NBS CIRCULAR 510

Tables of Chemical Kinetics
Homogeneous Reactions

UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

Tables of Chemical Kinetics

Homogeneous Reactions

These Tables are delivered in the form of punched loose sheets, temporarily assembled under a paper cover. This cover can be removed at the discretion of the subscriber upon receipt of a batch of supplementary sheets which can then be inserted at their right place as indicated by the number of the table, and the whole set can then be held in a suitable loose-leaf binder.

Each table is designated by a six-digit number, the first two of which refer to the type of reaction, the third to the phase of the homogeneous reaction, gaseous (1), liquid (2), or solid (3). The indication of the phase is repeated at the upper right-hand corner of the first sheet of each table. The second three-digit group of the table number refers to the types of substances involved. Within each table, reactions are numbered. In tables including more than one page, the table number is repeated at the head of each page, and the pages are numbered. Each table starts on a new sheet.

The first supplementary installment, to be delivered at a later stage, may include additional tables, additions to tables now delivered, and revised sheets canceling and replacing parts of the present tables. Such changes will be duly indicated on the new sheets. Further supplementary installments will be delivered at future dates as new or revised data material warrants it.

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Tables of Chemical Kinetics

Homogeneous Reactions

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Foreword

The publication of International Critical Tables in 1926 provided the world with a comprehensive and critical selection of the then existing scientific data. Scientists of many nations cooperated in its compilation. Since then, the immense growth and refinement of scientific data have made much of it obsolete and incomplete, but its revision would be an enterprise even more tremendous than the original collection. A cooperative effort has therefore been established among the National Research Council, the International Union of Pure and Applied Chemistry, the International Union of Pure and Applied Physics, the National Bureau of Standards, and other interested institutions to compile separate critical tables of data in selected fields. The selection is governed by the apparent need in particular fields and the availability of experts thoroughly familiar with the subjects to undertake the work.

The tables presented in this volume represent one of these cooperative efforts sponsored by the National Bureau of Standards, the Committee on Tables of Constants of the National Research Council, and Princeton University.

E. U. Condon, *Director.*

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V th " + I st " " (2)	732.510
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V th " + V th " " (1)	732.550
V th " + VI th " " (1)	732.560

SUBJECT INDEX *(continued)*

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VII th " + VI th " "	(2)	732.760
VII th " + VII th " "	(2)	732.770
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The first two digits indicate the corresponding **Section.** For the *tables* included under the section (designated by numbers beginning with these two digits), consult the Table of Contents.

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ALPHABETICAL INDEX *(continued)*

LITERATURE REFERENCES

Code abbreviations for the most frequently quoted Periodicals

Abbreviation	Title
ACJ	Amer. Chem. Journal
ACS	J. Amer. Chem. Soc.
APU	Acta physicochim. USSR
BCB	Bull. Soc. chim. Belg.
BCF	Bull. Soc. chim. France
BDC	Ber. Deutche Chem. Ges.
CIL	J. Soc. Chem. Ind. London
CJR	Canadian J. Res.
CRA	Compt. rend. Acad. Sci. Paris
CRV	Chem. Reviews
CSL	J. Chem. Soc. London
DAN	Doklady Akad. Nauk SSSR
GCI	Gazz. chim. Ital.
HCA	Helv. chim. Acta
HPA	Helv. phys. Acta
IEC	Indust. Engin. Chem.
JCC	J. chim. phys. et coll.
JCP	J. Chem. Phys.
JOC	J. Org. Chem.
JPC	J. Phys. Chem.
JPR	J. Phys. Radium
JPS	J. Polymer. Sci.
MHC	Monatshefte f. Chemie
PRS	Proc. Roy. Soc.
RTC	Rec. trav. chim. Pays Bas
TFS	Trans. Faraday Soc.
ZAC	Zeitschr. anorg. allg. Chem.
ZEC	Zeitschr. f. Elektrochem.
ZPC	Zeitschr. f. physik. Chem.
ZhFKh	Zhur. fizicheskoi Khim.
ZhOKh	Zhur. obshchei Khim.
ZhPKh	Zhur. priklad. Khim.

TABLES OF NUMERICAL DATA
of
HOMOGENEOUS CHEMICAL REACTION
KINETICS

INTRODUCTION

The purpose of these Tables is a critically evaluated compilation of the available *factual* numerical data on rates and rate constants of homogeneous chemical reactions. Stress was laid throughout on experimentally ascertained facts; data largely contingent on interpretations have generally not been included.

Reaction equations are written in the simplest possible way, on the sole basis of the *observed* overall chemical change. The products are specified for each reaction, unless all reactions of a table are of a common type; in that case, the *Reaction Type* is stated once and for all at the head of the table, and the products, being unequivocally obvious from the type of the reaction, are not repeated. Whenever a reaction gives rise to a variety of products in no simple stoichiometric relation to the reactants, as is the case especially in many gaseous reactions, the products are separated by commas.

Symbols for Reactants and Products. By convention, and for the purpose of formulation of the rate laws, reactants and products are designated by Roman-type capital letters $A + B + C.... \rightarrow L + M + N....$, in the order in which they are written down in the reaction equation. As an example, in the reaction written $CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$, A stands for $CH_3COOC_2H_5$, B for OH^-, L for CH_3COO^-, M for C_2H_5OH.

Units of amount. The unit of "amount" (concentration, pressure), in which the rates and rate constants are expressed, unless expressly given for each individual reaction, is stated at the head of each table. Generally, that unit is the concentration unit M/l (moles per liter); data originally expressed in other units have been mostly converted to

M/l. It is known, of course, that for first-order rate constants the unit of concentration is immaterial, if rate and mass-action are in the same unit.

Units of time and rate. Throughout these tables, *the unit of time is the second,* and rates are understood to be expressed in the stated "unit of amount" (mostly M/l) *per second.* Original data using units of time other than the second have been systematically converted to seconds. The greatest possible care was exercised to gain complete certainty about the time and rate units involved in the original data. Authors are all too often neglectfully reticent or even confusing on that point, and the process of ascertaining the units has often been laborious.

Base of logarithms. The integrated forms of the rate laws generally involve natural logarithms, and the correct value of the rate constant k is that calculated from the integrated equation with *natural logarithms.* Practically, numerical calculations are mostly made with the use of decimal logarithms, which amounts to a division of the true k by ln 10, and necessitates remultiplication by that factor. In all too many instances, this simple operation is either omitted, or, worse yet, there is no hint or clue as to whether it has or has not been carried out, with a resulting uncertainty in k by a factor of 2.303. It has been our strenuous endeavor to make sure, in each doubtful case, often at the cost of laborious search, of the kind of logarithm actually meant in the original. All k in these Tables are the *true* k, i.e. based on natural logarithms. The necessary conversions have been made wherever they were called for.

Uniformity of units. These recalculations have resulted in a tabulation of data in uniform units throughout these Tables, rates per second, rate constants calculated with natural logarithms. In many instances, rate constants, not included in the original publication, have been calculated in these units, from the experimental data material; the gain, in terms of ready comparison of data from different sources, and of intercommunication, is obvious.

Rate measured. The expression "rate of the reaction" is not necessarily unambiguous. It *may* make a difference whether the "rate" meant is that of the disappearance of a reactant or of the formation of a product, and it often does make a difference *which* reactant or *which* product is meant. There are instances where authors speak loosely of a "rate of the reaction" where a precision about the exact rate referred to would be essential. It has been our endeavor, throughout these Tables, to leave no doubt on that point, and to state the exact nature of the change referred to by the "rate" wherever there might be an ambiguity. In particular, in gaseous reactions giving rise to a variety of products, it is always essential to state whether the rate is that of the disappearance of a given reactant, of the formation of a product (and of which), or, as is often the case, merely of a change of pressure which often stands in no known relation to the rate of formation of a definite product. Similarly, in the case of a reactant undergoing parallel transformations in different directions, it is essential to state whether the rate refers to the total consumption of the reactant or to one or two specific reactions. The necessary statements are given either for separate reactions or, whenever they apply to a whole group of reactions of common type, at the head of the table. They are omitted wherever there can be no ambiguity.

Defined mass-action law. Empirical rate laws are tabulated in their differential form, the left-hand member of the equation (written down only if necessary to avoid ambiguity) being understood to be the momentary *rate* measured, in the stated unit of amount per second, and the right-hand member the mass-action law in the form of an algebraic function $k\,f(A, B, \ldots L, M, \ldots X)$ where A, B... are the momentary amounts of the reactants, L, M.... those of the products, X the amount of a catalytically active homogeneous catalyst or inhibitor, if any. Integrated rate equations, being merely a matter of mathematical technique, are not tabulated. Wherever necessary, the differential rate law was reconstituted from the integrated equation.

The "defined mass-action law" is given *primarily as a definition of the rate constants* k the values of which are listed in the tables. It is not necessarily, and often quite certainly is not, the "rate law" of the reaction. It could be a matter of choice; the rate of an actually overall second-order reaction, first-order in reactant A, and first-order in reactant B, normally to be represented by a mass-action function $k\,AB$, can be described by a first-order function k' A on the understanding that [B] is included in k' which, of course, will then vary with [B], unless, as is often the case, [B] is kept constant throughout the investigation. If the rate constant of a reaction between A and B is defined by a first-order mass-action function k' A, it means, generally, that the order of the mass-action of B is left open. In instances where the experimental material warranted it, we have often derived a more explicit "defined mass-action law" than that used by the original author, and recalculated k accordingly. In all cases, however, greatest care was taken to establish a clearcut correspondence between the *definition* of the k by the "defined mass-action law" and its tabulated numerical values. Unless otherwise stated, the defined k is understood to be constant over the reaction, and to reflect its order under the given conditions.

Temperature. All temperatures are in degrees Celsius (centigrade). Temperatures originally expressed on other scales have been converted to °C.

Rate constants as defined under "defined mass-action law", are given in the form $k = k^{\circ} \times 10^{n}$, with the values of k° and n tabulated in adjacent columns, opposite the temperature to which they refer. The symbol k° is the value of k in the order-of-magnitude unit 10^{n}, and must not be confused with any standard-state value.

Activation energies E, always in kcal/mole, are given with one digit at most after the decimal point.

Frequency factors A, defined by the Arrhenius equation $k = Ae^{-E/RT}$, are given in the same form as k, namely $A = A^{\circ} \times 10^{n}$, with A° and n tabulated in adjacent columns. A is of the same dimension and in the same units as k.

Activation heats, ΔH_{a} (kcal/mole), and **Activation entropies,** ΔS_{a} (cal/mole/degree °C), are given occasionally under these headings.

Empirical rates, in the stated units of amount per second, especially initial rates under fixed conditions, are reproduced occasionally as possibly useful factual numerical data where no mass-action law and no rate constant defined by a mass-action law can be derived from the available data.

By the same token, **Fractional times**, i.e. the time in seconds necessary for the completion of the stated fraction of the full conversion, have been tabulated occasionally, as empirical numerical material. The fraction of completion is stated in bold-face type, in parentheses. However, in all instances where a rate law could be inferred from the data, rate constants k, defined by that mass-action law, have been calculated and tabulated in preference to fractional times.

Initial concentrations. The range of amounts of reactants and products in which the rates and rate constants have been established is extremely important. A rate law may hold in one range but be utterly invalid in a different range. A statement of the initial range is included, under the heading "Amount of reactant," wherever that information is available. Reactants and products are referred to, as usual, by A, B..., L, M... . It is immediately obvious that the merits of the "defined mass-action law" and the strength of its claim to the dignity of a rate law, are largely dependent on the breadth of the concentration range in which the mass-action law was found to hold. It will be noted that not infrequently rates and rate constants have been determined only for one definite composition of the reactant mixture. Listing of data of k implies, of course, that k is satisfactorily constant throughout the reaction (except as qualified in the Comments), i.e. the given mass-action law renders the order of the reaction with the stated initial amounts.

Addend (Catalyst). Addends, other than the explicit participants A, B...., L, M...., are listed under that heading, with their amounts or ranges of amounts in the adjacent column. If the addend has a catalytic effect, its concentration is either implicitly contained in k, or explicitly in the mass-action function. The "defined mass-action law" is always so formulated that there can be no doubt on that point.

Solvent (Medium). In the case of liquid-phase reactions in solution, the solvent is stated in the column immediately following the Reaction equation. If the "solvent" is identical with one of the reactants, it is designated by the corresponding Capital-letter symbol. Composite solvents are frequently *coded,* e.g. Et 85 for C_2H_5OH 85 vol % + H_2O 15 %; explanation of the code designations will be found at the end of the table.

Agreeing and conflicting data. Reduction of the reaction equations to their simplest empirical form, expression of the mass-action functions in the most plausible form, and uniform expression of the rate constants k in standard units, have necessitated and permitted frequent cross-checks and comparisons of data from different sources. Very closely agreeing data have been averaged and are underlined in the Tables. Less closely concordant data, pertaining to overlapping conditions, unless there were reasonable grounds for a selection, have often been left side by side, the range of the variation being useful as a yardstick of the reproducibility of the rate of the reaction. Good agreement of data identically defined but determined in different ranges, adds greatly to the validity of the mass-action function as a true rate law. In the rarer instances of outright irreconcilable conflict, a motivated choice could mostly be made of the more reliable data; the editors do not, however, claim to be infallible, and will be receptive of criticisms. The degree of agreement or conflict of data from different sources is obvious from the tables, and is furthermore expressly stressed in the Comments placed at the end of the table.

Rate laws. The editors have knowingly refrained from committing themselves on the essentially controversial question of the true rate law of a reaction. The evaluation of the validity of a mass-action function as a rate law must be left to the judgment of the users of these Tables. The factual data given in these Tables, in particular the ranges of applicability of the "defined mass-action law", the degree of constancy or variation of k, its reproducibility as reflected by the agreement of data from different sources, are important elements in this evaluation. Further elements, such as systematic trends of k with the progress of the reaction i.e. as a function of the extent of the conversion, or the degree of homogeneity or partial heterogeneity of a gas-phase reaction, will be found in the Comments. It will be noted that, for a great number of extensively studied fundamentally important gaseous reactions, only *initial* rates and initial rate constants are available, and that reaction-rate orders inferred from variations of initial conditions, i.e. from one run to another, need not hold over the course of the reaction in one single run, partly on account of the yet insufficiently explored mixed homogeneous-heterogeneous and nonstationary character of these reactions. On many reactions, the scarcity of available numerical data, and their limitations, often contrasting with the imposing amount of existing brilliant even though maybe premature speculation, will be found disappointing. The Tables cannot, in this field, but tacitly dramatize the scantiness of our present factual knowledge.

Supplementary tables, placed after the main table, give additional useful numerical information which could not be fitted into the pattern of the table. The selection of topics was, of necessity, arbitrary. Secondary effects, in particular the great variety of salt effects, etc., especially if investigated for purposes outside the field of Kinetics, could not be included, but references thereto are generally given.

Comments at the end of the table cover, in a terse style, a variety of additional items of information both on the table as a whole and on particular reactions, including pertinent elements of evaluation. Reactions commented upon are marked in the table with an asterisk *.

Literature lists of references used or at least mentioned in Comments are placed at the very end of each table. References are arranged in the alphabetical order of the names of first authors, and are numbered in small type, e.g. ([12]). The sources of the data tabulated in the table are designated by these literature references numbers. Literature references examined but neither used nor mentioned are not included.

Order within the table. Reactions are arranged and numbered, without strict adherence to any ironclad system, in the usual order of increasing complexity of the key reactant, thus, in the case of organic compounds, in the order of increasing numbers of C atoms, branched isomers placed after the normal-chain isomers; not developed organic-compound formulas, e.g. $C_5H_{11}OH$, always mean the normal compound. Substituted derivatives are arranged in an order corresponding to that of the periodic system, e.g. alkyl-substituted, nitro-substituted, sulfo-substituted, halogen-substituted; the latter in the order F, Cl, Br, I. Longer tables are often subdivided, and the subdivisions are listed in the Comments of the table.

Pattern of the tables. The patterns of columns and headings vary somewhat from one table to another, depending on their contents. Where the width of a column was insufficient, and space was available in adjacent columns, free neighboring space was borrowed and the encroachment clearly marked by horizontal lines enclosing the extraneous parts.

Errors and omissions are unavoidable in Tables. The loose-leaf form has been chosen in view of the ease of subsequent revisions of individual sheets, including deletions, replacements, and additions. We shall welcome criticisms and communications pointing out errors and gaps.

Acknowledgments. The editor and his associates gratefully acknowledge the interest and help of the National Bureau of Standards, of the Committee on Tables of Constants, National Research Council, of Princeton University, and of the correspondents and authors to whom we have had many an occasion to turn for advice.

Editor

Tables of Chemical Kinetics

Homogeneous Reactions

ORTHO - PARA CONVERSION

Gas *phase*

Homogeneous Reactions

101.000.

Rates are in "unit of amount" per sec.

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
									k^o	n			
.1	$o\text{-H}_2 \rightleftarrows p\text{-H}_2$	thc	mm Hg	50 - 400			$k\ (A - A_e)(A + L)^{1/2}$	600	3.3	-5		*	(1) (11) (7)
								700	1.1	-3	58		
.2	$o\text{-H}_2 \rightarrow p\text{-H}_2$	from (.1)	"	"			$k_1\ A(A + L)^{1/2}$	600	8.0	-6			"
								700	2.7	-4	58		
.3	$p\text{-H}_2 \rightarrow o\text{-H}_2$	from (.1)	"	"			$k_2\ A(A + L)^{1/2}$	600	2.5	-5			
								700	8.0	-4	58		"
.4	$o\text{-H}_2 \rightleftarrows p\text{-H}_2$	thc	M/1	10 - 500 mm Hg	X =		$k\ (A - A_e)X$					*	(10)
						1 - 170							(8)
					O_2	mm Hg		-80	1.2	-1			(3)
								~20	1.5	-1			(13)
								100	1.7	-1			(9)
													(6)
													(12)
					NO^*	"	"	-80	6.0	-1			
								~20	6.0	-1			
					NO_2	"	"	~20	2.1	-1			
								100	2.3	-1			
					I		"	420	2.6	0			
								480	1.0	+1			

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
									k^o	n			
.4	$o\text{-}H_2 \rightleftarrows p\text{-}H_2$ *(continued)*	thc	M/l	10 - 500 mm Hg	B_2H_6		$k\,(A - A_e)X$	~ 20	1.8	-4			
								100	1.4	-1			
.5	$o\text{-}H_2 \rightarrow p\text{-}H_2$	from (.4)	M/l	10 - 500 mm Hg	X =		k_1 AX					*	
					O_2	1 - 170 mm Hg		-80	3.0	-2			
								~ 20	3.7	-2			
								100	4.2	-2			
				"	NO*	"		-80	1.5	-1			
								~ 20	1.5	-1			
				"	NO_2	"		~ 20	5.2	-2			
								100	5.5	-2			
				"	·I			420	6.5	-1			
								480	2.5	0			
				"	B_2H_6			~ 20	6.7	-5			
								100	3.5	-2			
.6	$p\text{-}H_2 \rightarrow o\text{-}H_2$	from (.4)	M/l	10 - 500 mm Hg	X =		k_2 AX					*	
					O_2	1 - 170 mm Hg		-80	9.0	-2			
								~ 20	1.1	-1			
								100	1.3	-1			
				"	NO*	"		-80	4.5	-1			
								~ 20	4.5	-1			
				"	NO_2	"		~ 20	1.6	-1			
								100	1.8	-1			

101.000.

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$: k^o	n	E	Comments	Literature
.6	$p\text{-}H_2 \rightarrow o\text{-}H_2$ *(continued)*	from (.4)	M/1	10 - 500 mm Hg	I		k_2 AX	420	1.9	0			
								480	7.5	0			
.7	$o\text{-}D_2 \rightleftarrows p\text{-}D_2$	thc	mm Hg	10			$k\ (A - A_e)(A + L)^{1/2}$	660	1.4	-4		*	(^{2})
								700	4.3	-4			
.8	$o\text{-}D_2 \rightarrow p\text{-}D_2$	from (.7)	mm Hg	10			$k_1\ A(A + L)^{1/2}$	660	4.6	-5			
								700	1.4	-4			
.9	$p\text{-}D_2 \rightarrow o\text{-}D_2$	from (.7)	mm Hg	10			$k_2\ A(A + L)^{1/2}$	660	9.2	-5			
								700	2.9	-4			
.10	$o\text{-}D_2 \rightleftarrows p\text{-}D_2$	thc	M/1		X =		$k\ (A - A_e)X$					*	(^{5}) (^{3}) (^{4})
					O_2			-80	1.2	-2			
								20	1.4	-2			
					NO*			-80	6.0	-2			
								20	6.0	-2			
.11	$o\text{-}D_2 \rightarrow p\text{-}D_2$	from (.10)	M/1		O_2		k_1 AX	-80	3.8	-3			
								20	4.7	-3			
					NO*		"	-80	2.0	-2			
								20	2.0	-2			
.12	$p\text{-}D_2 \rightarrow o\text{-}D_2$	from (.10)	M/1		O_2		k_2 AX	-80	7.7	-3		*	
								20	9.4	-3			
					NO*		"	-80	4.0	-2			
								20	4.0	-2			

COMMENTS

(.1) (.4) (.7) (.10) The kinetics of the conversion in both directions are represented by a single rate law with a single rate constant $k = k_1 + k_2$, with k_1 pertaining to the ortho → para, k_2 to the para → ortho conversion; the acting mass is the distance $(A - A_e)$ of the concentration of the reactant A from its equilibrium concentration A_e. The separate ortho → para rate constants k_1 (.2) (.5) (.8) (.11) and the para → ortho rate constants k_2 (.3) (.6) (.9) (.12) are derived from the corresponding ortho ⇄ para k and the equilibria. The equilibria give, at ∞ temperature (and with sufficient accuracy at the temperatures listed), for $o\text{-}H_2 \rightleftarrows p\text{-}H_2$, $k_1 = k/4$ and $k_2 = 3k/4$ and for $o\text{-}D_2 \rightleftarrows p\text{-}D_2$, $k_1 = k/3$ and $k_2 = 2k/3$. The experimentally feasible $(A - A_e)$ are positive with respect to $p\text{-}H_2$ and to $o\text{-}D_2$ at the temperatures listed.

Uncatalyzed reactions (.1) (.2) (.3) (.7) (.8) (.9): the form of the rate laws is accounted for by the catalytic action of H (D) atoms, exemplified by $o\text{-}H_2 + H \rightarrow H + p\text{-}H_2$.

Catalyzed reactions (.4) (.5) (.6) (.10) (.11) (.12): NO^* is the paramagnetic first excited state (353 cal); k at 20° calculated at total NO = 12 mm Hg. Iodine-catalyzed reaction calculated from conversion in $H_2 + I_2$, subtracting that due to atomic H. Catalysis by O_2, NO^*, NO_2, I, is attributed to magnetic moment; catalysis by B_2H_6 to exchange of H between B_2H_6 and H_2.

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(11) K.H.Geib, P.Harteck, *ZPC* 1931, *Bodensteinband*, 849. (12) E.J.Rosenbaum, T.R.Hogness, *JCP* 1934, 2, 267. (13) H.Sachsse, *ZEC* 1934, 40, 531.

ORTHO-PARA CONVERSION

Liquid phase

Homogeneous Reactions
102.000.

Rates are in "unit of amount" per sec.

No.	Reaction	Medium (solvent)	Method	Unit of amount	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
										k^o	n			
.1	$o - H_2 \rightarrow p - H_2$	pure	thc	M %	75			$k A^2$	~ 25	3.3	-8	~ 0		(3) (4) (9) (1)
.2	$o - H_2 \rightleftarrows p - H_2$	S = H_2O	thc	M/l	sat,			$k(A - {}'A_e)S$	~ 20	1.1	-6			(8) (5) (6)
		D_2O			1 atm					4.8	-7		*	
		C_6H_6								2.8	-6			
		CS_2								3.8	-7			
		CCl_4								4.5	-7			
		$C_6H_5NH_2$								3.9	-6			
		CH_3OH								2.0	-6			
		$C_6H_{11}OH$								2.7	-6			
.3	$o - H_2 \rightarrow p - H_2$	S = H_2O	from .2	M/l	sat,			$k_1 AS$	~ 20	2.8	-7			(8) (5) (6)
		D_2O			1 atm					1.2	-7		*	
		C_6H_6								7.2	-7			
		CS_2								1.0	-7			
		CCl_4								1.2	-7			
		$C_6H_5NH_2$								9.7	-7			
		CH_3OH								5.2	-7			
		$C_6H_{11}OH$								6.8	-7			

102.000.

No.	Reaction	Medium (solvent)	Method	Unit of amount	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.4	$p-H_2 \rightarrow o-H_2$	$S = H_2O$	from .2	M/1	sat,			k_2AS	~ 20	8.5	-7			(8)(5)(6)
		D_2O			1 atm					3.7	-7		*	
		C_6H_6								2.1	-6			
		CS_2								2.8	-7			
		CCl_4								3.3	-7			
		$C_6H_5NH_2$								2.9	-6			
		CH_3OH								1.5	-6			
		$C_6H_{11}OH$								2.0	-6			
.5	$o-H_2 \rightleftarrows p-H_2$	H_2O	thc	M/1	sat,	X =		$k(A - A_e)X$	~ 20					(7)(11)(10)(2)(5)
					1 atm	$PrCl_3$	0.0025 - 0.020			3.8	-2		*	
						$NdCl_3$				4.0	-2			
						$SmCl_3$				1.1	-2			
						$GdCl_3$				2.9	-1			
						$ErCl_3$				6.4	-1			
						$YbCl_3$				1.7	-1			
						$CuCl_2$				2.0	-2			
						$NiSO_4$				3.5	-2			
						$CoSO_4$	0.001 - 1.0			9.3	-2			
						$FeSO_4$				1.0	-1			
						$MnSO_4$				1.4	-1			
						$Fe_2(SO_4)_3$				8.3	-2			
						$Cr_2(SO_4)_3$				3.7	-2			

No.	Reaction	Medium (solvent)	Method	Unit of amount	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
										k°	n			
.5	$o - H_2 \rightleftarrows p - H_2$	H_2O	thc	M/1	sat,	O_2		$k(A - A_e)X$	~ 20	1.8	-1			
	(*continued*)				1 atm	NO				4.4	-1			
		C_2H_5OH	"	"	"	$NiSO_4$	0.001	"	"	3.3	-2			
						$FeSO_4$	"			1.0	-1			
						$MnSO_4$	"			9.8	-2			
						$Fe_2(SO_4)_3$	"			8.0	-2			
.6	$o - D_2 \rightleftarrows p - D_2$	$S = H_2O$	thc	M/1	sat,			$k(A - A_e)S$	~ 20	6.0	-7		*	(8)
		C_6H_6			1 atm					7.0	-7			
		CS_2								8.5	-8			
		CCl_4								8.5	-8			
.7	$o - D_2 \rightarrow p - D_2$	$S = H_2O$	from .6	M/1	sat,			k_1AS	~ 20	1.4	-7		*	(8)
		C_6H_6			1 atm					2.3	-7			
		CS_2								2.8	-8			
		CCl_4								2.8	-8			
.8	$p - D_2 \rightarrow o - D_2$	$S = H_2O$	from .6	M/1	sat,			k_2AS	~ 20	2.8	-7		*	(8)
		C_6H_6			1 atm					4.7	-7			
		CS_2								5.7	-7			
		CCl_4								5.7	-7			

COMMENTS

(.2) (.3) (.4) $k = k_1 + k_2$; $k_2/k_1 = 3$. The formulation (.2) is valid for the reaction in either direction, in terms of the mass action of the distance from equilibrium $(A - A_e)$. (.5) $k = k_1 + k_2$; the formulation of the rate law is analogous to that under (.2), in terms of the distance from equilibrium; the ratio k_2/k_1 remains = 3. (.6) (.7) (.8) Formulation (.6) analogous to that of (.2), in terms of distance from equilibrium $(A - A_e)$; $k = k_1 + k_2$; $k_2/k_1 = 2$.

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ORTHO-PARA CONVERSION

Amounts are in mole %.
Rates in mole % per sec.

No.	Reaction	Method	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
						k^o	n	
.1	$o-H_2 \rightarrow p-H_2$	thc	25 - 70	kA^2	~ - 263	5.4	-8	~ 0

COMMENTS

The rate constant *k* falls with the progress of the reaction as the molecules become increasingly separated in the lattice. With an initial $A_o = 75$ mole %, *k* begins to fall off at A = 25 %. The reaction comes to a halt at A = 19 %.

LITERATURE

E. Cremer, *ZPC*^{B} 1935, 28, 199
E. Cremer, M. Polanyi, *ZPC*^{B}, 21, 459

RACEMIZATION

Organic halogen compounds

Gas phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Active compound	Unit of amount	Amount of reactant	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Literature
							k^o	n		
.1	d-$C_2H_5CH(CH_3)I$	M/1	100 - 200	I_2	$k\,A(I_2)^{1/2}$	238.0 255.5 276.0	3.53 1.01 3.14	-2 -1 -1	32.2	(1)

COMMENTS

Catalyzed by I_2 formed through decomposition of A. The mechanism is: $I_2 \rightleftarrows I + I\,(K)$; $I + d - A \xrightarrow{1} l - A + I$; $k = 2k_1K^{1/2}$. See the decomposition reaction $2A \rightarrow C_4H_{10} + C_4H_{10} + I_2$, 521.477. Converted from M/ml to M/l.

LITERATURE

R.A.Ogg, Jr., M.Polanyi, *TFS* 1935, **31**, 482.

RACEMIZATION

C, H, O compounds

Liquid phase

Homogeneous Reactions
112.440

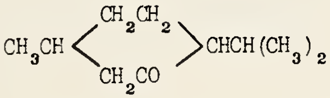
Method: polarimetry

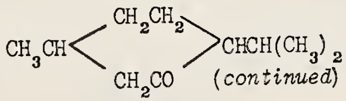
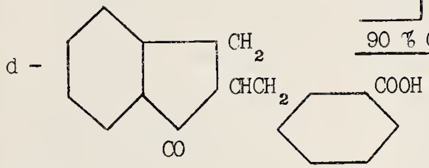
All rates are in "unit of amount" per sec.

No.	Initial active compound	Solvent (Medium)	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Fractional time	$k = k^o \times 10^n$		Comments	Literature
										k^o	n		
.1	(+) $C_2H_5CH(CH_3)CHO$	H_2O + dioxane, N	M/1		H^+	0.06 - 0.6	$k A[H^+]$						(1)
		0.274						25		4.65	-5		
		"						35		1.02	-4		
	[see Supplementary Table]	0.500						25		1.60	-4		
		"						35		5.09	-4		
		0.649						25		2.69	-4		
		"						35		1.33	-3		
		0.960						25		3.90	-3		
		"						35		4.60	-3		
.2	l - trans - $COOHCH(CH_3)CH{:}C(CH_3)COOH$	H_2O	M/1				$k A$		(0.5)				(8)
	COOH				HCl	0		100	6.42×10^4	1.07	-5		
						2		100.5	7.68×10^4	1.04	-5		
						5		101	1.95×10^4	3.55	-5		
			"		NaOH	1		101.5	1.47×10^3	4.73	-4		
		$(CH_3)_2CO$			-			56.5	2.88×10^5	2.44	-6		
.3	d - $CH_3COCH(CH_3)C_2H_5$	CH_3COOH	M/1	0.9	HNO_3	1.19	$k A$	25.0		4.13	-3		(2)
								38.7		2.17	-2		
.4	d - $C_2H_5COCH(CH_3)C_2H_5$	CH_3COOH	M/1	0.9	HNO_3	1.19	$k A$	25.0		1.72	-3		(2)
								38.7		5.66	-3		

112.440.

No.	Initial active compound	Solvent (Medium)	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Fractional time	$k = k^o \times 10^n$		Comments	Literature
										k^o	n		
.5	d - cyclo - $C_6H_{11}COCH(CH_3)C_2H_5$	CH_3COOH	M/1	0.9	HNO_3	1.19	k A	25.0		3.05	-4		(2)
.6	d - $C_6H_5COCH(CH_3)C_2H_5$	CH_3COOH	M/1	0.9	HNO_3	1.19	k A	36.7		4.94	-4		(2)
.7	1 - $C_6H_5COCH(CH_3)C_2H_5$	dioxane + D_2O 45.0	g/100 ml	7.5	NaOD	0.43		35.0					(5)
								(0.12)	3600				
								(0.41)	11700				
								(0.65)	23400				
.8	$C_6H_5COCH(CH_3)C_6H_5$	C_6H_5Cl	M/kg	0.025		c	$(k\ c + k' c^2)A$						
					CCl_3COOH	0.02 - 0.2		99.4	k	1.27	-4	*	(4)
								"	k'	7.42	-4		
					$CHCl_2COOH$	0.05 - 0.3	$(k\ c + k' c^{1/2})A$						
								99.4	k	3.35	-5	*	"
									k'	1.67	-6		
					$CH_2ClCOOH$	0.08 - 0.5	"	"	k	1.60	-6	*	"
									k'	1.47	-6		
					o - $NO_2C_6H_4COOH$	0.08 - 0.4	"	"	k	3.33	-6	*	"
									k'	1.75	-6		
.9	$C_6H_5COCH[CH(CH_3)C_2H_5]C_6H_5$	$C_6H_5OCH_3$	M/kg	0.028	$CHCl_2COOH$	0.6	k Ac	100		1.85	-6	*	(4)
					(c)	0.4				1.73	-6		
						0.2				7.67	-7		
		$C_6H_5NO_2$	"	"	"	0.6	"	"		3.62	-6		"
						0.4				4.43	-6		
						0.1				3.89	-6		

No.	Initial active compound	Solvent (Medium)	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Fractional time	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.9	$C_6H_5COCH[CH(CH_3)C_2H_5]C_6H_5$ *(continued)*	C_6H_5Cl	M/kg	0.028	$CHCl_2COOH$ (*c*)	0.6 0.4 0.1	$k\,Ac$	100		8.60 8.30 7.12	-6 -6 -6		(^{4})
		decalin	"	"	"	0.6 0.4 0.1	"	"		2.57 2.19 1.43	-5 -5 -5		"
.10	d - $C_6H_5CH_2COCH(CH_3)C_2H_5$	CH_3COOH	M/1	0.9	HNO_3	1.19	$k\,A$	25.0 44.6		1.97 1.18	-4 -3	*	(^{2})
.11	p - $CH_3C_6H_4CH(C_6H_5)COO^-$	H_2O + 3 % D_2O	M/1	0.2	NaOH	0.22	$k\,A$	100		6.4	-6	*	(^{7})
.12	p - $CH_3C_6H_4CD(C_6H_5)COO^-$	H_2O	M/1	0.2	NaOH	0.22	$k\,A$	100		1.4	-6	*	(^{7})
.13	 $CH_3CH\langle CH_2CH_2, CH_2CO\rangle CHCH(CH_3)_2$ (menthone)	C_6H_5Cl	wt % (A) M/kg (*c*)	6.2 ± 0.2		*c*	$(k\,c + k'c^{1/2})A$						
					C_6H_5COOH	0.07 - 0.6		99.4	k k'	7.35 5.50	-6 -6	*	(^{3})
		"		"	m - ClC_6H_4COOH	0.1 - 0.4	"	"	k k'	1.33 1.13	-5 -5		"
		"		"	$CH_2ClCOOH$	0.1 - 0.4	$(k\,c + k'c^2)\,A$	99.4	k k'	4.78 2.33	-5 -8		"
		"		"	o - $NO_2C_6H_4COOH$	0.1 - 0.3	"	"	k k'	1.33 3.33	-4 -8		"
		"		"	$CHCl_2COOH$	0.01 - 0.07	"	"	k k'	3.33 5.83	-4 -7		"

No.	Initial active compound	Solvent (Medium)	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature		$k = k^o \times 10^n$		Comments	Literature
										k^o	n		
.13	 (continued) (menthone)	C_6H_5Cl		6.2 ± 0.2	CCl_3COOH	0.01 – 0.05	$(k\ c + k'c^2)A$	99.4	k k'	1.23 5.68	-3 -6		(3)
		"		"	$C_6H_2(OH)(NO_2)_3$	0.1 – 0.25	"	"	k k'	9.68 1.03	-5 -7		"
.14	d –  (2 – o – carboxybenzylindan – 1 – one)	90 % $CH_3COOH + H_2O$	M/1	0.05	HBr	0.142	$k\,A$	25		1.25	-4		(6)
						0.245				2.57	-4		
						0.303				3.68	-4		
						0.352				4.95	-4		
.15	Strychnine hydrogen – L – trans – α, γ – dimethylglutaconate	H_2O					$k\,A$	100		1.61	-4		(8)
		$(CH_3)_2CO$					"	56.6		1.25	-4		"

SUPPLEMENTARY TABLE

(.1) *Activation functions*

Dioxane, N (mole fraction)	ΔH_a	ΔS_a	Dioxane, N (mole fraction)	ΔH_a	ΔS_a
0.274	16.6	-22.6	0.649	26.6	+14.4
0.500	19.0	-12.2	0.960	2.7	-60.4

COMMENTS

(.8) The $c^{1/2}$ term may arise from equilibrium between monomeric and dimeric forms of the acid. The c^2 term may arise from acid acting as proton acceptor. (.9) Only 40 % of the reaction (15 % in $C_6H_5NO_2$) followed.

(.11 - .12) Accompanied by H-D exchange at the same rate. Ionic mechanism. (.13) As (.8) The rate law holds to 60 - 80 % completion. At given c, $k = k_o(1 - nA)$.

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RACEMIZATION

Organic halogen compounds

Method: polarimetry

Liquid phase

All amounts are in M/l.

All rates in M/l per sec.

No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	d - $CH_3CHBrCOOH$	$(CH_3)_2CO$	0.3	Br^-	0.3	$kA[Br^-]$	22	5.23	-4	*	(1)
.2	d - $C_7H_{15}CHICH_3$	$(CH_3)_2CO$	0.138	I^-	0.160	$kA[I^-]$	30	1.30	-3	*	(2)
.3	$C_6H_5CHClCH_3$	$(CH_3)_2CO$	0.18	$HgCl_2$	0.15	kA	20	1.42	-5		(4)
					0.30		"	4.17	-5		
					0.60		"	1.67	-4		
					1.20		"	8.33	-4		
.4	d - $C_6H_5CHBrCH_3$	$(CH_3)_2CO$	0.2	Br^-	0.2	$kA[Br^-]$	15.2	1.85	-4	*	(3)
							30	8.00	-4		
							40.5	1.94	-3		

COMMENTS

(.1) The reverse reaction proceeds with the same k. Isotopic substitution of Br (see 302.477.) proceeds practically with the same k; consequently, the inversion takes place by way of substitution. (.2) The reverse reaction proceeds with the same rate constant; k calculated from the original N_1 = constant sum total of all rates of inversion occurring in the system; $k = N_1 A_0 [I^-]$. By the near equality of the rates of inversion and of isotopic substitution of I (see 302.477.), the inversion takes place by way of the substitution $I^- + A \rightarrow L + I^-$. (.4) As (.2).

LITERATURE

(1) W. A. Cowdrey, E. D. Hughes, J. P. Newell. C. L. Wilson, *CSL* **1938**, 209. (2) E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley, J. Weiss, *CSL* **1935**, 1525. (3) E. D. Hughes, F. Juliusberger, A. D. Scott, B. Topley, J. Weiss, *CSL* **1936**, 1173. (4) D. R. Read, W. Taylor *CSL* **1940**, 679.

CIS-TRANS ISOMERIZATION

C, H, O compounds

Gas phase

Amounts are in mm Hg.

Rates are in mm Hg per sec.

No.	Initial isomer	Method	Amount of reactant	Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.1	cis - $CH_3CH{:}CHCH_3$ (→ trans)	melt	103		kA	390	1.0	-6				*	(3)
			"			418	1.7	-6	~ 18				
			402			390	3.6	-6					
						416	6.9	-6					
			1440			390	3.8	-6					
.2	cis - $CH_3OCOCH{:}CHCOOCH_3$ (→ trans)	melt	732		kA	300	4.3	-6				*	(4)(5)
			2140			"	7.7	-6					
			4060			"	8.3	-6					
			∞			"	1.3	-5	26.5	1.3	5		
									(280 - 390°)				
.3	cis - $C_6H_5CH{:}CHCOOCH_3$ (→ trans)	melt	6 - 570		kA	380.5	4.53	-4	42	3.5	10	*	(2)
									(290 - 390°)				
.4	cis - $C_6H_5CH{:}CHC_6H_5$ (→ trans)	melt	5 - 380		kA	320	9.9	-4	43	6	12	*	(1)
.5	trans - $C_6H_5CH{:}CHC_6H_5$ (→ cis)	anal		N_2	kA	214	1.16	-6					(6)
						223	2.32	-6					

COMMENTS

(.1) Order lower than first with a given initial pressure; approximately A^2 with respect to initial pressure. **(.2)** E and A valid for pressure extrapolated to ∞. First order holds at high pressures. Corrected for partial decomposition of the product. **(.3)** Reverse reaction negligible. Rate falls off at lower pressures. **(.4)** Partial decomposition of cis, compensated by a conventional equilibrium constant.

LITERATURE

(1) G.B.Kistiakowsky, W.R.Smith, *ACS* 1934, **56**, 638.

(2) G.B.Kistiakowsky, W.R.Smith, *ACS* 1935, **57**, 269.

(3) G.B.Kistiakowsky, W.R.Smith, *ACS* 1936, **58**, 766.

(4) G.B.Kistiakowsky, M.Nelles, *ZPC* 1931, Bodenstein Festband 369. (5) M.Nelles, G.B.Kistiakowsky, *ACS* 1932, **54**, 2208. (6) T.W.Taylor, A.R.Murray, *CSL* **1938**, 2078.

CIS-TRANS ISOMERIZATION
C, H, N compounds

Amounts are in mm Hg.
Rates are in mm Hg per sec.

No.	Initial isomer (→ final)	Method	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	cis - $C_6H_5CH:CHCN$ (→ trans)	refr	>150	k A	352	4.00	-5	46	6	11	*	(1)
.2	trans - $C_6H_5CH:CHCN$ (→ cis)	refr	>150	k A	352	2.89	-5	46	4	11	*	(1)

COMMENTS

(.1 - .2) First-order homogeneous reaction holds at high pressures and temperatures. Heterogeneous reaction prevails at low pressure and temperature.

LITERATURE

(1) G.B.Kistiakowsky, W.R.Smith, *ACS* 1936, 58, 2428.

CIS-TRANS ISOMERIZATION

Organic halogen compounds

Gas phase

Amounts are in mm Hg.
Rates are in mm Hg per sec.

No.	Initial isomer (→ final)	Method	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	trans - ClCH:CHCl (→ cis)	refr	200 - 700	k A	312.5	8.76	-4	42	5	12	*	(¹)
							(290 - 335°)					
.2	α - $C_6H_5CCl:CHC_6H_5$ (→ β)	anal		k A	226 246	1.01 4.46	-5 -5	37				(²)
.3	α - $C_6H_5CCl:CClC_6H_5$ (→ β)	anal		k A	196	1.6	-6	34				(²)

COMMENTS

(.1) Some heterogeneous conversion and partial decomposition.

LITERATURE

(¹) J. Leslie Jones, R.L. Taylor, *ACS* 1940, **62**, 3480.

(²) T.W. Taylor, A.R. Murray, *CSL* **1938**, 2078.

CIS-TRANS ISOMERIZATION

C, H, O compounds

Liquid phase

Rates are in "unit of amount" per sec.

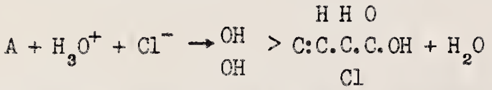
No.	Initial isomer (→ final)	Solvent (Medium)	Unit of amount	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.1	cis - COOHCH:CHCOOH(→ trans)	H_2O	M/1	0.24 - 0.88	X =		$k_1A[X]$; $k_2A^2[X]$					*	(3)
					HCl	1.6	k_1	99.9	1.82	-5			
						"	k_2	"	2.17	-5			
						2.7	k_1	79.8	4.98	-6			
						"	k_2	"	5.67	-6			
						"	k_1	99.9	3.33	-5			
						"	k_2	"	4.15	-5	24.9		
					HBr	1.6	k_1	99.9	1.13	-5			
							k_2	"	1.23	-5			
					H_2SO_4	2.7	k_1	99.9	1.56	-6			
							k_2	"	1.80	-6			
					$HClO_4$	5.2	k_1	99.9	6.17	-7			
							k_2	"	7.17	-7			
					KCNS	0.04 - 0.09	k_1	79.8	2.77	-4			
						"	k_2	"	3.87	-4			
						"	k_1	99.9	1.23	-3			
						"	k_2	"	1.62	-3	18.8		
					NaBr	1.8 - 5.3	k_1	99.9	1.20	-6			
							k_2	"	1.42	-6			

122.440.

No.	Initial isomer (→ final)	Solvent (Medium)	Unit of amount	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
									k^o	n			
.2	cis - $C_6H_5CH:CHCOOH$ (→ trans)	C_6H_6	M/ml	$10^5A = 3 - 9$	I_2	$10^5[I_2] = 0.15 - 2.4$	$kA[I_2]^{1/2}$	99.4	1.4	-3	24.2 (100 - 125°)	*	(²)

COMMENTS

(.1) In the presence of acids, the second-order k_2 is more nearly constant throughout a run than the first-order k_1 which falls off, particularly in HCl and HBr. With respect to the mass-action of the catalyst X, the order in acids is actually higher than first; this is attributed to catalysis by both the anion of the acid and the proton. With salts, the order with respect to the catalyst is actually first. The catalyzing proton donation is taken to be contributed by the reactant itself. The reaction is complicated by unavoidable simultaneous addition of the anion to the double bond. The true order with respect to the reactant appears to be, in the presence of acids, first, and in the presence of salts, between 1.5 and 2. The rate determining step is assumed to be represented by



$$A + H_3O^+ + Cl^- \rightarrow \begin{matrix} OH \\ OH \end{matrix} > \underset{Cl}{\overset{H\ H\ O}{C:C.C.C.OH}} + H_2O$$

(.2) Conductometric method. The rate of the photochemical reaction in C_6H_6 solution (¹)(²) at 35°C is governed by the same law, $k'A(I_2)^{1/2}$, with k' proportional to the square root of the incident light intensity.

LITERATURE

(¹) A.Berthoud, C.H.Urech, *JCP* 1937, 27, 291. (²) R.G.Dickinson and Lotzkar, *ACS* 1937, 59, 472. (³) R.Nozaki, R.Ogg, *ACS* 1941, 63, 2583.

CIS-TRANS ISOMERIZATION

Organic halogen compounds

Liquid phase

Rates are in "unit of amount" per sec.

No.	Initial isomer (⟶ final)	Solvent (Medium)	Unit of amount	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = k^\circ \times 10^n$		Comments	Literature
									k°	n		A°	n		
.1	*cis* - ClCH:CHCl (⟶ *trans*)	pure; C_4H_6; C_6H_{12}; $C_{10}H_{18}$	mole fraction	< 0.2	I_2	0.001 - 0.015	$kA[I_2]^{1/2}$	150	4.5	-5	31 (150 - 185°)			*	(3)
.2	*cis* - ICH:CHI (⟶ *trans*)	$C_{10}H_{18}$	M/ml	5 - 10 mole %	I_2	1.3 - 5.0 g/l	$kA[I_2]^{1/2}$	144	1.7	-3	29	1.3	11	*	(1)
.3	*trans* - ICH:CHI (⟶ *cis*)	$C_{10}H_{18}$	M/ml	5 - 10 mole %	I_2	1.3 - 5.0 g/l	$kA[I_2]^{1/2}$	144	1.3	-3	30	2.0	11	*	(1)

COMMENTS

(.1) Dielectric constant measurements. Rate practically identical in the pure liquid and in the solvents listed. The photochemical reaction (2) in $C_{10}H_{18}$ (decalin) has an activation energy of $E = 13.4$. **(.2) (.3)** Dielectric constant measurement. A is assumed from the isotopic exchange reaction

$$cis\ (trans) - C_2H_2I_2 + \tfrac{1}{2} I_2^* \rightarrow cis\ (trans) - C_2H_2I^*I + \tfrac{1}{2} I_2;$$

E is calculated from the assumed A and the observed k. The rate of the photochemical reaction (1) in decalin solution is governed by the same law $k' A[I_2]^{1/2}$, with k' proportional to the square root of the incident light intensity; E = 11 kcal (77° - 114°C) for *cis* → *trans*, and = 13 kcal (77° - 114°C) for *trans* → *cis*.

LITERATURE

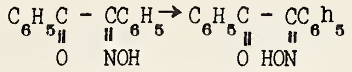
(1) R.M.Noyes, R.G.Dickinson, Verner Schomaker *ACS* 1945, **67**, 1319. (2) R.E.Wood; see *ACS* 1945, **67**, 1327 footnote (15). (3) R.E.Wood, G.Dickinson *ACS* 1939, **61**, 3259.

SYN-ANTI ISOMERIZATION

C, H, O, N compounds, aromatic

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent (Medium)	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
							k^o	n
.1	 $C_6H_5\underset{\underset{O}{\|}}{C} - \underset{\underset{NOH}{\|}}{C}C_6H_5 \rightarrow C_6H_5\underset{\underset{O}{\|}}{C} - \underset{\underset{HON}{\|}}{C}C_6h_5$ α-benzilmonoxime → β	pure liquid	HCl	0.5	k A	55	6.98	-5
				1.0		55	2.42	-4
				1.5		55	4.87	-4
		$H_2O + C_2H_5OH$ 96%	HCl	0.5	k A	55	5.25	-6
				1.5		55	3.54	-5
				2.0		55	1.40	-4
				3.0		55	7.52	-4
		$H_2O + C_2H_5OH$ 96%	LiCl	0.5	k A	55	2.79	-5
				1.5		55	8.41	-5
				2.0		55	2.46	-4
		$H_2O + C_2H_5OH$ 96%	$N(CH_3)_4Cl$	0.5	k A	55	1.58	-4
		$H_2O + C_2H_5OH$ 56%	HCl	0.5	k A	55	5.38	-7
				1.5		55	4.98	-6
		$H_2O + C_2H_5OH$ 56%	KCl	0.5	k A	55	3.19	-5

LITERATURE

T. W. J. Taylor, D. C. V. Roberts, *CSL* **1933**, 1439.

BRANCHING ISOMERIZATION

Liquid phase

Hydrocarbons

Rates and mass-action are in M/l per sec.

No.	Reaction	Medium	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
						k^o	n		A^o	n
.1	$CH_3CH_2CH_2CH_3 \longrightarrow (CH_3)_2CHCH_3$	pure liquid	(moles/mole A)	$k\,A\,[HAlBr_4]$						
			Al_2Br_6 0.0118 + HBr 0.0077		53.0	1.48	-4			
			0.00418 0.0077		"	1.70	-4			
			0.0162 0.00096		65.0	2.90	-4			
			0.0077 0.0020		"	2.80	-4			
			0.0273 0.00543		"	3.57	-4			
			0.0056 0.0077		"	2.73	-4			
			0.0082 0.0077		"	2.20	-4			
			0.00666 0.0077		"	2.88	-4			
			0.00845 0.0077		78.5	4.1	-4	9.2	2.5	2
.2	$(CH_3)_2CHCH_3 \longrightarrow CH_3CH_2CH_2CH_3$	pure liquid	Al_2Br_6 0.00968 + HBr 0.00204	$k\,A\,[HAlBr_4]$	65.0	1.8	-4			
			0.00965 0.00274		"	1.9	-4			
			0.0182 0.00644		"	1.4	-4			
			0.0214 0.0078		"	1.5	-4			
			0.00112 0.0078		"	1.3	-4			

COMMENTS

(.1) (.2) Conversion in sealed tubes followed by vapor pressure and density determinations. Catalysts dissolved homogeneously except for slight solid residue on walls. Data of rates with varying amounts of $AlBr_3$ and HBr prove that the catalyst is $HAlBr_4$, and the rate proportional to its concentration. Consequently, k was calculated on the basis of a rate law $kA[HAlBr_4]$, and shows sufficient constancy to bear out the conclusion. All data have been converted from M/ml to M/l.

LITERATURE

P. A. Leighton, J. D. Heldman, *ACS* 1943, **65**, 2276.

ISOMERIZATION

Liquid phase

Hydrogen migration with Double bond shift

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$CH_2:CHCH_2COO^- \rightarrow CH_3CH:CHCOO^-$	H_2O	1.0	NaOH	1.05	kA	100	9.7	-5	*	(1)
.2	$CH_3CH:CHCH_2COO^- \rightarrow CH_3CH_2CH:CHCOO^-$	H_2O	1.0	NaOH	1.2	kA	100	1.9	-6	*	(2)
.3	$CH_3CH_2CH:CHCOO^- \rightarrow CH_3CH:CHCH_2COO^-$	H_2O	1.0	NaOH	1.2	kA	100	1.0	-6	*	(2)

COMMENTS

(.1) D exchange determined simultaneously. Proposed mechanism: $A + OH^- \rightarrow CH_2:CHCHCOO^- + H_2O \rightarrow L + OH^-$.

(.2) (.3) From the rate of establishment of the equilibrium

$$\begin{tikzcd}
CH_3CH_2CH:CHCOO^- \arrow[rr, shift left] \arrow[dr, shift left] & & CH_3CH:CHCH_2COO^- \arrow[ll, shift left] \arrow[dl, shift left] \\
& CH_3CH_2CHOHCH_2COO^- \arrow[ul, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

from $CH_3CH_2CH:CHCOO^-$.

LITERATURE

(1) D.J.G. Ives, *CSL* **1938**, 91. (2) D.J.G. Ives, R.G. Kerlogue, *CSL* **1940**, 1362.

ISOMERIZATION

Liquid phase

Alkenyl group migration with Double bond shift on aliphatic C

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Medium	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
					k^o	n		A^o	n	
.1	$CH_3CH{:}CHC(CH_2{:}CHCH_2)(COOC_2H_5)_2 \rightarrow CH_3CH(CH_2{:}CHCH_2)CH{:}C(COOC_2H_5)_2$	pure liquid	kA	193.1	1.43	-4				(1)
.2	$C_2H_5CH{:}CHC(CH_2{:}CHCH_2)(COOC_2H_5)_2 \rightarrow C_2H_5CH(CH_2{:}CHCH_2)CH{:}C(COOC_2H_5)_2$	pure liquid	kA	193.1	1.84	-4				(1)
.3	$C_2H_5CH{:}C(CH_3)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow C_2H_5CH(CH_2{:}CHCH_2)C(CH_3){:}C(CN)(COOC_2H_5)$	pure liquid	kA	176.5	1.35	-3				(1)
.4	$(CH_3)_2CHCH{:}C(CH_3)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow (CH_3)_2CHCH(CH_2{:}CHCH_2)C(CH_3){:}C(CN)(COOC_2H_5)$	pure liquid	kA	180 200	3.54 1.40	-4 -3	28.6 $\Delta S_a = -14.0$	2.3	10	(2)
.5	$C_4H_9CH{:}C(CH_3)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow C_4H_9CH(CH_2{:}CHCH_2)C(CH_3){:}C(CN)(COOC_2H_5)$	pure liquid	kA	176.5	9.16	-4				(1)

152.441.

No.	Reaction	Medium	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Literature
					k°	n		A°	n	
.6	$CH_3CH{:}C(C_2H_5)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow$ $CH_3CH(CH_2{:}CHCH_2)C(C_2H_5){:}C(CN)(COOC_2H_5)$	pure liquid	kA	176.5	1.53	-3				(1)
.7	$CH_3CH{:}C(C_2H_5)C(CH_2{:}CHCH_2)(CN)_2 \rightarrow$ $CH_3CH(CH_2{:}CHCH_2)C(C_2H_5){:}C(CN)_2$	pure liquid	kA	120	4.02	-4				(2)
				130	9.12	-4	25.8	8.7	10	
				140	1.98	-3		$\Delta S_a = -11.1$		
.8	$CH_2{:}C(C_6H_5)C(CH_2{:}CHCH_2)(CN)(COOC_2H_5) \rightarrow$ $CH_2(CH_2{:}CHCH_2)C(C_6H_5){:}C(CN)(COOC_2H_5)$	pure liquid	kA	176.5	1.60	-3				(1)

COMMENTS

Refractive index measurements.

LITERATURE

(1) A.C.Cope, R.E.Hoyle, D.Heyl, *ACS* 1941, **63**, 1843.

(2) E.Gordon Foster, A.C.Cope, Farrington Daniels, *ACS* 1947, **69**, 1893.

ISOMERIZATION

Liquid phase

Alkenyl group migration with Double bond shift on alicyclic ring

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Medium	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
					k^o	n		A^o	n	
.1	$C(CN)_2(CH_2{:}CHCH_2)$ - *cyclo* - C_6H_9 → 1 - $(CH_2{:}CNCH_2)$ - 2 - $C(CN)_2$:*cyclo* - C_6H_9	pure liquid	kA	120	1.81	-4				(²)
				130	4.09	-4	26.2	6.3	10	
				140	9.14	-4		ΔS_a = -11.7		
.2	$C(CN)(COOC_2H_5)(CH_2{:}CHCH_2)$ - *cyclo* - C_6H_9 → 1 - $(CH_2{:}CHCH_2)$ - 2 - $C(CN)(COOC_2H_5)$:*cyclo* - C_6H_9	pure liquid	kA	176.5	1.13	-3				(¹)

LITERATURE

(¹) A.C.Cope, R.E.Hoyle, D.Heyl, *ACS* 1941, 63, 1843.

(²) E.Gordon Foster, A.C.Cope, Farrington Daniels, *ACS* 1947, 69, 1893.

ISOMERIZATION

Liquid phase

OH group migration with Double bond shift

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
								k^o	n	
.1	$CH_3CH:CHCH(OH)C:CH \rightarrow CH_3CH(OH)CH:CHC:CH$	$H_2O + C_2H_5OH$ 20 vol %	0.0729	HCl	0.1	kA	30	1.04	-5	
					0.4		"	5.46	-5	
					1.0		"	1.85	-4	
					4.0		"	6.18	-3	
					0.1		40	3.50	-5	
					0.4		"	2.03	-4	
					1.0		"	6.93	-4	
					0.1		50	1.07	-4	
					0.4		"	5.50	-4	23.5
					1.0		"	2.05	-3	24.2
					0.1		60	3.67	-4	23.2
				H_2SO_4	0.2		60	9.17	-4	23.8
				H_3PO_4	1.0		"	3.75	-4	21.6
				CH_3COOH	1.0		"	7.49	-6	22.2
		40 vol %	"	HCl	0.1	kA	30	3.49	-6	
					0.4		"	1.75	-5	
					1.0		"	7.19	-5	
					4.0		"	2.40	-3	

152.461.

No.	Reaction	Solvent	AAmount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperarure	$k = k^o \times 10^n$		E
								k^o	n	
.1	$CH_3CH{:}CHCH(OH)C\vdots CH \rightarrow CH_3CH(OH)CH{:}CHC\vdots CH$	$H_2O + C_2H_5OH$ 40 vol %			0.1		40	1.28	-5	
	(continued)				0.4		"	5.64	-5	
					1.0		"	2.73	-4	
					0.1		50	3.67	-5	
					0.4		"	2.49	-4	25.1
					1.0		"	8.63	-4	24.7
					0.1		60	9.48	-5	22.7
				H_2SO_4	0.2		60	3.35	-4	
				H_3PO_4	1.0		"	1.11	-4	
				CH_3COOH	1.0		"	1.65	-6	
		60 vol %		HCl	0.1	k A	30	9.71	-7	
					0.4		"	5.43	-6	
					1.0		"	2.55	-5	
					4.0		"	1.77	-3	
					0.1		40	3.71	-6	
					0.4		"	2.27	-5	
					1.0		"	8.30	-5	
					0.1		50	1.35	-5	
					0.4		"	7.16	-5	24.7
					1.0		"	2.87	-4	25.8
					0.1		60	4.68	-5	25.7
				H_2SO_4	0.2		60	1.24	-4	
				H_3PO_4	1.0		"	2.63	-5	
				CH_3COOH	1.0		"	4.17	-7	

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
								k^o	n	
.1	$CH_3CH{:}CHCH(OH)C{\vdots}CH \rightarrow CH_3CH(OH)CH{:}CHC{\vdots}CH$ *(continued)*	$H_2O + C_2H_5OH$ 80 vol %		HCl	0.1	k A	30	3.50	-7	
					0.4		"	1.87	-6	
					1.0		"	8.46	-6	
					0.1		40	1.42	-6	
					0.4		"	7.62	-6	
					1.0		"	3.64	-5	
					0.1		50	5.33	-6	
					0.4		"	3.33	-5	27.2
					1.0		"	1.21	-4	26.5
					0.1		60	1.67	-5	25.7
				H_2SO_4	0.2		60	5.38	-5	
				H_3PO_4	1.0		"	4.53	-6	
				CH_3COOH	1.0		"	3.33	-8	
		C_2H_5OH		HCl	1.0	k A	30	7.84	-5	
							40	2.60	-4	
							50	7.84	-4	22.5
				CH_3COOH	1.0		60	2.33	-8	
		H_2O		CH_3COOH	1.0		60	2.38	-5	

COMMENTS

Spectrophotometric determinations. Up to 80 vol % C_2H_5OH, and except with high HCl (= 4 M/l), the rate constant is related to dielectric constant ϵ by $\log k = m\epsilon + n$, with the following values of m and n (k in sec^{-1}):

Catalyst		*Temperature*	$10^2 m$	n
HCl	0.1	30	4.69	-4.17
	0.4	"	4.39	-3.27
	1.0	"	3.85	-1.197
	0.1	40	4.68	-3.347
	0.4	"	4.44	-2.573
	1.0	"	4.19	-1.873
	0.1	50	4.20	-2.601
	0.4	"	3.93	-1.853
	1.0	"	4.00	-1.166
	0.1	60	3.93	-1.897
H_2SO_4	0.2	60	3.74	-1.346
H_3PO_4	1.0	60	5.28	-2.580
CH_3COOH	1.0	60	6.21	-4.76

The rearrangement of the oxonium ion AH^+ is considered to be rate determining.

Previous data of E. R. H. Jones, J.,T. McCombie, *CSL* **1943**, 261, vitiated by heterogeneity, are not included.

LITERATURE

E. A. Braude, E. R. H. Jones, *CSL* **1944**, 436; E. A. Braude, *CSL* **1944**, 443.

ISOMERIZATION

H Substitution by NH_2 from side chain in aromatic ring

Liquid phase

Amounts are in M/1000 g

Rates are in M/1000 g per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
								k^o	n
.1	$C_6H_5NH \cdot N_2 \cdot C_6H_5 \longrightarrow p\text{-}NH_2C_6H_4 \cdot N_2 \cdot C_6H_5$	$C_6H_5NH_2$	0.25	HCl	0.025	k A	25	1.08	-6
					0.05		"	2.05	-6
					0.1		"	4.39	-6
					0.025	"	45	1.51	-5
					0.05		"	2.93	-5
					0.1		"	5.72	-5
					0.2		"	1.15	-4
			"	HBr	0.025	"	25	1.72	-6
					0.05		"	3.67	-6
					0.1		"	7.86	-6
					0.025	"	45	2.33	-5
					0.05		"	4.83	-5
					0.1		"	1.05	-4
					0.2		"	2.32	-4
		"	"	HNO_3	0.025	"	25	1.41	-6
					0.05		"	2.87	-6
					0.1		"	6.06	-6
					0.025	"	45	1.98	-5
					0.05		"	4.18	-5
					0.1		"	8.39	-5

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
								k^o	n
.1	$C_6H_5NH{\cdot}N_2{\cdot}C_6H_5 \rightarrow p\text{-}NH_2C_6H_4{\cdot}N_2{\cdot}C_6H_5$ *(continued)*	$C_6H_5NH_2$	0.25	$o\text{-}OHC_6HCOOH$	0.025	kA	25	1.85	−7
					0.05		"	4.21	−7
					0.1		"	1.00	−6
					0.2		"	2.41	−6
			"		0.025	"	45	2.05	−6
					0.05		"	4.46	−6
					0.1		"	1.02	−5
					0.2		"	2.62	−5
		"	"	$o\text{-}NO_2C_6H_4COOH$	0.025	"	45	1.17	−6
					0.05		"	2.60	−6
					0.1		"	6.22	−6
		"	"	$m\text{-}NO_2C_6H_4COOH$	0.025	"	45	2.46	−7
					0.05		"	6.33	−7
					0.1		"	1.55	−6
			"	$o\text{-}BrC_6H_4COOH$	0.025	"	45	2.90	−7
					0.05		"	5.53	−7
					0.1		"	1.42	−6
					0.2		"	4.16	−6
		$p\text{-}CH_3C_6H_4NH_2$	0.25	HBr	0.1	"	45	1.08	−5
				HCl	"		"	6.78	−6
				$(NO_3)_3C_6H_2OH$	"		"	1.41	−5
				$o\text{-}NO_2C_6H_4COOH$	"		"	1.11	−6
				$m\text{-}NO_2C_6H_4COOH$	"		"	3.96	−7
				$o\text{-}BrC_6H_4COOH$	"		"	3.88	−7

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$	
								k°	n
.1	$C_6H_5NH \cdot N_2 \cdot C_6H_5 \rightarrow p\text{-}NH_2C_6H_4 \cdot N_2 \cdot C_6H_5$ *(continued)*	$m\text{-}ClC_6H_4NH_2$	0.25	HBr	0.1	*k* A	25	4.74	-5
				$o\text{-}NO_2C_6H_4COOH$	"		"	9.64	-7
				$m\text{-}NO_2C_6H_4COOH$	"		"	1.85	-7
				$o\text{-}BrC_6H_4COOH$	"		"	1.66	-7

COMMENTS

In $C_6H_5NH_2$, at 45° C, k can be represented as a function of the concentration c of the catalyst, by $k = ac + bc^2$, with the following empirical values of a and b:

Catalyst	*a*	*b*
HCl, HBr	9.11×10^{-4}	1.27×10^{-3}
$o\text{-}OHC_6H_4COOH$	7.60×10^{-5}	2.63×10^{-4}
$o\text{-}NO_2C_6H_4COOH$	4.15×10^{-5}	2.07×10^{-4}
$m\text{-}NO_2C_6H_4COOH$	9.52×10^{-6}	6.20×10^{-5}
$o\text{-}BrC_6H_4COOH$	7.79×10^{-6}	6.39×10^{-5}

Other acids in original.

LITERATURE

H. Goldschmidt, R. W. Reinders, *BDC* 1896, **29**, 1369, 1899; H. Goldschmidt, S. Johnsen, E. Overwein, *ZPC* 1924, **110**, 251; H. Goldschmidt, *ZEC* 1930, **36**, 662.

ISOMERIZATION

Liquid phase

H substitution by halogen (X) from NX group in aromatic ring

Amounts are in M/1000 g.

Rates are per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
								k^o	n
.1	$C_6H_5NICHO \rightarrow$ *p*-IC_6H_4NH	$C_6H_5OCH_3$	0.010	$CH_2ClCOOH$	0.297	kA	25	1.32	-4
					1.26		"	6.15	-4
		"	"	$CHCl_2COOH$	0.381	"	25	2.34	-4
					0.926		"	6.41	-4
		"	"	$(CH_3)_3CCOOH$	2.46	"	25	4.02	-4
					5.84		"	9.38	-4
		"	"	C_6H_5COOH	1.85	"	25	2.38	-4
					7.98		"	1.15	-3
				o-$NO_2C_6H_4COOH$	0.523	"	25	2.34	-4
					1.13		"	5.94	-4
				m-$NO_2C_6H_4COOH$	0.704	"	25	1.11	-4
					3.16		"	1.17	-3
				$C_6H_5CH:CHCOOH$	1.49	"	25	1.53	-4
					6.94		"	6.98	-4
				2,4,6-$Cl_3C_6H_4COOH$	4.06	"	25	4.60	-4
					8.12		"	6.13	-4

152.752.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
								k^o	n
.2	$C_6H_5NClCOCH_3 \longrightarrow o,p\text{-}ClC_6H_4NHCOCH_3$	C_6H_5Cl	0.005	$CH_2ClCOOH$	0.116	kA	100	5.76	-6
					0.466		"	2.53	-5
			"	$CHCl_2COOH$	0.097	"	100	2.18	-5
					0.499		"	1.64	-4
				$o\text{-}NO_2C_6H_4COOH$	0.047	"	100	8.41	-6
					0.156		"	2.80	-5
				$p\text{-}NO_2C_6H_4COOH$	0.112	"	100	1.53	-6
					0.430		"	1.11	-5
				$C_6H_5CH_2COOH$	0.456	"	100	6.13	-6
					1.043		"	1.80	-5

COMMENTS

Initially first order; (.1) self-accelerating or self-inhibiting, (.2) self-accelerating owing to formation of traces of · HCl.

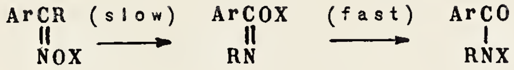
LITERATURE

R. P. Bell, P. V. Danckwerts, *CSL* **1939**, 1774.

ISOMERIZATION

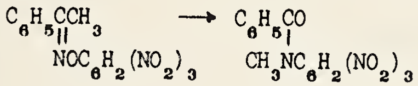
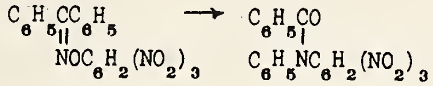
Beckmann rearrangement

Liquid phase

Reaction type 
$\underset{\substack{\Vert \\ NOX}}{ArCR} \xrightarrow{(slow)} \underset{\substack{\Vert \\ RN}}{ArCOX} \xrightarrow{(fast)} \underset{\substack{\vert \\ RNX}}{ArCO}$ (end product)

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Literature
								k^o	n		
.1	 $\underset{\substack{\Vert \\ NOC_6H_2(NO_2)_3}}{C_6H_5CCH_3} \longrightarrow \underset{\substack{\vert \\ CH_3NC_6H_2(NO_2)_3}}{C_6H_5CO}$	CCl_4	0.043			kA	99.3	1.30	-5		(¹)
							116	6.5	-5	~ 27	
		C_6H_6	"			"	85	2.88	-5		"
							99.1	1.26	-4	~ 27	
		CH_3Cl	"			"	75	6.5	-5		"
							85	1.92	-4	~ 27	
		$C_2H_4Cl_2$				"	65	6.8	-5		"
							75	2.04	-4		
							85	5.8	-4	~ 27	
		CH_3CN				"	60	1.03	-4		"
.2	 $\underset{\substack{\Vert \\ NOC_6H_2(NO_2)_3}}{C_6H_5CC_6H_5} \longrightarrow \underset{\substack{\vert \\ C_6H_5NC_6H_2(NO_2)_3}}{C_6H_5CO}$	CCl_4	0.078			kA	75	3.18	-5		(¹)
							85	9.6	-5		
							99.7	4.8	-4	~ 27	
		C_6H_6				"	50	9.2	-6		"
							70	1.19	-4		
							75	2.18	-4		
							79	3.37	-4	~ 27	

162.455

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Literature
								k^o	n		
.2	$C_6H_5\underset{\Vert}{C}C_6H_5$ $NOC_6H_2(NO_2)_3$ $\longrightarrow$ C_6H_5CO $C_6H_5NC_6H_2(NO_2)_3$	$CHCl_3$				k A	40	4.5	-5		(1)
							45	8.8	-5		
							50	1.5	-4		
							55	2.4	-4		
							60	4.0	-4		
	(continued)	$C_2H_4Cl_2$					50	3.2	-4		"
		CCl_4	0.0225			k A	70.5	1.84	-5		(2)
							80.5	5.87	-5		
							81.0	6.30	-5		
							92.8	2.10	-4		
							100.0	4.30	-4		
		CCl_4			k A; $k = k_o + aA$			k_o		$10^5 a$	(2)
			0.0225				70.5	(1.17)	-5		
			~ 0.01 - 0.03				80.5	4.40	-5	67	
			"				81.0	4.73	-5	67	
			"				85.9	7.9	-5		
			"				92.8	1.68	-4	190	
			"				100.0	3.41	-4	392	
		"	0.0225	c =	k A; $k = k_o + ac + bc^2$			k_o		$10^5 a$	$10^5 b$
				CH_3CN	0.3 - 0.6		81.0	4.73	-5	52	24
				$(CH_3)_2CO$	0.25 - 0.5		"	"		25	9.5
				C_4H_9Cl	0.38 - 0.73		"	"		5.3	
		"	0.0225	CH_3NO_2	0.0 - 1.0		70.5	1.17	-5	13.3	13
							81.0	4.73	-5	36.5	39
							92.8	1.68	-4	118	80
		"	0.0225	C_2H_4Cl	0.0 - 0.96		81.0	4.73	-5	6.8	2.4
					0.0 - 0.8		91.0			17.8	6.1
					0.0 - 0.38		100.1			40.5	9.3

COMMENTS

The increase of the first-order k with the concentration of A indicates self-catalysis by A itself, representable by $k = k_o + a\,A$ (2). In the presence of extraneous catalysts (concentration c), $k = k_o + ac + bc^2$, where k_o = rate constant of the uncatalyzed reaction. Data for further catalysts in original (2).

LITERATURE

(1) A. W. Chapman, C. C. Howis, *CSL* **1933**, 806.
(2) A. W. Chapman, *CSL* **1934**, 1550.

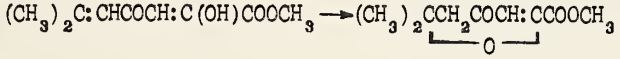
ISOMERIZATION

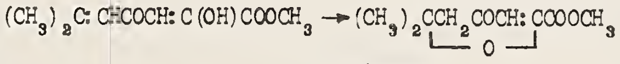
Double bond to Closed ring

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$ k°	n
.1	 $(CH_3)_2C{:}CHCOCH{:}C(OH)COOCH_3 \longrightarrow (CH_3)_2\underbrace{CCH_2COCH{:}C}_{O}COOCH_3$	C_6H_5Cl	0.01	X =		k A; $k = k_c k'X/(k' + k_cX) + aX$	99.0		
				$(C_2H_5)_3N$	0.003 - 0.1		k_c	2.37	-3
							k'	1.67	-4
							a	0	
				$(CH_3)_3N$	0.01 - 0.2		k_c	3.43	-3
							k'	3.00	-4
							a	0	
				$C_6H_5CON(C_2H_5)_2$	0.05 - 0.35		k_c	1.97	-4
							k'	1.12	-4
							a	0	
				$CHCl_2COOH$	0.001 - 0.2		k_c	4.18	-1
							k'	2.42	-3
							a	1.17	-3
				o-$NO_2C_6H_4COOH$	0.001 - 0.008		k_c	1.92	-1
							k'	2.39	-4
							a	0	
				C_6H_5COOH	0.003 - 0.2		k_c	4.18	-2
							k'	2.29	-4
							a	0	

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n
.1	 $(CH_3)_2C{:}CHCOCH{:}C(OH)COOCH_3 \rightarrow (CH_3)_2\underbrace{CCH_2COCH}_{O}{:}COOCH_3$ *(continued)*	C_6H_5Cl	0.01	$X = CH_3COOH$	0.003 - 0.2	k A; $k = k_c k'X/(k' + k_cX) + aX$		k_c 1.78 k' 2.22 a 0	-2 -4

COMMENTS

Selected bases and acids For basic catalysts and weak acids, $a = 0$. For basic catalysts, k are corrected for heterogeneous catalysis by glass; for acid catalysts, k are corrected for the heterogeneous inhibition by glass.

LITERATURE

R. P. Bell, S. M. Rybicka, *CSL* 1947, 24.

ISOMERIZATION

Ring closing - Ionization

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

Reaction type $ClCH_2(CH_2)_nSC_2H_5 \longrightarrow [\underline{CH_2(CH_2)_n\overset{+}{S}}C_2H_5]Cl^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$ClCH_2CH_2CH_2CH_2CH_2SC_2H_5$	$H_2O + (CH_3)_2CO$ 50 %	0.024	*k*A	68.6 80.4 88.6 (100)	7.5 1.8 3.8 (8.8)	-5 -4 -4 -4
.2	$ClCH_2CH_2CH_2CH_2CH_2CH_2SC_2H_5$	$H_2O + (CH_3)_2CO$ 50 %	0.0014 - 0.025	*k*A	100 116	1.17 4.54	-4 -4

COMMENTS

Analysis for Cl^-. (.1) *k* at 100°C extrapolated.

LITERATURE

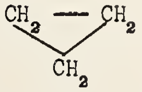
G. M. Bennett, E. G. Turner, *CSL* 1938, 813.

ISOMERIZATION

Ring opening to Double bond

Gas phase

Amounts are in mm Hg.
Rates and rate constants
are per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
					k^o	n		A^o	n		
.1	 → $CH_3CH{:}CH_2$	600	kA	440	1.5	-4				*	(1)(2)
		"		480	1.9	-4					
		"		500	5.6	-4					
		"		520	1.7	-3	65.0	2	15		(1)
		910	kA	500	5.7	-4				*	(2)
		703		"	5.9	-4					(1)
		600		"	5.6	-4					(2)
		383		"	6.3	-4					(1)
		251		"	5.2	-4					(2)
		109		"	5.1	-4					(2)
		10		"	3.4	-4					(2)

COMMENTS

Selected values. Proof of homogeneity given. H_2, C_2H_4, C_3H_8, have little effect on the rate. Decomposing C_4H_{10} accelerates the reaction. Data of (1) in essential agreement with (2). Rate-determining step assumed to be (1) $A \longrightarrow -CH_2CH_2CH_2-$, followed by (2) $-CH_2CH_2CH_2- \longrightarrow A$, (3) $-CH_2CH_2CH_2- \longrightarrow L$, (4) $-CH_2CH_2CH_2 + A \longrightarrow 2L$; $-dA/dt = k_1A\,(k_3 + 2k_4A)/(k_2 + k_3 + k_4A)$.

LITERATURE

(1) Chambers, G.B.Kistiakowsky, *ACS* 1934, 56, 399.

(2) E.S.Corner, R.N.Pease, *ACS* 1945, **67**, 2067.

ESTERIFICATION

Gas phase

Aliphatic acid anhydride + Alcohol

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant		Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$	$10^3A = 2.32$;	$10^3B = 2.68$	kAB	79.2	2.1	-3
		5.64	5.13		"	8.5	-3
		4.42	11.61		"	1.79	-2
		27.19	30.18		"	1.56	-2
		39.08	24.77		"	1.18	-2
		43.43	43.60		"	2.52	-2

COMMENTS

No marked change of k by change of the surface/volume ratio.

LITERATURE

E. A. Moelwyn-Hughes, C. N. Hinshelwood, *CSL* **1932**, 230.

ESTERIFICATION

Aliphatic carboxylic acid + Alcohol

Liquid phase

Reaction type $\underset{(A)}{RCOOH} + \underset{(B)}{R'OH} \rightarrow \underset{(L)}{RCOOR'} + \underset{(M)}{H_2O}$

Rate measured $-dA/dt = +dL/dt$

G* = Goldschmidt equation, $kA[H^+]r/(M + r)$; $r = [BH^+][M]/[MH^+]$

All rates are in M/l per sec.
All amounts in M/l.

Comments, Literature, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.1	$HCOOH + CH_3OH$	B	0.5	HCl	0.005	G*	0	1.84	-1	0.11				*	(14)
							20	6.32	-1	0.20					"
							30	1.10	0	0.25					"
							40	1.73	0	0.32	10.0	1.7	7		"
.2	$CH_3COOH + CH_3OH$	B	0.1	HCl	0.005	G*	20	4.93	-2	0.20				*	(19)
							30	9.02	-2	0.25					"
							40	1.53	-1	0.32					"
							50	2.48	-1	0.42	10.2				"
		B	0.5	HCl	0.001 - 0.005		0	1.18	-2	0.15					(19)
						G*	14	3.25	-2	0.18					"
							20	4.41	-2	0.20				(14)	"
							25	6.01	-2	0.22					"
							30	7.99	-2	0.25				(14)	"
							35	1.04	-1	0.31					"
							40	1.32	-1	0.32				(14)	"
							45	1.68	-1	0.49					"
							50	2.14	-1	0.42	10.2	1.2	6	(14)	"
							100	1.89	0		10.2	1.8	6		(9)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.2	$CH_3COOH + CH_3OH$ *(continued)*	B	1.0	HCl	0.001 - 0.005		0	1.06	-2	0.15				*	$(^{19})$
						G^*	14	2.89	-2	0.18					"
							25	5.52	-2	0.22					"
							45	1.47	-1	0.49					"
		$B + H_2O$(M/l)	0.1			G^*								*	$(^{2})$
		0		HCl	0.05		25	6.20	-2	0.21				*	$(^{2})$
		1					25	9.75	-3	0.21					"
		2					25	4.85	-3	0.21					"
.3	$CH_3COOH + CH_3OH$	B	0.1 - 1.0		-	$k A^2$	25	2.13	-7	-					$(^{13})$
							70	4.13	-6						"
							100	(7.6)	-6		(13.0)	(3.4)			$(^{9})$
							109	1.47	-5						$(^{13})$
							151	6.06	-5						"
		B	0.1 - 1.0	Buffer		$k A^2 + 0.032k$									$(^{13})$
							70	1.38	-6	-					"
							100	9.46	-6						"
							109	1.83	-5						"
							151	1.53	-4		13.0				"
		PhOMe	"	-	-	$k A^{1.5} B$					11.0				$(^{13})$
.4	$CH_3COOH + C_2H_5OH$	B	0.1	HCl	0.05	G^*	25	1.56	-2					*	$(^{3})$
.5	$CH_3COOH + C_2H_5OH$	B	1.0	-	-	$k A^2$	100	5.7	-6	-	15.2	4.9	3	*	$(^{1})$
		H_2O	1.0	-	-	$k AB$	50	2.34	-7	-					$(^{12})$
							60	4.20	-7						"
	(see Supplementary Table)						70	7.98	-7						"
							75	1.27	-6		13.8	4.6	2		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		r	E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n			A°	n		
.6	$CH_3COOH + C_3H_7OH$	$B + H_2O$(M/1)	0.1			G*									
		0		HCl	0.1		25	2.74	-3	0.11				*	(6)
		0.1			"		"	2.63	-3	"					"
		0.5			"		"	2.30	-3	"					"
		1.0			"		"	2.23	-3	"					"
.7	$CH_3COOH + (CH_3)_2CHOH$	B	1.0	-	-	$k A^2$	100	1.65	-6	-					(9)
							119	4.49	-6						"
							139	1.19	-5						"
							154	2.32	-5						"
							184	7.29	-5		15.3	1.6	3		"
.8	$CH_3COOH + C_4H_9OH$	H_2O		-	-	k AB	70	1.04	-6	-					(12)
							75	1.31	-6						"
	(see Supplementary Table)						80	1.73	-6		13.7	5.7	2		"
.9	$CH_3COOH + (CH_3)_2CHCH_2OH$	$B + H_2O$(M/1)	0.1			G*									
		0		HCl	0.1		25	1.31	-3	0.089				*	(5)
		0.4			"		"	1.25	-3	"					.
		2.0			"		"	1.46	-3	"					
.10	$CH_3COOH + (C_2H_5)(CH_3)CHOH$	H_2O		-	-	k AB	70	1.77	-7	-					(12)
							75	2.68	-7						"
							80	3.89	-7		17.5	2.5	4		"
.11	$CH_3COOH + (CH_3)_3COH$	B	1.0	-	-	$k A^2$	100	2.50	-8	-				*	(9)
							140	2.86	-7						"
							154	5.95	-7						"
							183	1.81	-6						"
							211	8.35	-6		18.8	2.7	3		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		r	E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n			A°	n		
.12	CH_3COOH + cyclo-$C_6H_{11}OH$	B	1.0	-	-	kA^2	100	3.18	-6	-	16.6	1.8	4		(^{1})
.13	$CH_3COOH + C_6H_5CH_2OH$	B	1.0	-	-	kA^2	100	7.1	-6	-					(^{9})
							119	2.08	-5						"
							140	5.82	-5						"
							154	9.49	-5		15.3	7.3	3		"
.14	$(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3COOH$	B	0.1 - 0.2	-	-	kA	50	8.0	-5	-	18.8				(^{11})
							75	6.6	-4						
		C_6H_{14}	0.158	-	-	kAB	50	1.62	-4	-				*	(^{10})
							60	3.84	-4						"
							70	1.02	-3						"
							100	2.66	-3		12.4				"
		CCl_4	0.1	-	-	kAB	50	2.6	-4	-				*	(^{10})
							60	6.28	-4						"
							70	1.14	-3						"
							100	4.50	-3		13.2				"
.15	$CH_2OHCOOH + C_2H_5OH$	B	0.1	HCl	0.05	G*	25	2.16	-2						(^{3})
.16	$CCl_3COOH + C_6H_5CH_2OH$	B	1.0	-	-	kA^2	24	2.94	-6	-				*	(^{9})
							35	6.42	-6						"
							53	2.11	-5						"
							65	4.73	-5						"
							78	9.15	-5						"
							100	2.76	-4		13.1	1.5	4		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		r	E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n			A°	n		
.17	$C_2H_5COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	4.00	-2	0.20				*	(14)
							25	5.73	-2	0.22					"
							30	6.70	-2	0.25					"
							40	1.11	-1	0.32					"
							50	1.93	-1	0.42	10.0	1.0	6		"
		B	0.1	HCl	0.002 - 0.006		20	(3.8)	-2	0.18	(11.6)	(9.1)	5	*	(1)
						G^*	20	4.23	-2	0.20					(17)
							30	7.58	-2	0.25					"
							40	1.31	-1	0.34					"
							50	2.07	-1	0.48	10.0				"
.18	$C_2H_5COOH + C_2H_5OH$	B	0.1	HCl	0.05	G^*	25	1.01	-2						(3)
.19	$C_2H_5COOH + C_2H_5OH$	B	1.0	-	-	kA^2	100	4.47	-6	-	15.0	2.9	3	*	(1)
											(75 - 153°)				
.20	$C_2H_5COOH + (CH_3)_2CHCH_2OH$	B	0.1	HCl	0.1	G^*	25	8.81	-4	0.089				*	(5)
.21	C_2H_5COOH + *cyclo*-$C_6H_{11}OH$	B	1.0	-	-	kA^2	100	2.24	-6	-	16.5	1.7	4	*	(1)
											(100 - 154°)				
.22	$C_3H_7COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.11	-2	0.20				*	(14)
							25	2.90	-2	0.22					"
							30	3.72	-2	0.25					"
							40	6.52	-2	0.32					"
							50	1.03	-1	0.42	10.0	5.7	5		"
		B	0.1	HCl	0.002 - 0.006		20	(2.28)	-2	0.16	(11.8)	1.5	7		(1)
											(75 - 150°)				

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.22	$C_3H_7COOH + CH_3OH$ *(continued)*	B	0.1	HCl	0.005	G^*	20	2.15	-2	0.20				*	(17)
							30	3.81	-2	0.25					"
							40	6.70	-2	0.34					"
							50	1.08	-1	0.48	10.0				"
		$B + H_2O(M/1)$	0.1			G^*									
		0		HCl	0.05		25	2.86	-2	0.21				*	(2)
		1					25	4.54	-3	"					
		2					25	2.20	-3	"					
.23	$C_3H_7COOH + C_2H_5OH$	B	0.1	HCl	0.05	G^*	25	5.30	-3						(3)
.24	$C_3H_7COOH + C_2H_5OH$	B	1.0	-	-	kA^2	100	3.0	-6	-	14.8	1.5	3	*	(1)
											(75 - 154°)				
.25	$C_3H_7COOH + C_3H_7OH$	$B + H_2O(M/1)$	0.1			G^*									
		0 - 0.1		HCl	0.1		25	8.82	-4	0.11				*	(6)
.26	$C_3H_7COOH + (CH_3)_2CHCH_2OH$	$B + H_2O(M/1)$	0.1			G^*									
		0		HCl	0.1		25	3.98	-3	0.089				*	(5)
		0.2					"	4.47	-3						
		2.0					"	6.08	-3						
.27	$C_3H_7COOH +$ *cyclo*-$C_6H_{11}OH$	B	1.0	-	-	kA^2	100	1.59	-6	-	15.7	2.7	3	*	(1)
											(100 - 154°)				
.28	$(CH_3)_2CHCOOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	1.47	-2	0.18				*	(15)
							30	2.63	-2	0.23					"
							40	4.40	-2	0.30					"
							50	7.27	-2	0.42					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		r	E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n			A°	n		
.28	$(CH_3)_2CHCOOH + CH_3OH$ *(continued)*	$B + H_2O$ (M/1)	0.1			G*									
		0		HCl	0.05		25	1.98	-2	0.21				*	(²)
		1					"	3.36	-3	"					"
		2					"	1.72	-3	"					"
.29	$(CH_3)_2CHCOOH + C_2H_5OH$	B	0.1	HCl	0.05	G*	25	4.04	-3						(³)
.30	$(CH_3)_2CHCOOH + (CH_3)_2CHCH_2OH$	$B + H_2O$ (M/1)	0.1			G*									
		0		HCl	0.1		25	2.60	-4	0.089				*	(⁵)
		1.0					"	2.81	-4	"					
		2.0					"	3.31	-4	"					
.31	$C_4H_9COOH + CH_3OH$	B	0.5	HCl	0.005	G*	20	2.14	-2	0.18				*	(¹⁴)
							25	3.08	-2	0.21					"
							30	4.02	-2	0.23					"
							40	6.55	-2	0.30					"
							50	1.03	-1	0.42	10.0	5.7	5		"
		B	0.1	HCl	0.005	G*	20	2.25	-2	0.20					(¹⁷)
							30	4.15	-2	0.25					"
							40	7.12	-2	0.34					"
							50	1.14	-1	0.48	10.2				"
.32	$C_4H_9COOH + C_2H_5OH$	B	0.1	HCl	0.05	G*	25	5.07	-3						(³)
.33	$(CH_3)_2CHCH_2COOH + CH_3OH$	B	0.5	HCl	0.005	G*	20	4.88	-3	0.18				*	(¹⁵)
							30	8.77	-3	0.23					"
							40	1.54	-2	0.30					"
							50	2.48	-2	0.42					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		r	E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n			A°	n		
.33	$(CH_3)_2CHCH_2COOH + CH_3OH$ *(continued)*	$B + H_2O$(M/1)	0.1			G^*									
		0		HCl	0.05		25	7.45	-3	0.21				*	(2)
		1					"	1.25	-3	"					"
		2					"	6.66	-4	"					"
.34	$(CH_3)_2CHCH_2COOH + C_2H_5OH$	B	0.1	HCl	0.05	G^*	25	1.21	-3						(3)
.35	$(CH_3)_2CHCH_2COOH + C_3H_7OH$	$B + H_2O$(M/1)	0.1			G^*									
		0		HCl	0.1		25	1.77	-4	0.11				*	(6)
		1.0					"	2.17	-4	"					"
		2.0					"	2.28	-4	"					"
.36	$(CH_3)_2CHCH_2COOH + (CH_3)_2CHCH_2OH$	$B + H_2O$(M/1)	0.1			G^*									
		0		HCl	0.1		25	7.17	-5	0.089				*	(5)
		1.0			"		"	1.24	-4	"					
		2.0			"		"	1.43	-4	"					
.37	$C_2H_5CH(CH_3)COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	4.05	-3	0.18				*	(15)
							30	7.20	-3	0.23					"
							40	1.31	-2	0.30					"
							50	2.19	-1	0.42					"
.38	$(CH_3)_3CCOOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	1.40	-3					*	(16)
							30	2.68	-3						"
							40	4.93	-3						"
							50	8.58	-3		11.4				"
.39	$(CH_3)_3CCOOH + C_2H_5OH$	B	0.1	HCl	0.05	G^*	25	2.44	-5						(3)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		r	E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n			A°	n		
.40	$C_5H_{11}COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.19	-2	0.18				*	(14)
							30	3.91	-2	0.25					"
							40	6.54	-2	0.30					"
							50	1.02	-1	0.42	10.0	5.7	5		"
		B	0.1	HCl	0.002 - 0.006		20	(2.08)	-2	0.14	(11.7) (75 - 154°)	(1.1)	6	*	(1)
		B	0.1	HCl	0.005	G^*	20	2.42	-2	0.20				*	(17)
							30	4.26	-2	0.25					"
							40	7.19	-2	0.34					"
							50	1.17	-1	0.48	9.9				"
.41	$C_5H_{11}COOH + C_2H_5OH$	B	1.0	-	-	$k\,A^2$	100	3.38	-6	-	15.1 (75 - 154°)	2.57	3	*	(1)
.42	$C_5H_{11}COOH +$ *cyclo*-$C_6H_{11}OH$	B	1.0	-	-	$k\,A^2$	100	1.89	-6	-	15 (100 - 154°)	1.25	2	*	(1)
.43	$(CH_3)_2CH(CH_2)_2COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.24	-2					*	(15)
							30	3.83	-2						
							40	6.34	-2						
							50	1.04	-1						
.44	$C_2H_5CH(CH_3)CH_2COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	4.63	-3					*	(16)
							30	8.05	-3						"
							40	1.43	-2						"
							50	2.40	-2		10.4				"

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.45	$(C_2H_5)_2CHCOOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	3.51	-4					*	$(^{16})$
							30	7.11	-4						"
							40	1.32	-3						"
							50	2.53	-3		12.4				"
.46	$C_6H_{13}COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.11	-2	0.11				*	$(^{14})$
							30	3.80	-2	0.20					"
							40	6.52	-2	0.25					"
							50	1.00	-1	0.42	10.0	5.7	5		"
		$B + H_2O$(M/l)	0.1			G^*									
		0		HCl	0.05		25	2.88	-2	0.21				*	$(^{2})$
		1					"	4.88	-3	"					"
		2					"	2.48	-3	"					"
.47	$C_6H_{13}COOH + C_2H_5OH$	B	0.1	HCl	0.05	G^*	25	5.11	-3						$(^{3})$
.48	$C_6H_{13}COOH + (CH_3)_2CHCH_2OH$	$B + H_2O$(M/l)	0.1			G^*								*	
		0		HCl	0.1		25	4.03	-4	0.089				*	$(^{5})$
		1.0			"		"	4.96	-4	"					
		2.0			"		"	5.82	-4	"					
.49	$(C_3H_7)_2CHCOOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.97	-4					*	$(^{16})$
							30	6.31	-4						"
							40	1.22	-3						"
							50	2.27	-3		12.4				"

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		r	E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k	n			A°	n		
.50	$C_8H_{17}COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.1	-2	0.11				*	$(^{14})$
							40	6.5	-2	0.25	10.0	5.7	5		"
		B	0.1	HCl	0.002 - 0.006		20	(1.98)	-2	0.39	(11.3) (0 - 45°)	(1.56)	6	*	$(^{1})$
.51	$C_8H_{17}COOH + C_2H_5OH$	B	1.0	-	-	kA^2	100	3.8	-6	-	14.9 (75 - 153°)	2.19	3	*	$(^{1})$
.52	$C_8H_{17}COOH$ + *cyclo*-$C_6H_{11}OH$	B	1.0	-	-	kA^2	100	1.9	-6	-	15.4 (100 - 153°)	2.16	3	*	$(^{1})$
.53	$(C_4H_9)_2CHCOOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.67	-4					*	$(^{16})$
							30	5.53	-4						"
							40	1.10	-3						"
							50	2.07	-3		12.9				"
.54	$[(CH_3)_2CHCH_2]_2CHCOOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	1.40	-4					*	$(^{16})$
							30	2.80	-4						"
							40	5.47	-4						"
							50	1.05	-3		12.6				"
.55	$C_{11}H_{23}COOH + CH_3OH$	B	0.1	HCl	0.005	G^*	20	2.23	-2	0.20				*	$(^{17})$
							30	4.04	-2	0.25					"
							40	6.89	-2	0.34					"
							50	1.13	-1	0.48	10.2				"
		B + H_2O(M/l)	0.1			G^*									
		0		HCl	0.05		25	2.88	-2	0.21				*	$(^{2})$
		1					"	4.70	-3	"					"
		2					"	2.39	-3	"					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.56	$C_{11}H_{23}COOH + (CH_3)_2CHCH_2OH$	$B + H_2O$(M/1)	0.1			G*									
		0		HCl	0.1		25	3.84	-4	0.089				*	(5)
		1.0			"		"	4.74	-4	"					"
.57	$C_{15}H_{31}COOH + CH_3OH$	B	0.1	HCl	0.002 - 0.006	G*	20	2.2	-12	0.13	11.8 (0 - 45°)	1.5	7	*	(1)
.58	$C_{15}H_{31}COOH + C_2H_5OH$	B	1.0	-	-	kA^2	100	4.27	-6	-	15.1 (75 - 154°)	3.2	3	*	(1)
.59	$C_{15}H_{31}COOH +$ *cyclo*-$C_6H_{11}OH$	B	0.5	-	-	kA^2	100	2.09	-6	-	15.4 (100 - 154°)	2.4	3	*	(1)
.60	$C_{21}H_{43}COOH + C_2H_5OH$	B	1.0	-	-	kA^2	100	4.3	-6	-	15.1 (75 - 154°)	3.2	3	*	(1)
.61	$C_{21}H_{43}COOH +$ *cyclo*-$C_6H_{11}OH$	B	0.08	-	-	kA^2	100	2.49	-6	-	14.3 (100 - 154°)	6.3	2	*	(1)
Aryl - substituted aliphatic acid															
.62	$C_6H_5CH_2COOH + CH_3OH$	B	0.5	HCl	0.005	G*	20	1.97	-2					*	(15)
							25	2.62	-2						"
							30	3.44	-2						"
							40	5.84	-2						"
							50	9.44	-2		9.9				"
		$B + H_2O$(M/1)	0.1			G*									
		0		HCl	0.05		25	2.85	-2	0.21				*	(2)
		1					"	4.97	-3	"					
		2					"	2.39	-3	"					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.63	$C_6H_5CH_2COOH + C_2H_5OH$	B	0.1	HCl	0.05	G*	25	6.02	-3						(^{3})
.64	$C_6H_5CH_2COOH + C_3H_7OH$	B + H_2O(M/l)	0.1			G*									
		0		HCl	0.01		25	7.18	-4	0.055				*	(^{6})
		0			0.1		"	1.23	-3	0.11					"
		0.1			"		"	1.23	-3	"					"
		0.5			"		"	1.06	-3	"					"
		2.0			"		"	1.01	-3	"					"
		0	"	HBr	0.01	"	"	7.72	-4	0.055				*	"
		0			0.1		"	1.51	-3	0.11					"
		0.1			"		"	1.51	-3	"					"
		0.5			"		"	1.06	-3	"					"
		2.0			"		"	9.92	-4	"					"
		0.1	"	HI	0.1	"	"	1.40	-3	0.11					"
.65	$C_6H_5CH_2COOH + C_4H_9OH$	B + H_2O(M/l)	0.1			G*									
		0	"	HCl	0.1		25	4.20	-4	0.12					(^{4})
		0.1	"		"		"	2.24	-4	"					"
		0.2	"		"		"	1.43	-4	"					"
		1.0	"		"		"	4.00	-4	"					"
		0	"	HBr	0.1	"	25	4.72	-4	"					"
		0	"	HI	0.1	"	25	4.78	-4	"					"
.66	$C_6H_5CH_2COOH + (CH_3)_2CHCH_2OH$	B	0.1	HCl	0.005	G*	25	2.49	-4	0.035				*	(^{5})
					0.01		"	2.74	-4	0.04					"
					0.05		"	4.17	-4	0.06					"
					0.1		"	6.01	-4	0.089					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.66	$C_6H_5CH_2COOH + (CH_3)_2CHCH_2OH$ *(continued)*	B	0.1	HBr	0.1	G^*	25	3.27	-4	0.089				*	(^{5})
		"	"	HI	"	"	"	3.32	-4	"					"
		B + H_2O(M/l)	"												
		0		HCl	0.1	"	"	6.01	-4	0.089				*	(^{5})
		0.2			"		"	6.20	-4	"					"
		2.0			"		"	7.34	-4	"					"
		B		$(NO_2)_2C_6H_2OH$	0.01	"	"	1.26	-4	0.25				*	(^{5})
			0.1		0.02		"	1.03	-4	"					"
.67	$C_6H_5CH(C_2H_5)COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	1.33	-3					*	(^{18})
							30	2.45	-3						"
							40	4.46	-3						"
							50	7.78	-3		11.1				"
		"	0.1	HCl	0.005	G^*	0	3.63	-4					*	(^{9})
							24	1.90	-3						"
							34	3.36	-3						"
							44	5.54	-3						"
							54	1.07	-2						"
							100	7.80	-2		10.8	1.8	5		"
.68	$(C_6H_5)_2CHCOOH + C_6H_5CH_2OH$	B	0.1	-	-	kA^2	100	2.10	-6					*	(^{9})
							119	6.73	-6						"
							140	1.81	-5						"
							155	3.80	-5						"
							163	1.08	-4		16.3	8.9	3		"

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		r	E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n			A^o	n		
.69	$C_6H_5(CH_2)_2COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.00	-2					*	(15)
							25	2.67	-2						"
							30	3.56	-2						"
							40	5.89	-2						"
							50	9.20	-2		10.1				"
.70	$C_6H_5(CH_2)_2COOH + C_2H_5OH$	B	0.1	HCl	0.005	G^*	25	6.34	-3						(3)
.71	$C_6H_5(CH_2)_3COOH + CH_3OH$	B		HCl	0.005	G^*	20	2.01	-2					*	(15)
							25	2.67	-2						"
							30	3.52	-2						"
							40	6.08	-2						"
							50	1.00	-1		9.6				"
Cycloalkyl - substituted aliphatic acid															
.72	*cyclo*-$C_6H_{11}CH_2COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	5.25	-3					*	(18)
							30	9.79	-3						"
							40	1.70	-2						"
							50	2.79	-2		10.5				"
.73	*cyclo*-$C_6H_{11}(CH_2)_2COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	2.10	-2					*	(18)
							30	3.54	-2						"
							40	5.98	-2						"
							50	1.06	-1		10.1				"
.74	*cyclo*-$C_6H_{11}(CH_2)_3COOH + CH_3OH$	B	0.5	HCl	0.005	G^*	20	1.94	-2					*	(18)
							30	3.28	-2						"
							40	5.74	-2						"
							50	9.56	-2		10.1				"

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SUPPLEMENTARY TABLES

Effect of pressure (12)

(.5) $CH_3COOH + C_2H_5OH$

°C	10^7k					
P (atm)	50	60	70	75	*E*	*A*
1	2.34	4.20	7.98	12.7	13.77	4.58×10^2
2000	12.35	20.88	41.42	58.10	13.79	2.40×10^2
3000	25.63	47.92	81.30	125.10	13.83	6.10×10^3
3750	-	-	-	227.5	-	-
4000	60.01	101.35	193.80	-	13.98	1.61×10^4

(.8) $CH_3COOH + n\text{-}C_4H_9OH$

°C	10^7k				
P (atm)	70	75	80	*E*	*A*
1	10.41	13.07	17.27	13.7	5.69×10^2
2000	32.20	51.88	73.70	14.58	7.0×10^3
3000	74.20	100.40	145.20	14.95	2.4×10^4
3750	123.0	167.0	226.0	15.19	5.72×10^4

SUPPLEMENTARY TABLES *(continued)*

(.10) $CH_3COOH + (C_2H_5)(CH_3)CHOH$

°C	$10^7 k$				
p (atm)	70	75	80	E	A
1	1.77	2.63	3.89	17.5	2.5×10^4
2000	9.68	14.13	21.14	19.8	3.5×10^6
3000	20.65	31.75	49.20	21.0	4.9×10^7
3750	30.22	57.60	90.50	21.7	2.2×10^8

General. (G*) The Goldschmidt equation, $kA[H^+]r/(M + r)$, $r = [BH^+][M]/[MH^+]$, integrated form

$$k = \frac{1}{t[H^+]} \left[(a + r) \ln \frac{ar}{a - x} - x\right],$$

accounts for the gradual decrease of the concentration of the catalytically active BH^+ with the progress of the esterification, through its increasing replacement by the less active MH^+. The empirical values of the parameter r, used for calculation, are included beside k whenever they are stated. The catalytic effect of the acid HX, assumed to be composed of the effect of BH^+ and of B.HX, was expressed by Goldschmidt (2, 3), by representation of k as the sum of two terms, $k = k_{BH^+} \gamma + k_{BHX} (1 - \gamma)$, and the two constants given separately; these data were not included in these tables. For weak acids, at the concentration c, the ratio $k/c\alpha$, where α = degree of dissociation, is fairly constant, thus, for reactions (.2) and (.62) in catalysis by $(NO_2)_3C_6H_2OH$, $(NO_2)_3 - m\text{-}C_6H(OH)CH_3$, CCl_3COOH (7), and catalysis by $(NO_2)_3 - m\text{-}C_6H(OH)CH_3$ of the reactions (.4), (.23), (.33), (.62) (8).

Data of Goldschmidt et al. (2) to (8), were recalculated from hour to sec. On the basis of comparisons particularly with data of H.A.Smith et al. (14) to (18), it appears certain that the data of (2) to (8) have been calculated with decimal logarithms. Consequently, all k values of (2) to (8) were multiplied by 2.303; thus converted to ln, data of (2) to (8) check fairly well, at times very well with those of (14) to (18) which are rated highly reliable. The two sets of data are, thus, satisfactorily comparable and mutually complementary for reactions covered only by one of the two sets.

Data of (2) to (8) and those of (14) to (18) even though close, are tabulated separately. Data of the H. A. Smith and the Hinshelwood schools have been amalgamated whenever possible; *very close* data from different sources have been averaged and are underlined.

Uncatalyzed esterification. In the absence of a catalyzing acid, (9) finds the law kA^2 to be valid. It accounts for the catalytic action of A itself.

Order of reactions. The reactions are arranged by acids, by increasing numbers of C atoms, and subdivided into purely aliphatic, aryl-substituted and cycloalkyl-substituted acids. Bulk formulae of alkyls refer to the normal unbranched structure. Branched acids follow, in the order of increasing branching, the normal acids. Under each acid, the reactions are ordered by the alcohols, on the same principle. Acid-catalyzed and uncatalyzed reactions are numbered separately.

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ESTERIFICATION

Aromatic carboxylic acid + Alcohol

Liquid phase

Reaction type $\underset{(A)}{ArCOOH} + \underset{(B)}{R'OH} \rightarrow \underset{(L)}{ArCOOR'} + \underset{(M)}{H_2O}$

Rate measured $-dA/dt = +dL/dt$

G* = Goldschmidt equation, $kA[H^+]r/(M + r)$ $r = [BH^+][M]/[MH^+]$

Amounts are in M/l.
Rates are in M/l per sec.
Comments, Literature, at the end of the table.

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.1	$C_6H_5COOH + CH_3OH$	B		HCl	G*	25	1.92	-4				*	(3)
				0.02 - 0.1		40	6.52	-4					"
						60	2.93	-3	15.5				"
		"	0.1	"	"	0	1.67	-5				*	(5)
				0.002 - 0.006		25	1.92	-4					"
						40	6.53	-4					"
						51	1.55	-3					"
						63	3.03	-3					"
						100	4.0	-2	15.7	6.0	7		"
		"	1.0		kA^2	100	5.11	-7					"
						120	1.71	-6					"
						139	5.61	-6					"
						153	1.11	-5	18.3	3.0	4		"
.2	$C_6H_5COOH + CH_3OH$	B + H_2O(M/1)	0.1		G*								(2a)
		0		HCl 0.05		25	8.65	-5	0.21				
		1				"	1.24	-5	"				
		2				"	5.5	-6	"				
.3	$C_6H_5COOH + (CH_3)_2CHOH$	B	1.0		kA^2	100	5.3	-8				*	(5)
						139	8.49	-7					

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^o \times 10^n$		$\mathcal{B}$	$\mathcal{A} = \mathcal{A}^o \times 10^n$		Comments	Literature
							k^o	n		$\mathcal{A}^o$	n		
.3	$C_6H_5COOH + (CH_3)_2CHOH$ (*continued*)	B	1.0		kA^2	153	1.70	-6					(5)
						183	9.12	-6					"
						211	4.04	-5	21.1	1.3	5		"
.4	$C_6H_5COOH + (CH_3)_3COH$	B	1.0		kA^2	100	1.71	-10				*	(5)
						183	1.49	-7					"
						194	3.10	-7					"
						211	8.85	-7	27.5	2.3	6		"
.5	$C_6H_5COOH +$ *cyclo* $- C_6H_{11}OH$	B	0.1	HCl 0.02 - 0.1	C*	55	1.56	-5				*	(4)
						65	4.26	-5					"
						75	9.08	-5					"
						85	1.97	-4	19.5	1.7	8		"
.6	$C_6H_5COOH + C_6H_5CH_2OH$	B	1.0		kA^2	100	4.2	-7				*	(5)
						121	1.71	-6					"
						139	5.46	-6					"
						154	1.19	-5	19.7	1.8	5		"
		C_6H_6		$p - CH_3C_6H_4SO_3H$	kAB							*	(1)
		A_o =	B_o =										
		0.2	0.1	0.01		100	6.0	-5					
		0.1	0.2	"		"	5.0	-5					
		"	0.1	0.02		"	1.67	-4					
		"	"	0.01		74.3	2.1	-5					
		"	"	"		100	6.9	-5					
		"	"	"		137	2.27	-4					
		"	"	0.002		100	3.3	-5					
		"	0.01	0.005		"	3.8	-5					
		0.01	0.1	0.002		"	2.9	-5					

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^o \times 10^n$		*E*	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.7	$o - CH_3C_6H_4COOH + CH_3OH$	B		HCl 0.02 - 0.1	G*	25	5.41	-5				*	(3)
						40	2.02	-4					
						50	4.09	-4					
						60	8.14	-4					
.8	$o - CH_3C_6H_4COOH + cyclo - C_6H_{11}OH$	B	0.1	HCl 0.02 - 0.1	G*	55	7.67	-6				*	(4)
						65	1.74	-5					"
						75	3.91	-5					"
						85	8.13	-5	18.4	1.41	7		"
.9	$m - CH_3C_6H_4COOH + CH_3OH$	B	"	"	"	25	2.17	-4				*	(3)
						40	6.55	-4					"
						50	1.37	-3					"
						60	2.65	-3	14.2				"
.10	$p - CH_3C_6H_4COOH + CH_3OH$	B	"	"	"	25	1.94	-4				*	(3)
						40	5.90	-4					"
						50	1.20	-3					"
						60	2.25	-3	13.8				"
.11	$2, 4, 6 - (CH_3)_3C_6H_2COOH + C_6H_4CH_2OH$	B	1.0		$k A^2$	100	7.41	-10	27.7	1.45	7	*	(5)
.12	$o - CH_3OC_6H_4COOH + cyclo - C_6H_{11}OH$	B	"	HCl 0.02 - 0.1	G*	55	5.23	-5				*	(4)
						65	1.26	-4					"
						75	2.53	-4					"
						85	5.61	-4	18.2	7.52	7		"
.13	$m - CH_3OC_6H_4COOH + cyclo - C_6H_{11}OH$	B	"	"	"	55	1.91	-5				*	(4)
						65	5.04	-5					"
						75	1.00	-4	19.3	1.4	8		"
						85	2.39	-4					"

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.14	$p - CH_3OC_6H_4COOH$ + *cyclo* $- C_6H_{11}OH$	B	0.1	HCl 0.02 - 0.1	G*	55	7.2	-6				*	(4)
						65	1.96	-5					"
						75	3.50	-5					"
						85	1.07	-4	20.2	2.13	8		"
.15	$o - C_2H_5OC_6H_4COOH$ + *cyclo* $- C_6H_{11}OH$	B	"	"	"	55	4.62	-5				*	(4)
						65	1.17	-4					"
						75	2.42	-4					"
						85	5.34	-4	18.8	1.69	8		"
.16	$m - C_2H_5OC_6H_4COOH$ + *cyclo* $- C_6H_{11}OH$	B	"	"	"	55	1.89	-5				*	(4)
						65	5.50	-5					"
						75	1.12	-4					"
						85	2.20	-4	18.9	7.91	7		"
.17	$p - C_2H_5OC_6H_4COOH$ + *cyclo* $- C_6H_{11}OH$	B	"	"	"	55	9.0	-6				*	(4)
						65	1.97	-5					"
						75	4.62	-5					"
						85	8.49	-5	17.7	5.74	6		"
.18	$o - NO_2C_6H_4COOH + CH_3OH$	B	"	"	"	25	5.46	-6				*	(3)
						40	2.43	-5					"
						60	1.72	-4	19.0				"
		"	"		kA^2	100	3.54	-7	20.7	5.4	5	*	(5)
.19	$m - NO_2C_6H_4COOH + CH_3OH$	B	"	"	G*	25	7.28	-5				*	(3)
						40	2.34	-4					"
						50	4.81	-4					"
						60	9.36	-4	14.6				"

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
							k°	n		A°	n		
.20	p - $NO_2C_6H_4COOH + CH_3OH$	B	0.1	HCl	G*	25	8.67	-5				*	(3)
				0.02 - 0.1		40	2.74	-4					"
						50	5.77	-4					"
						60	1.15	-3	14.7				"
.21	3, 5 - $(NO_2)_2C_6H_3COOH + CH_3OH$	B	"	"	"	30	3.33	-5				*	(2)
						40	8.37	-5					"
						50	1.73	-4					"
						60	3.50	-4	15.5				"
.22	o - FC_6H_4COOH + *cyclo* - $C_6H_{11}OH$	B	"	"	"	55	2.35	-5				*	(4)
						65	5.45	-5					"
						75	1.11	-4					"
						85	2.26	-4	17.5	1.11	7		"
.23	m - FC_6H_4COOH + *cyclo* - $C_6H_{11}OH$	B	"	"	"	55	2.21	-5				*	(4)
						65	4.93	-5					"
						75	1.03	-4					"
						85	2.34	-4	18.2	3.02	7		"
.24	p - FC_6H_4COOH + *cyclo* - $C_6H_{11}OH$	B	"	"	"	55	1.48	-5				*	(4)
						65	4.43	-5					"
						75	8.37	-5					"
						85	1.53	-4	17.9	1.4	7		"
.25	o - $ClC_6H_4COOH + CH_3OH$	B	"	"	"	25	7.83	-5				*	(3)
						40	2.51	-4					"
						50	5.02	-4					"
						60	1.02	-3	14.6				"

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.26	m - $ClC_6H_4COOH + CH_3OH$	B	0.1	HCl 0.02 - 0.1	G*	25	1.24	-4				*	(3)
						40	3.83	-4					"
						50	8.04	-4					"
						60	1.57	-3	14.6				"
.27	p - $ClC_6H_4COOH + CH_3OH$	B	"	"	"	25	1.14	-4				*	(3)
						40	3.66	-4					"
						50	7.66	-4					"
						60	1.54	-3	14.6				"
.28	2, 4 - $Cl_2C_6H_3COOH + CH_3OH$	B	"	"	"	30	4.56	-5				*	(2)
						40	1.27	-4					"
						50	3.25	-4					"
						60	7.10	-4	18.3				"
.29	2, 5 - $Cl_2C_6H_3COOH + CH_3OH$	B	"	"	"	30	5.35	-5				*	(2)
						40	1.17	-4					"
						50	2.36	-4					"
						60	4.75	-4	14.5				"
.30	3, 5 - $Cl_2C_6H_3COOH + CH_3OH$	B	"	"	"	30	9.08	-5				*	(2)
						40	2.16	-4					"
						50	5.48	-4					"
						60	1.23	-3	18.1				"
.31	o - $BrC_6H_4COOH + CH_3OH$	B	"	"	"	25	5.55	-5				*	(3)
						40	1.90	-4					"
						50	3.87	-4	15.2				"
.32	m - $BrC_6H_4COOH + CH_3OH$	B	"	"	"	25	1.25	-4				*	(3)
						40	4.02	-4					"

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.32	*m* - $BrC_6H_4COOH + CH_3OH$ (*continued*)	B	0.1	HCl	C*	50	8.25	-4					(3)
				0.02 - 0.1		60	1.57	-3	14.4				"
.33	*p* - $BrC_6H_4COOH + CH_3OH$	"	"	"	"	25	1.23	-4				*	(3)
						40	4.00	-4					"
						50	8.03	-4	14.6				"
.34	*o* - IC_6H_4COOH + *cyclo* - $C_6H_{11}OH$	B	"	"	"	55	6.6	-6				*	(4)
						65	1.87	-5					"
						75	3.40	-5					"
						85	6.68	-5	17.6	4.12	6		"
.35	*m* - IC_6H_4COOH + *cyclo* - $C_6H_{11}OH$	B	"	"	"	55	3.16	-5				*	(4)
						65	7.11	-5					"
						75	1.43	-4					"
						85	2.70	-4	16.7	4.4	6		"

COMMENTS

General. (G*) The Goldschmidt equation, $kA[H^+]r/(M + r)$, $r = [BH^+][M]/[MH^+]$ accounts for the decrease of the concentration of the catalytically active BH^+ with the progress of the esterification, through its increasing replacement by the less active MH^+. The empirical values of the parameter r used for the calculations of k are given in the following. For the uncatalyzed esterification, without H^+ ions added in the form of HCl, (5) find a rate law kA^2, accounted for by a catalytic action of A itself. Values of r used for the calculation of k:

°C	25	40	50	60
r	0.22	0.36	0.50	0.65

(3) (CH_3OH)

°C	30	40	50	60
r	0.26	0.36	0.42	0.56

(2) (CH_3OH)

°C	55	65	75	85
r	0.60	0.30	0.25	0.20

(4) (*cyclo*-$C_6H_{11}OH$)

(.6) The variation of k with A_o and B_o in the data of (1) is ascribed to dimerization of both A and B and formation of AB complexes. The activation energy for the esterification (excluding association processes) is estimated to 3.5 kcal. (.8) (.12 - .17) (.22 - .24) (.26 - .27) k valid between 20 % and 80 % conversion (4).

LITERATURE

(1) M.M.Davies, *TFS* 1937, 33, 331. (2) A.G.Gassman, R.J.Hartman, *ACS* 1941, 63, 2393. (2a) H.Goldschmidt et al., *ZPC* 1926, 124, 23. (3) R.J.Hartman, A.M.Borders, *ACS* 1937, 59, 2107. (4) R.J.Hartman, R.M.Hoogsteen, J. A. Moede, *ACS* 1944, 66, 1714. (5) C.N.Hinshelwood, A.R.Legard, *CSL* 1935, 587.

ESTERIFICATION

Aliphatic alcohol, Hydrohalic acid

Liquid phase

Reaction type $\underset{(A)}{ROH} + \underset{(B)}{HX} \rightarrow \underset{(L)}{RX} + \underset{(M)}{H_2O}$

Rate law $-dB/dt = + dL/dt = kAB$

All rates are in M/l per sec.
All amounts in M/l.
Comments, Literature, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
					k^o	n			
.1	$CH_3OH + HBr$	PhOH	A = 0.05; B = 0.1; M = 0.5	80	2.97	-4			(1)
				92	1.0	-3	26.6		"
.2	$C_2H_5OH + HBr$	"	"	80	5.29	-5			(1)
				92	2.20	-4	31.3		"
.3	$C_3H_7OH + HBr$	"	"	80	4.58	-5			(1)
				92	1.95	-4	31.7		"
.4	$C_4H_9OH + HBr$	"	"	80	4.70	-5			(1)
				92	1.83	-4	29.6		"
.5	$(CH_3)_2CHCH_2OH + HBr$	"	"	80	5.98	-6			(1)
				92	2.18	-5	28.4		"
.6	$(C_2H_5)(CH_3)CHOH + HBr$	"	"	80	2.89	-4			(1)
				92	1.13	-3	29.9		"
.7	$C_5H_{11}OH + HBr$	"	"	80	4.78	-5			(1)
				92	1.93	-4	30.6		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
					k^o	n			
.8	$(CH_3)_2CHCH_2CH_2OH + HBr$	PhOH	A = 0.05; B = 0.1; M = 0.5	80	1.21	-4			(1)
				92	4.82	-4	30.1		"
.9	$C_6H_{13}OH + HBr$	"	"	80	4.76	-5			(1)
				92	1.95	-4	30.9		"
.10	$C_7H_{15}OH + HBr$	"	"	80	4.87	-5			(1)
				92	1.93	-4	30.1		"
.11	$C_8H_{17}OH + HBr$	"	"	80	4.80	-6			(1)
				92	1.83	-4	29.5		"
.12	$C_{16}H_{33}OH + HBr$	"	"	80	4.80	-5	26.6		(1)
Halogen-substituted Alcohol									
.13	$CH_2ClCH_2OH + HBr$	PhOH	A = 0.05; B = 0.1; M = 0.5	97	0				(1)
.14	$CH_2Cl(CH_2)_2OH + HBr$	"	"	97	6.3	-5	26.6		(1)
.15	$CH_2Cl(CH_2)_3OH + HBr$	"	"	97	1.25	-4	26.6		(1)
.16	$CH_2Cl(CH_2)_6OH + HBr$	"	"	97	2.85	-4	26.6		(1)
Aryl-substituted Alcohol									
.17	$(C_6H_5)_2CHOH + HCl$	$(CH_3)_2CO + H_2O$ 0.5556	A = B = 0.1	50	1.83	-4		*	(3)

No.	Reaction	Medium (Solvent)	Amount of reactant	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
					k^o	n			
.17	$(C_6H_5)_2CHOH + HCl$ *(continued)*	$(CH_3)_2CO + H_2O$	A = B = 0.1						
		1.1112		50	1.54	-4			(3)
		2.7778		"	3.53	-5			"
		5.5556		"	5.18	-6			"
.18	$\left.\begin{matrix}(C_6H_5)_2CHOH \\ (C_6H_5)_2CHOC_2H_5\end{matrix}\right\} + HCl$	$C_2H_5OH + H_2O$ %	$A_o = B_o = 0$; $L_o = 0.03 - 0.14$						
		0		25	8.5	-5		*	(2)
		0.15		"	4.33	-5			"
		0.58		"	2.00	-5			"
		1.07		"	1.5	-5			"
		2.39		"	2.5	-5			"
		7.19		"	1.13	-4			"
.19	$C_6H_5O(CH_2)_2OH + HBr$	PhOH	A = 0.05; B = 0.1; M = 0.5	97	1.31	-5	26.6		(1)
.20	$o - CH_3C_6H_4O(CH_2)_2OH + HBr$	"	"	97	1.45	-5	26.6		(1)
.21	$m - CH_3C_6H_4O(CH_2)_2OH + HBr$	"	"	97	1.37	-5	26.6		(1)
.22	$p - CH_3C_6H_4O(CH_2)_2OH + Br$	"	"	97	1.67	-5	25.5		(1)
.23	$o - ClC_6H_4O(CH_2)_2OH + HBr$	"	"	97	9.3	-5	26.6		(1)
.24	$C_6H_5O(CH_2)_3OH + HBr$	"	"	86	4.62	-5			(1)
				97	1.57	-4	24.3		"
.25	$C_6H_5O(CH_2)_4OH + HBr$	"	"	86	1.82	-4	25.8		(1)
				97	5.86	-4			"

No.	Reaction	Medium (Solvent)	Amount of reactant	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
					k^o	n			
			Bialcohol						
.26	$OH(CH_2)_2OH + HBr$	PhOH	A = 0.05; B = 0.1; M = 0.5	76	1.5	-6			(1)
				85	5.08	-5			"
.27	$OH(CH_2)_3OH + HBr$	"	"	76	6.84	-5			(1)
				85	3.12	-4			"
.28	$OH(CH_2)_4OH + HBr$	"	"	76	4.55	-4			(1)
				85	2.24	-3			"
.29	$OH(CH_2)_5OH + HBr$	"	"	76	3.95	-4			(1)
				85	1.05	-3			"
.30	$OH(CH_2)_6OH + HBr$	"	"	76	2.18	-4			(1)
				85	5.9	-4			"
.31	$OH(CH_2)_7OH + HBr$	"	"	76	2.00	-4			(1)
				85	6.41	-4			"
.32	$OH(CH_2)_8OH + HBr$	"	"	76	2.48	-4			(1)
				85	5.14	-4			"
.33	$OH(CH_2)_9OH + HBr$	"	"	76	2.56	-4			(1)
				85	6.19	-4			"
.34	$OH(CH_2)_{10}OH + HBr$	"	"	76	2.30	-4			(1)

COMMENTS

Reverse reactions, see 212.471. (.17) Data not of high precision, owing to reaction between HCl and $(CH_3)_2CO$, resulting in a decrease of HCl; allowed for in the calculation of *k*. (.18) From reverse reaction.

LITERATURE

(1) G. M. Bennett, F. M. Reynolds, *CSL* 1935, 131. (2) J. Norris, A. Morton, *ACS* 1928, 50, 1795. (3) W. Taylor, *ACS* 1938, 60, 2094.

ESTERIFICATION

Polyalcohol and Hydrogen halide

Liquid phase

Amounts are in M/l.

Rates in M/l per sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
						k^o	n	
.1	$HO(CH_2)_2OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	1.5	−6	
					85.0	5.1	−6	26.6
.2	$HO(CH_2)_3OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	6.8	−6	
					85.0	3.1	−5	26.6
.3	$HO(CH_2)_4OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	4.2	−5	
					85.0	2.2	−4	26.6
.4	$HO(CH_2)_5OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	3.9	−5	
					85.0	1.0	−4	26.6
.5	$HO(CH_2)_6OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	2.2	−5	
					85.0	5.9	−5	26.6
.6	$HO(CH_2)_7OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	2.0	−5	
					85.0	6.4	−5	26.6
.7	$HO(CH_2)_8OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	2.5	−5	
					85.0	5.1	−5	26.6
.8	$HO(CH_2)_9OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	2.5	−5	
					85.0	6.2	−5	26.6
.9	$HO(CH_2)_{10}OH + 2\ HBr$	C_6H_5OH	A = 0.05; B = 0.1; M = 0.5	k AB	75.9	2.3	−5	

LITERATURE

G.M. Bennett, F.M. Reynolds, *CSL* **1935**, 131.

ESTER SOLVOLYSIS
Alkyl ester of aliphatic carboxylic acid

Liquid phase

Reaction types: $RCOOR' + R''OH \longrightarrow RCOOH + R'OR''$
(A) (B) (L) (M)
$RCOOR + OR''^- \longrightarrow RCOO^- + R'OR''$
(A) (B) (L) (M)

Amounts are in M/l.
Rates are in M/l per sec.
*Coded solvents, Comments, Literature, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$HCOOCH_3 + H_2O$	MW*	0.05	HCl	0.05	$kA[H^+]$	25	1.0	-3	15.6	(0° - 140°)			(12)
.2	$HCOOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$kA[H^+]$	25	1.07	-6	15.6	(0° - 140°)			(12)
.3	$HC(OC_2H_5)_3 + H_2O \rightarrow HCOOC_2H_5 + 2C_2H_5OH$	$H_2O + D_2O$ (N)		$c = H^+ + D^+$		kAc							*	(2)
			0.0				15.0	3.83	-6					
			0.925				"	9.58	-6					
			1.00				"	1.03	-5					
			0.0				35.0	2.28	-5	15.7				
			0.917				"	4.80	-5					
			1.00				"	5.28	-5	14.3				
.4	$CH_3COOCH_3 + H_2O$	MW*	0.05	HCl	0.05	$kA[H^+]$	25	5.49	-5	16.2	(0° - 140°)			(12)
.5	$CH_3COOCH_3 + H_2O$	DW*		HCl	0.1 - 0.2	kA		See Supplementary Table						(8)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.6	$CH_3COOCH_3 + H_2O$	H_2O		HCl	0.1	$k\,A[HCl]$	25	1.06	-4					([8])
					"		35.3	3.23	-4	17.1				"
					0.2		25	1.01	-4					"
		"	~ 0.7	"	0.1005	$k\,A[HCl]$	25	1.09	-4				*	([10])
					0.5020		"	1.17	-4					"
					0.8275		"	1.21	-4					"
					1.800		"	1.48	-4					"
					2.429		"	1.42	-4					"
					0.1005		35	2.77	-4					"
					0.5020		"	2.95	-4					"
					0.8275		"	3.07	-4					"
					1.800		"	3.50	-4					"
					2.429		"	3.73	-4					"
.7	$CH_3COOCH_3 + H_2O$	H_2O		H_2SO_4	0.7	$k\,A$	15	3.17	-5					([9])
							25	8.68	-5	17.0				"
		D_2O 97 %		"	0.85	"	15	6.83	-5					"
							25	1.67	-4	15.8				"
.8	$CH_3COOCH_3 + OH^-$	Mw*	A = B = 0.05			$k\,AB$	25	1.37	-1	11.5	(0° - 140°)			([12])
.9	$CH_3COOC_2H_5 + H_2O$	H_2O		HCl	0.1	$k\,A[H^+]$	25	4.8	-5					([13])
							See Supplementary Table							
.10	$CH_3COOC_2H_5 + H_2O$	H_2O	A = 0.4; L = 0.1		$k\,AL^{1/2} = k'AB[H^+]$								*	([4])
							25	k 4.34	-7					
							25	k' 1.90	-6					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.11	$CH_3COOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	$kA[H^+]$	25	4.51	-5				(17)	(3)
							35	1.09	-4				*	(3)
							45	2.47	-4	16.2	3.4	7		(3)
.12	$CH_3COOC_2H_5 + OH^-$	Et85*	A = B = 0.05		–	kAB	20	4.54	-3					(16)
							25	6.21	-3					(7)
							30	1.09	-2					(16)
							35	1.36	-2					(7)
							40	2.30	-2					(16)
							50	3.87	-2	14.2				(7)
							"	4.79	-2	14.7				(16)
.13	$CH_3COOC_2H_5 + OH^-$	AW*	A = B = 0.1	–	–	kAB	25	4.65	-2					(3)
							35	8.22	-2					"
							45	1.35	-1		7.9	5		"
.14	$CH_3COOC_2H_5 + OC_2H_5^- + H_2O \rightarrow CH_3COO^- + 2C_2H_5OH$	H_2O + EtOH	0.1	–	–	kA	25	See Supplementary Table						(15)
.15	$CH_3COOC(CH_3)_3 + OH^-$	H_2O	A = 0.014 – 0.019 B = 0.002 – 0.031			kAB	6.6	4.1	-4					(22)
.16	$CH_3COOCH_2C_6H_5 + H_2O$	WA*	0.05	HCl	0.05	$kA[H^+]$	15	1.15	-5					(21)
							25	2.99	-5					"
							40	1.23	-4					"
							60	5.80	-4					"
							80	2.28	-3	16.4	3.8	7		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.17	$CH_3COOCH_2C_6H_5 + OH^-$	WA*	A = B = 0.05			kAB	-10	4.35	-3					(21)
							0	1.02	-2					"
							15	3.44	-2					"
							25	6.99	-2					"
							40	1.90	-1	12.3	8.1	7		"
.18	$CH_3COOCH_2(m\text{-}C_6H_4CH_3) + H_2O$	WA*	0.05	HCl	0.05	kA[H⁺]	15	1.08	-5					(21)
							25	2.83	-5					"
							40	1.04	-4					"
							60	4.69	-4					"
							80	2.02	-3	16.2	2.24	7		"
.19	$CH_3COOCH_2(m\text{-}C_6H_4CH_3) + OH^-$	WA*	A = B = 0.05	-	-	kAB	-10	3.31	-3					"
							0	7.78	-3					"
							15	2.63	-2					"
							25	5.66	-2					"
							40	1.50	-1	12.4	7.6	7		"
.20	$CH_3COOCH_2(p\text{-}C_6H_4CH_3) + H_2O$	WA*	0.05	HCl	0.05	kA[H⁺]	25	2.98	-5					"
							40	1.24	-4					"
							60	5.71	-4					"
							80	2.28	-3	16.2	2.52	7		"
.21	$CH_3COOCH_2(p\text{-}C_6H_4CH_3) + OH^-$	WA*	A = B = 0.05	-	-	kAB	-10	2.95	-3					"
							0	7.17	-3					"
							15	2.38	-2					"
							25	4.88	-2					"
							40	1.37	-1	12.5	7.6	7		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$k = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.22	$CH_3COOCH_2(m\text{-}C_6H_4NO_2) + H_2O$	WA*	0.05	HCl	0.05	$kA[H^+]$	15	1.07	-5					$(^{21})$
							25	2.55	-5					"
							40	1.03	-4					"
							60	4.94	-4					"
							80	1.86	-3	16.1	1.95	7		"
.23	$CH_3COOCH_2(m\text{-}C_6H_4NO_2) + OH^-$	WA*	A = B = 0.05	-	-	kAB	15	1.98	-1					"
							25	2.09	-1					"
							40	5.65	-1	11.6	8.13	7		"
.24	$CH_3COOCH_2(p\text{-}C_6H_4NO_2) + H_2O$	WA*	0.05	HCl	0.05	$kA[H^+]$	15	1.07	-5					$(^{21})$
							25	2.72	-5					"
							40	1.07	-4					"
							60	5.08	-4					"
							80	1.98	-3	16.2	2.46	7		"
.25	$CH_3COOCH_2(p\text{-}C_6H_4NO_2) + OH^-$	WA*	A = B = 0.05			kAB	15	4.59	-2					$(^{21})$
							25	1.37	-1					"
							40	6.96	-1	11.5	7.42	7		"
.26	$CH_2ClCOOC_2H_5 + H_2O$	EW*		HCl	0.05	$kA[H^+]$	25	3.95	-5					$(^{20})$
							40	1.35	-4					"
							60	6.19	-4					"
							80	2.26	-3	15.3	7.25	6		"
.26.1	$CH_2ClCOOCH(CH_3)_2 + OH^-$	H_2O	$10^4A = 4 - 8$ $10^4A = 4 - 7$			kAB	6.6	2.0	-1					$(^{22})$

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.27	$CHCl_2COOC_2H_5 + H_2O$	EW*		HCl	0.05	$k\,A[H^+]$	25	2.13	-5					(20)
							40	6.59	-5					"
							60	2.70	-4					"
							80	9.25	-4	14.3	6.6	5		"
.28	$CCl_3COOC_2H_5 + H_2O$	EW*		HCl	0.05	$k\,A[H^+]$	25	8.26	-5					(20)
							40	2.39	-4					"
							60	7.61	-4					"
							80	2.17	-3	12.2	8.7	4		(20)
.29	$N(CH_3)_2CH_2COOC(CH_3)_3 + OH^-$	H_2O	A = 0.008 - 0.016 B = 0.007 - 0.014			$k\,AB$	10.2	3.72	-4					(22)
.30	$Cl(CH_3)N(CH_3)_2CH_2COOC(CH_3)_3 + OH^-$	H_2O	A = 0.0004 - 0.002 B = 0.0004 - 0.002			$k\,AB$	10.2	3.70	-1					(22)
.31	$C_2H_5COOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	$k\,A[H^+]$	25	$\underline{3.74}$	-5				(17)	(3)
							35.0	9.24	-5					(3)
							44.7	2.07	-4	16.2	2.9	7		"
.32	$C_2H_5COOC_2H_5 + OH^-$	AW*	A = B = 0.1			$k\,AB$	24.8	2.20	-2					(3)
							35.0	4.06	-2					
							44.7	6.83	-2		1.2	6		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.33	$C_2H_5COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	20	2.32	-3				*	(16)
							25	3.63	-3					(7)
							30	5.30	-3					(16)
							35	8.31	-3					(7)
							40	1.17	-2					(16)
							50	2.47	-2	14.5				(7)
							"	2.42	-2	14.7				(16)
.34	$C_2H_5COOC_2H_5 + OC_2H_5^- + H_2O \longrightarrow C_2H_5COO^- + 2C_2H_5OH$	Et85*	0.05	-	-	kAB	25	4.37	-6					(14)
.35	$C_3H_7COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	kA[H$^+$]	20	1.14	-5				*	(18)
			0.05 - 0.1		0.05 - 0.1		25	1.83	-5			(17)	(3)	(18)
			0.1		0.1		30	2.99	-5					(18)
			0.05		0.1		35	4.83	-5					(3)
			0.1		0.1		40	6.92	-5	16.5				(18)
			0.05		0.05		44.7	1.08	-4	16.1	2.2	7		(3)
.36	$C_3H_7COOC_2H_5 + OH^-$	"	A = B = 0.1	-	-	kAB	24.8	8.81	-3					(3)
							35.0	1.68	-2					"
							44.7	2.99	-2		1.3	7		"
.37	$C_3H_7COOC_2H_5 + OH^-$	Et85*		-	-	kAB	20	1.18	-3					(16)
							25	1.72	-3					(7)
							30	2.79	-3					(16)
							35	3.94	-3					(7)
							40	6.27	-3					(16)
							50	1.33	-3	15.1				(7)
							"	1.22	-3	15.0				(16)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.38	$(CH_3)_2CHCOOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	8.65	-6					(18)
			0.05 - 0.1		0.05 - 0.1		25	1.40	-5				(13)	(18)
			0.1		0.1		30	2.07	-5					(18)
			0.05		0.05		35	3.43	-5					(3)
			0.1		0.1		40	5.03	-5	16.4				(18)
			0.05		0.05		44.7	7.46	-5	15.3	2.5	6		(3)
.39	$(CH_3)_2CHCOOC_2H_5 + OH^-$	"	A = B = 0.1	-	-	kAB	24.8	5.5	-3					(3)
							35.0	1.03	-2					"
							44.7	1.80	-2		1	6		"
.40	$(CH_3)_2CHCOOC_2H_5 + OH^-$	EW*	A = B = 0.05	-	-	kAB	25	6.24	-6	11.0				(3)
.41	$(CH_3)_2CHCOOC_2H_5 + OH^-$	Et85*		-	-	kAB	25	8.01	-4					(7)
							35	1.84	-3					"
							50	5.72	-3	14.5				"
.42	$C_4H_9COOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	$kA[H^+]$	25	1.79	-5				(17)	(3)
							35	4.45	-5				*	(3)
							45	1.02	-4	16.5	2.2	7		"
.43	$C_4H_9COOC_2H_5 + OH^-$	"	A = B = 0.1	-	-	kAB	24.8	6.59	-3					(3)
							35.0	1.33	-2					"
							44.7	2.45	-2		7.9	6		"
.44	$C_4H_9COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	1.92	-3					(7)
							35	4.42	-3					"
							50	1.33	-2	14.7				"
.45	$(CH_3)_2CHCH_2COOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	$kA[H^+]$	24.8	5.72	-6					(3)
							35.0	1.46	-5					"
							44.7	3.30	-5	16.5	7.4	6		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.46	$(CH_3)_2CHCH_2COOC_2H_5 + OH^-$	AW*	A = B = 0.1		-	kAB	24.8	2.18	-3					(3)
							35.0	4.50	-3					"
							44.7	8.63	-3		1.3	7		"
.47	$(CH_3)_2CHCH_2COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	4.27	-4					(7)
							35	1.02	-3					"
							50	3.34	-3	15.7				"
.48	$C_2H_5CH(CH_3)COOC_2H_5 + OH^-$	"	"	-	-	kAB	25	3.08	-4					(7)
							35	7.35	-4					"
							50	2.36	-3	15.4				"
.49	$(CH_3)_3CCOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	kA[H⁺]	24.8	1.28	-6					(3)
							35.0	3.63	-6					"
							44.7	1.10	-5					"
.50	$(CH_3)_3CCOOC_2H_5 + OH^-$	"	A = B = 0.1	-	-	kAB	24.8	2.23	-4					(3)
							35.0	4.56	-4					"
							44.7	8.74	-4		7.9	5		"
.51	$(CH_3)_3CCOOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	2.54	-5					(7)
							35	6.35	-5					"
							50	2.41	-4	16.5				"
.52	$C_5H_{12}COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	kA[H⁺]	20	1.10	-5					(18)
			0.05 - 0.1		0.05 - 0.1		25	<u>1.77</u>	-5				(3)	(18)
			0.1		0.1		30	2.81	-5					(18)
			0.05		0.05		35	4.30	-5					(3)
			0.1		0.1		40	6.72	-5	16.4				(18)
			0.05		0.05		44.7	9.76	-5	16.2	1.35	7		(3)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.53	$C_5H_{11}COOC_2H_5 + OH^-$	Et85*		-	-	kAB	25	2.07	-3					(7)
							35	4.81	-3					"
							50	1.45	-2	14.8				"
.54	$(CH_3)_2CHCH_2CH_2COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	4.11	-4					(16)
							35	9.63	-4					"
							45	2.20	-4					"
							55	4.65	-3	15.7				"
.54.1	$(CH_3)_2CHCH_2CH_2COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	kA[H$^+$]	20	1.04	-5					(18)
							25	1.68	-5					
							30	2.68	-5					
							40	6.16	-5					
							50	1.45	-4	16.4				
.55	$C_2H_5CH(CH_3)CH_2COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	1.86	-3					(16)
							35	4.31	-3					"
							45	9.04	-3					"
							55	1.89	-2	15.0				"
.56	$(C_2H_5)_2CHCOOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	kA[H$^+$]	24.8	1.17	-6					(3)
							35.0	3.33	-6					"
							44.7	8.69	-6	19.1	1.2	8		"
.57	$(C_2H_5)_2CHCOOC_2H_5 + OH^-$	AW*	A = B = 0.1	-	-	kAB	24.8	8.3	-5					(3)
							35.0	1.84	-4					"
							44.7	3.71	-4		2.5	6		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.58	$(C_2H_5)_2CHCOOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	1.53	-5				(16)	(7)
							35	4.35	-5				"	"
							45	9.70	-5				*	(16)
							50	1.54	-4					(7)
							55	2.15	-4	17.3				(16)
.58.1	$CH_3COC(CH_3)_2COOC_2H_5 + OH^-$	H_2O	A = 0.03 B = 0.03 - 0.04			kAB	0.0	8.1	-4					(12a)
							24.9	4.2	-3					
.59	$C_6H_{13}COOC_2H_5 + H_2O$	AW*	0.05	HCl	0.05	kA[H$^+$]	24.8	1.64	-5					(3)
							35.0	4.09	-5					"
							44.7	9.07	-5	16.2	1.3	7		"
.60	$C_6H_{13}COOC_2H_5 + OH^-$	"	A = B = 0.05	-	-	kAB	24.8	6.08	-3					(3)
							35.0	1.19	-2					"
							44.7	2.21	-2		7.9	6		"
.61	$C_6H_{13}COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	kAB	25	1.79	-3					(7)
							35	4.06	-3					"
							50	1.27	-2					"
.61.1	$C_3H_7CH(CH_3)CH_2COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	kA[H$^+$]	20	2.50	-6					(18)
							25	4.05	-6					
							30	6.46	-6					
							40	1.52	-5					
							50	3.55	-5	16.4				
.62	$C_7H_{15}COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	kA[H$^+$]	24.8	1.55	-5					(3)
							35.0	3.85	-5					"
							44.7	8.70	-5	16.3	1.4	7		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.63	$C_7H_{15}COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	k AB	25	1.84	-3					(7)
							35	4.30	-3					"
							45	1.33	-2	15.0				"
.64	$(C_3H_7)_2CHCOOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	k AB	25	1.0	-5					(17)
							35	2.8	-5					"
							45	6.5	-5					"
							55	1.54	-4	17.2				"
.64.1	$C_8H_{17}COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	k A[H⁺]	20	8.68	-6					(18)
							25	1.40	-5					
							30	2.20	-5					
							40	5.19	-5					
							50	1.18	-4	16.4				
.65	$(C_4H_9)_2CHCOOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	k A	25	1.0	-5					(17)
							35	2.5	-5					"
							45	6.3	-5					"
							55	1.53	-4	17.7				"
.66	$C_{11}H_{23}COOC_2H_5 + OH^-$	Et85*	A = B = 0.05	-	-	k AB	25	1.84	-3					(17)
							35	4.11	-3					"
							45	9.27	-3					"
							55	1.87	-2	15.1				"
Cycloalkyl-substituted aliphatic carboxylic acid														
.67	*cyclo*-$C_6H_{11}CH_2COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	k A[H⁺]	20	3.00	-6					(17)
							25	4.81	-6					"
							30	7.80	-6					"
							40	1.90	-5					"
							50	4.41	-5	16.9				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$: k^o	n	E	$A = A^o \times 10^n$: A^o	n	Comments	Literature
.68	*cyclo*-$C_6H_{11}CH_2COOC_2H_5 + OH^-$	Et85*	0.05	-	-	kAB	25	5.09	-4					(17)
							65	1.16	-2	15.6				"
Aryl-substituted aliphatic carboxylic acid														
.69	$C_6H_5CH_2COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	9.34	-6				*	(17)
							25	1.52	-5				(17)	(3)
							30	2.37	-5					(17)
							35.0	3.84	-5					(3)
							40	5.50	-5					(17)
							44.7	8.84	-5	16.2	1.2	7		(3)
							50	1.20	-4	16.1				(17)
.70	$C_6H_5CH_2COOC_2H_5 + OH^-$	Et85*	0.05	-	-	kAB	25	1.01	-2					(17)
							55	8.83	-2	14.1				"
.71	$(C_6H_5)_2CHCOOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	2.96	-8					(17)
							25	5.03	-8					"
							30	8.36	-8					"
							40	2.09	-7					"
							50	5.06	-7	17.7				"
.72	$(C_6H_5)_2CHCOOC_2H_5 + OH^-$	Et85*	A = B = 0.05		-	kAB	25	5.60	-4					(17)
							65	1.37	-2	16.0				"
.73	$CH_3CH(C_6H_5)COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	1.71	-7					(17)
							25	2.77	-7					"
							30	4.47	-7					"
							40	1.11	-6					"
							50	2.51	-6	16.9				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.74	$CH_3CH(C_6H_5)COOC_2H_5 + H_2O$	Et85*	0.05	-	-	kAB	25	8.02	-4					(17)
							65	1.76	-2	15.4				"
.75	$C_2H_5CH(C_6H_5)COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	6.69	-8					(17)
							25	1.10	-7					"
							30	1.78	-7					"
							40	4.33	-7					"
							50	1.03	-6	17.1				"
.76	$C_2H_5CH(C_6H_5)COOC_2H_5 + OH^-$	Et85*	A = B = 0.05		-	kAB	25	2.64	-4					(17)
							65	6.28	-3	15.9				"
.77	$C_6H_5(CH_2)_2COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	8.05	-8					(17)
							25	1.28	-5					"
							30	2.05	-5					"
							40	4.76	-5					"
							50	1.10	-4	16.3				"
.78	$C_6H_5(CH_2)_2COOC_2H_5 + OH^-$	Et85*	A = B = 0.05		-	kAB	25	5.04	-3					(17)
							55	4.71	-2	14.5				"
.79	$C_6H_5(CH_2)_3COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	8.00	-6					(17)
							25	1.27	-5					"
							30	2.04	-5					"
							40	4.86	-5					"
							50	1.12	-4	16.5				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.80	$C_6H_5(CH_2)_3COOC_2H_5 + OH^-$	Et85*	A = B = 0.05			kAB	25	2.69	-3					(17)
							55	2.68	-2	14.7				"
.81	$C_6H_5(CH_2)_4COOC_2H_5 + H_2O$	AW*	0.1	HCl	0.1	$kA[H^+]$	20	8.61	-6					(17)
							25	1.39	-5					"
							30	2.24	-5					"
							40	5.35	-5					"
							50	1.21	-4	16.6				"
.82	$C_6H_5(CH_2)_4COOC_2H_5 + OH^-$	Et85*	A = B = 0.05			kAB	25	2.28	-3					(17)
							55	2.19	-2	14.7				"

SUPPLEMENTARY TABLES

(.5) $CH_3COOCH_3 + H_2O$ ([8])

Solvent DW* = 1, 4 - dioxane + H_2O (x %)

HCl	°C											
0.1	25	x =	0	10	20	30		45		75	80	90
		$10^4 k$ =	1.06	1.15	1.51	1.12		1.00		0.728	0.622	0.764
		E =	17.1	16.5	16.1	16.0		-		-	15.4	16.5
0.1	35.3	x =	0	9	20		40		60		80	90
		$10^4 k$ =	3.23	2.92	2.99		2.83		2.20		1.88	2.10
0.2	25	x =	0	10	20				60	70	80	90
		$10^4 k$ =	1.01	1.10	1.16				0.884	0.744	0.669	0.758

(.9) $CH_3COOC_2H_5 + H_2O$ ([13])

Salt effects (selected data); HCl = 0.1

Salt	M/l	$10^6 k$	Salt	M/l	$10^6 k$	Salt	M/l	$10^6 k$
NaCl	1	5.82	LiBr	1	4.80	$BaCl_2$	0.33	4.96
	4	9.78		3	3.65		1.33	6.37
$NaNO_3$	1	5.10	NaBr	2	5.93	$Ca(NO_3)_2$	1.06	5.15
	6	5.83		5	7.56		2.25	5.50

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SUPPLEMENTARY TABLES *(continued)*

(.14) $CH_3COOC_2H_5 + OC_2H_5^- + H_2O \rightarrow CH_3COO^- + 2C_2H_5OH$ (15)

Solvent: $H_2O + C_2H_5OH$ (x %)

x	0	20	40	50	65	75	96
$10^6 k$	100	81.8	48.4	35.0	20.0	12.0	1.83

SOLVENTS

MW*	$CH_3OH + H_2O$ 40 ml/100 ml solution (12)
EW*	$C_2H_5OH + H_2O$ 40 ml/100 ml solution (12)
DW*	1, 4-dioxane + H_2O (x %)
Et85*	C_2H_5OH 85 % + H_2O 15 % (7)(14)(16)(17)
AW*	$(CH_3)_2CO$ 70 % + H_2O 30 % (= ~ 56 wt % $(CH_3)_2CO$) (3)(17)
WA*	$(CH_3)_2CO + H_2O$ 40 ml/100 ml solution (21)

COMMENTS

General. Activation entropy calculations, see (17). **(.3)** Original time unit presumed to be min, on the basis of other papers of the same author; converted to sec. Value of k for 100 % D_2O is extrapolated. The rate is also represented in a two-term formula, $(k_H[H^+] + k_D[D^+])A$; for the calculation of $[H^+]$ and $[D^+]$ separately, see (2) p. 613. **(.7)** Viscosity measurements. **(.10)** k constant over half of the reaction, then falls slowly. The rate equation accounts for the increasing catalysis by the H^+ ions of L,, with $[H^+] = (KL)^{1/2}$, where $K = 1.85 \times 10^{-5}$. **(.11)** k at 25°C average of close data of (17) and (3). **(.12)** Combined data of (16) and (7) at temperatures alternating by 5°C; agreement satisfactory. **(.14)** Electric conductivity measurements. **(.31) (.35) (.42) (.69)** as (.11); Data of (3) and of (18) at temperatures alternating by 5°C, in good agreement. **(.37)** as (.12). **(.38) (.52)** Data of (3) and (18) at temperatures alternating by 5°C, in good agreement. **(.58)** k at 25 and 35°C average of close data of (16) and (7).

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ESTER SOLVOLYSIS

Aromatic carboxylic acid and Aliphatic alcohol

Liquid phase

Reaction types $\underset{(A)}{\mathrm{ArCOOR}} + \underset{(B)}{\mathrm{R'OH}} \quad \underset{(L)}{\mathrm{ArCOOH}} + \underset{(M)}{\mathrm{ROR'}}$

$\underset{(A)}{\mathrm{ArCOOR}} + \underset{(B)}{\mathrm{OR'^-}} \quad \underset{(L)}{\mathrm{ArCOO^-}} + \underset{(M)}{\mathrm{ROR'}}$

Amounts are in M/l.
Rates in M/l per sec.
*Coded solvents, Comments, Literature, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$C_6H_5COOCH_3 + H_2O$	MW*	0.05	HCl	0.05	$k\,A[H^+]$	25	2.67	-5					(5)
							100	1.68	-4					(7)
							121	5.56	-4					"
							139	1.56	-3					"
							154	3.21	-3	17.6	3.7	6		(7)
.2	$C_6H_5COOCH_3 + OH^-$	WA*	A = B = 0.05		-	$k\,AB$	0	1.00	-3					(8)
							15	4.04	-3					"
							25	9.01	-3					"
							40	2.89	-2	14.2	2.4	8		(8)
.3	$C_6H_5COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$k\,A[H^+]$	25	1.29	-7					(5)
							60	3.92	-6					(7)
							80	2.05	-5					"
							100	8.45	-5					"
							120	3.35	-4					"
							138	1.14	-3	19.6	2.8	7		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.4	$C_6H_5COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.05	$k\,A[H^+]$	80	2.09	-5					(7)
							100	9.44	-5					"
							121	3.95	-4					"
							139	1.28	-3	20.2	6.9	7		"
.5	$C_6H_5COOC_2H_5 + OH^-$	WA*	A = B = 0.05			$k\,AB$	0	3.02	-4					(8)
							15	1.27	-3					"
							25	2.87	-3					"
							40	9.56	-3	14.6	1.5	8		"
.6	$C_6H_5COOC_2H_5 + OH^-$	S*	A = B = 0.05			$k\,AB$	see Supplementary Table							(2)
.7	$C_6H_5COOC_2H_5 + OH^-$	Et85*				$k\,AB$	25	5.85	-4				(3)	(1)
							35	1.68	-3				*	(1)
							50	6.28	-3	17.7				"
							50	5.60	-3					(3)
.8	$C_6H_5C^{14}OOC_2H_5 + OH^-$	Et50*	A = 0.09			$k\,AB$		k^{14}/k						
			B = 0.5				25	0.86						(6)
.9	$o\text{-}CH_3C_6H_4COOC_2H_5 + OH^-$	Et85*				$k\,AB$	25	7.76	-5					(1)
							35	2.07	-4					"
							50	8.09	-4	18.0				"
.10	$m\text{-}CH_3C_6H_4COOC_2H_5 + OH^-$	Et85*				$k\,AB$	25	4.33	-4					(1)
							35	1.18	-3					"
							50	4.57	-3	17.9				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.11	m-$CH_3C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			kAB	0	1.64	-4					(8)
							15	7.22	-4					"
							25	1.71	-3					"
							40	5.56	-3	14.9	1.5	8		"
.12	p-$CH_3C_6H_4COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.05	kA[H$^+$]	80	1.68	-5					(7)
							100	8.31	-5					"
							120	3.49	-4					"
							139	1.05	-3	20.4	7.5	7		"
.13	p-$CH_3C_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	kA[H$^+$]	60	3.24	-6					(7)
							80	1.65	-5					"
							100	8.19	-5					"
							120	3.01	-4					"
							140	9.78	-4	19.7	2.9	7		"
.14	p-$CH_3C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05		-	kAB	0	1.06	-4					(8)
							15	4.77	-4					"
							25	1.16	-3					"
							40	3.90	-3	15.2	1.6	8		"
.15	p-$CH_3C_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1 B = 0.005		-	kA	25	2.51	-4					(3)
							50	2.71	-3	18.2	5.7	9		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.16	$p\text{-}CH_3OC_6H_4COOCH_3 + H_2O$	MW*	0.05	HCl	0.05	$kA[H^+]$	100	1.09	-4					(7)
							120	3.92	-4					"
							138	1.01	-3					"
							154	2.59	-3	18.3	5.3	6		"
.17	$p\text{-}CH_3OC_6H_4COOCH_3 + OH^-$	WA*	A = B = 0.05			kAB	0	2.00	-4					(8)
							15	9.04	-4					"
							25	2.22	-3					"
							40	7.70	-3	15.4	5.1	8		"
.18	$p\text{-}CH_3OC_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$kA[H^+]$	60	2.05	-6					(7)
							80	1.41	-5					"
							99	5.65	-5					"
							120	2.57	-4					"
							138	8.00	-4	20.5	6.9	7		"
.19	$p\text{-}CH_3OC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1 B = 0.005			kAB	25	1.15	-4					(3)
							50	1.31	-3	18.6	5.4	9		"
.20	$p\text{-}CH_3OC_6H_4COOC_2H_5 + OH^-$	EW*	A = B = 0.05			kAB	25	7.9	-4	15.3 (0°-40°)				(5)
.21	$2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CH\,C_6H_3 + OH^-$	Et85*				kAB	25	5.75	-5					(4)
							35	1.47	-4					"
							50	7.00	-4					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.22	$2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CH.C_6H_3COOC_2H_5 + OH^-$	Et85*		–	–	k AB	25	5.75	-5					(4)
							35	1.32	-4					"
							50	5.35	-4					"
.23	$3\text{-}CH_3\text{-}6\text{-}(CH_3)_2CH.C_6H_3COOCH_3 + OH^-$	Et85*		–	–	k AB	25	2.35	-5					(4)
							35	6.59	-5					"
							50	3.73	-4					"
.24	$3\text{-}CH_3\text{-}6\text{-}(CH_3)_2CH.C_6H_3COOC_2H_5 + OH^-$	Et85*		–	–	k AB	25	2.18	-5					(4)
							35	6.45	-2					"
							50	2.45	-4					"
.25	$p\text{-}OHC_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$k\,A[H^+]$	80	9.92	-6					(7)
							100	4.16	-5					"
							120	1.91	-4	20.4	4.1	7		(7)
							138	6.70	-4					"
.26	$p\text{-}OHC_6H_4COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.05	$k\,A[H^+]$	80	9.82	-6					(7)
							100	4.69	-5					"
							120	1.96	-4					"
							139	6.68	-4	20.7	6.7	7		"
.27	$m\text{-}NH_2C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	0	1.59	-4					(8)
							15	7.26	-4					"
							25	1.65	-3					"
							40	5.60	-3	15.0	1.8	8		"

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.28	*p*-$NH_2C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			kAB	25	8.40	-5					(8)
							40	2.41	-4					"
							60	1.74	-3					"
							80	7.14	-2	16.7	1.7	8		"
.29	*p*-$NH_2C_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1			kAB	25	1.27	-5					(3)
			B = 0.005				50	1.72	-4	20.0	5.42	9		"
.30	*o*-$NO_2C_6H_4COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.05	$kA[H^+]$	80	1.46	-6					(7)
							100	7.04	-6					"
							121	3.72	-5					"
							139	1.08	-4	21.1	1.6	7		"
.31	*o*-$NO_2C_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$kA[H^+]$	80	1.49	-6					(7)
							100	5.91	-6					"
							121	2.62	-5					"
							139	8.56	-5	20.1				"
.32	*o*-$NO_2C_6H_4COOC_2H_5 + OH^-$	Et85*		-	-	kAB	25	5.41	-3					(1)
							35	1.27	-2					"
							50	3.88	-2	14.5				"
.33	*m*-$NO_2C_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$kA[H^+]$	25	1.10	-7					(5)
							80	2.09	-7					(7)
							100	8.85	-5					"
							120	3.32	-4					"
							138	9.00	-4	18.8	9.5	6		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.34	m-$NO_2C_6H_4COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.08	$k\,A[H^+]$	60	3.48	-6					(^{7})
							80	1.93	-5					"
							100	8.64	-5					"
							120	3.68	-4					"
							139	1.15	-3	20.1	5.3	7		"
.35	m-$NO_2C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			$k\,AB$	0	1.85	-4					(^{8})
							15	6.68	-4					"
							25	1.37	-4					"
							40	3.86	-4	12.8	3.6	8		"
.36	m-$NO_2C_6H_4COOC_2H_5 + OH^-$	EW*	A = B = 0.05			$k\,AB$	0	2.31	-2					(^{5})
							15	8.15	-2					"
							25	1.71	-1					"
							40	4.88	-1	12.8				"
.37	p-$NO_2C_6H_4COOCH_3 + H_2O$	Et85*		-	-	$k\,AB$	25	4.29	-2					(^{1})
							35	1.00	-3	15.4				"
.38	p-$NO_2C_6H_4COOCH_3 + H_2O$	MW*	0.05	HCl	0.05	$k\,A[H^+]$	100	1.65	-4					(^{7})
							121	5.74	-4					"
							138	1.54	-3					"
							153	3.17	-3	17.5	3.3	6		"
.39	p-$NO_2C_6H_4COOCH_3 + OH^-$	WA*	A = B = 0.05			$k\,AB$	0	9.17	-2					(^{8})
							15	3.11	-2					"
							25	6.40	-1					"
							40	1.70	0	12.3	6.92	8		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.40	p-$NO_2C_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$k\,A[H^+]$	80	2.86	-5					(7)
							99	1.04	-4					"
							119	3.32	-4					"
							138	9.52	-4	17.5	1.9	6		"
.41	p-$NO_2C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05		-	$k\,AB$	0	3.58	-2					(8)
							15	1.21	-1					"
							25	2.44	-1					"
							40	6.87	-1	12.4	3.55	8		"
.42	o-$FC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1 B = 0.005		-	$k\,AB$	25	6.45	-4				(5)	(3)
							35	1.62	-3	14.8				(1)
							40	1.83	-3	14.5	2.3	9		(3)
.43	o-$FC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1 B = 0.005		-	$k\,AB$	25	2.32	-3					(1)
							35	5.81	-3					"
							50	2.10	-2	16.9				"
.44	p-$C_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1 B = 0.005		-	$k\,AB$	25	1.26	-3					(1)
							35	3.20	-3					"
							50	1.20	-2	17.2				"
.45	o-$ClC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1 B = 0,005			$k\,AB$	25	1.39	-3					(1)
							35	3.38	-2					"
							50	1.10	-2	15.7				"
.46	m-$ClC_6H_4COOC_2H_5 + OH^-$	Et85*				$k\,AB$	25	4.77	-3					(1)
							35	1.18	-2					"
							50	3.96	-2	16.4				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.47	p-$ClC_6H_4COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.05	$kA[H^+]$	80	1.85	-5					(7)
							100	8.75	-5					"
							120	3.55	-4					"
							139	1.18	-3	20.1	5.8	7		"
.48	p-$ClC_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$kA[H^+]$	80	1.86	-5					(7)
							100	8.12	-5					"
							121	3.12	-4					"
							139	8.61	-4	19.0	1	7		"
.49	p-$ClC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1			kAB	25	2.37	-2					(3)
			B = 0.005				50	2.13	-2	16.8	4.93	4		"
.50	p-$BrC_6H_4COOC_2H_5 + H_2O$	WA*	0.05	HCl	0.05	$kA[H^+]$	60	3.4	-6					(7)
							80	1.85	-5					"
							100	8.64	-5					"
							120	3.46	-4					"
							139	1.11	-3	20.1	5.2	7		"
.51	p-$BrC_6H_4COOC_2H_5 + H_2O$	EW*	0.05	HCl	0.05	$kA[H^+]$	80	2.0	-5					(7)
							100	8.62	-5					"
							120	3.02	-4					"
							139	9.55	-4	18.9	1	9		"
.52	p-$BrC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1			kAB	25	2.89	-3					(3)
			B = 0.005				50	2.60	-2	16.8	5.82	9		"
.53	p-$IC_6H_4COOC_2H_5 + OH^-$	Et85*	A = 0.1			kAB	25	2.78	-3					(3)
			B = 0.005				50	2.48	-2	16.7	4.9	9		"

SUPPLEMENTARY TABLE

(.6) $C_6H_5COOC_2H_5 + OH^-$ (^{2}) ; S* = Solvent:

(I-VI) H_2O 400 g + 1000 ml [$(CH_3)_2CO$ x wt % + C_2H_5OH $(1-x)$ wt %]

(I) $x = 100$
(II) 88.95
(III) 75
(IV) 50.50
(V) 36.97
(VI) 25.04

(VII - XI) $H_2O + C_2H_5OH$ x wt %

(VII) $x = 47.9$
(VIII) 66.5
(IX) 67.1
(X) 71.3
(XI) 93.5
(XII) 1,4-dioxane + H_2O 400 g/l

°C	0	16	25	39.7		$A = A^\circ \times 10^n$	
S*	$10^4 k$				E	A°	n
(I)	4.05	17.2	38.8	116.5	14.0	7.4	7
(II)	3.19	15.19	32.9	101.2	14.7	1.9	8
(III)	2.68	12.84	27.0	88.3	15.0	3.3	8
(IV)	2.17	10.78	24.02	77.6	15.2	3.9	8
(V)	1.79	9.49	21.4	73.3	15.8	9.1	8
(VI)	1.45	8.05	18.59	63.7	15.9	1	9
(VII)	1.78	9.20	21.05	68.4	15.6	6.6	8
(VIII)	1.29	6.54	15.3	55.5	16.0	1	9
(IX)	0.932	5.12	12.03	45.6	16.5	1.9	9
(X)	0.731	4.14	10.02	39.6	16.9	3.5	9
(XI)	0.183	1.17	3.56	15.57	19.0	3.5	10
(XII)	7.8	29.3	64.0	152.0	12.8	1.5	7

SOLVENTS

MW*	$CH_3OH + H_2O$ 40 ml/100 ml solution (5) (7)
WA*	$(CH_3)_2CO + H_2O$ 40 ml/100 ml solution (56 wt % $(CH_3)_2CO$) (7) (8)
EW*	$C_2H_5OH + H_2O$ 40 ml/100 ml solution (5) (7)
S*	See Supplementary Table (2)
Et85*	C_2H_5OH 85 vol % + H_2O 15 vol % (1) (3)
Et50*	C_2H_5OH 50 vol % + H_2O 50 vol % (6)

COMMENTS

(.7) (.42) At 25°, *k* of (1) averaged with the close value of (3).

LITERATURE

(1) D.P. Evans, J.J. Gordon, H.B. Watson, *CSL* **1937**, 1430. (2) R.A. Fairclough, C.N. Hinshelwood, *CSL* **1937**, 538. (3) C.K. Ingold, W.S. Nathan, *CSL* **1936**, 222. (4) C.T. Lester, C.F. Bailye, *ACS* 1946, **68**, 375. (5) W.B.S. Newling, C.N. Hinshelwood, *CSL* **1936**, 1357. (6) W.H. Stevens, R.W. Attree, *CJR*^{B} 1949, **27**, 807. (7) E.W. Timm, C.N. Hinshelwood, *CSL* **1938**, 862. (8) E. Tommila, C.N. Hinshelwood, *CSL* **1938**, 1801.

ESTER SOLVOLYSIS

Aliphatic carboxylic acid and Phenol

Reaction types $$\underset{(A)}{RCOOAr} + \underset{(B)}{R'OH} \longrightarrow \underset{(L)}{RCOOH} + \underset{(M)}{ArOR'}$$

$$\underset{(A)}{RCOOAr} + \underset{(B)}{OR'^{-}} \longrightarrow \underset{(L)}{RCOO^{-}} + \underset{(M)}{ArOR'}$$

Rate measured (unless otherwise stated) $-dA/dt = +dM/dt$

All rates are in M/l per sec.
All amounts in M/l.

*Coded Solvents, Comments, Literature, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
.1	$CH_3COOC_6H_5 + H_2O$	WA*	0.05	HCl	0.05	$k\,A[H^+]$	15	1.05	-5					(1)
							25	2.70	-5					"
							40	1.14	-4					"
							60	5.81	-4					"
							80	2.68	-3	17.2	1.26	8		"
.2	$CH_3COOC_6H_5 + OH^-$	WA*	A = B = 0.05	-	-	$k\,AB$	-20	1.26	-2					(1)
							-12	2.53	-2					"
							0	7.48	-2					"
							15	2.50	-1					"
							25	5.76	-1	12.5	9.34	8		"
.3	$CH_3COOC_6H_5 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow$	H_2O + c wt % C_2H_5OH		HCl	0.01 - 0.2	$+\,dM/dt = k\,A[H^+]$ $+\,dL/dt = k'\,A[H^+]$								(2)
	$\begin{cases} (L)\ CH_3COOH \\ (L')\ CH_3COOC_2H_5 \end{cases} + C_6H_5OH\ (M)$	c						k						
		50					25	5.83	-5				*	"
		"					40	2.18	-4					"
		70					25	5.53	-5					"
		"					40	2.10	-4					"
		95					25	1.83	-4					"
		"					35	2.58	-4					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.3	(*continued*) $CH_3COOC_6H_5 + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \rightarrow$ $\begin{cases} (L)\ CH_3COOH \\ (L')\ CH_3COOC_2H_5 \end{cases} + C_6H_5OH\ (M)$							k'						
		50					25	4.0	-5				*	(2)
		"					40	1.58	-4					"
		70					25	3.6	-5					"
		"					40	1.27	-4					"
		90					25	2.8	-5					"
		"					35	6.5	-5					"
.4	$CH_3COO\ (m - C_6H_4CH_3) + H_2O$	WA*	0.05	HCl	0.05	$k\,A[H^+]$	15	1.01	-5					(1)
							25	2.66	-5					"
							40	1.10	-4					"
							60	5.75	-4					"
							80	2.57	-3	17.2	1.2	8		"
.5	$CH_3COO\ (m - C_6H_4CH_3) + OH^-$	WA*	A = B = 0.05		-	$k\,AB$	-20	8.2	-3					(1)
							-10	1.95	-2					"
							0	5.22	-2					"
							15	1.80	-1					"
							25	3.80	-1	12.9	1.1	9		"
.6	$CH_3COO\ (p - C_6H_4CH_3) + H_2O$	WA*	0.05	HCl	0.05	$k\,A[H^+]$	25	2.93	-5					(1)
							40	1.18	-4					"
							60	6.19	-4					"
							80	2.84	-3	17.2	1.23	8		"
.7	$CH_3COO\ (p - C_6H_4CH_3) + OH^-$	WA*	A = B = 0.05		-	$k\,AB$	-20	6.5	-3					(1)
							-10	1.75	-2					"
							0	4.50	-2					"
							15	1.54	-1					"
							25	3.10	-1	12.9	9.78	8		"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.13	$CH_3COO\ (m - C_6H_4NO_2) + H_2O$	WA*	0.05	HCl	0.05	$k\,A[H^+]$	15	7.00	-6					(1)
							20	1.94	-5					"
							40	7.61	-5					"
							60	3.79	-4					"
							80	1.58	-3	16.7	4.07	7		"
.14	$CH_3COO\ (m - C_6H_4NO_2) + OH^-$	WA*	A = B = 0.05		–	$k\,AB$	-20	1.83	-1					(1)
							-10	4.10	-1					"
							0	9.70	-1					"
							15	2.80	0					"
							25	5.49	0	11.3	1.15	9	*	"
.15	$CH_3COO\ (p - C_6H_4NO_2) + OH^-$	WA*	A = B = 0.05		–	$k\,AB$	-20	2.90	-1					(1)
							-10	7.00	-1					"
							0	1.40	0					"
							15	4.30	0					"
							25	8.05	0	11.0	1	9	*	"

SOLVENTS

WA* $(CH_3)_2CO + H_2O$ 400 ml/l solution, (~ 56 wt % $(CH_3)_2CO$)

COMMENTS

(.3) Selected data; *k*' is from initial stage of the reaction. With increasing *c*, *k* appears to pass through a minimum at about 60 - 70 % , then to increase; *k*' decreases with increasing *c*. (.14) (.15) *k* at 25°C extrapolated.

LITERATURE

(1) E. Tomila, C.N. Hinshelwood, *CSL* 1938, 1801. (2) W.A. Waters, *CSL* 1936, 1014.

ESTER SOLVOLYSIS

Aliphatic carboxylic acid and Polyalcohol

Liquid phase

Amounts are in M/l.
Rates are in M/l sec.
Comments, Literature, at the end of the table.

Rate measured $-dB/dt = dM/dt$

$Ac = CH_3CO$

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$AcOCH_2CH_2OAc + 2OH^- \rightarrow OHCH_2CH_2OH + 2AcO^-$	H_2O	A = 0.005 - 0.25 B = 0.01 - 0.5	kAB	18 25	1.27 2.72	-1 -1
.2	$AcOCH_2CH_2OAc + OH^- \rightarrow AcOCH_2CH_2OH + AcO^-$	"	"	"	18 25	2.70 5.28	-1 -1
.3	$AcOCH_2CH_2OH + OH^- \rightarrow OHCH_2CH_2OH + AcO^-$	"	"	"	18 25	1.35 2.72	-1 -1
.4	$AcOCH_2CH(OAc)CH_2OAc + 3OH^- \rightarrow OHCH_2CHOHCH_2OH + 3AcO^-$	"	10^3A = 3.3 - 6.7 B = 0.1 - 0.2	"	18 25	1.32 2.89	-1 -1
.5	$AcOCH_2CH(OAc)CH_2OAc + OH^- \rightarrow AcOCH_2CH(OAc)CH_2OH + AcO^-$	"	"	"	18 25	4.08 8.62	-1 -1
.6	$AcOCH_2CHOHCH_2OAc + 2OH^- \rightarrow OHCH_2CHOHCH_2OH + 2AcO^-$	"	A = 0.005 - 0.01 B = 0.1 - 0.2	"	18 25	1.31 2.97	-1 -1
.7	$AcOCH_2CHOHCH_2OAc + OH^- \rightarrow AcOCH_2CHOHCH_2OH + AcO^-$	"	10^3A = 3.3 - 6.7 B = 0.01 - 0.02	"	18 25	2.71 5.75	-1 -1
.8	$OHCH_2CH(OAc)CH_2OH + OH^- \rightarrow OHCH_2CHOHCH_2OH + AcO^-$	"	"	"	18 25	1.35 2.87	-1 -1

COMMENTS

Reaction (.1) is composed of the two consecutive steps (.2) and (.3); with the subscripts referring to the reaction designated by that number, $k_1 \approx k_3$, and $k_2 = 2k_3$. Reaction (.4) is composed of the three consecutive steps (.5), (.7) and (.8); $k_4 \approx k_8$, $k_5 = 3k_8$ and $k_1 = 2k_8$. Reaction (.6) is composed of the two consecutive steps (.7) and (.8); $k_6 \approx k_8$, $k_7 = 2k_8$.

LITERATURE

J. Meyer, *ZPC* 1909, 67, 257; E. Abel, *ZPC* 1906, 56, 558.

ESTER SOLVOLYSIS

Liquid phase

Aliphatic carboxylic polyacid and Alcohol

Rate measured $-dB/dt = + dM/dt$

Amounts are in M/l.
Rates are in M/l per sec.
Comments, literature, at the end of the table

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^{\circ} \times 10^{n}$	
						k°	n
.1	$CH_3OCOCH_2CH_2COOCH_3 + 2OH^- \rightarrow {}^-OCOCH_2CH_2COO^- + 2CH_3OH$	H_2O	see Reactions (.2) (.3)				
.2	$CH_3OCOCH_2CH_2COOCH_3 + OH^- \rightarrow CH_3OCOCH_2CH_2COO^- + CH_3OH$	"	0.01 - 0.05	k AB	18 25	2.08 3.42	-1 -1
.3	$CH_3OCOCH_2CH_2COO^- + OH^- \rightarrow {}^-OCOCH_2CH_2COO^- + CH_3OH$	"	"	"	18 25	2.17 3.50	-2 -2
.4	$C_2H_5OCOCH_2CH_2COOC_2H_5 + 2OH^- \rightarrow {}^-OCOCH_2CH_2COO^- + 2C_2H_5OH$	"	see Reactions (.5) (.6)				
.5	$C_2H_5OCOCH_2CH_2COOC_2H_5 + OH^- \rightarrow C_2H_5OCOCH_2CH_2COO^- + C_2H_5OH$	"	0.01 - 0.05	k AB	18 25	1.84 2.84	-1 -1
.6	$C_2H_5OCOCH_2CH_2COO^- + OH^- \rightarrow OCOCH_2CH_2COO^- + C_2H_5OH$	"	"	"	18 25	1.72 2.77	-2 -2
.7	$CH_3OCOCHOHCOOCH_3 + 2OH^- \rightarrow CHOH(COO^-)_2 + 2CH_3OH$	"	see Reactions (.8) (.9)				
.8	$CH_3OCOCHOHCOOCH_3 + OH^- \rightarrow CH_3OCOCHOHCOO^- + CH_3OH$	"	0.01 - 0.05	k AB	18 25	1.45 2.85	0 0
.9	$CH_3OCOCHOHCOO^- + OH^- \rightarrow CHOH(COO^-)_2 + CH_3OH$	"	"	"	18 25	1.75 3.07	-2 -2

212.447.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.10	$C_2H_5OCOCHOHCOOC_2H_5 + 2OH^- \rightarrow CHOH(COO^-)_2 + 2C_2H_5OH$	H_2O	see Reactions (.11) (.12)				
.11	$C_2H_5OCOCHOHCOOC_2H_5 + OH^- \rightarrow C_2H_5OCOCHOHCOO^- + C_2H_5OH$	"	0.01 - 0.05	k AB	18 25	1.04 2.25	-1 -1
.12	$C_2H_5OCOCHOHCOO^- + OH^- \rightarrow CHOH(COO^-)_2 + C_2H_5OH$	"	"	"	18 25	1.40 2.44	-2 -2

COMMENTS

Reaction (.1) is composed of the consecutive steps (.2) and (.3). Reaction (.4) is composed of the consecutive steps (.5) and (.6). Reaction (.7) is composed of the consecutive steps (.8) and (.9). Reaction (.10) is composed of the consecutive steps (.11) and (.12). Rates of (.2), (.5), (.8), (.11), by extrapolation to zero time of, respectively, the rates of (.1), (.4), (.7), (.10).

LITERATURE

J. Meyer, *ZPC* 1909, 67, 257.

SOLVOLYSIS

Alkyl arylsulfonates

Liquid phase

Reaction type $ArSO_3R + OR'^- \rightarrow ROR' + ArSO_3^-$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$	
						k°	n		A°	n
.1	$C_6H_5SO_3C_2H_5 + OC_2H_5^-$	C_2H_5OH	A = B = 0.05	kAB	35	1.28	-7			
					45	3.92	-3	21.7	6.0	10
.2	p-$CH_3C_6H_4SO_3C_2H_5 + OC_2H_5^-$	C_2H_5OH	A = B = 0.05	kAB	35	8.06	-4			
					45	2.36	-3	20.8	8.2	9
.3	p-$CH_3OC_6H_4SO_3C_2H_5 + OC_2H_5^-$	C_2H_5OH	A = B = 0.05	kAB	35	5.35	-4			
					45	1.62	-3	21.7	2.2	10
.4	p-$NO_2C_6H_4SO_3C_2H_5 + OC_2H_5^-$	C_2H_5OH	A = B = 0.05	kAB	25	3.85	-3			
					35	1.50	-2	24.0	3.0	13
.5	p-$BrC_6H_4SO_3C_2H_5 + OC_2H_5^-$	C_2H_5OH	A = B = 0.05	kAB	35	2.87	-3			
					45	8.98	-3	22.2	3.0	11

LITERATURE

M.S.Morgan, L.M.Fletcher, *ACS* 1948, 70, 375.

212.463.

SOLVOLYSIS

Phenol sulfates

Liquid phase

Reaction type $ArOSO_3K + H_2O \longrightarrow ArOH + KHSO_4$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E
.1	$C_6H_5OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	8.9	-5	
							78.7	3.35	-3	27.0
.2	o-$CH_3C_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	7.75	-5	
							78.7	2.72	-3	26.5
.3	m-$CH_3C_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	8.8	-5	
							78.8	3.2	-5	26.7
.4	o-$CH_3OC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	1.33	-4	
							78.7	4.53	-3	
.5	m-$CH_3OC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	1.02	-4	
							78.7	3.4	-3	26.1
.6	p-$CH_3OC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	4.5	-5	
							78.7	1.80	-5	27.4
.7	o-$NO_2C_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	3.58	-4	
							78.7	8.8	-3	23.8

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E
								k°	n	
.8	m-$NO_2C_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	2.05	-4	
							78.7	5.8	-3	24.8
.9	p-$NO_2C_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	4.45	-4	
							78.7	1.2	-2	24.7
.10	o-$ClC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	1.30	-4	
							78.7	4.42	-3	26.2
.11	m-$ClC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	1.63	-4	
.12	p-$ClC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	1.08	-4	
							78.7	3.62	-3	26.2
.13	p-$BrC_6H_4OSO_3K + H_2O$	H_2O	0.08	HCl	0.04	kA	48.6	1.15	-4	

LITERATURE

G.N.Burkhardt, W.G.K.Ford, E.Singleton, *CSL* **1936**, 17.

ESTER SOLVOLYSIS

Aliphatic alcohol and Hydrohalic acid

Liquid phase

Reaction types $RX + R'OH \rightarrow HX + ROR'$

$(A) \quad (B) \qquad (L) \quad (M)$

$RX + OR'^{-} \rightarrow X^{-} + ROR'$

Rate measured $-dA/dt = + dL/dt$
(unless otherwise stated)

Rates are in M/l per sec.

Amounts are in M/l.

Solvents, Comments, Literature, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
						k°	n		A°	n		
	Saturated alkyl halide											
.1	$CH_3Cl + H_2O$	H_2O	0.1	kA	25	3.32	-10	27.7			*	(21)
					100	1.80	-6	27.7				"
		"	0.033	kA	37.8	1.27	-7					(21a)
					60.0	2.16	-6					
.1.1	$CH_3Cl + OH^-$	H_2O	A = 0.033; B = 0.099	kAB	37.8	3.55	-5					(21a)
					49.4	1.46	-4					
					55.5	3.00	-4					
					60.0	4.88	-4					
					66.6	9.	-4	24.3	4.1	12		
.2	$CH_3Br + H_2O$	H_2O	0.1	kA	25	6.00	-9				*	(21)
					100	2.09	-5	26.5				
		"	0.063	kA	24.5	3.21	-7					(21a)
					35.4	1.46	-6					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.2	$CH_3Br + H_2O$ *(continued)*	Et60		-	-	kA	25	2.47	-7					(28)
							55	8.32	-6	22.8				"
		Et80		-	-	"	25	1.22	-7					"
							55	5.86	-6	23.7				"
		Me_2CO	B = 5 %			kAB	50	2.63	-8					(29)
			10 %				"	4.31	-8					
		PhOH	B = 0.5; L = 0.1; M = 0.05			kAB	80	9.56	-6					(4)
							92	3.19	-5	26.6				
.2.1	$CH_3Br + OH^-$	H_2O	A = 0.063; B = 0.105			kAB	19.6	7.08	-5					(21a)
							24.5	1.37	-4					
							30.3	2.87	-4					
							35.4	5.33	-4					
							40.2	9.31	-4					
							49.8	2.91	-3	23.0	1.0	13		
		Et80			$k_1A + k_2AB$		55							(16a)
							k_1	3.49	-6					
							k_2	2.14	-2					
.3	$CH_3I + H_2O$	H_2O	0.1	-	-	kA	25	1.14	-9	28.1			*	(21)
							100	7.46	-6	23.1				"
		"	0.012	-	-	kA	69.7	2.45	-5					(21a)
.3.1	$CH_3I + OH^-$	H_2O	A = 0.012; B = 0.104			kAB	29.9	1.16	-4					(21a)
							39.1	3.45	-4					
							41.7	4.52	-4					
							48.9	1.06	-3					
							59.9	3.21	-3					
							69.7	8.54	-3	22.2	1.2	12		

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.4	$C_2H_5Cl + OC_2H_5^-$	EtOH	A = B = 0.05	kAB	40	1.1	-5				*	(10)
					60	9.9	-5					"
					71	3.06	-4					"
					80	7.73	-4		7.93$T^{1/2}$	9		"
					91	1.89	-3	23.0				"
.5	$C_2H_5Br + H_2O$	Et60		kA	25	1.01	-7					(28)
					55	4.00	-6	23.8				"
		Et80		"	25	5.06	-8					"
					55	2.00	-6	23.8				"
		$(Me)_2CO$	B = 5 %	kAB	50	8.40	-9					(29)
			10 %		"	1.45	-8					"
		PhOH	B = 0.5; L = 0.1; M = 0.05	kAB	80	2.69	-6					(4)
					92	1.28	-5	31.3				"
.6	$C_2H_5Br + OH^-$	WAn		kAB	25	5.68	-5					(8)
					40	2.66	-4					"
					60	1.66	-3					"
					80	8.01	-3	18.5	2.5	9		"
		WEt		kAB	25	4.71	-5					"
					40	2.69	-4					"
					60	2.02	-3					"
					80	1.05	-2	20.1	3.16	10		"
		Et80		$k_1A + k_2AB$	55							(16a)
					k_1	1.39	-6					
					k_2	1.71	-3					

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.6.1	$C_2H_5Br + OC_2H_5^-$	EtOH	A = 0.01 - 0.1	-	-	kAB	16	2.37	-5				*	(10)
			B = 0.01 - 0.1				25	7.63	-5					"
							32	1.83	-4					"
							40	4.66	-4					"
							50	1.35	-3					"
							60	3.31	-3					"
							71	1.02	-2					"
							80	2.26	-2		1.28 $T^{1/2}$	10		"
							90	5.28	-2	21				"
			B = 0.0125		-	kAB	60	4.3	-3					"
			0.025				60	3.7	-3					"
			0.05				60	3.2	-3					"
			0.1				60	2.8	-3					"
.7	$C_2H_5I + H_2O$	H_2O		-	-	kA	60	1.67	-5					(20)
							77	7.96	-5					"
							100	5.13	-4	21.2				"
.8	$C_2H_5I + \begin{cases} H_2O & (=B) \\ C_2H_5OH & (=B') \end{cases} \longrightarrow HI + \begin{cases} C_2H_5OH & (a) \\ C_2H_5OC_2H_5 & (b) \end{cases}$		A = 0.01 - 0.17		(a + b)=	kA=	k'A(B + B')							(7)
		$H_2O + C_2H_5OH$ %		-	-		25							"
			18.4				k	1.17	-7					"
			"				k'	2.87	-9					"
			100				k	8.18	-9					"
			100				k'	4.84	-10					"
							50							
			18.4				k	3.83	-6					"
			"				k'	8.17	-9	28.0				"
			55.5				k	1.38	-6					"
			"				k'	4.17	-9					"
			100				k	2.16	-7					"
			100				k'	1.30	-8	21.5				"

No.	Reaction	Medium (Solvent)	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$: k°	n	E	$A = A^\circ \times 10^n$: A°	n	Comments	Literature
.9	$C_2H_5I + \begin{cases} H_2O \\ C_2H_5OH \\ (C_2H_5)_3N\ (=B) \end{cases} \longrightarrow \begin{cases} HI + C_2H_5OH & (a) \\ HI + C_2H_5OC_2H_5 & (b) \\ (C_2H_5)_4NI & (c) \end{cases}$	$H_2O + C_2H_5OH$ %	-	$(a + b + c) = k_1A + k_2AB = k'AB$									(7)
						25							"
		36.9				k_2	4.92	-5					"
		"				k'	5.14	-5					"
		55.5				k_2	2.08	-5					"
		"				k'	2.18	-5					"
	[See reaction (a + b), (.8)]	100				k_2	2.67	-6					"
		"				k'	2.81	-6					"
						50							
		18.1				k_2	6.18	-4					"
		"				k'	9.15	-4					"
		55.5				k_2	2.12	-4					"
		"				k'	2.40	-4					"
		100				k_2	3.83	-5					"
		"				k'	4.17	-5					"
.10	$C_2H_5I + \begin{cases} H_2O \\ C_2H_5OH \\ CH_3COO^-\ (=B) \end{cases} \longrightarrow \begin{cases} HI + C_2H_5OH & (a) \\ HI + C_2H_5OC_2H_5 & (b) \\ I^- + CH_3COOC_2H_5 & (c) \end{cases}$	$H_2O + C_2H_5OH$ %	-	$(a + b + c) = k_1A + k_2AB = k'AB$									(7)
						25							"
		55.5				k_2	1.05	-5					"
		"				k'	1.50	-5					"
		100				k_2	1.00	-5					"
	[See reaction (a + b), (.8)]	"				k'	1.17	-5					"
						50							
		36.9				k_2	2.03	-5					"
		"				k'	4.18	-5					"
		55.5				k_2	1.87	-5					"
		"				k'	3.16	-5	22.0				"
		75.8				k_2	2.47	-5					"
		"				k'	4.16	-5					"
		100				k_2	2.05	-5					"
		"				k'	2.50	-5	23.2				"

No	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.11	$C_2H_5I + \left\{\begin{matrix} H_2O \\ C_2H_5OH \\ OH^- \\ OC_2H_5^- \end{matrix}\right\}$ (=B) $\nearrow$ $HI + \left\{\begin{matrix} C_2H_5OH \\ C_2H_5OC_2H_5 \end{matrix}\right.$ (a) (b) $\searrow$ $I^- + \left\{\begin{matrix} C_2H_5OH \\ C_2H_5OC_2H_5 \end{matrix}\right\}$ (c)		A = 0.06 - 0.15 B = 0.007 - 0.5			(a + b + c) = $k_1A + k_2AB = k'AB$								(^{7})
		$H_2O + C_2H_5OH$ %					25							〃
			36.9				k_2	5.33	-5					〃
			〃				k'	5.68	-5					〃
			66.3				$k_2 = k'$	7.67	-5					〃
			100				〃	1.03	-4					〃
	[See reaction (a + b), (.8)]						50							〃
			18.1				$k_2 = k'$	3.76	-4					〃
			36.9				〃	7.50	-4	19.8				〃
			55.5				〃	8.25	-4	18.8				〃
			75.4				〃	1.35	-3	20.7				〃
			100				〃	1.38	-3	19.8				〃
.12	$C_2H_5I + .OC_2H_5^-$	EtOH	A = B = 0.05		-	k AB	18	5.03	-5				*	(^{10})
							25	1.53	-4					〃
							32	3.68	-4					〃
							40	9.58	-4					〃
							50	2.70	-3					〃
							60	6.71	-3					〃
							71	1.99	-2					〃
							80	4.60	-2		2.70 $T^{1/2}$	10		〃
							91	1.19	-1	21.0				〃
.13	$C_3H_7Br + H_2O$	PhOH	B = 0.5; L = 0.1; M =0.05											
						k AB	80	2.02	-6					(^{4})
							92	9.50	-6	31.7				〃
.14	$(CH_3)_2CHCl + H_2O$	Et80	0.1	-	-	k A	90	2.21	-7					(^{15})
							110	1.15	-6					〃
.15	$(CH_3)_2CHCl + OH^-$	Et80		-	-	k AB	70	5.08	-6					(^{15})
							90	3.27	-5					〃

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.16	$(CH_3)_2CHBr + H_2O$	Et60		–	–	kA	25	2.64	−7					(28)
							55	7.13	−6	22.7				"
		Et80		–	–	kA	25	7.84	−8					"
							55	2.37	6	23.2				"
		$(Me)_2CO$	B = 5 %	–	–	kAB	50	1.34	−8					(29)
			10 %				"	2.03	−8					"
.17	$(CH_3)_2CHBr + OH^- \longrightarrow Br^- + (CH_3)_2CHOH$	Et60	A = 0.1;	B = 0-0.005		kA	45	2.23	−6				*	(13)
							55	6.67	−6					"
							65	1.87	−5					"
							75	4.92	−5	22.7				"
		Et60	A = 0.1;	B = 0.85		kAB	45	1.38	−5					"
							60	6.00	−5					"
							75	2.35	−4	20.7				"
		Et80	A = 0.1;	B = 0-0.005		kA	45	7.70	−7					"
							55	2.38	−6					"
							65	6.81	−6					"
							75	1.81	−5	23.2				"
		Et80	A = 0.1;	B = 0.85	–	kAB	50	2.80	−5					"
							80	4.98	−4	21.7				"
		EtOH				$kA + k_2AB$	55							(16a)
							k_1	2.37	−6					
							k_2	4.75	−5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.18	$(CH_3)_2CHBr + OH^- \longrightarrow Br^- + \begin{cases} (CH_3)_2CHOH & (a) \\ CH_3CH{:}CH_2 + H_2O & (b) \end{cases}$	Et60	A = 0.1;	B = 0.85										
						(a + b) = kAB	45	2.94	-5					(13)
			"	"			60	1.35	-4					"
	[See reaction (a), (.17)]		"	"			75	5.55	-4	21.5				"
			"	0.1		"	45	5.08	-5					"
			"	0.2			"	4.70	-5					"
	(See Supplementary table)		"	0.5			"	3.72	-5					"
			"	1.0			"	2.94	-5					"
		Et80	A = 0.1;	B = 0.85		"	50	6.70	-5					"
							80	1.28	-3	22.2				"
.19	$(CH_3)_2CHI + H_2O$	Et60	0.1	-	-	kA	50	4.94	-6					(15)
							60	4.26	-5					"
.20	$(CH_3)_2CHI + OH^-$	Et60		-	-	kAB	70	5.08	-6					(15)
							90	3.28	-5					"
.21	$C_4H_9Br + H_2O$	PhOH	B = 0.5;	L = 0.1;	M = 0.05									
						kAB	80	2.17	-6					(4)
							92	8.16	-6	29.6				"
.22	$(CH_3)_2CHCH_2Br + H_2O$	PhOH	B = 0.5;	L = 0.1;	M = 0.05									
						kAB	80	9.32	-7					(4)
							92	2.07	-6	28.4				"
.22.1	$(CH_3)_2CHCH_2Br + OC_2H_5^-$	C_2H_5OH				kAB	55	5.8	-2					(16a)
.23	$(C_2H_5)(CH_3)\ CHBr + H_2O$	PhOH	B = 0.5;	L = 0.1;	M = 0.05									
						kAB	80	1.58	-5					(4)
							92	5.84	-5	29.9				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.24	$(CH_3)_3CCl + \left\{\begin{matrix}H_2O\\CH_3OH\end{matrix}\right.$ → $HCl + (CH_3)_3COH$ (a) → $\left\{\begin{matrix}HCl + (CH_3)_3COCH_3\\CH_3Cl + (CH_3)_3COH\end{matrix}\right\}$ (b)	MeOH		–		(a + b) = kA	25	8.20	-7				*	(11)
		MeOH + H_2O (N)												"
			0.070				"	1.75	-6					"
			0.175				"	4.33	-6					"
			0.230				"	7.14	-6					"
			0.282				"	1.13	-5					"
	(See Supplementary table)		0.346				"	2.12	-5					"
			0.432				"	5.28	-5					"
			0.497				"	9.75	-5					"
		H_2O	1.000				"	3.3	-2					"
.25	$(CH_3)_3CCl + \left\{\begin{matrix}H_2O\\C_2H_5OH\end{matrix}\right.$ → $HCl + (CH_3)_3COH$ (a) → $\left\{\begin{matrix}HCl + (CH_3)_3COC_2H_5\\C_2H_5Cl + (CH_3)_3COH\end{matrix}\right\}$ (b)	EtOH %,	H_2O (N)	–		(a + b) = kA							(32)	(11)
		100	0.000				25	9.70	-8				*	"
		90	0.262				"	1.73	-6					"
		80	0.448				"	9.24	-6					"
	(See Supplementary table)	70	0.582				"	4.07	-5					"
		60	0.684				"	1.27	-4					"
		50	0.765				"	3.67	-4					"
		40	0.829				"	1.29	-3					"
		0	1.000				"	3.3	-2					"
.26	$(CH_3)_3CCl + H_2O$	H_2O + EtOH %												
		40	0.05-0.08	OH^-	< A	kA	25	1.29	-3				*	(12)
		50	"	"	"	"	8	3.53	-5					"
							16	1.10	-4					"
							25	3.67	-4	22.9	2.8	13		"
		70	"	"	"	"	25	4.03	-4					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.26	$(CH_3)_3CCl + H_2O$ *(continued)*	80	0.05-0.08	OH^-	$< A$	kA	8	8.62	-7					(12)
							16	2.72	-6					"
							35	3.15	-5					"
							45	1.04	-4	23.1	6.9	11		"
		EtOH				kA	25	8.54	-6					(16a)
		An80	0.05-0.08	OH^-	$< A$	kA	35	6.61	-6				*	(12)
							45	2.12	-5	22.9	7.8	10		"
.27	$(CH_3)_3CBr + H_2O$	Et60		–	–	kA	15	1.17	-3					(28)
							25	3.20	-3	17.2				"
		Et80		–	–	"	15	1.02	-4					"
							25	3.31	-4	20.0				"
		$(Me)_2CO$	B = 5 %		–	kAB′	50	1.67	-5					(29)
			10%				"	5.12	-5					"
.28	$(CH_3)_3CBr + OH^-$	Et80				kAB	55	1.0	-2					(16a)
.29	$C_5H_{11}Br + H_2O$	An50	0.01			kA	50	7.7	-7				*	(22b)
							60	2.2	-6	22.1	5.2	8		
		"	"	KOH	0.05	kA	50	5.8	-6					"
					"		60	1.5	-5					
					0.10		50	1.0	-5					
					"		60	2.7	-5					
					0.25		50	2.0	-5					
					"		60	4.9	-5					
.30	$C_5H_{11}Br + H_2O$	PhOH	B = 0.5;	L = 0.1;	M = 0.05									
						kAB	80	2.47	-6					(4)
							92	8.28	-6	30.8				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.31	$(CH_3)_2CH(CH_2)_2Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05											
						kAB	80	9.00	-6					(4)
							92	3.60	-5	30.1				"
.31.1	$C_2H_5C(CH_3)_2Cl + H_2O$	Et80				kA	25	1.50	-5					(16a)
.32	$C_2H_5C(CH_3)_2Cl + OH^-$	Et60	B = 0.212; A = 0.073			kA	25.2	1.1	-4				*	(14a)
		Et80	B = 0.212; A = 0.161			kA	25.2	9.4	-6				"	"
			0.078				"	1.0	-5					
			0.147				50.0	1.7	-4					
.33	$C_2H_5C(CH_3)_2Br + OH^-$	Et80	B = 0.118; A = 0.072			kA	25.2	4.3	-4				*	"
			0.005					4.0	-4					
.33.1	$(CH_3)_3CCH_2Br + OC_2H_5^-$	C_2H_5OH				kAB	95	5.0	-4					(16a)
.34	$CH_3N(CH_2CH_2Cl)_2 + 2\ OH^-$	DiW	A = B = 0.01 - 0.05			kA	25.0	3.0	-4				*	(2b)
.35	$CH_3N(CH_2CH_2Cl)_2 + H_2O$	DiW	See Comments										*	(2b)
.36	$C_2H_5N(CH_2CH_2Cl)_2 + H_2O$	DiW	See Comments										*	(2a)
.37	$C_6H_{13}Cl + H_2O$	An50	0.01			kA	50	2.2	-8				*	(22b)
							60	6.7	-8					
		"	"	KOH	0.05	kA	50	1.5	-7					"
					"		60	4.3	-7					
					0.10		50	2.7	-7					
					"		60	7.7	-7					
					0.25		50	4.5	-7					
					"		60	1.5	-6					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.38	$C_6H_{13}Br + H_2O$	An50	0.01			k A	50	7.0	-7				*	(^{22b})
							60	2.0	-6	22.6	1.1	9		
		"	"	KOH	0.05	k A	50	5.2	-6					"
					"		60	1.35	-5					
					0.10		50	9.2	-6					
					"		60	2.3	-5					
					0.25		50	1.7	-5					
					"		60	4.4	-5					
		AnD50				k A	50	5.8	-7					"
							60	1.6	-6					
.39	$C_6H_{13}Br + H_2O$	PLOH	B = 0.5; L = 0.1; M = 0.05											
						k AB	80	1.96	-6					(^{4})
							92	8.18	-5	30.9				"
.40	$(CH_3)_2CHCH_2CH_2CH_2Br + H_2O$	An50	0.01			k A	50	7.3	-7				*	(^{22b})
							60	2.1	-6	22.3	7.5	8		
		"	"	KOH	0.05	k A	50	5.5	-6					"
					"		60	1.35	-5					
					0.10		50	9.0	-6					
					"		60	2.4	-5					
					0.25		50	1.7	-5					
					"		60	4.5	-5					
.41	$C_2H_5CH(CH_3)CH_2CH_2Br + H_2O$	An50	0.01			k A	50	5.0	-7				*	(^{22b})
							60	1.4	-6	21.75	2.1	8		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.41	$C_2H_5CH(CH_3)CH_2CH_2Br + H_2O$ *(continued)*	An50	0.01	KOH	0.05	kA	50	1.5	-6					(^{22b})
					"		60	8.9	-6					
					0.10		50	6.0	-6					
					"		60	1.6	-5					
					0.25		50	1.1	-5					
					"		60	2.8	-5					
.42	$C_7H_{15}Br + H_2O$	An50	0.01			kA	50	6.6	-7					(^{22b})
							60	1.85	-6	22.1	4.7	8		
		"	"	KOH	0.05	kA	50	4.8	-6					"
					"		60	1.2	-5					
					0.10		50	8.5	-6					
					"		60	2.1	-5					
					0.25		50	1.5	-5					
					"		60	4.1	-5					
.43	$C_7H_{15}Br + H_2O$	PhOH	B = 0.5;	L = 0.1; M = 0.05		kAB	80	3.02	-6					(^{4})
							92	1.12	-5	30.1				"
.44	$C_5H_{11}CH(CH_3)Br + H_2O$	An50	0.01			kA	50	3.7	-6				*	(^{22b})
							60	1.0	-5	21.9	2.0	9		
		"	"	KOH	0.05	kA	50	7.7	-6					"
					"		60	2.1	-5					
					0.10		50	1.1	-5					
					"		60	2.8	-5					
					0.25		50	1.7	-5					
					"		60	4.5	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.45	$C_8H_{17}Br + H_2O$	An50	0.01			kA	50	6.3	-7					(22b)
							60	1.8	-6	22.2	5.1	8		
		"	"	KOH	0.05	kA	50	4.6	-6					"
					"		60	1.15	-5					
					0.10		50	7.9	-6					
					"		60	2.0	-5					
					0.25		50	1.45	-5					
					"		60	3.6	-5					
.46	$C_8H_{17}Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			kAB	80	2.36	-6					(4)
							92	8.90	-6	29.5				"
.47	$C_6H_{13}CH(CH_3)Cl + \left\{\begin{matrix} H_2O \\ C_2H_5OH \end{matrix}\right. \longrightarrow HCl + \left\{\begin{matrix} C_6H_{13}CH(CH_3)OH & \text{(a)} \\ C_6H_{13}CH(CH_3)OC_2H_5 & \text{(b)} \\ C_8H_{16} + H_2O & \text{(c)} \end{matrix}\right.$	Et60	0.057	(a + b + c) = kA			100	8.05	-6				*	(14)
			See following reaction (a + b)											
.48	$C_6H_{13}CH(CH_3)Cl + \left\{\begin{matrix} H_2O \\ C_2H_5OH \end{matrix}\right. \longrightarrow HCl + \left\{\begin{matrix} C_6H_{13}CH(CH_3)OH & \text{(a)} \\ C_6H_{13}CH(CH_3)OC_2H_5 & \text{(b)} \end{matrix}\right.$	Et60	0.057	-	(a + b) = kA		100	7.00	-6					(14)
.49	$C_6H_{13}CH(CH_3)Br + \left\{\begin{matrix} H_2O \\ C_2H_5OH \end{matrix}\right. \longrightarrow HBr + \left\{\begin{matrix} C_6H_{13}CH(CH_3)OH & \text{(a)} \\ C_6H_{13}CH(CH_3)OC_2H_5 & \text{(b)} \\ C_8H_{16} + H_2O & \text{(c)} \end{matrix}\right.$	Et60	0.057	(a + b + c) = kA			80	5.18	-5				(14)	(16)
							100	2.86	-4	22			*	"
			See following reaction (a + b)											

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.50	$C_6H_{13}CH(CH_3)Br + \left\{\begin{matrix} H_2O \\ C_2H_5OH \end{matrix}\right. \longrightarrow HBr + \left\{\begin{matrix} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \end{matrix}\right.$	Et60	0.057	-	(a + b) =	kA	80 100	4.66 2.30	-5 -4				(14)	(16) ″
.51	$C_6H_{13}CH(CH_3)Br + \left\{\begin{matrix} OH^- \\ OC_2H_5^- \end{matrix}\right. \longrightarrow Br^- + \left\{\begin{matrix} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \\ C_8H_{16} + H_2O & \end{matrix}\right.$	Et60	A = 0.057 B = 0.80	(a + b + c) =		kAB	80	7.96	-4				(14) *	(16)
			See following reaction (a + b)											
.52	$C_6H_{13}CH(CH_3)Br + \left\{\begin{matrix} OH^- \\ OC_2H_5^- \end{matrix}\right. \longrightarrow Br^- + \left\{\begin{matrix} C_6H_{13}CH(CH_3)OH & (a) \\ C_6H_{13}CH(CH_3)OC_2H_5 & (b) \end{matrix}\right.$	Et60	A = 0.057 B = 0.80	-	(a + b) =	kAB	80	3.56	-4				(14)	(16)
.52.1	$(CH_3)_3C.C(C_2H_5)_2Cl + H_2O$	Et80				kA	25	1.17	-4					(16a)
			Carboxyl - substituted alkyl											
.53	$CH_2(COO^-)Cl + H_2O$	H_2O	0.2	$NaNO_3$	1 - A	kA	25	2.75	-8				*	(6)
.54	$CH_2(COO^-)Cl + H_2O \longrightarrow CH(COO^-)(OH_3^+) + Br^-$	H_2O	0.2	$NaNO_3$	1 - A	kAB	25	5.0	-10				*	(5) (25)
.55	$CH_2(COO^-)Br + H_2O$	H_2O	0.2	$NaNO_3$	1 - A	kA	25	5.40	-8				*	(6)
.56	$CH_2(COO^-)Br + H_2O \longrightarrow CH(COO^-)(OH_3^+) + Br^-$	H_2O	0.2	$NaNO_3$	1 - A	kAB	25	1.0	-9				*	(5) (25)
.57	$CH_2(COO^-)Br + OH^-$	H_2O	A = 0.05 - 0.5 B = 0 - 0.7 $NaNO_3$ = 1 - (A + B)			kAB	25	6.9	-5					(5) (25)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
	Halogen - substituted alkyl													
.58	$BrCH_2CH_2Br + H_2O$	An25	0.01			kA	60	1.7	-7				*	(^{22b})
		"	"	KOH	0.375	kA	30	7.8	-5					"
							60	fast						
.59	$CH_3CHBr_2 + H_2O$	An25	0.01			kA	60	4.3	-8				*	(^{22b})
		"	"	KOH	0.375	kA	30	3.8	-7				*	"
							60	1.35	-5					
.60	$ClCH_2CH_2CH_2Br + H_2O$	PhOH				kAB	97	2.81	-6	26.6				(^{4})
			B = 0.5; L = 0.1; M = 0.05											
.61	$ClCH_2CH_2CH_2CH_2Br + H_2O$	PhOH				kAB	97	6.40	-6	26.6				(^{4})
			B = 0.5; L = 0.1; M = 0.05											
	Unsaturated alkenyl halide													
.62	$CH_2:CHCH_2CH_2Cl + H_2O$	Et50	0.1	-	-	kA	25	1.48	-6					(^{33})
.63	$CH_2:CHCH_2CH_2Cl + OH^-$	Et50	A = 0.1; B =			$k_1A + k_2AB$	25							(^{33})
				0.00			k_1	1.48	-6					"
				"			k_2	0						"
				0.05			k_1	1.42	-6					"
				"			k_2	3.08	-4					"
				0.1			k_1	1.33	-6					"
				"			k_2	2.92	-4					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.63	$CH_2:CHCH_2CH_2Cl + OH^-$ *(continued)*	Et50	A = 0.2; B = 0.27			k AB	25	5.61	-5				*	$(^{33})$
.64	$CH_2:CHCH(CH_3)Cl + H_2O \rightarrow HCl + \begin{cases} CH_2:CHCH(CH_3)OH & (a) \\ OHCH_2CH:CH(CH_3) & (b) \end{cases}$	Et50	0.13	-	(a + b) =	k A	25	1.14	-5					$(^{33})$
.65	$CH_2:CHCH(CH_3)Cl + OH^- \longrightarrow Cl^- + \begin{cases} CH_2:CHCH(CH_3)OH & (a) \\ OHCH_2CH:CH(CH_3) & (b) \end{cases}$	Et50	A = 0.07 - 0.13;		(a + b)=	k A							*	$(^{33})$
			B = 0.00			"	25	1.14	-5					"
				0.05			"	1.21	-5					"
				0.2			"	1.28	-5					"
			A = 0.2; B = 0.2		(a + b)=	k AB	25	1.01	-6				*	"
				"			40	6.25	-6					"
				0.1			"	7.56	-6					"
.66	$CH_3CHClCH:CHCl + H_2O$	Et50	0.08			k A	25	1.1	-4					$(^{01})$
.67	$CH_3CHClCH:CHCl + OC_2H_5^-$	EtOH abs.	A = 0.08; B = 0.1 - 0.4			k AB	25	4.1	-6					$(^{01})$
.68	$CH_2OHCH:CHCH_2Cl + H_2O$	H_2O	0.1	-	-	k A	30	2.0	-5					$(^{17})$
							50	3.67	-4					"
.69	$CH_2OHCH:CHCH_2Cl + OH^-$	H_2O				k AB	30	1.48	-2					$(^{17})$
.69.1	$ClCH:CHCH_2Cl + H_2O$	H_2O		See Supplementary table										$(^{11b})$

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
	Mono-aryl-substituted alkyl halide													
.70	$C_6H_5CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	1.81	-7				*	(19)
					0.03		"	9.25	-7					"
					0.3		"	1.46	-5					"
.71	$C_6H_5CH_2F + OH^-$	Et64	A = 0.07; B = 0.3			kAB	81	4.15	-5					(19)
.72	$C_6H_5CH_2F + OC_2H_5^-$	Et95	A = B = 0.22			kAB	76	2.64	-5					(19)
.73	$C_6H_5CH_2Cl + H_2O$	An50	~ 0.01			kA	30	3.7	-7				*	(22b)
							60	7.7	-6	20.6	2.1	8		
				KOH	0.05	kA	30	2.8	-6					(22b)
					"		60	4.3	-5					
					0.10		30	5.2	-6					
					"		60	8.3	-5					
					0.26		30	1.0	-5					
					"		60	1.7	-4					
		Et50	~ 0.01			kA	30	1.85	-6					(22a)
							83	2.6	-4					
				See Comments										(11a)
.73.1	$C_6H_5CH_2Cl + C_2H_5OH$	EtE	~ 0.001			kA	25	4.17	-10				*	(21b)
.74	$dl\text{-}C_6H_5CH(CH_3)Cl + H_2O$	$(Me)_2CO$	A = 0.2 B = 2.77	$HCl + HgCl_2$	0.05	kAB								(24)
					0.0		50	5.43	-8					"
					0.1		"	3.89	-6					"
					0.2		"	2.17	-4					"
					0.3		"	2.65	-4					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.74	$dl\text{-}C_6H_5CH(CH_3)Cl + H_2O$ *(continued)*		5.55		0.0		50	2.16	−7					(24)
					0.1		"	1.05	−5					"
					0.3		"	1.87	−4					"
.75	$dl\text{-}C_6H_5CH(CH_3)Br + H_2O$	$(Me)_2CO$	A = 0.2	HCl + $HgBr_2$	0.05	*k* AB								(24)
			B = 2.77		0.0		50	1.92	−6					"
					0.05		"	9.74	−5					"
					0.1.		"	2.57	−4					"
			5.55		0.0	"	"	4.39	−6					"
					0.05		"	8.66	−5					"
.76	$m\text{-}CH_3C_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	*k* A	81	5.18	−7				*	(19)
					0.03		"	2.56	−6					"
					0.3		"	3.34	−5					"
.77	$m\text{-}CH_3C_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22			*k* AB	76	2.50	−5					(19)
.78	$p\text{-}CH_3C_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	*k* A	81	1.55	−7				*	(19)
					0.03		"	1.91	−6					"
					0.3		"	1.93	−5					"
.79	$p\text{-}CH_3C_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3			*k* AB	81	6.00	−5				*	(19)
.80	$p\text{-}CH_3C_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22			*k* AB	76	3.33	−6					(19)
.81	$o\text{-}CH_3C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			*k* A	30	1.6	−6				*	(22b)
							60	3.2	−5	20.2	4.7	8		
		"	"	KOH	0.05	*k* A	30	7.0	−6				*	"
					0.10		"	9.7	−6					
					0.26		"	2.1	−5					
		Et50	~ 0.01			*k* A	30	9.2	−6					(22a)
							83	1.25	−3					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.82	*m*-$CH_3C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	4.6	-7				*	(22b)
							60	9.2	-6	20.4	1.8	8		
		"	"	KOH	0.05	kA	30	2.7	-6				*	"
					0.10		"	4.7	-6					
					0.26		"	8.8	-6					
		Et50	~ 0.01			kA	30	2.4	-6					(22a)
							83	3.6	-4					
.83	*p*-$CH_3C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	2.9	-6				*	(22b)
							60	6.7	-5	21.4	6.4	9		
		"	"	KOH	0.05	kA	30	6.2	-6				*	"
					0.10		"	9.7	-6					
					0.26		"	1.6	-5					
		Et50	~ 0.01			kA	30	1.7	-5					(22a)
							83	2.7	-3					
.84	*m*-$COOHC_6H_4CH_2Cl + H_2O$	Et50	~ 0.01			kA	30	3.15	-7					(22a)
							83	6.3	-5					
		An50	~ 0.01			kA	30	9.2	-8				*	(22b)
							60	2.2	-6	21.7	3.1	8		
		"	"	KOH	0.05	kA	30	2.75	-6					"
					0.10		"	6.0	-6					
					0.26		"	1.6	-5					
	m-$COOHC_6H_4CH_2Cl + OH^-$	"	A ~ 0.01; B = 0.05 - 0.26			kAB	30	6.55	-5					"

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.85	p-$COOHC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	6.5	-8				*	(^{22b})
							60	1.4	-6	21.1	8.2	7		
		Et50	~ 0.01			kA	30	2.0	-7					"
							83	4.3	-5					
.86	m-$(CONH_2)C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	50	1.3	-6					(^{22b})
							60	3.4	-6	20.9	1.4	8		
.87	p-$(CONH_2)C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	50	9.2	-7					(^{22b})
							60	2.4	-6	21.0	1.2	8		
.88	o-$CNC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	50	3.0	-7				*	(^{22b})
							60	8.2	-7	21.4	7.7	7		
		"	"	KOH	0.05	kA	30	4.0	-6					"
					0.10		"	7.7	-6					
					0.26		"	1.7	-5					
.89	m-$CNC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	50	3.95	-7				*	(^{22b})
							60	1.03	-6	20.7	3.2	7		
		"	"	KOH	0.05	kA	30	2.8	-6					"
					0.10		"	5.5	-6					
					0.26		"	1.5	-5					
.90	p-$CNC_6H_4CH_2Cl + H_2O$	An50	~ 0.10			kA	50	3.6	-7				*	(^{22b})
							60	9.7	-7	21.5	9.3	7		
		"	"	KOH	0.05	kA	30	3.7	-6					"
					0.10		"	7.2	-6					
					0.26		"	1.5	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
.91	m-$NO_2C_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	3.42	-8				*	(19)
					0.03		"	3.42	-8					"
					0.3		"	8.20	-7					"
.92	m-$NO_2C_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3	-	-	kAB	81	9.30	-5				*	(19)
.93	m-$NO_2C_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		-	kAB	76	8.95	-5				*	(19)
.94	p-$NO_2C_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	2.67	-8				*	(19)
					0.03		"	2.70	-8					"
					0.3		"	8.70	-7					"
.95	o-$NO_2C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	2.7	-8					(22b)
							60	7.5	-7	22.7	4.7	8		
		Et50	~ 0.01			kA	30	8.7	-8					(22a)
							83	2.2	-5					
.96	m-$NO_2C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	3.6	-8					
							60	8.5	-7	21.7	1.2	8		(22b)
		Et50	~ 0.01			kA	30	1.05	-7					(22a)
							83	2.3	-5					
.97	p-$NO_2C_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	3.3	-8					(22b)
							60	7.7	-7	21.5	8.2	7		
		Et50	~ 0.01			kA	30	8.2	-8					(22a)
							83	1.9	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.98	m-$FC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	6.29	-8				*	(19)
					0.03		"	1.08	-7					"
					0.3		"	1.22	-6					"
.99	m-$FC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		-	kAB	81	3.35	-5				*	(19)
.100	m-$FC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		-	kAB	76	2.69	-5				*	(19)
.101	p-$FC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	2.41	-7				*	(19)
					0.03		"	1.60	-6					"
					0.3		"	2.55	-5					"
.102	p-$FC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		-	kAB	81	6.00	-5				*	(19)
.103	p-$FC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		-	kAB	76	3.61	-5					(19)
.104	o-$ClC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	1.04	-7				*	(19)
					0.03		"	3.25	-7					"
					0.3		"	2.65	-6					"
.105	o-$ClC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		-	kAB	81	4.48	-5				*	(19)
.106	m-$ClC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	5.76	-8				*	(19)
					0.03		"	1.01	-7					"
					0.3		"	1.09	-6					"
.107	m-$ClC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		-	kAB	81	3.38	-5				*	(19)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^n$		E	$A = A^{\circ} \times 10^n$		Comments	Literature
								k°	n		A°	n		
.108	p-$ClC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	1.44	-7				*	$(^{19})$
					0.03		"	5.43	-7					"
					0.3		"	6.22	-6					"
.109	p-$ClC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3	-	-	kAB	81	7.10	-5				*	$(^{19})$
.110	o-$ClC_6H_4CH_2Cl + H_2O$	An50	$\sim$0.01			kA	30	1.02	-7					$(^{22b})$
							60	2.3	-6	21.2	1.6	8		
		Et50	$\sim$0.01			kA	83	9.2	-5					$(^{22a})$
.111	m-$ClC_6H_4CH_2Cl + H_2O$	An50	$\sim$0.01			kA	30	6.7	-8					$(^{22b})$
							60	1.55	-6	21.5	1.6	8		
		Et50	$\sim$0.01			kA	30	2.5	-7					$(^{22a})$
							83	6.1	-5					
.112	p-$ClC_6H_4CH_2Cl + H_2O$	An50	$\sim$0.01			kA	30	2.1	-7					$(^{22b})$
							60	4.5	-6	20.9	1.8	8		
		Et50	$\sim$0.01			kA	30	8.7	-7					$(^{22a})$
							83	1.6	-4					
.113	o,p-$Cl_2C_6H_4CH_2Cl + H_2O$	An50	$\sim$0.01			kA	60	1.7	-8				*	$(^{22b})$
		"	"	KOH	0.05	kA	60	>3	-8					"
					0.10		"	>3.5	-8					
					0.28		"	>5.5	-8					
.114	o-$BrC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	5.22	-8				*	$(^{19})$
					0.03		"	1.28	-7					"
					0.3		"	1.60	-6					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.115	$o\text{-}BrC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		–	kAB	81	2.50	-5				*	(19)
.116	$o\text{-}BrC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		–	kAB	76	1.53	-5					(19)
.117	$m\text{-}BrC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	6.34	-8				*	(19)
					0.03		"	9.06	-8					"
					0.3		"	1.04	-6					"
.118	$m\text{-}BrC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		–	kAB	81	3.62	-5				*	(19)
.119	$m\text{-}BrC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		–	kAB	76	3.33	-5					(19)
.120	$p\text{-}BrC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	1.35	-7				*	(19)
					0.03		"	4.80	-7					"
					0.3		"	5.06	-6					"
.121	$p\text{-}BrC_6H_4CH_2F + OH^-$	Et64	A = 0.07; B = 0.3		–	kAB	81	6.25	-5				*	(19)
.122	$p\text{-}BrC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		–	kAB	76	3.97	-5					(19)
.123	$o\text{-}BrC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	9.2	-8				*	(22b)
							60	2.15	-6	21.5	2.4	8		
		"	"	KOH	0.05	kA	30	1.8	-6				*	(22b)
					0.10		"	3.7	-6					
					0.26		"	7.8	-6					
		Et50	~ 0.01			kA	30	3.9	-7					(22a)
							83	7.4	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.124	m-$BrC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	6.5	-8				*	$(^{22b})$
							60	1.55	-6	21.7	2.05	8		
		"	"	KOH	0.05	kA	30	1.5	-6					"
					0.10		"	2.8	-6					
					0.26		"	6.2	-6					
		Et50	~ 0.01			kA	30	2.45	-7					$(^{22a})$
							83	5.6	-5					
.125	p-$BrC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	1.8	-7				*	$(^{22b})$
							60	3.9	-6	20.9	1.6	8		
		"	"	KOH	0.05	kA	30	2.85	-6				*	"
					0.10		"	5.7	-6					
					0.26		"	1.67	-5					
		Et50	~ 0.01			kA	30	7.6	-7					$(^{22a})$
							83	1.3	-4					
.126	o,o-$Br_2C_6H_3CH_2Cl + H_2O$	An50	~ 0.01			kA	30	4.2	-8				*	$(^{22b})$
		"	"	KOH	0.05	kA	30	2.4	-6				*	$(^{22b})$
					0.10		"	4.3	-6					
					0.26		"	7.5	-6					
.127	m,m-$Br_2C_6H_3CH_2Cl + H_2O$	An50	~ 0.01			kA	30	2.2	-8				*	$(^{22b})$
		"	"	KOH	0.05	kA	30	1.5	-6				*	$(^{22b})$
					0.10		"	2.8	-6					
					0.26		"	6.0	-6					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.128	o,p-$Br_2C_6H_3CH_2Cl + H_2O$	An50	~ 0.01			kA	30	7.0	-8				*	$(^{22b})$
		"	"	KOH	0.05	kA	30	3.0	-6				*	$(^{22b})$
					0.10		"	5.8	-6					
					0.28		"	1.2	-5					
.129	m-$IC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	6.34	-8				*	$(^{19})$
					0.03		"	9.06	-8					"
					0.3		"	1.02	-6					"
.130	m-$IC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		-	kAB	76	3.58	-5					$(^{19})$
.131	p-$IC_6H_4CH_2F + C_2H_5OH$	Et64	0.07	HCl	0	kA	81	1.12	-7				*	$(^{19})$
					0.03		"	4.6	-7					"
					0.3		"	4.8	-8					"
.132	p-$IC_6H_4CH_2F + OH^-$	Et64	A = B = 0.22		-	kAB	81	7.16	-5				*	$(^{19})$
.133	p-$IC_6H_4CH_2F + OC_2H_5^-$	Et95	A = B = 0.22		-	kAB	76	4.45	-5					$(^{19})$
.134	o-$IC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	9.7	-8					$(^{22b})$
							60	2.1	-6	20.9	8.2	7		
		Et50	~ 0.01			kA	30	4.1	-7					$(^{22a})$
							83	7.4	-5					
.135	m-$IC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	6.6	-8					$(^{22b})$
							60	1.5	-6	21.2	1.1	8		
		Et50	~ 0.01			kA	30	2.5	-7					$(^{22a})$
							83	5.2	-5					

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
.136	p-$IC_6H_4CH_2Cl + H_2O$	An50	~ 0.01			kA	30	1.7	-7					(22b)
							60	3.6	-6	20.9	1.6	8		
		Et50	~ 0.01			kA	30	6.95	-7					(22a)
							83	1.2	-4					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
	Aryloxy-substituted primary alkyl halide													
.137	$C_6H_5O(CH_2)_2Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	97	2.61	−7					(4)
.138	*o*-$CH_3C_6H_4O(CH_2)_2Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	97	3.29	−6					(4)
.139	*m*-$CH_3C_6H_4O(CH_2)_2Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	97	2.72	−6					(4)
.140	*p*-$CH_3C_6H_4O(CH_3)_2Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	97	3.55	−6					(4)
.141	*p*-$ClC_6H_4O(CH_2)_2Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	97	1.55	−6					(4)
.142	$C_6H_5O(CH_2)_3Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	86	2.35	−6					(4)
							97	8.32	−6	24.3				"
.143	$C_6H_5O(CH_2)_4Br + H_2O$	PhOH	B = 0.5; L = 0.1; M = 0.05			k AB	86	8.82	−6	25.8				(4)
	Arylthio substituted primary alkyl halide													
.144	*p*-$CH_3C_6H_4S(CH_2)_2Cl + H_2O$	An50	0.005			k A	25	1.70	−3				*	(1)
							55	3.05	−2	18.8				"
.145	s-$(CH_3)_3C_6H_2S(CH_2)_2Cl + H_2O$	An50	0.005			k A	25	3.23	−3				*	(1)
							55	6.53	−2	19.6				"
.146	*p*-$CH_3OC_6H_4S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	4.34	−2				*	(1)
.147	*p*-$NO_2C_6H_4S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	7.5	−4				*	(1)
							75	4.17	−3	19.8				"
.148	*p*-$ClC_6H_4S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	1.02	−2				*	(1)
							75	4.35	−2	16.2				"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.149	p-$BrC_6H_4S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	8.45	-3				*	(1)
							75	3.32	-2	15.6				"
.150	p-$IC_6H_4S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	7.10	-3				*	(1)
							75	3.57	-2	18.4				"
.151	2, 5-$Cl_2C_6H_3S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	1.05	-3				*	(1)
							75	4.62	-3	16.9				"
.152	s-$Cl_3C_6H_2S(CH_2)_2Cl + H_2O$	An50	0.005			k A	55	5.33	-4				*	(1)
							75	3.30	-3	20.8				"
Di-aryl-substituted alkyl halide														
.153	$(C_6H_5)_2CHCl + H_2O$	$(Me)_2CO$	A ~ 0.1			k AB								(30)
			B = 0.5556				50	6.39	-7					"
			1.1112				"	1.15	-6					"
			2.7778				"	4.75	-6					"
			5.5556				"	1.77	-5					"
.154	$(C_6H_5)_2CHCl + \begin{cases} C_2H_5OH & (a) \\ H_2O & (b) \end{cases}$	$EtOH + H_2O$ %	0.03 – 0.14										*	(22)
		0				(a + b) = k A	0	1.80	-6					"
		0				"	25	4.84	-5	21.3				
		0				(a + b) = k AB	25	4.85	-5				*	"
		0.15					"	5.28	-5					"
		0.58					"	5.98	-5					"
		1.07					"	6.80	-5					"
		2.39					"	8.86	-5					"
		7.19					"	1.92	-4					"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.155	$(C_6H_5)_2CHCl + C_2H_5OH$	B	0.4 – 0.1			k A	25	5.76	–5				*	(9)
			0.6 – 0.1	H_2O	0.86	"	"	6.70	–5					"
				"	1.58	"	"	1.15	–4					"
			0.1	$PhNO_2$	0.3 – 0.6	"	"	4.36	–5					"
			0.09	HCl	0.2 – 0.4	"	"	6.80	–5					"
.156	$(C_6H_5)_2CHCl + C_2H_5OH$	EtE	~ 0.001			k A	25	8.41	–7				*	(21b)
							30	2.0	–6	26.6	5.0	11		
.157	$(p\text{-}CH_3OC_6H_4)_2CHCl + CH_3OH$	$PhNO_2$	A ~ 0.07;	Et_3N	~ 0.1	k AB + k'AB^2								(2c)
			B = 0.07 – 0.2			k	25	2.22	–3					
						k'	"	1.0	–2					
	Tri - aryl - substituted alkyl halide													
.158	$(C_6H_5)_3CCl + H_2O$	Diox	A = 0.1 – 0.2; B = 0.1 – 0.5			k AB	50	3.3	–4					(23a)
.159	$(C_6H_5)_3CCl + CH_3OH$	C_6H_6	A = 0.1	C_5H_5N	0.1	k AB^2	25	4.33	–3	6.6	(25 – 60°)		*	(27)
			B = 0.03 – 0.19											
.160	$(C_6H_5)_3CCl + C_6H_5OH$	"	"	"	"	k AB^2	25	6.7	–5				*	(27)
.161	$(C_6H_5)_3CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	1.57	–3				*	(21b)
							25	1.24	–2	13.4	1.45	6		
.162	$(C_6H_5)_3CBr + H_2O$	C_6H_6	A = 0.1	C_5H_5N	0.1		25	very fast					*	(27)
			B = 0.03 – 0.19											
.163	$(C_6H_5)_3CBr + CH_3OH$	"	"	"	"	k AB^2	25	~ 3.7	–1				*	(27)
.164	$(C_6H_5)_3CBr + (C_6H_5)_3COH$	"	"	"	"	k AB^2	60	2.3	–5				*	(27)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.165	$(p\text{-}CH_3C_6H_4)(C_6H_5)_2CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	7.18	-3				*	(^{21b})
							25	1.60	-2	12.4	1.1	6		
.166	$(p\text{-}CH_3OC_6H_4)_3CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	> 1.5	-1	26.6	5.0	11	*	(^{21b})
.167	$(p\text{-}(CH_3)_3C.C_6H_4)_3CCl + CH_3OH$	C_6H_6	A = 0.1	C_5H_5N	0.1	k AB^2	25	1.3	-1				*	(^{27})
		B = 0.03 - 0.19												
.168	$(1\text{-}C_{10}H_7)(C_6H_5)_2CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	2.14	-3				*	(^{21b})
							25	1.59	-2		9.2	5		
.169	$(2\text{-}C_{10}H_7)(C_6H_5)_2CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	2.63	-3				*	(^{21b})
							25	1.97	-2	13.0	1.15	6		
.170	$(p\text{-}NO_2C_6H_4)_3CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	1.02	-5				*	(^{21b})
							25	1.36	-4	16.7	4.0	6		
.171	$(p\text{-}FC_6H_4)_3CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	1.15	-3				*	(^{21b})
							25	9.34	-3	13.6	1.4	6		
.172	$(p\text{-}ClC_6H_4)_3CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	4.96	-4				*	(^{21b})
							25	3.97	-3	13.5	2.8	5		
.173	$(p\text{-}BrC_6H_4)_3CCl + C_2H_5OH$	EtE	~ 0.001			k A	0	5.44	-4				*	(^{21b})
							25	3.58	-3	13.2	3.3	5		
Aryl-substituted halogen-substituted alkyl halide														
.174	$C_6H_5CHCl_2 + H_2O$	An50	~ 0.01			k A	30	3.8	-6				*	(^{22b})
							60	1.10	-4					
		"	"	KOH	0.05	k A	30	3.8	-6				*	(^{22b})
					"		60	1.12	-4					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.174	$C_6H_5CHCl_2 + H_2O$ *(continued)*	An50	~ 0.01	KOH	0.10	k A	30	3.7	−6					
					"		60	1.07	−4					
					0.26		30	3.2	−6					
					"		60	0.87	−4					
.175	$C_6H_5CCl_3 + H_2O$	An50	0.01			k A	30	1.8	−4				*	$(^{22b})$
		"	"	KOH	0.05	k A	30	1.8	−4				*	"
					0.10		"	1.8	−4					
					0.26		"	1.45	−4					
		"	"	CH_3COOK	0.25	"	30	1.43	−4				*	"
		"	"	KNO_3	0.25	"	30	1.75	−4				*	"
.176	o-$ClC_6H_4CHCl_2 + H_2O$	An50	~ 0.01			k A	60	2.2	−6				*	$(^{22b})$
		"	"	KOH	0.05	k A	60	2.5	−6				*	"
					0.10		"	2.8	−6					
					0.26		"	3.3	−6					
.177	m-$ClC_6H_4CHCl_2 + H_2O$	An50	~ 0.01			k A	60	1.3	−6				*	$(^{22b})$
		"	"	KOH	0.05	k A	60	1.8	−6				*	$(^{22b})$
					0.10		"	2.3	−6					
					0.26		"	3.0	−6					
.178	p-$ClC_6H_4CHCl_2 + H_2O$	An50	~ 0.01			k A	60	4.5	−5				*	$(^{22b})$
		"	"	KOH	0.05	k A	60	4.5	−5				*	"
					0.10		"	4.2	−5					
					0.26		"	3.5	−5					

SUPPLEMENTARY TABLES

Fraction of (elimination) reaction (b) (13)						
(.18)	$(CH_3)_2CHBr + OH^-$					
°C	45	50	60	75	80	100
Solvent: Et60	0.532	-	0.557	0.575	-	0.636
Et80	-	0.581	-	-	0.612	0.665

Composition of products (molefraction, *N*) at 25° C (3)										
(.24) $(CH_3)_3CCl + \left\{\begin{matrix}H_2O\\CH_3OH\end{matrix}\right.$						(.25) $(CH_3)_3CCl + \left\{\begin{matrix}H_2O\\C_2H_5OH\end{matrix}\right.$				
Solvent			Product			Solvent		Product		
MeOH %	MeOH (*N*)	H_2O	$(CH_3)_3COH$	$(CH_3)_3COCH_3$	C_4H_8	EtOH %	H_2O	$(CH_3)_3COH$	$(CH_3)_3COC_2H_5$	C_4H_8
70	0.510	0.490	0.55	0.36	0.09	60	0.683	0.715	0.155	0.13
85	0.716	0.284	0.28	0.59	0.13	80	0.447	0.56	0.27	0.17
92	0.836	0.164	0.14	0.68	0.18	90	0.264	0.37	0.41	0.22

(.69.1) $CHCl{:}CHCH_2Cl + H_2O \longrightarrow CHCl{:}CHCH_2OH + HCl$

Solvent H_2O; Temperature 80° C ; x = % hydrolyzed after 30 minutes

Catalyst	Isomer	x
0.2 % CuCl, 1.5 % HCl	α	30
	β	73
1 % NaOH	α	39
	β	32
1.5 % HCl	α	8
	β	4

SOLVENTS

Diox	1,4 - Dioxane
DiW	1,4 - Dioxane: H_2O = 2:1 (vol)
Et 50 (60, 64, 80, 95)	C_2H_5OH (vol % as indicated) + H_2O
EtE	C_2H_5OH 40 % + $(C_2H_5)_2O$ 60 % (21b)
An 50 (80)	$(CH_3)_2CO$ (vol % as indicated) + H_2O
AnD 50	$(CH_3)_2CO$ 50 vol % + D_2O 50 vol %
WAn	1 l $(CH_3)_2CO$ + 400 g H_2O
WEt	1 l C_2H_5OH + 400 g H_2O

COMMENTS

Classification. The aliphatic halides undergoing solvolysis are grouped under the headings: Saturated alkyl halide; Carboxyl - substituted alkyl halide; Halogen - substituted alkyl halide; Unsaturated alkenyl halide; Mono-aryl-substituted alkyl halide; Aryloxy - substituted alkyl halide; Arylthio - substituted alkyl halide; Di-aryl-substituted alkyl halide; Tri-aryl-substituted alkyl halide; Aryl-substituted halogen-substituted alkyl halide. In each group, the halides are arranged as usual in the order of increasing numbers of C atoms in the alkyl, straight-chain isomers preceding the branched-chain isomers; the order of halides is F, Cl, Br, I.

Comments by Literature References. (1) Original k assumed to be in minutes. (4) From reverse reaction. (19) For alkaline hydrolysis, k calculated from fractions of completion of the reaction in 10 hours, assuming second order. For HCl-catalyzed hydrolysis, k was calculated assuming first order, from fractions of completion in, respectively, 120, 120, and 10 hours, with 0, 0.03, and 0.3 M/l HCl (21b) The values of k as listed are valid only for the given concentration; the variation of k with the concentration c = ester + ether is $k = k_1 + k_2/(k_3 + c)$, where the second term stems from a second mechanism, contributing the rate-constant term k_2/k_3 at $c = 0$. The preexponential factor is formulated $a + b/(k_3 + c)$. (22a) (22b) Rates of the nonalkaline hydrolyses are unaffected by H_2SO_4 up to 0.5 M/l. The rates of the alkaline hydrolyses are represented by first-order equations and rate constants; consequently, in the tables, KOH is listed as "addend" not as reactant. KOH is said to exert, in addition to the solvolytic mass-action of OH^-, a retarding effect on account of the hydrophilic nature of K^+. For the alkaline hydrolysis (.73) and analogous reactions, a good second-order k can be given up to about 0.1 M/l KOH, but this second-order k falls off at higher concentrations of KOH. However, the second-order k remains satisfactorily constant in (.88) owing to presence of the COOH group. In reaction (.158), CH_3COOK has the same effect as KOH, whereas KNO_3 has none. (27) C_5H_5N acts only as acceptor for the hydrogen halide formed; its occasional replacement by $C_6H_5N(C_2H_5)_2$, C_9H_7N, or α-$CH_3C_9H_6N$, does not affect k much. In solvolysis by CH_3OH mixed with C_6H_5OH or substituted phenols, the rate law is $k\,AB\,[PhOH]$ (data of k in original). See further displacement reactions with amines, 332.751.

Comments by Reactions. **(.1)** In H_2O: Arrhenius equation not applicable; $\log k = 110.223 - (10403/T) - 33.559 \log T$. (.2) In H_2O Arrhenius equation not applicable; $\log k = 112.656 - (10236/T) - 34.259 \log T$. (.3) In H_2O Arrhenius equation not applicable; $\log k = 111.859 - (10534/T) - 33.821 \log T$. (.4) Reaction with KOH in

COMMENTS *(continued)*

abs. EtOH. (.6.1) As (.4); k independent of A, but varying with B. Data of k are averages for B = 0.01 - 0.1. (.12) As (.4). (.17) The second-order k are derived from the overall reaction (a + b) (.18). (.24) (.25) (.26) The kinetics of the simultaneous hydrolysis + alcoholysis have been represented ([23]) by two-term second-order rate equations, in terms of partial vapor pressures of the components, of the type $-d(A/A_o)/dt = k_w AB_w + k_a AB_a$, with the notation A = tert-BuCl, $B_w = H_2O$, B_a = alcohol (CH_3OH or C_2H_5OH), subscript $_o$ referring to the pure substance; The constant k_w was derived from the experimental rates of pure hydrolysis in acetone, or in dioxane on the assumption of a second-order law $k_w AB_w$, and, thence, by difference, from the experimental rate of hydrolysis + alcoholysis, on the assumption of the second-order law, the constants k_a. However, this formulation fails to render the experimental compositions of the products (see Supplementary Tables). This can be achieved by assuming hypothetical higher-molecular reactions of the type $A + 2B_w$, $A + 2B_a$, and $A + B_w + B_a$, with a three-term and three-constant third-order rate law, or, better, by assuming similar polymolecular reactions of even higher orders, resulting in higher-order rate laws. These laws, and the high-order k, obviously purely hypothetical, have not been included in these Tables, and the advantage of expressing mass action in terms of partial pressures has not been deemed convincing. In the judgement of the editor, the experimental data warrant only evaluation in terms of an overall first-order constant for the hydrolysis + alcoholysis. According to ([11]), this constant can be represented by $\log k = 1.232 \log H - 9.811$, where H = Henry's constant of tert-BuCl in the given solvent. (.26) Data for hydrolysis; alcoholysis is disregarded. Under identical conditions, with excess A, k remains constant when, after consumption of the initially present OH^-, the solution passes the neutral point into the acid region. (.32) (.33) Accompanied by elimination reaction which see 422.471.

(.34) (.35) (.36) Reaction (.34) measured directly; similarly, the reactions $CH_3N(CH_2CH_2Cl)_2 + (C_2H_5)_3N \longrightarrow CH_3N(CH_2CH_2Cl)(CH_2CH_2)N(C_2H_5)_3Cl$, with $k = 4.2 \times 10^{-4}$, and $CH_3N(CH_2CH_2Cl)_2 + 2\,Na_2S_2O_3 \longrightarrow CH_3N(CH_2CH_2S_2O_3Na)_2 + 2\,NaCl$, with $k = 3.0 \times 10^{-4}$ (converted to sec from the presumably original hours). The rate-determining step of all these reactions is assumed to be the ionization $CH_3N(CH_2CH_2Cl)_2 \longrightarrow CH_3\overset{+}{N}(CH_2CH_2Cl){:}(CH_2CH_2) + Cl^-$. This step, and its reverse, is assumed to underlie reactions (.35) and (.36), and the simultaneous dimerizations of the type $2\,RN(CH_2CH_2Cl)_2 \longrightarrow R(CH_2CH_2Cl)\overset{+}{N}{:}(CH_2CH_2)_2{:}\overset{+}{N}(CH_2CH_2Cl)R + 2\,Cl^-$ (where R = CH_3 or C_2H_5). For the hydrolyses (.35) and (.36), and the accompanying dimerizations, ([2b]) and ([2a]) give fractional times, and rate constants of the constituent steps calculated with the aid of a differential analyzer on the basis of the

COMMENTS *(continued)*

assumed mechanisms. (.46) (.49) Elimination reaction (c) is about 10 % of the total. (.51) (.52) Second-order constants obtained after deduction of first-order terms determined in acid and neutral solutions.

(.53) (.54) The hypothetical second-order reaction (.54) is considered to be the rate-determining step (followed by $CH(COO^-)(OH_3^+) \longrightarrow CH_2(COO^-)OH + H^+$) of the observed reaction (.53). (.55) (.56) As (.53) (.54). (.59) Second step of hydrolysis becomes noticeable at 60°C.

(.65) First-order *k* falls with time, indicating presence of some second-order reaction; second-order *k* calculated disregarding the first-order reaction. (.73) See comments on Literature reference (^{22b}). No reaction occurs between the saturated vapors slightly above 100° C, except in contact with a liquid water surface. At 100° C, the rate of production of HCl, in contact with liquid water, can be calculated from the original data to about 2.2×10^{-8} moles /sec/cm^2(GSF). (.77) First-order *k* constant over 25 % of the reaction, then falling off. Second-order holding in any direction if difference of forward and back reaction is integrated as a whole. (.78) A second-order law in terms of partial pressures, proposed by (^{23}), and involving two separate terms, for hydrolysis and alcoholysis, fails to account for the composition of the products (^{3}). The catalytic effect of H_2O exceeds greatly its participation as reactant (^{9}). (.84) (.175) See comments on Literature reference (^{22b}).

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SOLVOLYSIS

Aryl halides

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $ArX + OR^- \rightarrow ArOR + X^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$p\text{-}NO_2C_6H_4Br + OCH_3^-$	CH_3OH	A = B = 0.002	k AB	99	7.8	−4
.2	$p\text{-}(CH_3SO_2)C_6H_4Br + OCH_3^-$	CH_3OH	A = B = 0.002	k AB	99	2.8	−5

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T. F. Bunnet, Arnold Levitt, *ACS* 1948, 70, 2778.

ESTER SOLVOLYSIS

Alkyl halide + Phenolate

Liquid phase

Reaction type RX + ArO$^-$ ⟶ ROAr + X$^-$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
						k^o	n			
.1	$CH_3I + CH_2:CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	kAB	42.5	1.23	-3			(²)
			0.250		"	1.50	-3			
			0.1875		"	1.64	-3			
			0.125		"	2.11	-3			
			0.375	"	50	2.57	-3			
			0.250		"	2.85	-3			
			0.1875		"	3.27	-3			
			0.125		"	4.18	-3			
			0.100		"	5.18	-3			
			0.500	"	55	3.63	-3			
			0.375		"	3.76	-3			
			0.250		"	4.59	-3			
			0.1875		"	5.02	-3			
			0.125		"	6.16	-3	18.9		
.2	$C_2H_5I + CH_2:CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	kAB	50	5.94	-4		*	(²)
			0.250		"	7.96	-4			
			0.125		"	1.09	-3			

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
						k^o	n			
.2	$C_2H_5I + CH_2:CHCH_2C_6H_3(OCH_3)O^-$ *(continued)*		0.500	k AB	57.7	1.17	-3			(2)
			0.250		"	1.46	-3			
			0.125		"	2.07	-3			
			0.250	"	68	3.49	-3			"
			0.125		"	4.98	-3	19.0		
.3	$C_2H_5I + C_6H_5O^-$	CH_3OH	0.1	k AB	58.5	4.61	-4		*	(1)
		C_2H_5OH	"		"	1.04	-3			
		C_3H_7OH	"		"	6.36	-4			
		iso - C_4H_9OH	"		"	3.12	-4			
		iso - $C_5H_{11}OH$	"		"	2.08	-4			
.4	$C_3H_7I + C_6H_5O^-$	CH_3OH	0.1	k AB	58.5	1.92	-4		*	(1)
		C_2H_5OH	"		"	4.15	-4			
		C_3H_7OH	"		"	2.69	-4			
		iso - C_4H_9OH	"		"	1.33	-4			
		iso - $C_5H_{11}OH$	"		"	9.00	-5			
		$(CH_3)_2CO$	0.05		"	1.09	-3			
.5	$C_3H_7I + CH_2:CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	k AB	57.5	4.24	-4		*	(2)
			0.250		"	5.28	-4			
			0.500	"	68	1.12	-3			"
			0.250		"	1.40	-3			
			0.125		"	2.08	-3			

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
						k^o	n			
.5	$C_3H_7I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ *(continued)*		0.250		75	2.05	-3			(2)
			0.125		"	3.50	-3			
			0.100		"	4.01	-3	21.0		
.6	$(CH_3)_2CHI + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	k AB	57.5	3.06	-4		*	(2)
			0.250		"	4.08	-4			
			0.500		68	8.28	-4			"
			0.250		"	1.05	-3			
			0.125		"	1.56	-3			
			0.500		75	1.54	-3			"
			0.250		"	1.92	-3			
			0.100		"	3.15	-3			
.7	$C_4H_9I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	k AB	57.5	3.97	-4		*	(2)
			0.250		"	5.00	-4			
			0.500		68	9.92	-4			"
			0.250		"	1.23	-3			
			0.100		"	2.18	-3			
			0.500		75	1.77	-3			"
			0.250		"	2.25	-3			
			0.100		"	3.57	-3	20.6		
.8	$C_2H_5CH(CH_3)I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	k AB	57.5	1.43	-4		*	(2)
			0.250		"	1.82	-4			
			0.500		68	3.72	-4			"
			0.250		"	4.46	-4			
			0.125		"	7.30	-4			

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k =$ $k^o \times 10^n$		E	Comments	Literature
						k^o	n			
.8	$C_2H_5CH(CH_3)I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$ (*continued*)		0.500		75	5.45	-4			
			0.250		"	7.46	-4			
			0.125		"	1.64	-3	19.6		
.9	$C_2H_5I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	k AB	57.5	3.77	-4		*	(2)
			0.250		"	4.80	-4			
			0.375		68	1.01	-3			"
			0.125		"	1.67	-3			
			0.500		75	1.69	-3			"
			0.100		"	3.33	-3	20.3		
.10	$C_3H_7CH(CH_3)I + CH_2{:}CHCH_2C_6H_3(OCH_3)O^-$	C_2H_5OH	A = B = 0.500	k AB	57.5	2.18	-4		*	(2)
			0.250		"	2.82	-4			
			0.500		68	4.85	-4			"
			0.250		"	6.82	-4			
			0.125		"	1.13	-3			
			0.500		75	8.32	-4			"
			0.250		"	1.69	-3			
			0.100		"	2.13	-3	19.4		

COMMENTS

(.1) (.2) Addition of NaI lowers k slightly. Data of (2): selected points.

LITERATURE

(1) D.Segaller, *CSL* 1914, **105**, 113. (2) S.S.Woolf, *CSL* **1937**, 1172.

SOLVOLYSIS

Mercaptyl carboxylate

Liquid phase

Reaction type $R'COSR + \left\{\begin{matrix} H_2O \\ OH^- \end{matrix}\right\} \longrightarrow RSH + \left\{\begin{matrix} R'COOH \\ R'COO^- \end{matrix}\right.$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
								k^o	n		A^o	n
.1	$CH_3COSC_2H_5 + H_2O$	$H_2O + (CH_3)_2CO$ 24.6 wt %	0.1	HCl	0.1	$kA[H^+]$	30.0	8.0	-6			
							40.0	2.05	-5	17.5		
		43.0	0.15	"	0.24	"	30.0	3.83	-6			
							40.0	1.08	-5	18.0		
		62.0	0.1	"	0.1	"	30.0	2.30	-6			
							40.0	5.82	-6	18.0		
.2	$CH_3COSC_2H_5 + OH^-$	$H_2O + (CH_3)_2CO$ 24.6 wt %	A = 0.03 - 0.06; B = 0.06 - 0.1			kAB	10.0	2.08	-2			
							20.0	4.67	-2	13.0	1.6	10
		43.0	"			"	10.0	1.43	-2			
							20.0	3.26	-2	13.8	4.0	10
		62.0	"			"	10.0	1.07	-2			
							20.0	2.57	-2			
							30.0	5.76	-2	14.4	8.0	10

LITERATURE

J.R.Schaefgren, *ACS* 1948, 70, 1308.

ESTER EXCHANGE

Aliphatic alcohol + Alkyl carboxylate

Liquid phase

Reaction type $R_1OH + R'COOR_2 \rightarrow R_2OH + R'COOR_1$
(A) (B) (L) (M)

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Medium	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
								k^o	n	
.1	$C_4H_9OH + CH_3COOC_2H_5$	pure liquid	A/B = 1	H_2SO_4	0.1 %	k AB	60	3.2	-5	
			1.55		"		"	3.4	-5	
			1		0.2		"	6.1	-5	
			1.55		"		"	6.1	-5	
			1		0.1	"	70	5.2	-5	
			1.55		"		"	5.5	-5	
			1		0.2		"	1.10	-4	
			1.55		"		"	1.12	-4	
			1		0.1		80	9.0	-5	
			1		0.2		"	1.85	-4	12.8
.2	$C_2H_5OH + CH_3COOC_4H_9$	pure liquid	A/B = 1	H_2SO_4	0.1 %	k AB	60	3.2	-5	
							70	5.5	-5	
							80	8.3	-5	

COMMENTS

The rate constants of the two opposing reactions (.1) and (.2) are derived from the integrated form of the total rate equation $k_1AB - k_2LM$ which, with one of the k expressed by the equilibrium constant $K = 0.96$, and with the amounts of reactants expressed in *mole fractions*, becomes $kt = \ln A_oB_o / (A_oB_o - L)$. In the given range of H_2SO_4, k is proportional to $[H_2SO_4]$. The mechanism is conceived as $B + H^+ \rightarrow BH^+$, and $A + BH^+ \rightleftarrows L + MH^+$.

LITERATURE

L. Farkas, O. Schächter, B. H. Vromen, *ACS* 1949, 71, 1991.

ESTER EXCHANGE

Phenol carboxylate + Aliphatic alcohol

Liquid phase

Reaction type $\underset{(A)}{R'COOAr} + \underset{(B)}{ROH} \rightarrow \underset{(L)}{R'COOR} + \underset{(M)}{ArOH}$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
								k^o	n	
.1	$CH_3COOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	6.30	-3	
.2	$CH_3COOC_{10}H_7(\beta) + C_2H_5OH$	B	0.006 - 4.0	HCl	1	kA	25	1.52	-3	
.3	$CH_3COOC_{10}H_7(\beta) + C_3H_7OH$	B	0.006 - 4.0	HCl	1	kA	25	1.46	-3	
								3.90	-3	12.1
.4	$CH_3COOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	9.0	-5	
							40	2.52	-4	12.7
.5	$C_2H_5COOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	3.96	-3	
.6	$C_2H_5COOC_{10}H_7(\beta) + C_2H_5OH$	B	0.006 - 4.0	HCl	1	kA	25	8.45	-4	
.7	$C_2H_5COOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	4.4	-5	
							40	1.3	-4	13.4
.8	$C_2H_5COOC_{10}H_7(\beta) + (C_2H_5)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	7.6	-4	
.9	$C_3H_7COOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	2.32	-3	

222.443.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
								k^o	n	
.10	$C_3H_7COOC_{10}H_7(\beta) + C_3H_7OH$	B	0.006 - 4.0	HCl	1	kA	25	4.0	-4	
							40	1.15	-3	13.0
.11	$C_3H_7COOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	2.26	-5	
							40	6.34	-5	12.7
.12	$(CH_3)_2CHCOOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	9.15	-4	
.13	$(CH_3)_2CHCOOC_{10}H_7(\beta) + C_2H_5OH$	B	0.006 - 4.0	HCl	1	kA	25	1.43	-4	
.14	$(CH_3)_2CHCOOC_{10}H_7(\beta) + C_3H_7OH$	B	0.006 - 4.0	HCl	1	kA	25	1.22	-4	
.15	$(CH_3)_2CHCOOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	5.0	-6	
							40	1.4	-5	12.7
.16	$C_4H_9COOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	1.93	-3	
.17	$C_4H_9COOC_{10}H_7(\beta) + C_3H_7OH$	B	0.006 - 4.0	HCl	1	kA	25	3.9	-4	
							40	1.07	-3	12.4
.18	$C_4H_9COOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	2.06	-5	
							40	5.90	-5	12.9
.19	$(CH_3)_3CCOOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	4.5	-5	
.20	$(CH_3)_3CCOOC_{10}H_7(\beta) + C_3H_7OH$	B	0.006 - 4.0	HCl	1	kA	25	3.5	-6	
							40	1.2	-5	12.7

No	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
								k^o	n	
.21	$(CH_3)_3CCOOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	9.9	-8	
							40	4.3	-7	
.22	$(C_2H_5O)COOC_{10}H_7(\beta) + CH_3OH$	B	0.006 - 4.0	HCl	1	kA	25	1.58	-5	
.23	$(C_2H_5O)COOC_{10}H_7(\beta) + C_3H_7OH$	B	0.006 - 4.0	HCl	1	kA	25	3.1	-6	
							40	1.05	-5	
.24	$(C_2H_5O)COOC_{10}H_7(\beta) + (CH_3)_2CHOH$	B	0.006 - 4.0	HCl	1	kA	25	2.35	-7	
							40	8.0	-7	

LITERATURE

M.Harfenist, R.Baltzly, *ACS* 1947, 69, 362

ESTER EXCHANGE

Alkyl halide + carboxylic acid

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, Comments, Literature, at the end of the table.

Reaction types $$RX + \begin{Bmatrix} R'COOH \\ R'COO^- \end{Bmatrix} \longrightarrow R'COOR + \begin{Bmatrix} HX \\ X^- \end{Bmatrix}$$

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$C_2H_5I + CH_3CHOHCOO\ Ag$	Et 60	A = B ~ 0.014 – 0.015			k AB	25	2.7	-2	*	(2)
							→	2.1	-2		
			~ 0.03			"		5.0	-2		
							→	2.0			
.2	$(COO^-)CH_2Br + HCOO^-$	H_2O	A = 0.05 – 0.5 B = 0 – 0.7	$NaNO_3$	1 – (A + B)	k AB	25	5.5	-7	*	(4) (1)
.3	$(COO^-)CH_2Br + CH_3COO^-$	H_2O	A = 0.05 – 0.5 B = 0 – 0.7	$NaNO_3$	1 – (A + B)	k AB	25	8.3	-7	*	(4) (1)
.4	$(COO^-)CH_2Br + CH_2OHCOO^-$	H_2O	A = 0.05 – 0.5 B = 0 – 0.7	$NaNO_3$	1 – (A + B)	k AB	25	5.8	-7	*	(4) (1)
.5	$(COO^-)CH_2Br + CH_2ClCOO^-$	H_2O	A = 0.05 – 0.5 B = 0 – 0.7	$NaNO_3$	1 – (A + B)	k AB	25	2.3	-7	*	(4) (1)
.6	$(COO^-)CH_2Br + CH_2BrCOO^-$	H_2O	A = 0.05 – 0.5 B = 0 – 0.7	$NaNO_3$	1 – (A + B)	k AB	25	3.2	-7	*	(4) (1)
.7	$CH_3CH{:}CHCH_2Cl + CH_3COOH.NH_2C(NH)N(C_6H_5)_2$	CH_3COOH	A = B ~ 1.0			k AB	78.6	3.06	-5	*	(3)

222.471.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.8	$CH_3CH:CHCH_2Cl + CH_3COOK$	CH_3COOH	A = 1.0; B = 0.2 - 1.0			k AB	78.6	2.08	-5	*	([3])
.9	$CH_2:CHCH(CH_3)Cl + CH_3COOK$	CH_3COOH	A = B ~ 1.0			k AB	78.6	9.5	-6		([3])
							→	1.0	-5		
			A = 1.0; B ~ 0.2			"		1.44	-5		
							→	1.77	-5		
.10	$CH_2:CHCH(CH_3)Cl + CH_3COOH.NH_2C(NH)N(C_6H_5)_2$	CH_3COOH	A = B ~ 0.1			k AB	78.6	1.02	-5		([3])
			A = 1.0; B ~ 0.2			k A	"	4.45	-6		"
.11	$d\text{-}C_6H_5CH(CH_3)Cl + CH_3COOH$	CH_3COOH	A = 0.075 - 0.160	CH_3COOLi	0.2	k A	50	3.25	-6	*	([5])
				LiCl 0.15 + CH_3COOLi	0.5		"	4.85	-6		
				LiCl 0.5 + CH_3COOLi	0.15		"	3.56	-6		
			H_2O 0.141 +	LiCl 0.1 + CH_3COOLi	0.1		"	5.20	-6		
			H_2O 2.18 +	LiCl 0.1 + CH_3COOLi	0.1		"	6.05	-6		
			H_2O 3.09 +	LiCl 0.1 + CH_3COOLi	0.1		"	8.60	-6		
.12	$d\text{-}C_6H_5CH(CH_3)Cl + CH_3COON(C_2H_5)_4$	$(CH_3)_2CO$	0.05 - 0.15			k AB	50	4.7	-4		([5])

SOLVENTS

Et 60 C_2H_5OH 60 vol % + H_2O 40 vol %

COMMENTS

(.1) Partial solvolysis of the $CH_3CHOHCOOC_2H_5$ produced. Considerable fall of *k* with the progress of the reaction; the lower values of *k* refer to the reaction after about 3000 sec. (.2)-(.6) log *k* is a linear function of log K_b (base dissociation constant). (.7) (.8) With the progress of the reaction, increasing amount of $CH_2:CHCH(CH_3)OCOCH_3$ in the products. With B = 0.2, some upward drift of *k* at late stages of the reaction. (.9) Upward drift of *k* (upper figure after 10 hours) indicates some amount of first-order reaction. Products $CH_2:CHCH(CH_3)OCOCH_3$ and $CH_3CH:CHCH_2OCOCH_3$ in 51:49% ratio. (.11) (.12) Selected points.

LITERATURE

(1) H. M. Dawson, N. B. Dyson, *CSL* 1933, 49.
(2) F. G. Donnan, H. E. Potts, *CSL* 1910, 1882.
(3) J. D. Roberts, W. G. Young, S. Winstein, *ACS* 1942, 64, 2157.
(4) G. F. Smith, *CSL* 1943, 521.
(5) J. Steigman, L. P. Hammett, *ACS* 1937, 59, 2536.

ESTER EXCHANGE

Carboxylic acid ester + Hydrogen halide

Liquid phase

Reaction type $RCOOR' + HX \rightarrow RCOOH + R'X$

Rate measured $-dB/dt$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$CH_3COOCH_3 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	1.44	-8
.2	$CH_3COOC_2H_5 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	2.50	-9
.3	$CH_3COOC_3H_7 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	2.00	-9
.4	$CH_3COOCH(CH_3)_2 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	2.45	-9
.5	$CH_3COOCH_2CH{:}CH_2 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	5.92	-8
.6	$CH_3COOC_4H_9 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	1.33	-9
.7	$CH_3COOCH_2CH(CH_3)_2 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	2.22	-10
.8	$CH_3COOCH(CH_3)C_2H_5 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	2.25	-9
.9	$CH_3COOC(CH_3)_3 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	3.00	-4
.10	$CH_3COOCH_2CH_2OOCCH_3 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	3.11	-7
.11	$CH_3COOCH_2CH_2CH(CH_3)_2 + HBr$	CH_3COOH	$A = B \sim 0.06$	kAB	18 - 21	1.11	-9

222.741.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.12	$CH_3COOC(CH_3)_2C_2H_5$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	4.40	-4
.13	$CH_3COOCH_2CH_2CH_2OOCCH_3$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	3.97	-8
.14	$CH_3COOCH_2CH(CH_3)OOCCH_3$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	2.92	-7
.15	$CH_3COOC_6H_{13}$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	1.67	-8
.16	$CH_3COO(cyclo\text{-}C_6H_{11})$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	1.17	-8
.17	$CH_3COOCH_2CH(OCOCH_3)CH_2OOCH_3$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	2.09	-6
.18	$CH_3COOCH_2C_6H_5$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	3.15	-7
.19	$CH_3COOCH_2CH_2C_6H_5$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	4.72	-10
.20	$CH_3COOC_6H_5$ + HBr	CH_3COOH	A = B ~ 0.06	k AB	18 - 21	no reaction	

COMMENTS

(.10) (.13) (.14) No allocation for partial reaction with the second CH_3CO group.

(.20) No allocation for partial reaction with the second and third CH_3CO group.

LITERATURE

B.W.Tronow, N.C.Ssigbatullin, *BDC*^{B} 1929, 62, 2850.

Homogeneous Reactions
232.445.

CONDENSATION

Liquid phase

Aromatic aldehyde + Ketone

Reaction type $ArCHO + CH_3COR \longrightarrow ArCH{:}CHCOR + H_2O$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E
								k°	n	
.1	$C_6H_5CHO + CH_3COCH_3$	H_2O + dioxane 70 %	A = 0.025; B = 0.100	NaOH	0.036	kAB	25	1.37	-3	
					0.056		"	1.67	-3	
					"		50	4.65	-3	7.8
.2	$C_6H_5CHO + CH_3COC_2H_5$	H_2O + dioxane 70 %	B ~ 0.1	NaOH	0.051	kAB	25	6.7	-4	
			A = 0.025 - 0.030				50	1.25	-3	4.8
		60	A = 0.025		0.053		50	1.29	-3	
		50	"		"		50	1.30	-3	

LITERATURE

J. D. Gettler, L. P. Hammett, *ACS* 1943, 65, 1825.

232.451.

CONDENSATION

C = N bond formation

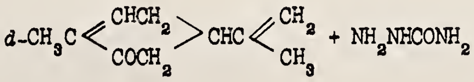
Liquid phase

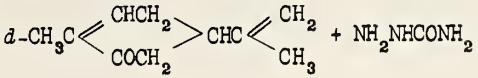
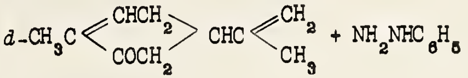
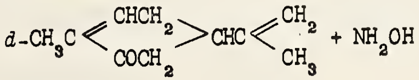
Amounts are in M/l.
Rates are in M/l per sec.
Solvents, Comments, Literature, at the end of the table

Reaction type $R_1R_2CO + H_2NR \longrightarrow R_1R_2C{:}NR + H_2O$

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
							k^o	n			
.1	$CH_3CHO + NH_2NHCONH_2$	H_2O; pH 7		k AB	25		6.0	0		*	(1)
.2	$(CH_3)_2CO + NH_2NHCONH_2$	H_2O; pH 7		k AB	0.0		6.35	-2			(3)
					25.1		8.61	-2	2.0		
		CeW; b 1		k AB	25		9.7	-2		*	(5)
		b 2			"		3.97	-1			
.3	$(CH_3)_2CO + NH_2OH.H^+$	H_2O; pH 1.22	0.003	k AB	17 – 19		2.16	-2		*	(2)
		2.18					1.89	-1			
		3.80					1.23	0			
		4.86					1.50	0			
		6.39					5.85	-1			
		7.97					1.06	-1			
.4	$CH_3COCOOH + NH_2NHCONH_2$	H_2O; pH 7		k AB	25		1.23	-1		*	(1)
.5	$C_3H_7CHO + NH_2NHCONH_2$	CeW; b 1		k AB	25		1.9	0		*	(5)
		b 2					fast				

232.451.

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$		ΔH	Comments	Literature
							k^o	n			
.6	$(C_2H_5)_2CO + NH_2NHCONH_2$	H_2O; pH 7		k AB	0.0		6.9	-3			(3)
					25.0		8.5	-3	1.4		
		CeW; b 1		k AB	25		2.83	-2		*	(5)
		b 2			"		1.85	-1			
.7	$(CH_3)_3CCHO + NH_2NHCONH_2$	H_2O; pH 7		k AB	25		3.33	-1			(1)
.8	$(CH_3)_3CCOCH_3 + NH_2NHCONH_2$	H_2O; pH 7		k AB	0.0		7.71	-4			(3)
					25.0		1.00	-3	1.8		
		CeW; b 1		k AB	25		6.8	-3		*	(5)
		b 2			"		2.47	-2			
.9	$\underline{CH_2(CH_2)_3}CO + NH_2NHCONH_2$	H_2O; pH 7		k AB	0.0		8.2	-3			(3)
					25.0		1.5	-2	4.0		
.10	$\underline{CH_2(CH_2)}_4CO + NH_2NHCONH_2$	H_2O; pH 7		k AB	0.0		4.37	-1			(3)
					25.1		5.12	-1	1.1		
		CeW; b 1		k AB	25		4.15	-1		*	(5)
		b 2			"		fast				
.11	$C_6H_{13}CHO + NH_2NHCONH_2$	CeW; b 1		k AB	25		1.13	0		*	(5)
		b 2					fast				
.12	$C_9H_{17}CHO + NH_2NHCONH_2$ citronellal	CeW; b 1		k AB	25		5.3	-1		*	(5)
		b 2		"	"		fast				
.13	 $d\text{-}CH_3C \ll \begin{smallmatrix} CHCH_2 \\ COCH_2 \end{smallmatrix} > CHC \ll \begin{smallmatrix} CH_2 \\ CH_3 \end{smallmatrix} + NH_2NHCONH_2$ (carvone)	Et 83	A = B = B.HCl = 0.015	k A	30		6.24	-5		*	(1a)
					40		1.28	-4			
			See Supplementary table		50		2.67	-4			

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	ΔH_a	Comments	Literature
.14	 $d\text{-}CH_3C{<}\genfrac{}{}{0pt}{}{CHCH_2}{COCH_2}{>}CHC{<}\genfrac{}{}{0pt}{}{CH_2}{CH_3} + NH_2NHCONH_2$ (carvone)	Et 83	A = 0.022; B = B.HCl = 0.05	k AB	30		5.2	-3			(^{3a})
.15	 $d\text{-}CH_3C{<}\genfrac{}{}{0pt}{}{CHCH_2}{COCH_2}{>}CHC{<}\genfrac{}{}{0pt}{}{CH_2}{CH_3} + NH_2NHC_6H_5$ (carvone)	Et 83	A = 0.02; B = 0.14; B.HCl = 0.01	k AB	30		3.7	-4			(^{3a})
.16	 $d\text{-}CH_3C{<}\genfrac{}{}{0pt}{}{CHCH_2}{COCH_2}{>}CHC{<}\genfrac{}{}{0pt}{}{CH_2}{CH_3} + NH_2OH$ (carvone)	Et 83	A = 0.065; B = B.HCl = 0.09 See Supplementary table	k AB	30		4.0	-3			(^{3a})
.17	$C_6H_5CH{:}CHCHO + NH_2NHCONH_2$	CeW; b 1		k AB	25		1.13	-1		*	(^{5})
		b 2		"	"		1.11	0			
.18	$C_6H_5CHO + NH_2NHCONH_2$	H_2O; pH 7		k AB	25		3.4	-2		*	(^{1})
		CeW; b 1		k AB	25		8.5	-2		*	(^{6})
		b 2			"		2.4	0			
.19	$C_6H_5CHO + NH_2NHC_6H_5.HCl$	Et 75			0	540					(^{4})
.20	$C_6H_5CHO + l\text{-}C_{10}H_{19}NH_2$ menthyl	C_2H_5OH			18	1920					(^{4})
		$C_6H_5CH_2OH$	0.05		"	960					
		$O{:}(CH_2)_4{:}O$	"		"	1860					
		$C_6H_5NO_2$	"		"	4200					
		$C_6H_5CH_3$	"		"	8600					
		$CHCl_3$	"		"	27000					

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
							k^o	n			
.21	$C_6H_5COCH_3 + NH_2NHCONH_2$	H_2O; pH 7		k AB	0.0		2.04	−4			(3)
				"	25.0		4.1	−4	4.6		
		OeW; b 1		k AB	25		5.5	−3		*	(5)
		b 2		"	"		4.7	−2			
				See supplementary table (.13)							(1a)
.22	$C_6H_5COCH_3 + NH_2NHC_6H_5\cdot HCl$	Et 75			0	10800					(4)
.23	$C_6H_5COCH_3 + NH_2OH.HCl$	Et 75	A = 0.2; B = 0.1		35	1440					(4)
.24	p-$CH_3C_6H_4COCH_3 + NH_2NHCONH_2$	Et 83		See supplementary table (.13)							(1a)
.25	1, 4-$(CH_3)_2$-C_6H_3-2-CHO + $NH_2NHC_6H_5\cdot HCl$	Et 75			0	3000					(4)
.26	1, 4-$(CH_3)_2$-C_6H_3-2-CHO + $NH_2OH.HCl$	Et 75	A = 0.2; B = 0.1		0	180					(4)
.27	o-$CH_3OC_6H_4CHO + NH_2NHC_6H_5\cdot HCl$	Et 75			0	60					(4)
.28	o-$CH_3OC_6H_4CHO$ + l-$C_{10}H_{19}NH_2$ menthyl	C_2H_5OH			18	720					(4)
		$C_6H_5CH_2OH$	0.05		"	840					
		O: $(CH_2)_4$:O	"		"	1020					
		$C_6H_5NO_2$	"		"	1080					
		$C_6H_5CH_3$	"		"	4000					
		$CHCl_3$	"		"	4115					
.29	p-$CH_3OC_6H_4CHO + NH_2NHCONH_2.HCl$	Et 70	A = 0.025; B = 0.050		0	840					(4)
				See supplementary table (.13)							(1a)

No.	Reaction	Solvent (Medium	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
							k^o	n			
.30	$p\text{-}CH_3OC_6H_4CHO + NH_2NHC_6H_5.HCl$	Et 75			0	3000					(4)
.31	$p\text{-}CH_3OC_6H_4CHO + NH_2OH.HCl$	Et 75	A = 0.2; B = 0.1		0	900					(4)
.32	$p\text{-}CH_3OC_6H_4CHO + l\text{-}C_{10}H_{19}NH_2$ menthyl	C_2H_5OH			18	4200					(4)
		$C_6H_5CH_2OH$	0.05		"	4200					
		$O:(CH_2)_4:O$	"		"	13800					
		$C_6H_5NO_2$	"		"	30200					
		$C_6H_5CH_3$	"		"	43000					
		$CHCl_3$	"		"	174000					
.33	$1, 2\text{-}(CH_3O)_2\text{-}C_6H_3\text{-}3\text{-}CHO + NH_2NHC_6H_5.HCl$	Et 75			0	720					(4)
.34	$1, 2\text{-}(CH_3O)_2\text{-}C_6H_3\text{-}4\text{-}CHO + NH_2NHC_6H_5.HCl$	Et 75			0	11400					(4)
.35	$o\text{-}OHC_6H_4CHO + l\text{-}C_{10}H_{19}NH_2$ menthyl	$O:(CH_2)_4:O$	0.05		18	300					(4)
		$C_6H_5NO_2$	"		"	540					
		$C_6H_5CH_3$	"		"	420					
		$CHCl_3$	"		"	3960					
.36	$p\text{-}OHC_6H_4CHO + NH_2NHCONH_2.HCl$	Et 70			0	900					(4)
.37	$p\text{-}OHC_6H_4CHO + NH_2NHC_6H_5.HCl$	Et 75			0	12000					(4)
.38	$p\text{-}OHC_6H_4CHO + NH_2OH.HCl$	Et 75	A = 0.2; B = 0.1		0	540					(4)

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^\circ \times 10^n$ k°	n	ΔH_a	Comments	Literature
.39	$p\text{-OHC}_6\text{H}_4\text{CHO} + l\text{-C}_{10}\text{H}_{19}\text{NH}_2$	$\text{C}_2\text{H}_5\text{OH}$			18	4900					$(^4)$
	menthyl	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	0.05		"	2640					
		$\text{O:(CH}_2)_4\text{:O}$	"		"	6000					
		$\text{C}_6\text{H}_5\text{NO}_2$	"		"	2100					
		$\text{C}_6\text{H}_5\text{CH}_3$	"		"	2600					
		CHCl_3	"		"	7200					
.40	$o\text{-OHC}_6\text{H}_4\text{COCH}_3 + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			35	12600					$(^4)$
.41	$o\text{-OHC}_6\text{H}_4\text{COCH}_3 + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		35	13800					$(^4)$
.42	$p\text{-OHC}_6\text{H}_4\text{COCH}_3 + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			35	19200					$(^4)$
.43	$p\text{-OHC}_6\text{H}_4\text{COCH}_3 + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		35	6600					$(^4)$
.44	$\text{1-OH-2-CH}_3\text{O-C}_6\text{H}_3\text{-4-CHO} + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			0	12000					$(^4)$
.45	$\text{1-OH-2-CH}_3\text{O-C}_6\text{H}_3\text{-4-CHO} + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		0	600					$(^4)$
.46	$\text{1-OH-2-CH}_3\text{O-C}_6\text{H}_3\text{-4-CHO} + l\text{-C}_{10}\text{H}_{19}\text{NH}_2$	$\text{C}_2\text{H}_5\text{OH}$			18	5300					$(^4)$
	menthyl	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	0.05		"	3300					
		$\text{O:(CH}_2)_4\text{:O}$	"		"	17400					
		$\text{C}_6\text{H}_5\text{NO}_2$	"		"	9300					
		$\text{C}_6\text{H}_5\text{CH}_3$	"		"	6000					
		CHCl_3	"		"	4300					

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
							k^o	n			
.47	$1\text{-OH-2-CH}_3\text{O-C}_6\text{H}_3\text{-6-CHO} + l\text{-C}_{10}\text{H}_{19}\text{NH}_2$	O: $(\text{CH}_2)_4$:O	0.05		18	180					
	menthyl	$\text{C}_6\text{H}_5\text{NO}_2$	"		"	300					
		$\text{C}_6\text{H}_5\text{CH}_3$	"		"	210					
		CHCl_3	"		"	1320					
.48	$1\text{-OH-3, 5-(CH}_3)_2\text{-C}_6\text{H}_2\text{-2-CHO} + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			0	120					(^{4})
.49	$1\text{-OH-3, 5-(CH}_3)_2\text{-C}_6\text{H}_2\text{-2-CHO} + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		0	240					(^{4})
.50	$1\text{-OH-3, 5-(CH}_3)_2\text{-C}_6\text{H}_2\text{-4-CHO} + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			0	5100					(^{4})
.51	$1\text{-OH-3, 5-(CH}_3)_2\text{-C}_6\text{H}_2\text{-4-CHO} + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		0	7800					(^{4})
.52	$o\text{-NO}_2\text{C}_6\text{H}_4\text{CHO} + \text{NH}_2\text{NHCONH}_2$	CeW; b 1		k AB	25		2.7	−2		*	(^{5})
		b 2		"	"		1.3	0			
.53	$o\text{-BrC}_6\text{H}_4\text{CHO} + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			0	300					(^{4})
.54	$p\text{-BrC}_6\text{H}_4\text{CHO} + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			0	1140					(^{4})
.55	$p\text{-BrC}_6\text{H}_4\text{CHO} + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		0	120					(^{4})
.56	$p\text{-ClC}_6\text{H}_4\text{COCH}_3 + \text{NH}_2\text{NHCONH}_2$	Et 83		See Supplementary table (.13)							(^{1a})
.57	$p\text{-BrC}_6\text{H}_4\text{COCH}_3 + \text{NH}_2\text{NHCONH}_2$	Et 83		"	"	"	"				(^{1a})
.58	$\alpha\text{-C}_{10}\text{H}_7\text{CHO} + \text{NH}_2\text{NHC}_6\text{H}_5\text{.HCl}$	Et 75			0	11700					(^{4})
.59	$\alpha\text{-C}_{10}\text{H}_7\text{CHO} + \text{NH}_2\text{OH.HCl}$	Et 75	A = 0.2; B = 0.1		0	300					(^{4})

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
							k^o	n			
.60	1-OH-$C_{10}H_6$-4-CHO + $NH_2OH.HCl$	Et 75	A = 0.2; B = 0.1		0	7200					(^{4})
.61	C_4H_3OCHO + $NH_2NHCONH_2$ furfural	H_2O; pH 7		k AB	0.0		6.5	-2		*	(^{1}) (^{3})
					25.0		1.2	-1	4.1		
		CeW; b 1		k AB	25		2.7	-2		*	(^{5})
		b 2		"	"		9.7	-1			

SOLVENTS

(1) 0.07 Na_2HPO_4 + 0.03 NaH_2PO_4; pH = 7

(2) Phosphate buffers; selected points

(4) Et 75 = C_2H_5OH 75 vol % + H_2O 25 vol %

(5) CeW = $CH_3OCH_2CH_2OH$ (cellosolve) 60 % + H_2O 40 %

b 1 = basic CH_3COONa buffer solution

b 2 = 0.02 ($CH_2ClCOOH$ + $CH_2ClCOONa$) buffer, corresponding to maximum rate

COMMENTS

(.1) From reverse reaction and equilibrium. (.3) Heats of activation ΔH_a given. For reaction (.53), very good agreement between the values of k of (1) and (3) in H_2O at pH 7. (.5) The reactions with $NH_2NHCONH_2$ are acid catalyzed. In chloroacetate buffers, there is a downward trend of k as the reaction progresses.

SUPPLEMENTARY TABLES

(.13) $ArCOCH_3$ + $NH_2NHCONH_2$ Solvent Et 83 (1a)

The rate constant $k = Ae^{-E/RT}$, defined as first-order, is won by comparison with the rate of reaction (.13), *d*-carvone + $NH_2NHCONH_2$, at equal concentrations of the reactants. The tables give A (sec^{-1}) and E (kcal) (30 - 50° C).

SUPPLEMENTARY TABLES *(continued)*

(.13) *(continued)*

$ArCOCH_3$	*A*	*E*
$C_6H_5COCH_3$	3.6	7.8
p-$CH_3C_6H_4COCH_3$	0.4	6.5
p-$CH_3OC_6H_4COCH_3$	0.0045	4.0
p-$ClC_6H_4COCH_3$	460	10.3
p-$BrC_6H_4COCH_3$	1670	11.0

(.14) (.15) (.16) General acid catalysis (at constant pH)

Reaction		Buffer		*k*
(.14)	Formic acid	0.076 + Formate	0.074	9.2×10^{-3}
		0.114	0.111	1.0×10^{-2}
		0.152	0.148	1.1×10^{-2}
(.15)	Acetic acid	0.0128 + Acetate	0.0112	3.3×10^{-4}
		0.0256	0.0223	5.8×10^{-4}
		0.0384	0.0335	7.8×10^{-4}
(.16)	Hydrogen maleate	0.032 + Maleate	0.032	3.0×10^{-3}
		0.048	0.048	3.5×10^{-3}
		0.064	0.064	3.8×10^{-3}

LITERATURE

(1) J.B.Conant, P.D.Bartlett, *ACS* 1932, 54, 2881. (1a) R.P. Cross, P. Fugassi, *ACS* 1949, 71, 223. (2) A.Ölander, *ZPC*^{A} 1927, 129, 1. (3) F.P.Price, L.P.Hammett, *ACS* 1941, 63, 2387. (3a) G.H.Stempel,Jr., G.S.Schaffel, *ACS* 1944, 66, 1158. (4) G.Vavon, P.Montheard, *BCF*, 1940, 7, 551, 560. (5) F.H.Westheimer, *ACS* 1934, 56, 1962.

CONDENSATION

Aliphatic alcohol + Alkyl halide

Liquid phase

Reaction type $ROH + R'X \rightarrow ROR' + HX$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	Comments	Literature
								k°	n			
.1	$CH_3OH + (C_6H_5)_3CCl$	C_6H_6	A = 0.03 - 0.19	C_5H_5N	0.1	kA^2B	25	4.34	-3	6.6	*	(4)
			B = 0.1	α-$CH_3C_9H_6N$	"	"	"	3.50	-3	(25° - 60°)		
				C_9H_7N	"	"	"	5.84	-3			
				$C_6H_5N(C_2H_5)_2$	"	"	"	4.17	-3			
	$CH_3OH + (C_6H_5)_3CCl(+ C_6H_5OH)$	"	"	C_5H_5N	0.1	$kABC$	25	3.14	-2	6.6	*	(4)
					0.2	"	"	2.0	-2	(25° - 60°)		
				α-$CH_3C_9H_6N$	"	"	"	3.34	-2			
.2	$CH_3OH + (C_6H_5)_3CCl(+ p\text{-}NO_2C_6H_4OH)$	"	"	C_5H_5N	0.1	$kABC$	25	~ 8	-2	6.6 (25° - 60°)	*	(4)
.3	$CH_3OH + (C_6H_5)_3CBr$	C_6H_6	A = 0.03 - 0.19	C_5H_5N	0.1 - 0.2	kA^2B	25	~ 3.7	-1	6.6	*	(4)
			B = 0.1	Et_3N	"	"	"	~ 3	-1	(25° - 60°)		
	$CH_3OH + (C_6H_5)_5CBr(+ C_6H_5OH)$	"	"	C_5H_5N	0.1	$kABC$	25	~ 3	0	6.6	*	(4)
.4	$CH_3OH + p\text{-}[(CH_3)_3CC_6H_4]_3Cl$	C_6H_6	A = 0.03 - 0.19	C_5H_5N	0.09	kA^2B	25	~ 1.3	-1	6.6	*	(4)
			B = 0.1							(25° - 60°)		

232.471.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.5	$C_2H_5ONa + CH_3I$	C_2H_5OH	A = 1 B = 0.5 - 2			k AB	0	2.8	-5			(2)
							6	5.9	-5			
							12	1.2	-4			
							18	2.4	-4			
							24	5.0	-4			
							30	1.0	-3			
.6	$C_4H_9S^- + C_4H_9Br$	CH_3OH	A = B = 0.10			k AB	25	7.34	-5		*	(3)
							35	1.83	-4			
							45	3.33	-4			
		C_2H_5OH	A = B = 0.05			"	25	3.33	-4			
							35	8.5	-4			
							45	1.48	-3			
		"	0.10			"	25	3.0	-4			
							35	8.0	-4			
							45	1.46	-3			
		"	0.20			"	25	3.0	-4			
							35	7.5	-4			
							45	1.27	-3			
.7	$C_6H_5CH_2O^- + CH_3I$	C_2H_5OH	0.1			k AB	30	2.65	-3		*	(1)
							40	8.75	-3	21.6		
.8	$C_6H_5CH_2O^- + C_2H_5I$	C_2H_5OH	0.1			k AB	30	2.37	-4		*	(1)
							40	7.82	-4	21.6		
.9	$C_6H_5CH_2O^- + C_3H_7I$	C_2H_5OH	0.1			k AB	30	9.26	-5		*	(1)
							40	3.06	-4	21.6		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.10	$C_6H_5CH_2O^- + (CH_3)_2CHI$	C_2H_5OH	0.1			k AB	30	5.50	-5		*	(1)
							40	1.81	-4	21.6		
.11	$C_6H_5CH_2O^- + C_4H_9I$	C_2H_5OH	0.1			k AB	30	6.67	-5		*	(1)
							40	2.20	-4	21.6		
.12	$C_6H_5CH_2O^- + (CH_3)_2CH_2CH_2I$	C_2H_5OH	0.1			k AB	30	8.68	-5		*	(1)
							40	2.86	-4	21.6		
.13	$C_6H_5CH_2O^- + (CH_3)_2CH_2CH_2CH_2I$	C_2H_5OH	0.1			k AB	30	3.33	-5		*	(1)
							40	1.10	-4	21.6		
.14	$C_6H_5CH_2O^- + C_4H_9CH(CH_3)I$	C_2H_5OH	0.1			k AB	30	9.67	-5		*	(1)
							40	3.19	-4	21.6		
.15	$C_6H_5CH_2O^- + C_7H_{15}I$	C_2H_5OH	0.1			k AB	30	6.67	-5		*	(1)
							40	2.20	-4	21.6		
.16	$C_6H_5CH_2O^- + C_8H_{17}I$	C_2H_5OH	0.1			k AB	30	6.67	-5		*	(1)
							40	2.20	-4	21.6		
.17	$C_6H_5CH_2O^- + C_6H_{13}CH(CH_3)I$	C_2H_5OH	0.1			k AB	30	7.25	-5		*	(1)
							40	2.40	-4	21.6		
.18	$C_6H_5CH_2O^- + C_{16}H_{33}I$	C_2H_5OH	0.1			k AB	30	6.84	-5		*	(1)
							40	2.26	-4	21.6		
.19	$(C_6H_5)_3COH + (C_6H_5)_3CBr$	C_6H_5	A = 0.03 - 0.19 B = 0.1	C_5H_5N	0.1	k A^2B	60	2.3	-5	6.6 (25° - 60°)	*	(4)

COMMENTS

(4) (.1) (.2) (.3) (.4) (.19) Mechanism assumed to be $2A + RX \rightarrow A_2RX$ (rate determining) ; $A_2RX \rightarrow R^+ + X^- + 2A$(fast); $R^+ + A \rightarrow$ ether + H^+(fast). The rate determining step gives the third-order law kA^2B. In the presence of phenol, one molecule of the latter replaces one molecule of A, hence the third-order law $kABC$. The phenol undergoes no change in the overall reaction. (3) (.6) Some decrease of k with increasing ionic strength. (1) (.7) - (.18) Rate law and values of k valid only at the given concentration.

LITERATURE

(1) P.C.Haywood, *CSL* 1922, **121**, 1904. (2) W.Hecht, M.Conrad, *ZPC* 1889, **3**, 450.
(3) O.R.Quayle, E.E.Royals, *ACS* 1942, **64**, 226. (4) C.G.Swain, *ACS* 1948, **70**, 1119.

CONDENSATION
Phenol + Alkyl halide

Reaction type $ArOH + RX \longrightarrow ArOR + HX$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	Comments	Literature
								k^{o}	n			
.1	$C_6H_5O^- + C_4H_9Br$	CH_3OH	0.10			kAB	25	6.67	-8			(^{1})
							35	2.17	-7			
							45	5.84	-7	23		
		C_2H_5OH	0.05			kAB	25	2.19	-7			
							35	6.50	-7			
							45	1.35	-6			
			0.10			"	25	1.66	-7			
							35	5.33	-7			
							45	1.35	-6	23		
			0.20			"	25	1.45	-7			
							35	4.67	-7			
							45	1.12	-6			
.2	$C_6H_5S^- + C_4H_9Br$	CH_3OH	0.10			kAB	25	7.5	-5		*	(^{1})
							35	1.8	-4			
							45	3.76	-4	17.8		
		C_2H_5OH	0.05			kAB	25	2.17	-4			
							35	5.68	-4			
							45	1.10	-3	17.4		

232.472.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	Comments	Literature
								k°	n			
.2	$C_6H_5S^- + C_4H_9Br$ *(continued)*		0.10			kAB	25	2.09	-4			
							35	5.18	-4			
							45	9.18	-4	15.7		
			0.20			kAB	25	2.0	-4			
							35	4.66	-4			
							45	7.91	-4	14.1		
		C_6H_6	0.10			kAB	35	2.0	-5			
.3	$C_6H_5OH + (C_6H_5)_3CCl$	C_6H_6	A = 0.03 - 0.19 B = 0.1	C_5H_5N	0.1	kA^2B	25	6.7	-6	6.6 (25°-60°)	*	(2)
.4	$C_6H_5OH + (C_6H_5)_3CBr$	C_6H_6	A = 0.03 - 0.19 B = 0.1	C_5H_5N	0.07	kA^2B	25	6.7	-5	6.6 (25°-60°)	*	(2)
					0.22		25	3.0	-3			
.5	$p - NO_2C_6H_4OH + (C_6H_5)_3CBr$	C_6H_6	A = 0.03 - 0.19 B = 0.1	C_5H_5N	0.055	kA^2B	25	1.3	-2	6.6 (25°-60°)	*	(2)
					0.110		25	2.8	-3			

COMMENTS

(.2) Some decrease of k with increasing ionic strength. The reaction in C_2H_5OH is retarded by LiCl.

(.3) (.4) (.5) The mechanism accounting for the third-order rate law is assumed to be $2\ ArOH + RX \longrightarrow (ArOH)_2RX$ (rate determining); $(ArOH)_2RX \longrightarrow R^+ + X^- + 2\ ArOH$ (fast); $ArOH + R^+ \longrightarrow ArOR + H^+$ (fast).

LITERATURE

(1) O.R. Quayle, E.E. Royals, *ACS* 1942, 64, 226. (2) C.G. Swain, *ACS* 1948, 70, 1119.

SOLVOLYSIS

Ethers

Liquid phase

Reaction type $ROR' + H_2O \rightarrow ROH + R'OH$

Amounts are in M/l.

Rates in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$C_2H_5OC_2H_5 + H_2O$	H_2O	0.48	$X = p\text{-}CH_3C_6H_4SO_3H$	0.5	kAX	25	(2.44)	-13				*	(1)
							65	7.24	-10	36.4	3.3	14		
							75	3.33	-9	34.6	2.2	13		
							85	1.30	-8	32.7	3.3	12		
							95	4.38	-8	30.8	1.1	7		
							125	(7.85)	-8					
.2	$(CH_3)_2CHOC_2H_5 + H_2O$	H_2O	0.48	$X = p\text{-}CH_3C_6H_4SO_3H$	0.5	kAX	25	2.50	-12				*	(1)
							55	1.21	-9	37.8	2.2	16		
							65	6.42	-9	36.3	2.2	15		
							75	3.04	-8	34.8	2.7	14		
							85	1.17	-7	31.8	3.3	11		
							125	8.38	-6					
.3	$(CH_3)_2CHOCH(CH_3)_2 + H_2O$	H_2O	0.48	$X = p\text{-}CH_3C_6H_4SO_3H$	0.5	kAX	25	1.10	-11				*	(1)
							55	5.20	-9	37.1	2.7	16		
							65	2.67	-8	35.3	2.2	15		
							75	1.18	-8	33.4	1.3	14		
							85	4.37	-7	31.5	8.5	12		
							125	2.14	-5					

COMMENTS

(.1) (.2) (.3) Converted to seconds from original k in minutes. Arrhenius law not obeyed, E and A vary with the temperature. Empirical formulas (k in min^{-1}) (.1) $\log k = (-14535/T) - 0.057476T + 55.069$; (.2) $\log k = (-13456/T) - 0.048120T + 49.6355$; (.3) $\log k = (-14592/T) - 0.060150T + 57.711$. Values of k at 25° and at 125°C extrapolated with the aid of the above formulas. The rates of hydrolysis of these ethers are exceedingly slow; that of $C_2H_5OC_2H_5$ is, roughly, 10^{16} slower than hydrolysis of $CH_3COOC_2H_5$. The half-time of the hydrolysis of $C_2H_5OC_2H_5$ in 1M solution is 90300 years.

LITERATURE

A. Skrabal, A. Zahorka, *MHC* 1933, 63, 1.

SOLVOLYSIS

Acetals

Reaction type $R_1R_2C(OR)_2 + H_2O \longrightarrow R_1R_2CO + 2\ ROH$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
								k^o	n			
.1	$HCH(OC_3H_7)_2 + H_2O$	H_2O		Sat C_6H_5COOH + NaCl	0.00	$kA[H^+]$	25	1.04	-1		*	(^{3})
					0.008		"	1.09	-1			
					0.10		"	1.29	-1			
					0.40		"	1.80	-1			
					1.00		"	2.96	-1			
				HCl 0.01 + NaCl	0.0	"	25	1.08	-1			"
					0.60		"	2.1	-1			
					2.00		"	7.2	-1			
				KCl	1.0	"	"	2.8	-1			
				KBr	1.0		"	3.8	-1			
				KI	1.0		"	5.3	-1			
				HCl 0.5 + NaCl	0.0	"	"	1.77	-1			"
					0.80		"	3.64	-1			
.2	$CH_3CH(OCH_3)_2 + H_2O$	H_2O		Sat C_6H_5COOH + NaCl	0.00	$kA[H^+]$	25	2.74	-1			(^{3})
					0.02		"	2.84	-1			
					0.08		"	3.10	-1			
					0.56		"	4.75	-1			
					2.00		"	1.30	0			
					3.00		"	2.65	0			

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.3	$CH_3CH(OC_2H_5)_2 + H_2O$	H_2O	0.01	H^+	0.001	$kA[H^+]$	25	1.35	0			(6)
		H_2O		Sat C_6H_5COOH + NaCl	0.00	$kA[H^+]$	25	1.32	0			(3)
					0.04		"	1.36	0			
					0.10		"	1.56	0			
					0.40		"	1.84	0			
					0.50		"	1.94	0			
					1.00		"	2.92	0			
				Sat $C_6H_5COOH + C_6H_5COONa$	0.40	"	"					"
		H_2O		+ NaCl	0.00		"	1.48	0			
					0.40		"	2.17	0			
					1.00		"	3.46	0			
					2.10		"	7.66	0			
					2.74		"	1.19	+ 1			
		H_2O		HCl	0.001	kA	15(?)	3.16	-4			(2)
				$(COOH)_2$	0.01			5.5	-4			
				HCOOH	0.0104			7.6	-5			
				CH_3COOH	0.0096			1.1	-5			
		D_2O		HCl	0.001	"	"	8.4	-4			"
				$(COOH)_2$	0.01			1.40	-3			
				HCOOH	0.0104			7.5	-5			
				CH_3COOH	0.0096			1.06	-5			
.4	$CH_3CH(OC_4H_9)_2 + H_2O$	H_2O	0.02	HCl	0.007	kAB	25	1.27	0			(4)
							35	4.44	0	22.7		
		Dx 60	0.02	HCl	0.007	kAB	15	2.11	-2			"
							25	7.99	-2	22.7		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$		E	Comments	Literature
								k^0	n			
.5	$(CH_3)_2C(OCH_3)_2 + H_2O$	H_2O, buffers	~ 0.1	H^+	1.0×10^{-7}	$kA[H^+]$	25	6.4	−2		*	(5)
					2.0×10^{-7}		"	5.7	−2			
.6	$(CH_3)_2C(OC_2H_5)_2 + H_2O$	H_2O, buffers	~ 0.1	H^+	2.0×10^{-7}	$kA[H^+]$	25	2.3	−3		*	(5)

SOLVENTS

Dx 60 = H_2O + 60 vol % dioxane (4).

COMMENTS

Methods. (2) interferometric; (3) dilatometric. **Reactions.** (.1) Selected points. Original (3) gives k in HCl solutions under the erroneous heading "$k \times 10^3$"; it should evidently read "k". The original data of (3) have been converted to sec and ln. (.2) Further data in the presence of $C_6H_5COOH + C_6H_5COONa + NaCl$ in original (3). (.3) Data of (2): no indication of the temperature, but from the context it appears that it is 15° C. If so, extrapolation to 25°C gives a catalytic constant, defined by $kA[H^+]$, in fair agreement with (3).

LITERATURE

(1) R.P. Bell, W.C.F. Higginson, Proc. Roy. Soc., 1949, A197, 141. (2) J.C. Hornel, J.A.V. Butler, *CSL* 1936, 1361. (3) A. R. Olson, L.K.J. Tong, *ACS* 1944 66, 1555. (4) F.N. Prilezhaeva, F.S. Shapiro, M.F. Shostakovskii, *ZOK* 1948, 18, 1663. (5) A. Skrabal, F. Bilger, *ZPC* 1927, 130, 29. (6) L.K.J. Tong, A.R. Olson, *ACS* 1943, 65, 1704.

SOLVOLYSIS

Acid anhydrides

Liquid phase

Reaction type $Ac_2O + H_2O \rightarrow 2\ AcOH$

Amounts are in M/l.

Rates in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$(CH_3CO)_2O + H_2O$	H_2O	A = 0.5			kA	0	4.7	-4	*	(1)
							15	1.2	-3		
		H_2O	A = 0.02			kA	25	2.7	-3	*	(3)
			0.116				"	2.6	-3		
			0.235				"	2.7	-3		
			0.735				"	2.4	-3		
			1.070				"	2.2	-3		
		$H_2O + CH_3COOH$ %	A = 0.08; B = 0.18			kA					(1)
		50					15	2.7	-4		
		80					"	9.4	-5		
		90					"	4.7	-5		
		CH_3COOH	A = 0.08; B = 0.18			kAB	15	7.0	-6		"
		$(CH_3)_2CO$	A = 10; B = 1.8			kAB	15	1.2	-6		
		$H_2O + CH_3COOH$ 90%	A = 0.08; B = 0.18			kA; $k'A[H_2SO_4]$					"
				H_2SO_4	0		15	4.7	-5		
					0.0166		k	1.8	-5		
					"		k'	1.1	-2		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		
.1	$(CH_3CO)_2O + H_2O$ *(continued)*				0.033		k	3.3	-4		
					"		k'	1.0	-2		
					0.05		k	5.8	-4		
					"		k'	1.2	-2		
					0.1		k	1.3	-3		
							k'	1.3	-2		
		A = 62g; B = 1.12g; CH_3COOH = 267g				k_{AB}	70.1	6.0	-5	*	(2)
							80.5	1.05	-4		

COMMENTS

Date of (3), converted to the base e from decimal log, are consistent with those of (1). Only one composition in (2) (preliminary communication).

LITERATURE

(1) K.J.P.Orton, M.Jones, *CSL* 1912, **101**, 1708. (2) J.C.Phillip, *CSL* 1912, **28**, 259. (3) A.C.D.Rivett, N.V.Sidgwick, *CSL* 1910, **97**, 732.

SOLVOLYSIS

C : N bond

Liquid phase

Reaction type $R_1R_2C{:}NR + H_2O \longrightarrow R_1R_2CO + H_2NR$

Amounts are in M/l.

Rates in M/l per sec.

No.	Reaction	Medium (Solvent)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
					k^o	n			
.1	$(CH_3)_2C{:}NOH + H_2O$	H_2O; pH 1.22	kA	17 - 19	4.0	-4		*	(2)
		1.70			7.5	-4			
		2.15			1.0	-3			
		2.58			9.2	-4			
		3.15			5.9	-4			
		4.25			9.0	-5			
		5.27			1.7	-5			
.2	$CH_3CH{:}NNHCONH_2 + H_2O$	H_2O; pH 7	kAB	25	1.73	-4		*	(1)
.3	$(CH_3)_2C{:}NNHCONH_2 + H_2O$	H_2O; pH 7	kA	0.0	5.11	-5		*	(3)
				25.1	2.78	-4	11.0		
.4	$COOH.C(CH_3){:}NNHCONH_2 + H_2O$	H_2O; pH 7	kAB	25	6.3	-7		*	(1)
.5	$(C_2H_5)_2C{:}NNHCONH_2 + H_2O$	H_2O; pH 7	kA	0.0	6.09	-5		*	(3)
				25.0	2.26	-4	8.5		

No.	Reaction	Medium (Solvent)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		ΔH_a	Comments	Literature
					k^o	n			
.6	$(CH_3)_3CCH:NNHCONH_2 + H_2O$	H_2O; pH 7	k AB	25	6.2	-6		*	(1)
.7	$(CH_3)_3CC(CH_3):NNHCONH_2 + H_2O$	H_2O; pH 7	k AB	25	1.4	-5		*	(1)
.8	$\underbrace{CH_2(CH_2)_4C}:NNHCONH_2 + H_2O$	H_2O; pH 7	k A	0.0	2.23	-4		*	(3)
				25.1	1.06	-3	10.1		
.9	$C_6H_5CH:NNHCONH_2 + H_2O$	H_2O; pH 7	k AB	25	1.0	-7		*	(1)

COMMENTS

(1) Buffer solution 0.07 Na_2HPO_4 + 0.03 NaH_2PO_4. Rate constants k from the rates of the reverse reaction and equilibrium constant. (2) Phosphate buffers. (3) From reverse reaction and equilibrium constant.

LITERATURE

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SOLVOLYSIS

CO - NH_2 bond (Acyl amide solvolysis)

Liquid phase

Reaction types $RCONH_2 + H_2O \rightarrow RCOO^- + NH_4^+$

$RCONH_2 + OH^- \rightarrow RCOO^- + NH_3$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$HCONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$k\,A[H^+]$	42.1	8.8	-4		*	(2)
							63.2	5.8	-3			
							70.3	1.1	-2			
							80.7	2.1	-2	19.1		
		H_2O	0.05 - 0.8	HCl	2	$k\,A$	25	2.3	-4			(7)
					4		"	4.4	-4			
					6		"	5.1	-4			
					8		"	4.5	-4			
					9.5		"	3.5	-4			
				H_2SO_4	1	"	"	3.0	-4			(7)
					1.75		"	4.5	-4			
					2.25		"	4.8	-4			
					3		"	4.3	-4			
					4		"	3.1	-4			

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	Comments	Literature
								k^{o}	n			
.2	$CH_3CONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$k\,A[H^+]$	42.1	4.43	-6		*	(2)
							63.2	3.60	-4			
							70.8	6.83	-4			
							80.7	1.48	-3	20.7		
		H_2O	0.05 - 0.8	HCl	1.50	$k\,A$	25	6.9	-6		*	(7)
					2.91		"	1.08	-5			
					4.13		"	9.7	-5			
					5.00		"	7.2	-5			
				H_2SO_4	0.49		"	6.7	-6			"
					1.25		"	9.2	-6			
					2.07		"	7.5	-6			
		H_2O	~ 0.15	HCl	1.0	$k\,A$	18	3.4	-6		*	(8)
							25	6.4	-6			
					0.5		25	2.8	-6			"
		H_2O	~ 0.15	HCl	0.5 - 1.0	$k\,A[H^+]$	25	6.0	-6		*	(8)
		H_2O	0.166	HCl	= B	$k\,A[H^+]$	65	5.0	-4		*	(1)
			0.333				"	4.1	-4			
			0.666				"	3.8	-4			
			1.333				"	3.4	-4			
		H_2O	0.1	HCl	~ A	$k\,A[H^+]$	49.3	1.28	-4		*	(5)
							64.3	3.71	-4	15.4		
		H_2O		pH	1.04	$k\,A[H^+]$	50	1.24	-4		*	(4)
					0.76		"	1.19	-4			
					0.59		"	1.17	-4			
					0.30		"	1.02	-4			
					0.05		"	9.20	-5			

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.2	$CH_3CONH_2 + H_2O$ *(continued)*				−0.15		50	7.98	−5			
					−0.30		"	6.93	−5			
					−0.45		"	4.96	−5			
					−0.58		"	3.72	−5			
		H_2O	0.05	H_2SO_4	2	kA	25	9.92	−6		*	(12)
				"	2.5		"	1.10	−5			
				HCl	3		"	1.00	−5			
				"	4		"	8.55	−6			
				"	5		"	6.02	−6			
				HBr	4		"	6.72	−6			
				"	5		"	5.44	−6			
				HCl4 +	LiCl1		"	8.51	−6			"
				"	NaCl1		"	9.81	−6			
				"	KCl1		"	9.70	−6			
				HBr4 +	LiBr1		"	5.99	−6			
				"	NaBr1		"	6.68	−6			
				"	KBr1		"	7.63	−6			
				HCl	4		25	8.55	−6			"
				"	"		40	4.56	−5			
				HCl	5		25	6.02	−6			
				"	"		41	3.66	−5			
.3	$CH_3CONH_2 + OH^-$	H_2O	A = 0.15; B = 0.6 − 1.0			kAB	18	2.0	−5		*	(8)
							25	4.0	−5			
		H_2O	A = 0.05; B = 1			kA	25	4.0	−5		*	(12)

No.	Reaction	Medium, (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	Comments	Literature
								k^{o}	n			
.4	$C_2H_5CONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$k\,A[H^+]$	42.1	5.9	-5		*	(2)
							63.2	4.3	-4			
							70.3	9.2	-4			
							80.7	1.9	-3	19.8		
		H_2O	0.05 - 0.8	HCl	1.5	$k\,A$	25	9.40	-6		*	(7)
					3.0		"	1.39	-5			
					3.5		"	1.39	-5			
					4.0		"	1.33	-5			
					5.0		"	1.17	-5			
				H_2SO_4	0.093	"	"	3.3	-6			"
					0.49		"	1.14	-5			
					0.825		"	1.47	-5			
					1.53		"	1.44	-5			
					2.06		"	1.25	-5			
					2.65		"	8.9	-6			
					3.00		"	7.2	-6			
					3.75		"	4.7	-6			
					5.60		"	1.7	-6			
		H_2O	~ 0.15	HCl	1.0	$k\,A$	18	4.6	-6		*	(8)
							25	8.3	-6			
			"	"	0.5	"	25	4.3	-6			
.5	$C_2H_5CONH_2 + OH^-$	H_2O	A = 0.15; B = 0.6 - 1.0			$k\,AB$	18	2.2	-5			(8)
							25	3.8	-5			

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No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.6	$C_3H_7CONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$kA[H^+]$	42.1	3.0	-5		*	(2)
							63.2	2.0	-4			
							70.3	4.0	-4			
							80.7	1.0	-3	20.1		
		H_2O	~ 0.15	HCl	1.0	kA	18	2.0	-6		*	(8)
							25	4.1	-6			
			"	"	0.5	"	25	2.0	-6			"
.7	$C_3H_7CONH_2 + OH^-$	H_2O	A = 0.15; B = 0.6 - 1.0			kAB	18	7.6	-6		*	(8)
							25	1.5	-5			
.8	$(CH_3)_2CHCONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$kA[H^+]$	42.1	3.5	-5		*	(2)
							63.2	2.5	-4			
							70.3	4.7	-4			
							80.7	1.05	-3	19.5		
		H_2O	~ 0.15	HCl	1.0	kA	18	2.6	-6		*	(8)
							25	6.0	-6			
.9	$(CH_3)_2CHCONH_2 + OH^-$	H_2O	A = 0.15; B = 0.6 - 1.0			kAB	18	7.1	-6		*	(8)
							25	1.35	-5			
.10	$C_4H_9CONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$kA[H^+]$	63.2	5.6	-5		*	(2)
							70.3	1.0	-4			
							80.7	2.5	-4	20.1		
		H_2O	~ 0.15	HCl	1.0	kA	18	4.0	-6		*	(8)
							25	8.8	-6			
		"	"	"	0.5	"	25	4.4	-6			"

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.11	$C_4H_9CONH_2 + OH^-$	H_2O	A = 0.15; B = 0.6 - 1.0			kAB	18	1.25	-6			(8)
							25	2.5	-6			
.12	$C_5H_{11}CONH_2 + H_2O$	H_2O	0.25 - 2.0	HCl	~ A	$kA[H^+]$	63.2	2.0	-4		*	(2)
							70.3	4.5	-4			
							80.7	1.05	-3			
		H_2O	~ 0.15	HCl	1.0	kA	18	2.8	-6		*	(8)
							25	4.8	-6			
			"	"	0.5	"	25	1.8	-6			"
.13	$C_5H_{11}CONH_2 + OH^-$	H_2O	A = 0.15; B = 0.6 - 1.0			kAB	18	7.1	-6		*	(8)
							25	1.3	-5			
.14	$NH_2COCONH_2 + OH^-$	H_2O	$10^3A = 1 - 3$; $10^3B = 2 - 4$			kAB	30.1	2.3	-2			(13)
.15	$NaOCOCONH_2 + OH^-$	H_2O	$10^2A = 1 - 5$; $10^2B = 1.4 - 5.5$			kAB	30.1	2.3	-4			(13)
.16	$\underbrace{COCONH} + OH^-$	H_2O	$10^3A = 1 - 3$; $10^3B = 2 - 5$			kAB	30.1	2.3	-2			(13)

COMMENTS

Literature references: (2) Definition of k, not clear from the original, was assumed to be second-order $kA[H^+]$. (5) The values of k are "means of 5 middle determinations"; actually, k falls with the progress of the reaction, paralleling the fall of the electrometrically measured $[H^+]$ which remains at all stages practically equal to the momentary $[A]$, in accordance with the formulation of the reaction $RCONH_2 + H_2O + H^+ \longrightarrow RCOOH + NH_4^+$. (8) Authors erroneously term their k as "bimolecular". Actually it is first-order. For the alkaline hydrolyses with OH^-, true second-order constants, as defined in the tables, have been calculated from the original, actually first-order k, and found to hold in the given range of variation of $[OH^-]$, 0.6 - 1.0. **Reactions.** (.2) Fair agreement for first-order k at 25° between (7) and (8). Plot of the first-order k against the concentration of the acid by (12), combining his own data and those of (8) at 25° C, and his own data and those of (4) and 50° C, shows increase of the first-order k with increasing concentrations of HCl up to about 2.5 - 3.0 M/l, a maximum, and then decrease of k with further increasing concentration of the acid. Order of magnitude of second-order k at 63 - 64° C, $\sim 3.6 \times 10^{-4}$, in fair agreement between (2), (1), and (4). A second-order rate constant defined by $kA[H^+]$ at 25° C, $k = 6.0 \times 10^{-6}$, has been averaged from data of (8). (.3) Second-order k of (12) at 25° C, since given for $[OH^-] = 1$, is in agreement with the first-order k of (8). No significant salt effects of 1 *N* NaCl, NaBr, NaI with NaOH, or KCl, KBr, KI with KOH (12).

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SOLVOLYSIS

C : N bond solvolysis

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$HCN + 2H_2O \rightarrow HCOONH_4$	H_2O	0.08 - 2.5	HCl	0.302	k A	65	8.06	-8				*	(9) (11)
					1.02		"	5.00	-7					
					3.17		"	2.64	-5					
					5.52		"	3.51	-4					
			"	HBr	0.30	"	65	8.06	-8					"
					4.45		"	1.31	-5					
					7.13		"	4.56	-4					
			"	H_2SO_4	0.508		65	1.72	-7					
					3.82		"	2.99	-5					
					5.49		"	5.45	-5					
		H_2O	0.22	HCl	8.47	k A	0.0	2.37	-6				*	(12) (13)
							19.8	3.50	-5					
							29.7	1.09	-4					
							34.7	2.05	-4	21.5	4.5	10		
			0.44	"	1.00	"	65	5.01	-7					
							80.3	2.41	-6					
							99.9	1.36	-5	24.7	4.5	9		
		CH_3COOH 95 %	0.1 - 1.0	HCl	0.8	k A	0	1.15	-5				*	(8)
					1.65		"	2.60	-4					
					2.65		"	3.48	-3					
					2.80		"	6.96	-3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$HCN + 2H_2O \longrightarrow HCOONH_4$ *(continued)*	CH_3COOH 95 %	0.1 - 1.0	HCl	0.85	kA	10	6.44	-5					(8)
					1.65		"	1.07	-3					
					2.0		"	5.50	-3					
		CH_3COOH 99.97 %	"	"	1.15	"	0	1.26	-4					"
					1.75		"	1.04	-3					
					2.45		"	6.52	-3					
		"	"	"	1.0	"	10	6.20	-4					"
					1.55		"	3.06	-3					
					1.85		"	8.65	-3					
.2	$HCN + H_2SO_4 + H_2O \longrightarrow CO + NH_4HSO_4$ $(HCN{\cdot}H_2SO_4 + H_2O \longrightarrow CO + NH_4HSO_4)$	$H_2O + H_2SO_4$ (%)	A ~ 0.05			kA							*	(1)
		73.1					80	9.17	-5					
		79.0					"	3.95	-4					
		82.5					"	2.27	-4					
		64.8	"			"	90	3.34	-5					"
		79.0					"	8.84	-4	22.3				
		91.3					"	8.38	-5	22.9				
		64.8	"			"	100	1.18	-4	33.3				"
		78.1					"	2.37	-3					
		95.9					"	5.33	-5	23.5				
.2.1	$HCN + H_2SO_4 \longrightarrow HCN{\cdot}H_2SO_4$	H_2SO_4 100 %	B/A = 1			k	0	5.66	-4				*	(1)
							10	2.00	-3	18.6				
		96.2 %	"			"	0	9.02	-5					"
							10	3.50	-4	20.8				
		H_2SO_4 100 %	B/A ⩾ 7			kA	0	1.64	-4					"
							10	3.10	-4	15.9				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2.1	$HCN + H_2SO_4 \rightarrow HCN \cdot H_2SO_4$ (*continued*)	96.2 %	B/A ⩾ 7			k A	0	5.13	-5					
							10	1.86	-4	19.5				
.3	$HCN + H_3PO_4 + H_2O \rightarrow CO + NH_4H_2PO_4$	$H_2O + H_3PO_4$ (%)	A ~ 0.05			k A								
		100					100	1.44	-4				*	(1)
	($HCN \cdot H_3PO_4 + H_2O \rightarrow CO + NH_4H_2PO_4$	100					110	3.44	-4					"
		93.3					"	9.25	-5					
		88.0					"	3.45	-5					
		100					120	7.38	-4					"
		93.3					"	2.24	-4					
		88.0					"	8.87	-5					
		100					130	1.60	-3	23.5				"
		93.3					"	5.32	-4					
		88.0					"	2.10	-4					
		93.3					140	1.05	-3	25.8				"
		88.0					"	4.55	-4	26.9				
.4	$NH_2CN + H_2O \rightarrow (NH_2)_2CO$	H_2O	0.5	H_2SO_4	0.06	k A	50	3.1	-5				*	(5)
		H_2O	0.25	H_2SO_4	0.036	k A	50.4	1.63	-5				*	(2)
					0.0675		"	3.13	-5					
					0.135		"	6.21	-5					
					0.494		"	2.48	-4					
			"	HNO_3	0.059	"	50.4	2.14	-5					"
					0.118		"	4.15	-5					
					0.237		"	8.35	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$NH_2CN + H_2O \rightarrow (NH_2)_2CO$ *(continued)*		0.23	HNO_3 + $CO(NH_2)_2$	0.249 1.0	k A	50.4	4.22	-5					(2)
			0.25	HNO_3	0.126	"	25.0	3.41	-6					"
					0.252		"	6.88	-6					
					0.526		"	2.00	-5					
					1.05		"	3.48	-5					
					2.14		"	9.62	-5					
					4.26		"	3.71	-4					
		H_2O	0.21 - 0.25	HNO_3	0.5947	k A	25.0	1.99	-5				*	(15) (7)
					1.490		"	6.27	-5					
					2.512		"	1.49	-4					
					3.881		"	3.70	-4					
			"	"	0.9944	"	30.0	6.27	-5					"
					1.490		"	1.09	-4					
					2.512		"	2.56	-4	19.3				
					3.881		"	6.28	-4					
		H_2O	0.036	$HClO_4$	0.4844	k A	30.0	2.48	-5					"
		H_2O	0.045	HCl	0.2474	k A	25.0	7.37	-6				*	"
					0.9820		"	3.33	-5					
					1.613		"	4.93	-5					
					2.066		"	4.48	-5					
					2.935		"	1.81	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$NH_2CN + H_2O \longrightarrow (NH_2)_2CO$ (*continued*)		0.045	HCl	0.0959	k A	30.0	4.73	-6					$(^{15})$ $(^{7})$
					0.2474		"	1.28	-5	19.9				
					0.9820		"	5.68	-5					
					1.613		"	8.63	-5					
					2.066		"	7.89	-5	20.3				
					2.935		"	3.34	-5	22.0				
		H_2O	0.25	NaCl + HCl = 4.0		k A								
				HCl	0.500		30.0	3.51	-5				*	$(^{15})$ $(^{7})$
					1.000		"	4.46	-5					
					2.000		"	3.21	-5					
					4.000		"	9.03	-6					
					0.500	"	40.0	1.01	-4					"
					1.000		"	1.10	-4					
					2.000		"	9.83	-5					
					4.000		"	3.14	-5					
		H_2O	0.21 - 0.25	HBr	1.010	k A	25.0	3.36	-5				*	$(^{15})$ $(^{7})$
					1.499		"	5.55	-5					
					2.097		"	9.00	-5					
					2.534			1.16	-4					
			"	"	0.7492	"	30.0	3.98	-5				*	"
					1.010		"	5.63	-5	18.4				
					1.499		"	9.28	-5	19.0				
					2.097		"	1.54	-4	19.4				
					2.534		"	2.01	-4	19.6				
					2.642		"	2.09	-4					
					3.038		"	2.47	-4					
					4.027		"	1.89	-4					
					5.178		"	3.95	-5					

242.453.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$NH_2CN + H_2O \rightarrow (NH_2)_2CO$ (*continued*)		0.21 - 0.25	HBr	0.7492	kA	40.0	1.07	-4	18.4			*	(15) (7)
					2.642		"	5.85	-4	19.4				
					3.038		"	6.88	-4	19.4				
					4.027		"	5.68	-4	20.6				
					5.178		"	1.36	-4	23.3				
		H_2O	0.19 - 0.25	CCl_3COOH	0.2497	kA	25.0	1.62	-5				*	"
					1.022		"	9.48	-5					
					2.040		"	2.34	-4					
					2.905		"	3.39	-4					
					3.971		"	4.33	-4					
.5	$CH_3CN + 2H_2O \rightarrow CH_3COONH_4$	H_2O	~ 0.22	HCl	0.51	kA	59.6	3.65	-8					(12) (13)
			"	"	1.00	"	59.6	8.03	-8					
							83.5	1.20	-6					
							93.3	3.23	-6					
							99.7	6.32	-6					
							111.8	1.84	-5	26.5	2.1	10		
				"	2.00	"	59.6	2.13	-7					
				"	4.00	"	49.6	2.78	-7					
							59.6	9.10	-7					
							80.6	9.36	-6					
							94.1	3.82	-5					
							99.5	6.33	-5	25.8	2.0	10		
			"	"	5.00	"	59.6	2.66	-6					"
							70.1	8.49	-6					
							83.1	2.98	-5					
							99.7	1.37	-4	24.2	4.0	9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.5	$CH_3CN + 2H_2O \rightarrow CH_2COONH_4$ *(continued)*		~ 0.22	HCl	8.47	k A	28.4	5.77	−6					(12) (13)
							42.7	2.74	−5					
							49.6	5.68	−5					
							59.6	1.52	−4	21.0	1.3	9		
.6	$CH_3CN + H_2O \rightarrow CH_3CONH_2$	H_2O		HCl	2	k A	65	1.66	−7					(10)
					4		"	5.65	−7					
					6		"	2.16	−6					
					8		"	1.07	−5					
					10		"	2.99	−5					
				H_2SO_4	2	"	65	2.36	−7					"
					4		"	7.36	−7					
					6		"	1.68	−6					
					8		"	2.95	−6					
.7	$C_2H_5CN + 2H_2O \rightarrow C_2H_5COONH_4$	H_2O	0.20	HCl	0.51	k A	59.6	7.2	−8	25.6	1.1	10	*	(13)
			"	"	2.00	"	59.6	4.2	−7					
		"	0.40	HBr	1.00	"	86.7	2.84	−6				*	(14)
							124.8	8.55	−5	25.7	1.1	10		
		"	0.40	H_2SO_4	1.00	"	86.5	3.20	−6				*	"
							113.6	3.94	−5					
							125.3	1.05	−4		1	10		
		"	0.40	HNO_3	1.00	"	80.5	2.60	−6				*	"
							124.8	9.20	−5	26.5	5	10		
		"	"	"	4.00	"	78.7	1.29	−5					"
							107.4	2.05	−4					

242.453.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.8	$C_2H_5CN + H_2O \rightarrow C_2H_5CONH_2$	H_2O		HCl	4	kA	65	1.00	-6					(10)
					6		"	4.00	-6					
					8		"	2.17	-5					
					14.9		"	3.90	-5					
		"		H_2SO_4	4	"	65	1.28	-6					
					6		"	2.52	-6					
.9	$C_2H_5CN + \left\{ \begin{matrix} H_2O \\ 2H_2O \end{matrix} \right. \rightarrow \left\{ \begin{matrix} C_2H_5CONH_2 & (a) \\ C_2H_5COONH_4 & (b) \end{matrix} \right.$	H_2O			$(a + b) = k$A									
			0.1995	HCl	6.48		3.83	2.76	-6				*	(13)
							49.9	9.75	-6					
							59.6	2.78	-5					
							72.6	9.00	-5	21.8	8	8		
		"	0.1770	"	10.13	"	0.0	4.8	-6					"
							16.8	3.36	-5					
							24.7	8.45	-5					
							34.5	2.21	-4	18.9	6	8		
		"	0.1638	HBr	7.68	"	48.7	1.01	-5				*	(14)
							79.7	2.22	-4	22.6	3.5	5		
		"	0.5244	H_2SO_4	5.30	"	58.5	5.75	-6				*	"
							80.6	5.74	-5	24.4	1.1	10		
		"	0.3883	"	9.43	"	48.7	3.42	-5				*	"
							68.1	1.88	-4	23.0	3.0	10		
		"	0.2593	HNO_3	13.01	"	48.7	1.36	-5				*	"
							68.1	8.30	-5					
							80.5	2.50	-4	20.7	1.3	9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.10	$CH_2OHCH_2CN + H_2O \longrightarrow CH_2OHCH_2CONH_2$	H_2O		HCl	4	k A	65	5.15	-7					(10)
					6		"	1.83	-6					
					8		"	9.64	-6					
				H_2SO_4	4	"	65	7.5	-7					"
					6		"	1.75	-6					
.11	$CH_3CHOHCN + H_2O \longrightarrow CH_3CHOHCONH_2$	H_2O		HCl	4	k A	65	7.77	-6					(10)
					6		"	7.[illegible]	-5					
					8		"	2.80	-4					
				H_2SO_4	4	"	65	1.69	-6					"
					6		"	4.86	-6					
.12	$COOHCH_2CN + 2H_2O \longrightarrow COOHCH_2COONH_4$	H_2O	0.185	HCl	1.00	k A	99.5	2.81	-6					(12) (13)
							110.2	7.40	-6					
							125.4	2.82	-5	26.3	7.9	9		
			"	"	4.00	"	59.6	6.23	-7					"
							90.5	1.57	-5					
							99.5	3.75	-5					
							109.9	1.02	-4	25.5	7.9	9		
.13	$COOHCH_2CN + H_2O \longrightarrow COOHCH_2CONH_2$	H_2O		HCl	2	k A	65	7.80	-8					(10)
					4		"	3.34	-7					
					6		"	2.30	-6					
					8		"	1.72	-5					
		"		H_2SO_4	4	"	65	3.5	-7					"
					6		"	7.4	-7					
					8		"	1.57	-6					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.14	2, 7 - $C_{10}H_6(CN)_2 + OH^- + H_2O$ $\rightarrow$ 2, 7 - $C_{10}H_6(CN)COO^- + NH_3$	$C_5H_{11}OH$	A = 0.0056 - 0.013 B = 0.011 - 0.016			k A	121 - 126	~ 2.5	-4				*	(6)
.15	2, 7 - $C_{10}H_6(CN)COO^- + OH^- + H_2O$ $\rightarrow$ 2, 7 - $C_{10}H_6(COO^-)_2 + NH_3$	$C_5H_{11}OH$	"			"	121 - 126	3.5 ~ 4.2	-5 -5				*	(6)

COMMENTS

(.1) Data of (9) (12) at 65° C in HCl 1M/l, $k = 5.0 \times 10^{-7}$ (underlined in table), in excellent agreement with (12) (13). In CH_3COOH, hydrolysis is about 10^6 times faster than in H_2O under the same conditions (8). Further data in different $CH_3COOH + H_2O$ solutions, and with $(CH_3CO)_2O$ added, in original (8). Rates clearly increase very much faster than proportionally to the acid concentration. Mechanism discussion, see (7). (.2) (.2.1) In concentrated H_2SO_4, the rate is strictly first-order in HCN in the presence of a large excess of H_2SO_4, but becomes more nearly of the zero order when the concentration of HCN becomes comparable to that of H_2SO_4. Convincing evidence is given (1) for a mechanism involving reaction (.2.1) as a first step of the overall reaction (.2). The compound $HCN \cdot H_2SO_4$ was actually isolated, and this justifies the alternative formulation of reaction (.2) written in the table in parentheses. $HCN \cdot H_2SO_4$ is assumed to react further according to $HCN \cdot H_2SO_4 + H_2O \rightleftarrows HCONH_2 \cdot H_2SO_4$ (this intermediate not actually isolated) $\rightarrow CO + NH_4HSO_4$. Evidence for this mechanism is the observation that, in H_2SO_4 of the same high concentration, the half-lives of HCN and of $HCONH_2$ are very exactly equal. Reaction (.2.1), the rate-determining step of (.2), is zero-order k at comparable concentrations of HCN and H_2SO_4, first-order (k A) in the presence of a large excess of H_2SO_4. The zero-order rate given in the table was recalculated to M/l per sec from the original M/ml per min; the first-order k was calculated from the original half-lives (1). For the overall reaction (.2), note the maxima of k at 78 - 79 % H_2SO_4; on each side of the maximum, $\Delta \log k/\Delta(\% \ H_2SO_4)$ is constant. In $H_2SO_4 > 90$ %, some SO_2 and CO_2 is formed in addition to CO. Data at further temperatures in original (1). (.3) Same mechanism and same considerations as for (.2) (.2.1). The compound $HCN \cdot H_3PO_4$ was isolated. The system is two-phase; the reaction takes place in the H_3PO_4 phase. For the rate-determining step $HCN + H_3PO_4$ in 100 % H_3PO_4 is 3.6 days. In the same concentrated H_3PO_4, the half-lives of HCN and of $HCONH_2$ are equal, which bears out the assumed intermediate $HCONH_2 \cdot H_3PO_4$. (.4) Selected points. The k data of (2) had to be multiplied by 2.3 (conversion from $\log_{10}$ to ln) to fall in line with the figure of (5), and to check with (15). Proportionality of k with the acid concentration is approximately fulfilled only at very low acid concentrations; in stronger acid, k increases much faster than linearly with the acid concentration (2). This increase is represented by (3) as exponential, the rate $v = v_o e^{kc}$, where v_o is the rate at zero concentration c of the acid; for HNO_3 at 25° C, $k = 0.265$ in the HNO_3 concentration range 0.05 - 5.0. (3). Values of

COMMENTS *(continued)*

k are given also for salts (KNO_3, NH_4NO_3, $NaNO_3$, $LiNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$) at constant $[HNO_3]$. In HNO_3, the activation energy *E* is independent of $[HNO_3]$ in the range 0.12 - 1.98, but it varies in HCl (7) (15). With increasing concentration of HCl or HBr, *k* increases to a maximum, then falls off (7). In [HCl] + [NaCl] = constant = 4.0, log (*k*/[HCl]) is a linear function of [HCl] (7). In CCl_3COOH, the plot of *k* against $[CCl_3COOH]$ approaches a straight line passing through the origin (7). Further data of *k* in dilute acids and in buffer solutions, see original (7). The mechanism is represented by $NH_2CN + H^+ \rightarrow NH_2CN \cdot H^+$, followed by $NH_2CN \cdot H^+ + H_2O \rightarrow NH_2CN \cdot H_3O^+$; subsequent reactions, and mechanism discussions, see in particular (15), and (4). **(.5) (.6) (.7) (.8) (.9)** Selected points. Salt effects present. **(.14) (.15)** From overall rate of two-step reaction.

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SOLVOLYSIS

N_2:C bond Solvolysis

Reaction type $N_2CHCOOR' + ROH \rightarrow N_2 + ROCH_2COOR'$

Rate measured $+ d[N_2]/dt$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.1	$N_2CHCOOC_2H_5 + H_2O \rightarrow$	H_2O	10^2A =	HNO_3; 10^4 $[H^+]$ =	$k\,A\,[H^+]$							*	(10)
			3.76	53.67		0.1	4.08	-2					
			3.09	107.4		"	4.36	-2					
			1.31	286.5		"	4.45	-2					
			3.94	17.90		5.0	7.24	-2					
			1.67	107.4		"	7.85	-2					
			0.95	214.9		"	7.75	-2					
			3.22	26.85		10.0	1.25	-1					
			2.24	107.4		"	1.29	-1					
			1.38	286.5		"	1.39	-1					
			3.62	26.83		14.9	2.17	-1					
			1.28	107.3		"	2.27	-1					
			1.50 - 3.26	26.80		20.3	3.82	-1					
			1.90	107.2		"	3.91	-1					
			2.80 - 3.84	13.40		25.0	5.99	-1					
			1.93	35.70		"	6.36	-1					
			0.67 - 3.36	71.39		"	6.22	-1					
			1.19 - 1.49	107.1		"	6.42	-1					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$N_2CHCOOC_2H_5 + H_2O$ (*continued*)		3.48		5.350		30.0	6.78	-1					
			1.76		53.50		"	1.02	0					
			4.36		5.342		35.2	1.25	0					
			2.04		26.69		"	1.58	0					
			2.72		5.325		40.1	1.92	0					
			1.92		13.36		"	2.30	0					
			1.91		26.65		"	2.62	0					
			2.60		1.329		45.1	1.55	0					
			3.11		5.318		"	2.83						
			1.68		8.888		"	3.53	0					
			1.53		1.323		55.1	4.45	0					
			1.17		3.529		"	5.69	0					
			1.07		7.057		"	7.06	0					
			1.69		2.634		65.1	1.01	+1					
			0.78		5.267		"	1.26	+1	17.5	4.27	12		
		H_2O		X =	10^3X =	$kA[H^+]$	25.0	<u>6.42</u>	-1				*	(7)
				o-$NH_2C_6H_4COOH$	2 - 16		"							
				p-$NH_2C_6H_4COOH$	5 - 16		"							
				m-$NH_2C_6H_4COOH$	5 - 16		"							
				d-$COOHCH(NH_2)CH_2COOH$	2 - 4		"							
				d-$COOHCH(NH_2)CH_2CH_2COOH$	2 - 4		"							
.1.1	$N_2CHCOOC_2H_5 + H_2O$	$H_2O + D_2O(N)$	0			kA	15	2.37	-1				*	(5)
			0.204				"	3.19	-1					
			0.447				"	3.97	-1					
			0.585				"	4.71	-1					
			0.843				"	6.08	-1					
			1.00				"	7.48	-1					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1.1	$N_2CHCOOC_2H_5 + H_2O$ (*continued*)	H_2O				k A	0	4.17	-2					
							15	2.37	-1					
							25	6.50	-1					
							35	1.67	0	17.8				
		D_2O (98 - 99 %)					0	1.38	-1					
							15	7.18	-1					
							25	1.80	0					
							35	5.00	0	17.0				
.2	$N_2CHCOOCH_3 + C_2H_5OH$	B + H_2O (M/1)	0.0	CCl_3COOH	0.0909	k A	25	2.40	-4				*	(1)
			0.152		"		"	1.19	-4					
			0.352		"		"	7.10	-5					
			0.0	$(NO_2)_3C_6H_2OH$	0.00227	"	"	2.92	-4					
			0.069		"		"	2.15	-4					"
			0.0	"	0.00455	"	"	4.74	-4					"
			0.106		"		"	2.89	-4					
			0.344		"		"	1.32	-4					
			0.0		0.00909	"	"	7.80	-4					"
			0.0975		"		"	4.63	-4					
			0.344		"		"	2.15	-4					
.3	$N_2CHCOOC_2H_5 + CH_3OH$		0.08 - 0.55	$(NO_2)_3C_6H_2COOH$		k A							*	(8)
		B + H_2O (M/1)	0.0		0.00909		25	6.12	-3					
			0.64		"		"	3.12	-3					
			1.91		"		"	1.49	-3					
			0.0	"	0.00455	"	"	3.60	-3					"
			0.32		"		"	2.24	-3					
			1.28		"		"	1.08	-3					

242.455.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.3	$N_2CHCOOC_2H_5 + CH_3OH$ (*continued*)		0.0	$(NO_2)_3C_6H_2COOH$	0.00227	kA	25	2.05	-3					(8)
			0.32		"	"	"	1.19	-3					
			1.28		"	"	"	5.58	-4					
.4	$N_2CHCOOC_2H_5 + C_2H_5OH$		0.08 - 0.55	$(NO_2)_3C_6H_2COOH$		kA								
		$B + H_2O$ (*M*/1)	0.0		0.00909		25	9.50	-4				*	(8)
			0.32		"		"	4.26	-4					
			2.56		"		"	1.07	-4					
			5.12		"		"	7.25	-5					
			10.2		"		"	8.16	-5					
			15		"		"	1.16	-4					
			0.0	"	0.00455	"	"	5.72	-4					"
			0.16		"		"	3.54	-4					
			0.64		"		"	1.56	-4					
			0.0	"	0.00114	"	"	1.83	-4					"
			0.08		"		"	1.28	-4					
		$B + H_2O$ (*M*/1)	0.0	CCl_3COOH	0.0445	kA	25	1.92	-4				*	(1)
			0.0445		"		"	1.45	-4					
			0.149		"		"	1.00	-4					
			0.288		"		"	6.88	-5					
			0.0	"	0.182	"	"	4.62	-4					"
			0.0427		"		"	3.74	-4					
			0.205		"		"	2.04	-4					
			0.336		"		"	1.51	-4					
			0.0	$(NO_2)_3C_6H_2COOH$	0.0445	"	"	1.10	-4					"
			0.33		"		"	3.67	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$N_2CHCOOC_2H_5 + C_2H_5OH$ *(continued)*		0.0	$(NO_2)_3C_6H_2COOH$	0.182		25	4.62	-4					(1)
			0.107		"		"	2.73	-4					
			0.336		"		"	1.46	-4					
			0.0	$HSO_3C_6H_3(OH)COOH$	0.00182	kA	"	1.18	-3					(1)
			0.103				"	7.13	-4					
			0.426				"	2.86	-4					
.5	$N_2CHCOOC_2H_5 + (CH_3)_2CHCH_2OH$		0.08 - 0.55	$(NO_2)_3C_6H_2COOH$		kA								
		$B + H_2O$ (M/1)	0.0		0.00909		25	1.62	-4				*	(8)
			0.32		"		"	4.50	-5					
.6	$N_2CHCOOC_2H_5 + CH_2ClCOOH$	C_6H_6	$10^3A = 7.5 - 11$			kA	15							
			$10^2B = 6 - 64$			$k = aB^2 + bB$	a	2.00	-4				*	(2)
							b	7.50	-6					
		$C_6H_5CH_3$	B = 0.25 - 0.80			kA	25.0							
						$k = aB^2 + bB$	a	2.24	-4				*	(6)
							b	3.10	-5					
		$C_6H_5NO_2$	0.15 - 1.2			"	a	1.10	-3					"
							b	7.50	-4					
		o-$CH_3C_6H_4NO_2$	0.26 - 0.83			"	a	1.50	-3					"
							b	1.67	-4					
		m-$CH_3C_6H_4NO_2$	0.15 - 0.97			"	a	8.33	-4					"
							b	5.00	-4					
		C_6H_5Cl	0.22 - 0.69			"	a	7.48	-4					"
							b	8.80	-5					
		C_6H_5Cl	0.11 - 0.70			"	a	9.13	-4					"
							b	7.63	-5					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.7	$N_2CHCOOC_2H_5 + CHCl_2COOH$	C_6H_6	$10^3A = 7.5 - 11$ $10^2B = 2.5 - 11.4$			kA	15						*	(2)
						$k = aB^2 + bB$	*a*	5.57	-2					
							b	1.40	-3					
		$C_6H_5CH_3$	B = 0.033 - 0.25			"	25.0						*	(6)
							a	4.50	-1					
							b	4.18	-2					
		$C_6H_5NO_2$	0.051 - 0.16			"	*a*	2.50	-1					"
							b	1.03	-2					
		C_6H_5Cl	0.033 - 0.25			"	*a*	4.25	-1					
							b	5.18	-2					
		C_6H_5Br	0.036 - 0.27			"	*a*	4.18	-1					
							b	8.68	-2					
		C_6H_5I	0.046 - 0.19			"	*a*	5.50	-1					
							b	6.50	-2					
.8	$N_2CHCOOC_2H_5 + CH_2BrCOOH$	C_6H_6	$10^3A = 7.5 - 11$ $10^2B = 3 - 50$			kA	15						*	(2)
						$k = aB^2 + bB$	*a*	3.92	-4					
							b	8.68	-5					
		$C_6H_5CH_3$	B = 0.27 - 0.86				25.0						*	(6)
							a	2.23	-4					
							b	3.11	-5					
		$C_6H_5NO_2$	0.40 - 1.3				*a*	7.32	-4					"
							b	3.83	-4					
		C_6H_5Cl	0.16 - 0.99				*a*	4.03	-4					"
							b	3.57	-5					
		C_6H_5Br	0.33 - 1.1				*a*	4.41	-4					"
							b	4.16	-5					

242.455.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$ k°	n	E	$A = A^{\circ} \times 10^{n}$ A°	n	Comments	Literature
.9	$N_2CHCOOC_2H_5 + CH_3CHBrCOOH$	C_6H_6	$10^3A = 7.5 - 11$ $10^2B = 9 - 50$			kA	15						*	(2)
					$k = aB^2 + bB$		a	2.64	-5					
							b	2.92	-6					
.10	$N_2CHCOOC_2H_5 + CH_2ICOOH$	C_6H_5Cl	B = 0.17 - 0.14			kA	25.0							
					$k = aB^2 + bB$		a	8.82	-5				*	(6)
							b	8.90	-6					
.11	$N_2CHCOOC_2H_5 + (NO_2)_3C_6H_2COOH$	C_6H_6	$10^3A = 7.5 - 11$; B = 0.068 0.136			kA	15	4.9	-7				*	(2)
							"	1.1	-6					

COMMENTS

(.1) Variation of k with $[H^+]$ is representable (10) by $k = (a/[H^+]) + b + c[H^+]$, where a (not evaluated) is not necessarily zero; at 10.1°C, $b = 0.124$ and $c = 0.525$. The temperature variation of k is representable (10) by $k = 4.27 \times 10^{12} e^{-17500/RT}$ or by $\ln k = 44.6801 - 4.615 \ln T - 18890/RT$. The first order in A and in $[H^+]$ is well followed in HNO_3, but k falls with the progress of the reaction in HCl at $A \geqslant 0.01$, owing to the substitution side reaction $A + HCl \rightarrow N_2 + CH_2ClCOOC_2H_5$ which consumes the catalyst. The value of k in H_2O solution, defined by the rate law $kA[H^+]$, at 25°C, is $k = \mathbf{6.42 \times 10^{-1}}$, in very good agreement between (7) ($[H^+] = 0.002$-0.015), (3) (0.0009-0.09), and (10) (at high $[H^+]$). **(.1.1)** Agreement of the value of k in H_2O at 25°C, 6.50×10^{-1}, with the 6.42×10^{-1} of (10) (7) (2), indicates that these first - order k refer to $[H^+] = 1M$. Picric-acid catalyzed reaction with H_2O, at different concentrations of the acid, in $H_2O + D_2O$ mixtures, see (4). **(.2) (.3) (.4) (.5)** For the reactions with

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COMMENTS *(continued)*

alcohol in alcohol-water solvents, up to $[H_2O] = 3\ M/l$, the first - order k (in A) is representable by $k = K/(r + N)$, where N = concentration of H_2O (in M/l), K = constant proportional to the concentration and the degree of dissociation of the catalyzing acid, and $r = [BH^+][H_2O]/[B][H_3O^+]$. This equation, analogous to the Goldschmidt equation obtaining in esterification of carboxylic acids (see Comments, 202.441) expresses the retardation of the reaction with the alcohol by H_2O, owing to a competition between H_3O^+ and BH^+ ($=ROH_2^+$) assumed to be rate determining through the step $A + ROH_2^+ \rightarrow N_2 + ROCH_2COOC_2H_5 + H^+$. The values of r are: $r = 0.15$, for both $N_2CHCOOCH_3$ and $N_2CHCOOC_2H_5$, and CCl_3COOH, $(NO_2)_3C_6H_2COOH$, $HSO_3C_6H_3(OH)COOH$.

(8)

Reaction	$(NO_2)_3C_6H_2OH$	r
(.3)	0.00909	0.63
	0.00455	0.55
	0.00227	0.49
(.4)	0.00909	0.14
	0.00455	0.16
	0.00227	0.15
(.5)	0.00909	0.12

For (.4), satisfactory agreement between (1) and (8). All acid-catalyzed reactions in alcohol-water mixtures are accompanied by side reactions with the acid itself. Further data on reaction (.4) catalyzed by $(NO_2)_3C_6H_2COOH$ plus picrates, see (11); the first-order $k = [\gamma k_H + (1 - \gamma) k_M]\,c$, where c = concentration of the acid, γ = degree of dissociation, k_H and k_M corresponding, respectively, to the catalytic effects of the dissociated and the undissociated parts of the acid. The alleged catalysis by undissociated picric acid is considered inconclusive by (2). (.6) (.7) (.8) (.9) (.10) The first-order law in A is justified by near constancy of the acid concentration (not over 8% change) (2). The second-order term in the acid is interpreted as acceleration of the reaction by dissociation of dimeric acid molecules (2). Original (2) gives further data for pairs of acids, and for acid catalysis in the presence of C_2H_5OH and C_6H_5OH. The effective apparent order in B in the aprotic solvents ranges from 1.3 to 1.9 (6).

LITERATURE

(1) H. Braune, *ZPC* 1913, **85**, 170. (2) J.N.Brönsted, R.P.Bell, *ACS* 1931, **53**, 2478. (3) W. Fraenkel, *ZPC* 1907, **60**, 202, 207. (4) Ph. Gross, H.Steiner, F. Krauss, *TFS* 1936, **32**, 877. (5) Ph. Gross, H. Steiner, F. Krauss, *TFS* 1938, **34**, 351. (6) R.J. Hartman, C. J . Hochanandel, E.G.Bobalek, *ACS* 1946, **68**, 2071. (7) B.Holmberg, *ZPC* 1908, **62**, 726. (8) W.S.Millar, *ZPC* 1913, 85, 129. (9) E.A.Moelwyn-Hughes, P. Johnson, *TFS* 1940, **36**, 949. (10) E.A.Molewyn-Hughes, P.Johnson, *TFS* 1941 **37**, 282. (11) H.C.S. Snethlage, *ZPC* 1913, **85**, 211.

242.456.

SOLVOLYSIS

of N_2:C bond by aromatic carboxylic acids

Reaction type N_2CR_2 + ArCOOH → N_2 + $ArCOOCHR_2$
(A) (B) (L) (M)

Method Measurement of N_2 evolved

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$N_2C(p - C_6H_4CH_3)_2 + C_6H_5COOH$	C_7H_8	A = B ~ 0.03	kAB	25	1.06	-3
.2	$N_2C(p - C_6H_4CH_3)_2 + o - CH_3C_6H_4COOH$	C_7H_8	A = B ~ 0.03	kAB	25	4.22	-3
.3	$N_2C(p - C_6H_4CH_3)_2 + m - CH_3C_6H_4COOH$	C_7H_8	A = B ~ 0.03	kAB	25	6.32	-3
.4	$N_2C(p - C_6H_4CH_3)_2 + o - CH_3OC_6H_4COOH$	C_7H_8	A = B ~ 0.03	kAB	25	4.65	-5
.5	$N_2C(p - C_6H_4CH_3)_2 + o - OHC_6H_4COOH$	C_7H_8	A = B ~ 0.03	kAB	25	~ 3	-1
.6	$N_2C(p - C_6H_4CH_3)_2 + o - NO_2C_6H_4COOH$	C_7H_8	A = B ~ 0.03	kAB	25	8.78	-3
		$CH_3COOC_2H_5$	A = B ~ 0.03	kAB	25	5.48	-3
.7	$N_2C(p - C_6H_4CH_3)_2 + m - NO_2C_6H_4COOH$	$CH_3COOC_2H_5$	A = B ~ 0.03	kAB	25	5.62	-3
.8	$N_2C(p - C_6H_4CH_3)_2 + p - NO_2C_6H_4COOH$	$CH_3COOC_2H_5$	A = B ~ 0.03	kAB	25	4.75	-3
.9	$N_2C(p - C_6H_4CH_3)_2 + o - ClC_6H_4COOH$	C_7H_8	A = B ~ 0.03	kAB	25	1.74	-2
.10	$N_2C(p - C_6H_4CH_3)_2 + m - ClC_6H_4COC$	C_7H_8	A = B ~ 0.03	kAB	25	1.02	-2

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.11	$N_2C(p - C_6H_4CH_3)_2 + p - ClC_6H_4COOH$	$CH_3COOC_2H_5$	A = B ~ 0.03	k AB	25	5.90	-5
.12	$N_2C(p - C_6H_4CH_3)_2 + o - BrC_6H_4COOH$	C_7H_8	A = B ~ 0.03	k AB	25	2.30	-2
		$CH_3COOC_2H_5$	A = B ~ 0.03	k AB	25	1.45	-2
.13	$N_2C(p - C_6H_4CH_3)_2 + m - BrC_6H_4COOH$	C_7H_8	A = B ~ 0.03	k AB	25	1.08	-2
		$CH_3COOC_2H_5$	A = B ~ 0.03	k AB	25	1.25	-3
.14	$N_2C(p - C_6H_4CH_3)_2 + p - BrC_6H_4COOH$	$CH_3COOC_2H_5$	A = B ~ 0.03	k AB	25	6.52	-4

LITERATURE

J. F. Norris, W. H. Strain *ACS* 1935, 57, 187

SOLVOLYSIS

Aromatic acyl halides

Reaction type $ArCOX + ROH \rightarrow ArCOOR + HX$

Amounts are in M/l.

Rates are in M/l per sec.

Coded solvents, at the end of the table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.1	$C_6H_5COCl + H_2O$	An50	0.02	kA	0	4.3	-4	(1)
.2	$C_6H_5COCl + CH_3OH$	B		kA	0 25	4.4 4.25	-4 -3	(2)
.3	$C_6H_5SO_2Cl + H_2O$	An50	0.04	kA	25	2.4	-4	(1)
		Et50	0.02	kA	25	5.2	-4	(1)
.4	*o* - $CH_3C_6H_4COCl + H_2O$	An50	0.02		0	very fast		(1)
.5	*o* - $CH_3C_6H_4COCl + CH_3OH$	B		kA	0	2.28	-3	(2)
.6	*o* - $CH_3C_6H_4COCl + C_2H_5OH$	B		kA	25	3.48	-3	(2)
.7	*m* - $CH_3C_6H_4COCl + H_2O$	An50	0.02	kA	0	6.3	-4	(1)
.8	*m* - $CH_3C_6H_4COCl + CH_3OH$	B		kA	0	4.93	-4	(2)
.9	*m* - $CH_3C_6H_4COCl + C_2H_5OH$	B		kA	0 25	6.28 7.88	-5 -4	(2)
.10	*p* - $CH_3C_6H_4COCl + H_2O$	An50	0.02	kA	0	1.25	-3	(1)

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.11	p - $CH_3C_6H_4COCl + CH_3OH$	B		kA	0	3.0	-4	(2)
.12	p - $CH_3C_6H_4COCl + C_2H_5OH$	B		kA	25	6.0	-4	
.13	2,4,6 - $(CH_3)_3C_6H_2COCl + CH_3OH$	B		kA	0	very fast		(2)
.14	p - $C_6H_5C_6H_4COCl + CH_3OH$	B		kA	0	3.3	-4	(2)
.15	p - $CH_3C_6H_4SO_2Cl + H_2O$	An50	0.04	kA	25	1.8	-4	(1)
		Et50	0.02	kA	25	4.45	-4	"
.16	o - $CH_3OC_6H_4COCl + C_2H_5OH$	B		kA	0	2.12	-3	(2)
.17	m - $CH_3OC_6H_4COCl + C_2H_5OH$	B		kA	0	7.69	-5	(2)
.18	o - $NO_2C_6H_4COCl + H_2O$	An50	0.02	kA	0	7.7	-4	(1)
.19	o - $NO_2C_6H_4COCl + CH_3OH$	B		kA	0	7.9	-4	(2)
.20	o - $NO_2C_6H_4COCl + C_2H_5OH$	B		kA	25	1.22	-3	(2)
.21	m - $NO_2C_6H_4COCl + H_2O$	An50	0.02	kA	0	3.0	-3	(1)
.22	m - $NO_2C_6H_4COCl + CH_3OH$	B		kA	0	5.48	-3	(2)
.23	p - $NO_2C_6H_4COCl + H_2O$	An50	0.02	kA	0	5.0	-3	(1)
.24	p - $NO_2C_6H_4COCl + CH_3OH$	B		kA	0	6.88	-3	(2)
.25	2,4,6 - $(NO_2)_3C_6H_2COCl + CH_3OH$	B		kA	25	very slow		(2)
.26	m - $NO_2C_6H_4SO_2Cl + H_2O$	An50	0.04	kA	25	7.3	-4	(1)
		Et50	0.02	kA	25	9.7	-4	(1)

242.472.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n	Literature

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$: k^o	n	Literature
.27	*o* - $ClC_6H_4COCl + H_2O$	An50	0.02	*k* A	0	6.3	-4	(1)
.28	*o* - $ClC_6H_4COCl + CH_3OH$	B		*k* A	0	1.23	-3	(2)
.29	*o* - $ClC_6H_4COCl + C_2H_5OH$	B		*k* A	25	2.1	-3	(2)
.30	*m* - $ClC_6H_4COCl + H_2O$	An50	0.02	*k* A	0	6.3	-4	(1)
.31	*m* - $ClC_6H_4COCl + CH_3OH$	B		*k* A	0	1.48	-3	(2)
.32	*m* - $ClC_6H_4COCl + C_2H_5OH$	B		*k* A	0 25	4.10 2.57	-4 -3	(2)
.33	*p* - $ClC_6H_4COCl + H_2O$	An50	0.02	*k* A	0	3.7	-4	(1)
.34	*p* - $ClC_6H_4COCl + CH_3OH$	B		*k* A	0	7.19	-4	(2)
.35	*p* - $ClC_6H_4COCl + C_2H_5OH$	B		*k* A	25	1.21	-3	(2)
.36	*o* - $BrC_6H_4COCl + H_2O$	An50	0.02	*k* A	0	5.8	-4	(1)
.37	*o* - $BrC_6H_4COCl + CH_3OH$	B		*k* A	0	1.22	-3	(2)
.38	*m* - $BrC_6H_4COCl + H_2O$	An50	0.02	*k* A	0	7.3	-4	(1)
.39	*m* - $BrC_6H_4COCl + CH_3OH$	B		*k* A	0	1.53	-3	(2)
.40	*p* - $BrC_6H_4COCl + H_2O$	An50	0.02	*k* A	0	4.0	-4	(1)
.41	*p* - $BrC_6H_4COCl + CH_3OH$	B		*k* A	0	8.0	-4	(2)
.42	*o*, *o* -$Br_2C_6H_3COCl + H_2O$	An50	0.01	*k* A	0 25	4.8 6.8	-6 -5	(3)

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.43	o, p - $Br_2C_6H_3COCl + H_2O$	An50	0.004	k A	0	9.2	-4	(³)
.44	m, m - $Br_2C_6H_3COCl + H_2O$	An50	0.004	k A	0	5.8	-3	(³)
.45	2,4,6 - $Br_3C_6H_2COCl + CH_3OH$	B		k A	25	3.1	-6	(²)
.46	o - $IC_6H_4COCl + C_2H_5OH$	B		k A	0	2.12	-4	(²)
.47	m - $IC_6H_4COCl + C_2H_5OH$	B		k A	0	3.0	-4	(²)
.48	p - $IC_6H_4COCl + C_2H_5OH$	B		k A	0	1.39	-4	(²)

SOLVENTS

An50	$(CH_3)_2CO$ 50 vol % + H_2O 50 vol %
Et50	C_2H_5OH 50 vol % + H_2O 50 vol %
B	The second reactant is the solvent (in great excess)

LITERATURE

(¹) G. Berger, S.C.J. Olivier, *RTC*, 1927, 46, 516.

(²) J.F.Norris, H.H.Young, *ACS* 1935, 57, 1420.

(³) S.C.J. Olivier, *RTC* 1929, **48**, 227.

SOLVOLYSIS

CN halides

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^{o} \times 10^{n}$		E
								k^{o}	n	
.1	$CNBr + OH^{-} \longrightarrow CNOH + Br^{-}$ $(CNBr + 2OH^{-} \longrightarrow CNO^{-} + Br^{-} + H_2O)$	H_2O	$10^3A = 0.6 - 6$; $10^3B = 3 - 12$			k AB	0.2	9.7	−2	
			1.8 − 6; 3 − 6			"	10	2.7	−1	
			0.8 − 1.6; 2 − 6			"	20	7.0	−1	15.3
.2	$CNI + OH^{-} \longrightarrow CNOH + I^{-}$ $(CNI + 2OH^{-} \longrightarrow CNO^{-} + I^{-} + H_2O)$	H_2O	$10^3A = 5$; $10^3B = 10$			k AB	20	7.4	−3	
			" 165				"	5.2	−3	
			" 41				0.2	5.9	−4	
							20	6.9	−3	
							30	2.05	−2	19.5
			$10^3A = 5$; $10^3B = 82$			k AB	20	6.2	−3	
				$NaNO_3$	0.1	"	"	6.05	−3	
				KCl	"	"	"	6.0	−3	
				KI	"	"	"	5.75	−3	
				KCN	"	"	"	4.95	−3	

LITERATURE

R. O. Griffith, R. S. Jobin, A. McKeown, *TFS* 1938, 34, 316.

SOLVOLYSIS

P - O bond

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $(OH)_2OP\text{-}O\text{-}PO(OH)_2 + H_2O \rightarrow 2(OH)_3PO$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	pH	$k = k^o \times 10^n$	
							k^o	n
.1	$Na_4P_2O_7 + H_2O \rightarrow 2Na_2HPO_4$	H_2O	0.012	k A	100	9.33	1.7	-6
.2	$Na_3P_2O_7 + H_2O \rightarrow Na_2HPO_4 + NaH_2PO_4$	"	"	"	"	7.34	7.8	-5
.3	$Na_2H_2P_2O_7 + H_2O \rightarrow 2NaH_2PO_4$	"	"	"	"	3.21	1.44	-4
.4	$NaH_3P_2O_7 + H_2O \rightarrow NaH_2PO_4 + H_3PO_4$	"	"	"	"	2.07	2.40	-4
.5	$H_4P_2O_7 + H_2O \rightarrow 2H_3PO_4$	"	"	"	"	1.92	8.30	-4

LITERATURE

L. M. Postnikov, *Vestnik Moskov. Univ.* 1950, 5, No. 5, 63.

ISOTOPE EXCHANGE

H - D exchange on aliphatic C

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Fractional time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$C_2H_5OH + HDO \longrightarrow C_2H_5OD + H_2O$	H_2O	B = 20 %			kAB	25.0		2.4 ±0.2	-6				*	(5)
.2	$C_2H_5OD + H_2O \longrightarrow C_2H_5OH + HDO$	H_2O				kAB	25.0		2.2 ±0.2	-6				*	(5)
.3	$CH_3COCH_3 + D_2O \longrightarrow CH_2DCOCH_3 + HDO$	H_2O + B;	A =	$[OH^- + OD^-]$ =		kA$[OD^- + OH^-]$									(7)
		% D = 99.6	1.5	0.003 - 0.0086			25		3.6	-5					
		"	"	0.0014			"		2.9	-5					
		97.5	3.2	0.006			"		3.2	-5					
		92.6	1.7	"			"		2.5	-5					
		51.6	1.6	"			"		4.5	-6					
.4	$CD_3COOH + H_2O \longrightarrow CD_2HCOOH + H_2O$	H_2O;	A = 0.14 - 2.5		-	kA	183		1.8	-5					(1)
		pH > 8.5					206		9.2	-5	32				
			A = 0.22 - 0.77	HCl = 0.15 - 0.8		kA[HCl]									"
		pH < 2.5					183		2.3	-4					
							206		1.06	-3	26				
			A = 0.3 - 2.0	KOH = 0.04 - 1.0		kA$[OH^-]$									"
		pH > 8.5					183		1.4	-3					
							206		5.4	-3	22				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Fractional time	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.5	$CH_3COOD + D_2O \longrightarrow CH_2DCOOD + HDO$	D_2O; $pH > 8.5$	A = 0.5 - 2.8		-	kA	183		3.5	-5					(1)
							206		2.0	-3					
		$pH < 2.5$	A = 0.5 - 1.8	DCl = 0.3 - 2.0		kA[DCl]	183		4.8	-4					(1)
							208		1.8	-3					
		$pH > 8.5$	A = 0.4 - 1.0	KOD = 0.03 - 3.1		$kA[OD^-]$	183		3.1	-3					(1)
							206		6.6	-3					
.6	$CH_2:CHCH_2COO^- + HDO \longrightarrow CH_2:CHCHDCOO^- + H_2O$	$H_2O + D_2O$ 2.5 %	A = 1.0	NaOH	1.05	kA	100		1.5	-4				*	(3)
.7	$C_6H_5COCH(CH_3)C_2H_5 + OD^- \longrightarrow C_6H_5COCD(CH_3)C_2H_5 + OH^-$	dioxane + $D_2O \sim 1.5$ (M/1)	A ~ 0.3; B ~ 0.125				35.0	(0.10) 3.6×10^3 (0.25) 7.2×10^3 (0.41) 1.4×10^4 (0.57) 2.3×10^4						*	(2)
.8	$p - CH_3C_6H_4CH(C_6H_5)COO^- + D_2O \longrightarrow p - CH_3C_6H_4CD(C_6H_5)COO^- + HDO$	H_2O; B = 3 %	A + L = 0.2	NaOH	0.22	kA	100		2.2	-6				*	(4)
.9	$p - CH_3C_6H_4CD(C_6H_5)COO^- + H_2O \longrightarrow p - CH_3C_6H_4CH(C_6H_5)COO^- + HDO$	H_2O	A + L = 0.2	NaOH	0.22	kA	100		1.4	-6				*	(4)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Fractional time	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.10	$p - CH_3OC_6H_4CH{:}NCH_2C_6H_5 + C_2H_5OD \longrightarrow$	C_2H_5OH + B	A + L = 1.78				74.0							*	$(^6)$
	$\left\{ \begin{array}{l} p - CH_3OC_6H_4CH{:}NCHDC_6H_5 \\ p - CH_3OC_6H_4CHD.N{:}CHC_6H_5 \\ \text{etc.} \end{array} \right\} + C_2H_5OH$	31.5 mole %		$OC_2H_5^-$	0.1		(0.045)		1.44×10^4						
							(0.0845)		2.88×10^4						
							(0.188)		8.64×10^4						
							(0.628)		2.68×10^6						
		94.4 "		"	"		(0.054)		1.8×10^3						
							(0.126)		3.6×10^3						

COMMENTS

(.1) (.2) Rate determining step $C_2H_5OH + HDO \underset{b}{\overset{a}{\rightleftarrows}} C_2H_5OHD^+ + OH^-$, gives, on the assumption $k_b \equiv$ collision frequency, $k_a = 2.8 \times 10^{-6}$. (.6) Data corrected for irreversible isomerization to $CH_2DCH{:}CHCOO^-$, $CH_3CH{:}CHCDCOO^-$, and $CH_2DCH{:}CDCOO^-$; k for H - D exchange is 1.55 × k for isomerization to crotonic acid. Mechanism $A + OH^- \longrightarrow CH_2{:}CH\bar{C}HCOO^- + H_2O$; $CH_2{:}CH\bar{C}HCOO^- + HDO \longrightarrow CH_2{:}CHCHDCOO^- + OH^-$. (.7) Assuming 12-fold transfer rate of protons, exchange rate is identical with racemization rate. (.8) (.9) Accompanied by racemization; ionic mechanism. (.10) Data refer to exchange of one H atom per molecule.

LITERATURE

$(^1)$ I.D.C.Bok, K.H.Geib, *ZPA*^{A} 1939, **183**, 353. $(^2)$ S.K.Hsu, C.K.Ingold, C.L.Wilson, *CSL* **1938**, 78. $(^3)$ D.J.G.Ives, *CSL* **1938**, 91. $(^4)$ D.J.G.Ives, G.C.Wilks, *CSL* **1938**, 1455. $(^5)$ W.J.C.Orr, *TFS* 1936, **32**, 1033. $(^6)$ E.de Salas, C.L.Wilson, *CSL* **1938**, 319. $(^7)$ W.D.Walters, K.F.Bonhoeffer, *ZPC*^{A} 1938, **182**, 265.

ISOTOPE EXCHANGE

H - D exchange on aromatic C

Liquid phase

The position of the substitution is indicated in parentheses after the arrow.

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Fractional time	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
									k°	n		A°	n		
.1	$2,4,6 - CD_3H(OD)_2 - 1,3 + H_2O \longrightarrow$ (2)	H_2O	A + L = 0.01 - 0.6	HCl	0.01 - 0.1	k A [HCl]	64.7		1.55	-1				*	(1)
	$\longrightarrow$ (4) or (6)	"	"	"	"	"	"		1.55	-1	20.6 (34.7 - 100°C)	3	11		"
.2	$C_6H_3(OD)_3 - 1,2,3 + H_2O \longrightarrow$ (5)	H_2O	A + L = 0.16	HCl	0.01 - 2.3	k A [HCl]	64.7		3	-4				*	(1)
	$\longrightarrow$ (4) or (6)	"	"	"	"	"	"		5.5	-1	19				"
.3	$C_6H_3(OH)_3 - 1,3,5 + D_2O$	D_2O 0.995	A/B = 1	NaOH	0.1		100							*	(2)
						(0.995 - 0.28)		9.0×10^3							
						(0.995 - 0.27)		1.8×10^4							
						(0.995 - 0.26)		∞							

COMMENTS

In all cases, hydroxyl-D is exchanged for H instantaneously.

(.1) (.2) Data of fractional times for the uncatalyzed, the NaOH-, and the $CH_3COOH + CH_3COONa$-catalyzed reactions, and for the exchange $m - C_6H_4(OH)_2 + D_2O$, in original (¹).

(.3) The bold-face decimal fractions refer to the fall of the fraction of D_2O in the solvent from the initial fraction 0.995. At the limit (D_2O in solvent = **0.26**), the number of H atoms exchanged is ~ 5.5.

LITERATURE

(¹) K. H. Geib, *ZPC*^{A} 1937, **180**, 211.

(²) F. K. Munzberg, *ZPC*^{B} 1936, **33**, 26.

ISOTOPE EXCHANGE

Oxygen isotope exchange

Liquid phase

Amounts are in M/l. Rate and mass-action of A and L are in M/l per second and M/l of A and L, or in atom fraction O^{18}/O per second and atom fraction of A and L.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$	
								k^{o}	n
.1	$C_6H_5CO^{18}O^{18}H + H_2O^{16} \longrightarrow C_6H_5CO^{16}O^{18}H + H_2O^{18}$	H_2O	C_6H_5COOH = 0.05 - 0.10	HCl	0.1 - 0.5	$k\ (A - L)\ [H^+]$	80	2.34	-4

COMMENTS

The same rate law and the same k is valid for the reverse reaction. No effect of KCl.

LITERATURE

J. Roberts, H.C. Urey, *ACS* 1939, **61**, 2580.

ISOTOPE EXCHANGE

Halogen for halogen, in organic compounds

Liquid phase

Reaction types $\underset{(A)}{RX} + \underset{(B)}{X^{*-}} \longrightarrow \underset{(L)}{RX^{*}} + \underset{(M)}{X^{-}}$

or $RX + 1/2\ X_2^{*} \longrightarrow RX^{*} + 1/2\ X_2$

Amounts are in M/l.

Rates are in M/l per sec.

Coded solvents, see at the end of the table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
			Aliphatic carbon											
.1	$C_2H_5I + I^{*-}$	C_2H_5OH	(A + L) = 0.02; (B + M) = 0.017			k AB	50	4.8	-5				*	(13)
							60	1.3	-4					
							70	3.45	-4	21.3	5.3	8		
		C_2H_5OH	(A + L) = (B + M) = 0.1			k AB	10	2.3	-5				*	(11)
							20	9.2	-5					
							30	2.15	-4					
							40	4.2	-4					
							80	1.5	-2	19.0				
.2	*trans*-CHI:CHI + 1/2 I_2^{*}	decalin	A = 0.005 - 0.03; B = 0.003 - 0.013			$k\ AB^{1/2}$	100	1.0	-1	26	6.6	12	*	(12)
.3	$C_3H_7Br + Br^{*-}$	An 90	(A + L) = 0.05-0.1; (B + M) = 0.03- 0.06			k AB	0	1.6	-5					(9)
							25	3.7	-4					
							34.5	~ 1.0	-3					
							65.6	~ 1.3	-2	18.1				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$(CH_3)_2CHBr + Br^{*-}$	$(CH_3COOCH_2)_2$	(A + L) = 0.05-0.1; (B + M) = 0.03-0.06			k AB	40	1.5	-6					(^{10}) (^{8})
							80	5.0	-5					
							100	2.6	-4					
							140	~ 4	-3	19.7				
		An 90	" "			k AB	25	1.2	-5					"
							34	3.9	-5					
							44	1.37	-4					
							70	2.27	-3	22.9				
.5	$(CH_3)_2CHBr + 1/2\ Br_2^*$	An 90	(A + L) = 0.15; (B + M) = 0.03-0.07			k $AB^{1/2}$	25	1.2	-5					(^{3})
							44.5	1.37	-4					
							70	2.27	-3	23	4.7	10		
.6	$CH_3CHBrCOOH + Br^{*-}$	$(CH_3)_2CO$	(B + M) = 0.3			k AB	22	5.15	-4					(^{2})
		H_2O	(A + L) ~ 0.03; (B + M) = 0.002-0.04			k AB								
				H_2SO_4	1		60	2.0	-4					(^{6})
							70	5.0	-4					
							80	1.15	-3					
							100	6.4	-3	20.9	9	7		
.7	$C_3H_7I + I^{*-}$	C_2H_5OH	(A + L) = 0.02; (B + M) = 0.017			k AB	50	3.25	-5				*	(^{13})
							60	8.84	-5					
							70	2.27	-4	20.8	2.1	8		
.8	$(CH_3)_2CHI + I^{*-}$	C_2H_5OH	(A + L) = 0.02; (B + M) = 0.017			k AB	45	1.0	-6				*	(^{13})
							60	5.0	-6	23.8	1.3	9		
.9	$(CH_3)_3CCl + Cl^{*-}$	HCOOH				k A	15	3	-4					(^{7})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.10	$C_4H_9Br + Br^{*-}$	$(CH_3COOCH_2)_2$	(A + L) = 0.05-0.1; (B + M) = 0.03-0.06			k AB	25	1.1	−5					(10)(8)
							50	1.15	−4					
							80	1.3	−3					
							100	~ 5.2	−2	17.8				
		$(CH_3)_2CO$	" "			"	−10	9.0	−6					"
							0	4.6	−5					
							20	1.0	−3					
							40	~ 4.5	−2	19.8				
		An 90	" "			"	34.5	9.0	−5					"
							44.5	2.3	−4	18.9				
.11	$C_4H_9Br + 1/2\ Br_2^*$	An 90	(A + L) $<$ 0.15; (B + M) $<$ 0.15			k AB$^{1/2}$	0	1.7	−6				*	(8)
							25	3.3	−5					
							65	1.5	−3					
.12	$(CH_3)_2CHCH_2Br + 1/2\ Br_2^*$	An 90	(A + L) = 0.1-0.2; (B + M) = 0.03-0.06			k AB$^{1/2}$	25	1.4	−5					(3)
							49	2.4	−4					
							70	1.7	−3	20.2	7.1	8		
.13	$(CH_3)_3CBr + Br^{*-}$	$(CH_3COOCH_2)_2$	(A + L) = 0.05-0.1; (B + M) = 0.03-0.06			k AB	40	5.0	−6					(10)
							60	1.0	−4					
							80	2.1	−4					
							100	~ 2.4	−3					
							120	~ 1	−2	9.3				
.14	$dl\text{-}C_7H_{15}CH(CH_3)I + I^{*-}$	$(CH_3)_2CO$	(A + L) = 0.138; (B + M) = 0.160			k AB	30	1.35	−3				*	(4)
.15	$d\text{-}C_6H_5CH(CH_3)Br + Br^{*-}$	$(CH_3)_2CO$	(A + L) = (B + M) = 0.2			k AB	30	8.70	−4				*	(5)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
							Aromatic carbon							
.16	p-$NO_2C_6H_4Cl + Cl^{*-}$	An 90				k AB	30	1.81	-5					(1)
							50	1.42	-4					
							70	1.01	-3	20.8	1.8	10		
.17	p-$NO_2C_6H_4Br + Br^{*-}$	An 90				k AB	0	1.29	-3					(1)
							15	6.43	-3					
							30	3.56	-2	18.0	3.8	11		
.18	2, 4-$(NO_2)_2C_6H_3Br + Br^{*-}$	$(CH_3COOCH_2)_2$	(A + L) = 0.05-0.1; (B + M) = 0.03-0.06			k AB	70	2.1	-5					(10)
							90	1.1	-4					
							100	2.4	-4					
							120	~ 9	-4					
							130	~ 1.6	-3	19.3				

SOLVENTS

An90 $H_2O + (CH_3)_2CO$ 90 vol %.

COMMENTS

General. The halogens marked X^* are radioactive isotopes. The reaction kinetics were followed by G. M. counter. The same rate law and the same second-order rate constant hold for the forward and the reverse reaction; the total rate from left to right is thus expressed by k (AB - LM), and k is determined from its integrated form. The sums (A + L) and (B + M) remain constant throughout the course of the reaction in either direction. (.1) Values of k of (^{13}) and (^{11}) are not in agreement; I^* (^{13}) is I^{128}; in (^{11}), "a mixture of long-lived isotopes." (.2) k and A converted to M/l from mM/l. Simultaneous isomerization is negligible. The photochemical reaction in hexane at 15 - 50°C follows the same rate law, with E = 8.5. (.6) Reverse reaction proceeds with the same k. Walden inversion proceeds with practically the same k, consequently, the inversion proceeds over substitution. (.7) (.8) Hydrolysis proceeds over the same mechanism. (.11) Acids and bases have no catalytic effect. (.14) (.15) k calculated (by the editors) from the original N_s = constant sum total of all rates of exchanges occurring in the system, and related to the rate by $+ dL/dt = N_s\ (B/M_o)(A/A_o)$, hence $k = N_s A_o M_o$, where the subscript $_o$ refers to initial amounts. The sum of rates of exchange is equal to the sum of rates of Walden inversions in the same systems; consequently, inversion proceeds over substitution. The reverse reaction proceeds with the same k.

LITERATURE

(1) T.A.Bither, J.M.Sturtevant, H.C.Thomas, *ACS* 1945, **67**, 1562. (2) W.A.Cowdrey, E.D.Hughes, J.P.Newell, C.L.Wilson, *CSL* **1938**, 209. (3) G.A.Elliot, S.Sugden, *CSL* **1939**, 1837. (4) E.D.Hughes, F.Juliusberger, S.Masterman, B.Topley, J.Weiss, *CSL* **1935**, 1525. (5) E.D.Hughes, F.Juliusberger, A.D.Scott, B.Topley, J.Weiss, *CSL* **1936**, 1173. (6) W.Koskoski, R.W.Dodson, R.D.Fowler, *ACS* 1941, **63**, 2149. (7) W.Koskoski, H.Thomas, R.D.Fowler, *ACS* 1941, **63**, 2451. (8) L.J.Le Roux, S.Sugden, *CSL* **1939**, 1279. (9) L.J.Le Roux, S.Sugden, *CSL* **1939**, 1836. (10) L.J.Le Roux, C.S.Lu, S.Sugden, K.Thomson, *CSL* **1945**, 586.

(11) M.B.Neiman, R.V.Protsenko, DAN 1950, **71**, 327. (12) R.M.Noyes, R.G.Dickinson, V.Schomaker, *ACS* 1945, **67**, 1319. (13) H.Seelig, D.E.Hull, *ACS* 1942, **64**, 941.

EXCHANGE

H for S on aliphatic carbon

Gas phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
					k^o	n		A^o	n
.1	$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$	A = 0.02 - 0.04 B = 0.02 - 0.04	k AB	550	1.1	0			
				575	1.9	0			
				600	3.0	0			
				625	6.4	0	34.4	1.4	9

COMMENTS

Flow. Homogeneous in stainless steel. Order based on constancy of k on variation of A/B by a factor of 2.

LITERATURE

R. A. Fisher, J. M. Smith, *IEC* 1950, 42, 704.

EXCHANGE
Hydrogen - Halogen
Hydrogen halide formation and decomposition

Gas phase

Reaction types $H_2 + X_2 \rightarrow 2\ HX$

$2\ HX \rightarrow H_2 + X_2$

Amounts are in M/l.
Rates in M/l per sec.

No.	Reaction	Method	Amount of reactant		Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
							k°	n		A°	n		
.1	$H_2 + Cl_2 \rightarrow 2\ HCl$	flow	A/B = 1/3 - 3/1		k AB	230	1.7	-1				*	(12)
						240	2.5	-1					
						250	3.7	-1	18				
		stat;	10^3A	10^3B	k A^{2}B/L								
		pyrex vessel	6.70	12.4		184	6.5	-3				*	(11)
			"	16.6		"	2.6	-3					
			13.6	5.85		"	1.4	-2					
			"	4.45		"	3.4	-3					
			"	6.35		"	1.07	-2					
			6.90	17.0		"	2.6	-3					
		stat;	5.50	11.6	k AB$^{1/2}$	184	1.59	-3				*	(11)
		KCl-coated vessel	10.8	11.4		"	9.6	-4					
			16.0	6.7		"	7.9	-4					
			10.8	11.6		"	3.4	-4					

No.	Reaction	Method	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$ k°	n	E	$A = A^{\circ} \times 10^{n}$ A°	n	Comments	Literature
.2	$H_2 + Br_2 \longrightarrow 2\ HBr$	stat anal (B)	0.006 - 0.04	$k\,AB^{1/2}/[m + (L/B)]$		k						
					225.7	9.93	-5				*	(^{16})
					251.4	8.02	-4					"
					275.8	3.86	-3					(^{1})
					277.5	4.91	-3					(^{6})
					301.3	2.64	-2					"
					313.3	6.08	-2					(^{1})
					338.9	1.88	-1	40				"
						m						
						1.0	1					(^{6})
						8.4	0					(^{5})
.3	$D_2 + Br_2 \longrightarrow 2\ DBr$	stat anal (B)	0.002 - 0.005	as (.2)		k					*	(^{1})
					275.8	6.79	-4					
					312.4	8.35	-3					
					317.1	1.18	-2					
					335.7	3.21	-2					
					350.6	8.48	-2					
					366.3	1.75	-1					
					379.5	3.67	-1	44				
						m						
						1.0	1					
						k						
.4	$H_2 + I_2 \longrightarrow 2\ HI$	stat anal (B)	0.02 - 1.00	$k\,AB$	283	4.45	-5				*	(^{3})
					302	1.32	-4					"
					356	2.52	-3					"
					374	5.22	-3					"
					393	1.42	-2					"
					"	1.56	-2					(^{13})

No.	Reaction	Method	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
						k^{o}	n		A^{o}	n		
.4	$H_2 + I_2 \rightarrow 2 HI$ *(continued)*	stat	0.02 - 1.00	$k AB$	410	2.46	-2					(3)
		anal (B)			425	6.70	-2					(13)
					427	6.43	-2					(3)
					443	1.40	-1					"
					508	1.34	0	~ 39				"
.5	$2 HI \rightarrow H_2 + I_2$	stat	0.02 - 1.0	$k A^2$	283	3.52	-7				*	(3)
		anal (B)			300	1.18	-6					(9)
					302	1.22	-6					(3)
					321	3.95	-6					(9)
					356	3.02	-5					(3)
					374	8.59	-5					"
					393	2.19	-4					"
					"	2.59	-4					(13)
					410	5.12	-4					(3)
					425	1.24	-3					(13)
					427	1.16	-3					(3)
					443	2.50	-3					"
					508	3.95	-2	~ 44				"
		"	0.02 - 1.0	"	321	3.95	-6					(9)
			2.0		"	4.2	-6					
			3.0		"	4.6	-6					
			4.0		"	4.8	-6					
			6.0		"	5.5	-6					
			7.0		"	~ 7	-6					

311.700.

No.	Reaction	Method	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.6	$D_2 + I_2 \rightarrow 2\ DI$	stat anal (B)	$(1 - 2) \times 10^{-5}$	$k\ AB$	393	7.95	-3				*	(13)
					425	3.45	-2					
.7	$2\ DI \rightarrow D_2 + I_2$	stat anal (B)	$(1 - 2) \times 10^{-5}$	$k\ A^2$	387	1.19	-4				*	(2)
					393	1.68	-4					(13)
					425	7.77	-4					"
					435	1.11	-3					(2)
					446'	1.83	-3					"

COMMENTS

(.1) The data of (12) and (11) supersede previous work, such as that of Christiansen. For the flow-system reaction (12), the second-order k and E were calculated from the original data. These figures can lay claim to no accuracy, and are given in the way of illustration of the order of magnitude. Over longer times, k falls sharply and depends strongly on surface conditions. The simple second-order rate law kAB is derivable from the simple Nernst-chain mechanism

$Cl_2 \rightarrow 2\,Cl;\ Cl + H_2 \rightarrow HCl + H;$ etc.

which also accounts for the main features of the photochemical reaction, including in particular the variation in the order in $[Cl_2]$ with the presence or absence of inhibitors. The flow-system thermal reaction (12) is inhibited by O_2, but in the presence of high amounts of O_2 packing accelerates the rate, which is taken to indicate chain generation at the wall. The reaction is thus, essentially, partly heterogeneous, partly homogeneous. The effect of the condition of the reaction vessel wall is illustrated by the static-system reactions (11) where the very rate law varies with the nature of the wall. Selected illustrative data are included in the table.

In the uncoated pyrex vessel, the rate is very strongly dependent on the kind of surface; all data listed refer to a constant surface/volume ratio of ~ 1.2 cm^{-1}. For the KCl-coated vessel, k falls strongly with the progress of the reaction (the data included refer to 900, 1800, 3600, 36000 sec). On account of the obvious inconstancy of k in both cases. the rate laws quoted can claim no absolute validity. The law proposed for the reaction in the KCl-coated bulb is derivable from a mechanism involving generation of only Cl atoms at the wall, whereas both Cl and H appear to be generated at the uncoated wall. The chain length is estimated to $\sim 10^4$. The second-order k from the flow experiments, (12), when extrapolated down to 284°C with the aid of the temperature coefficient holding between 230 and 250°C, becomes $\sim 2.4 \times 10^{-2}$, i.e. it is not unreasonably close, as far as order of magnitude goes, to the experimental k in the static experiments (11) in an uncoated bulb, particularly if it is borne in mind that the second-order flow-system k refers to an early stage of the reaction. The values of k thus appear to be little sensitive to the form of the rate law.

(.2) Data of (8) and of (1) are combined. The discrepancy

COMMENTS *(continued)*

between (6) and (1) is equivalent to almost 10° difference in temperature but it is improbable that the deviations should be due to that factor. The temperature effect is the same in (6) and in (1). The chain mechanism is now classic, (1) $Br_2 \rightleftarrows 2Br$, (2) $Br + H_2 \longrightarrow HBr + H$, (3) $H + Br_2 \longrightarrow HBr + Br$, (4) $H + HBr \longrightarrow H_2 + Br$, and hence $+\ dL/dt = 2\ (k_2 k_3/k_4)\ K^{1/2} AB^{1/2}/[(k_3/k_4) + (L/B)]$. For step (2), $E = 17.7$, $A = 7 \times 10^{10}$. The same mechanism and rate law, with the same value of m, render the photochemical reaction. (.3) Mechanism as in (.2). For step (2), $E = 19.9$, $A = 8 \times 10^{10}$. (.4) (.5) Combined data of (3) and (13) for (.4) and of (3), (9), and (13), for (.5). Data of (13) give the temperature variation of the equilibrium constant in agreement with that calculated from the free energy function (2), whereas the data of (3) do not. The latter data fail to give a linear plot of log k as a function of $1/T$ (8), hence E is somewhat uncertain. The reaction may be catalyzed by very extensive pyrex surface (14). Loss of H_2 by diffusion through quartz cannot be disregarded (13). Intensive drying is without effect (9). Apparent effect of drying with P_2O_5 (10) is due to oxidation(4). For reaction (.5) at higher concentrations, selected points from the 50-point experimental curve of (9); the variation of k with the concentration N is expressible by $k = k_o/(1 - Nb)$ where $k_o = 3.95 \times 10^{-6}$ is the rate constant at 0.02 - 1.0 M/1; the "van der Waals-like" constant $b = 4.7 \times 10^{-2}$ 1/M in the range 2 - 4.5 M/1. (.6) (.7) Combined data of (2) and (13), for reaction (.7), in satisfactory agreement. Data of (7) are doubtful on account of the uncertainties involved in the analytical procedure (nonmonochromatic extinction).

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EXCHANGE

Liquid phase

Nitration of aromatic compounds

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$	CH_3NO_2	A ~ 0.1	HNO_2	0.006 - 0.15	$k_o = (a + b[HNO_2]^{1/2})^{-1}$				*	(1)
			B = 3.0			a	0	1.57	5		
			"			b	"	1.88	6		
			3.5			a	"	1.72	5		
			"			b	"	7.00	5		
			4.0			a	"	8.3	4		
			"			b	"	4.75	5		
			4.5			a	"	5.0	4		
			"			b	"	2.70	5		
			5.0			a	"	1.74	4		
			"			b	"	1.73	5		
			5.5			a	"	1.74	4		
			"			b	"	8.80	4		
			6.0			a	"	7.4	3		
			"			b	"	7.03	4		
			6.5			a	"	5.6	3		
			"			b	"	4.85	4		
			7.0			a	"	3.5	3		
			"			b	"	3.30	4		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		
.1	$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$ *(continued)*		B = 3.0			a	0	1.57	5		
			"			"	20	2.15	4		
			"			b	0	1.88	6		
			"			"	20	1.52	5		
			B = 5.0			a	0	1.74	5		
			"			"	10	6.0	3		
			"			b	-10	5.70	4		
			"			"	0	1.73	4		
			"				10	4.8	3		
			B = 4.0	HNO_2	0.073		0				
						+dL/dt =		5.3	-3		
.2	$C_6H_5CH_3 + HNO_3 \longrightarrow CH_3C_6H_4NO_2 + H_2O$	CH_3NO_2	A ~ 0.1; B = 4.0	HNO_2	0.073	+dL/dt =		5.3	-3	*	(1)
.3	$C_6H_5C_2H_5 + HNO_3 \longrightarrow C_2H_5C_6H_4NO_2 + H_2O$	CH_3NO_2	A ~ 0.1; B = 4.0	HNO_2	0.073	+dL/dt =		5.3	-3	*	(1)
.4	$C_6H_5F + HNO_3 \longrightarrow FC_6H_4NO_2 + H_2O$	CH_3NO_2		See Comments						*	(1)
.5	$C_6H_5Cl + HNO_3 \longrightarrow ClC_6H_4NO_2 + H_2O$	CH_3NO_2		See Comments						*	(1)
.6	$C_6H_5Br + HNO_3 \longrightarrow BrC_6H_4NO_2 + H_2O$	CH_3NO_2		See Comments						*	(1)
.7	$C_6H_5I + HNO_3 \longrightarrow IC_6H_4NO_2 + H_2O$	CH_3NO_2		See Comments						*	(1)
.8	$C_6H_5NO_2 + HNO_3 \longrightarrow C_6H_4(NO_2)_2 + H_2O$	$H_2O + H_2SO_4$ %	A = B =			k AB				*	(5)
		95.6	0.04 0.04				5	3.7	-3		
		93.0	0.02 0.02				"	6.7	-3		
		90.0	0.04 0.04				"	9.2	-3		
		87.5	0.02 0.02				"	5.5	-3		
		86.0	0.04 0.04				"	2.1	-3		

No.	Reaction	Solvent	Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
									k^o	n		
.8	$C_6H_5NO_2 + HNO_3 \longrightarrow C_6H_4(NO_2)_2 + H_2O$ *(continued)*	95.6	0.02	0.02				25	3.27	-2		
		"	0.01	0.01				"	3.67	-2		
		93.0	0.02	0.02				"	5.30	-2		
		92.0	0.02	0.02				"	5.70	-2		
		90.0	0.01	0.01				"	7.00	-2		
		85.0	0.02	0.02				"	5.20	-2		
		82.5	0.05	0.05				"	2.2	-4		
		80.0	0.04	0.04				"	2.3	-5		
		95.6	0.02	0.02	$KHSO_4$	0.46		"	3.7	-2		([5])
		93.0	0.02	0.02	"	"		"	6.5	-2		
		92.0	0.02	0.02	"	"		"	5.5	-2		
		90.0	0.02	0.02	"	"		"	6.2	-2		
		85.0	0.02	0.02	"	0.70		"	2.3	-3		
		96.5	0.02	0.02				40	1.4	-1		
		93.0	0.01	0.01				"	1.67	-1		
		91.5	0.01	0.01				"	1.73	-1		
		90.0	0.01	0.01				"	1.92	-1		
		87.5	0.02	0.02				"	9.3	-2		
		85.0	0.02	0.02				"	1.45	-2		
		82.5	0.02	0.02				"	1.63	-3		
.9	*o* - $CH_3C_6H_4NO_2 + HNO_3 \longrightarrow CH_3C_6H_4(NO_2)_2 + H_2O$	$H_2O + H_2SO_4$ 82.5 %	0.02	0.02			kAB	25	1.25	-1		([5])
.10	*m* - $CH_3C_6H_4NO_2 + HNO_3 \longrightarrow CH_3C_6H_4(NO_2)_2 + H_2O$	$H_2O + H_2SO_4$ 82.5 %	0.02	0.02			kAB	25	5.3	-2		([5])
.11	*p* - $CH_3C_6H_4NO_2 + HNO_3 \longrightarrow CH_3C_6H_4(NO_2)_2 + H_2O$	$H_2O + H_2SO_4$ 80.0 %	0.01	0.01			kAB	25	7.0	-3		([5])
		82.5	0.02	0.02				"	6.5	-2		

No.	Reaction	Solvent		Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
										k^o	n		
.12	$CH_3C_6H_3(NO_2)_2 + HNO_3 \longrightarrow CH_3C_6H_2(NO_2)_3 + H_2O$	$H_2O + H_2SO_4$	95.6 %	0.12	0.12			kAB	100	3.8	-4		(5)
			90.0	"	"				"	3.5	-4		
.13	$m - (CH_3)_2C_6H_2(NO_2)_2 + HNO_3 \longrightarrow$ $m - (CH_3)_2C_6H(NO_2)_3 + H_2O$	$H_2O + H_2SO_4$	100.1 %	0.48	0.08			kAB	50	5.8	-4		(5)
			"	0.51	1.01				"	1.15	-4		
			95.6	0.02	0.02				"	7.7	-4		
			93.0	0.02	0.40				"	3.0	-3		
			"	0.09	0.09				"	2.7	-3		
			90.0	0.02	0.40				"	1.4	-3		
.14	$(CH_3)_3CH(NO_2)_2 + HNO_3 \longrightarrow (CH_3)_3C(NO_2)_3 + H_2O$	$H_2O + H_2SO_4$	95.6 %	0.02	0.02			kAB	25	1.03	-2		(5)
			91.5	0.01	0.01				"	1.8	-2		
			90.0	0.02	0.02				"	2.3	-2		
			88.5	0.01	0.01				"	1.23	-2		
			85.0	0.01	0.01				"	2.7	-3		
.15	$C_6H_5CH_2COOH + HNO_3 \longrightarrow C_6H_4(NO_2)CH_2COOH + H_2O$	$H_2O + H_2SO_4$	90.0 %	0.02	0.02			kAB	25	6.5	-2		(5)

COMMENTS

(.1) (.2) (.3) With a large excess of HNO_3, the reaction in organic solvents (CH_3NO_2, dioxane, CH_3COOH, CH_3CN, $(CH_3CO)_2O$) is zero-order in A; the zero-order rate constant k_o is a function of $[HNO_2]$, as given in the table. Empirically, the parameters a and b, at 0°C, are functions of $B = [HNO_3]$ of the form $a = 8.4 \times 10^9 B^{-6}(27 - B)^{-1}$ and $b = 11.3 \times 10^9 B^{-5}(27 - B)^{-1}$. The rates of reactions (.1) (.2) (.3) are practically the same. Strong acids (H_2SO_4) accelerate the rate; NO_3^- ion retards it. Discussion of the data (2) (3) (4) leads to the conclusion

COMMENTS *(continued)*

that the rate determining step is 2 $HNO_3 \longrightarrow H_2NO_3^+ + NO_3^-$, ($H_2NO_3^+ \rightleftarrows H_2O + NO_2^+$), with the nitronium ion NO_2^+ the effective nitrating agent. In reactions (.1) (.2) (.3), the reaction of NO_2^+ with A is rapid as compared with the rate-determining step, hence the zero-order in A. (.4) (.5) (.6) (.7) The order of these reactions is between 0 and 1, as the rates of the reactions between A and NO_2^+ are comparable with the rate of the rate determining step 2 $HNO_3 \longrightarrow NO_3^- + H_2NO_3^+$ ($\rightleftarrows H_2O + NO_2^+$). (.8) - (.15) In $H_2O + H_2SO_4$, the nitration proceeds over $HNO_3 + H_2SO_4 \rightleftarrows HSO_4^- + H_2NO_3^+$; $H_2NO_3^+ + H_2SO_4 \rightleftarrows HSO_4^- + H_3O^+ + NO_2^+$.

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Sulfonation of aromatic compounds

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.1	p - $CH_3C_6H_4NO_2$ + H_2SO_4 $\longrightarrow$ 1 - CH_3 - 2 - SO_3H - C_6H_3 - 4 - NO_2	H_2SO_4 97.6 % + SO_3 2.4 %	A = 0.1	kA	25	5	-5	(1)
					35	1	-4	
					45	2.5	-4	
		H_2SO_4 100 %	"	"	25	7	-6	"

COMMENTS

The values of k are *initial.* H_2O formed in the course of the reaction acts as inhibitor, and k falls with time, particularly in the absence of initial SO_3.

Sulfonation of C_6H_6, $CH_3C_6H_5$, $C_{10}H_8$, C_6H_5OH, $C_6H_5C_6H_5$, etc., with H_2SO_4 in the presence of BF_3 (catalyst): data of times of completion, see (2).

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EXCHANGE

of H for halogen on aliphatic C.

Liquid phase

Reaction type $RH + X_2 \rightarrow RX + HX$

(A) (B) (L) (M)

Rate measured -dB/dt

Amounts are in M/l.

Rates are in M/l per sec.

Where there may be doubt about the position of the substitution, the H exchanged is printed in bold-face type.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
					Aliphatic-aliphatic Ketone									
.1	$CH_3COCH_3 + Cl_2$	H_2O	A = 0.068; B = 0.0014	NaOH	0.035	*k* A	0	1.03	-3					(1)
			0.223		"		0	1.25	-3					
			0.0015		0.070		0	1.54	-3					
.2	$CH_3COCH_3 + Br_2$	A + 9.1 vol % H_2O	10^3B = 1 - 3	HCl	0.0108	-dB/dt	-20.6	3.8	-8				*	(3)
					0.0427		"	2.04	-7					
					0.0744		"	4.3	-7					
					0.117		"	8.5	-7					
					0.145		"	1.14	-6					
		A + 9.1 vol % H_2O	10^3B = 1 - 3	HBr	0.0375	-dB/dt	-20.6	1.07	-7				*	(3)
					0.045		"	1.4	-7					
					0.0818		"	2.1	-7					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.2	$CH_3COCH_3 + Br_2$ *(continued)*			HBr	0.0251	-dB/dt	-11.3	3.1	-7					(3)
					0.045		"	5.75	-7					
				"	0.0118	"	0.0	7.75	-7					"
					0.045		"	3.8	-6					
					0.0624		"	4.5	-6					
		H_2O	A = 0.1	HCl	0.5	-dA/dt	5	2.55	-7				*	(4)
							15	9.20	-7					
							25	3.07	-6					
							35	1.03	-5	20.3				
		Ac 25	"	"	"	"	15	1.15	-6					"
							25	3.70	-6					
							35	1.15	-5	20.0				
		Ac 50	"	"	"	"	0	2.28	-7					"
							15	1.54	-6					
							25	4.98	-6	19.7				
		Ac 75	"	"	"	"	0	4.53	-7					"
							15	3.27	-6					
							25	1.06	-5	20.1				
		H_2O	"	CH_3COO^-	0.147	"	35	1.78	-7				*	"
							45	5.15	-7					
							55	1.41	-6	20.7				
		Ac 25	"	"	"	"	35	3.08	-7					"
							45	8.65	-7					
							55	2.23	-6	19.0				
		Ac 50	"	"	"	"	35	4.67	-7					"
							45	1.28	-6					
							55	3.37	-6	19.4				"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.2	$CH_3COCH_3 + Br_2$ *(continued)*	Ac 75	A = 0.1	CH_3COO^-	0.147	$-dA/dt$	35	5.83	-7					(4)
							45	1.53	-6					
							55	3.77	-6	18.5				
		Ac 90	"	"	"	"	35	5.63	-7					"
							45	1.50	-6					
							55	3.62	-6	19.3				
		A + 9.1 vol % H_2O	10^3B = 1 - 3 M ~ 0.01 - 0.1	kM; $k'M(1 + 1.5\ M)$										(3)
						k	-20.6	2.8	-6					
							0.0	7.0	-5					
						k'	-40.0	6.7	-6					"
							-20.6	1.76	-6					
							0.0	3.60	-5					
							+10.1	1.33	-4	19.9	4.9	11		
		H_2O	A ~ 0.5; B ~ 0.003	HCl	~ 0.1 - 0.3	$kA[H^+]$	25	2.8	-5					(19)
		D_2O	"	DCl	"	"	"	5.9	-5					"
.3	$CD_3COCD_3 + Br_2$	H_2O	A ~ 0.5 B ~ 0.03	HCl	0.1 - 0.3	$kA[H^+]$	25	3.7	-6					(17)
		D_2O	"	DCl	"	$kA[D^+]$	25	7.7	-6					"
.4	$CH_3COCH_3 + I_2$	H_2O	A = 0.028 10^3B = 4 - 5	HCl	$(2 - 8)10^{-5}$	$kA[H^+]$	25	$\underline{2.90}$	-5				*	(8)
		"	"	"	0.01 - 0.1	$kA[H^+]$	25	$\underline{2.83}$	-5	See Supplementary Table			*	(9)
					0.2		"	2.91	-5					
					0.5		"	2.99	-5					
					1.0		"	3.05	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$CH_3COCH_3 + I_2$ *(continued)*	H_2O	0.03 - 0.10	HCl	0.03 - 0.11	$k\,A[H^+]$	0	1.15	-6				*	(21)
							25	$\underline{2.86}$	-5					
							27	3.60	-5					
							35	8.80	-5	20.6				
			"	HNO_3	"	"	25	$\underline{2.87}$	-5					"
			"	H_2SO_4	"	"	25	2.60	-5					"
				"	0.05 - 0.07	"	20	1.37	-5				*	(20)
							25	2.40	-5					
.5	$C_2H_5CH(CH_3)COCH_3 + I_2$	CH_3COOH	A = 0.9	HNO_3	1.19	$k\,A$	15	9.6	-3					(2)
							25	2.3	-2					
							38.7	7.6	-2					
.6	$C_2H_5CH(CH_3)COC_2H_5 + I_2$	CH_3COOH	A = 0.9	HNO_3	1.19	$k\,A$	15	5.5	-3					(2)
							25	1.42	-2					
							38.7	7.58	-2					
.7	$C_2H_5CH(CH_3)COCH_2C_6H_5 + I_2$	CH_3COOH	A = 0.9	HNO_3	1.19	$k\,A$	24.5	5.1	-3					(2)
							38.7	2.1	-3					
	Keto-Ketones													
.8	$CH_3COCH_2COCH_3 + Br_2$	H_2O	A = 0.0004 B = 0.025			$k\,A$	25	1.72	-2				*	(2a)
		"	"	X =		$k\,A[X]$								
				CH_2ClCOO^-			25	3.3	-1				*	"
				$m\text{-}NO_2C_6H_4COO^-$			"	7.5	-1					
				CH_2OHCOO^-			"	8.3	-1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.8	$CH_3COCH_2COCH_3 + Br_2$ *(continued)*			X =										
				$CH_2ClCH_2COO^-$			25	1.28	0					
				$C_6H_5CH_2COO^-$			"	1.50	0					
				$C_6H_5COO^-$			"	1.60	0					
				CH_3COO^-			"	2.66	0					
				$C_6H_5CH_2CH_2COO^-$			"	3.00	0					
				$C_2H_5COO^-$			"	3.17	0					
				$(CH_3)_3CCOO^-$			"	3.66	0					
				$(CH_3)_2CHCH_2COO^-$			"	4.17	0					
9	$CH_3COCHBrCOCH_3 + Br_2$	H_2O	A = 0.0004 B = 0.025			kA	25	2.32	-2				*	(^{2a})
		"	"	X =		kA[X]								
				CH_2ClCOO^-			25	6.01	-1				*	"
				m-$NO_2C_6H_4COO^-$			"	3.25	0					
				CH_2OHCOO^-			"	1.66	0					
				$CH_2ClCH_2COO^-$			"	3.75	0					
				$C_6H_5CH_2COO^-$			"	6.66	0					
				$C_6H_5COO^-$			"	4.66	0					
				CH_3COO^-			"	4.50	0					
				$C_6H_5CH_2CH_2COO^-$			"	1.30	+1					
				$C_2H_5COO^-$			"	6.17	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.9	$CH_3COCHBrCOCH_3 + Br_2$ *(continued)*			$(CH_3)_3CCOO^-$			25	1.20	+1					
				$(CH_3)_2CHCH_2COO^-$			"	1.00	+1					
.10	$CH_3COCH_2COOC_2H_5 + Br_2$	H_2O	A = 0.0004 B = 0.025			kA	25	1.20	-3				*	(2a)
		"	"	X =		$kA[X]$								
				$CHCl_2COO^-$			25	3.80	-2				*	"
				$m\text{-}NO_2C_6H_4COO^-$			"	1.08	-1					
				CH_2OHCOO^-			"	1.33	-1					
				$C_6H_5COO^-$			"	2.5	-1					
				$C_6H_5CH_2COO^-$			"	3.3	-1					
				CH_3COO^-			"	4.8	-1					
				$C_2H_5COO^-$			"	5.3	-1					
				$C_6H_5CH_2CH_2COO^-$			"	5.7	-1					
				$(CH_3)_2CHCOO^-$			"	6.5	-1					
				$(CH_3)_2CHCH_2COO^-$			"	6.8	-1					
				$(CH_3)_3CCOO^-$			"	7.2	-1					
				$n\text{-}C_4H_9COO^-$			"	7.3	-1					
.11	$C_6H_5COCH_2COCH_3 + Br_2$	H_2O	A = 0.0004 B = 0.025			kA	25	1.83	-4				*	(2a)
		"	"	X =		$kA[X]$								
				CH_2ClCOO^-			25	6.10	-3				*	"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.11	$C_6H_5COCH_2COCH_3 + Br_2$ *(continued)*			CH_2OHCOO^-			25	2.08	-2					
				$CH_2ClCH_2COO^-$			"	3.94	-2					
				m-$NO_2C_6H_4COO^-$			"	4.00	-2					
				$C_6H_5COO^-$			"	4.06	-2					
				$C_6H_5CH_2COO^-$			"	5.62	-2					
				CH_3COO^-			"	6.17	-2					
				$(CH_3)_3CCOO^-$			"	1.11	-1					
				$(CH_3)_2CHCH_2COO^-$			"	1.17	-1					
				$C_6H_5CH_2CH_2COO^-$			"	1.61	-1					
.12	$C_6H_5COCHBrCOCH_3 + Br_2$	H_2O	A = 0.0004 B = 0.025			kA	25	5.5	-3				*	([2a])
		"	"	X =		kA[X]								
				CH_2ClCOO^-			25	1.80	-1					
				CH_2OHCOO^-			"	6.25	-1					
				$CH_2ClCH_2COO^-$			"	1.18	0					
				m-$NO_2C_6H_4COO^-$			"	1.20	0					
				$C_6H_5COO^-$			"	1.22	0					
				$C_6H_5CH_2COO^-$			"	1.73	0					
				CH_3COO^-			"	1.85	0					
				$(CH_3)_3CCOO^-$			"	3.33	0					
				$(CH_3)_2CHCH_2COO^-$			"	3.50	0					
				$C_6H_5CH_2CH_2COO^-$			"	4.83	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
Aromatic-aliphatic Ketone														
.13	$CH_3COC_6H_5 + Br_2$	Ac 25	A = 0.1	HCl	0.5	-dA/dt	25	1.43	-6				*	(4)
							35	4.27	-6					
							45	1.15	-5	19.4				
		Ac 50	"	"	"	"	25	1.83	-6					"
							35	5.37	-6					
							45	1.47	-5	19.2				
		Ac 75	"	"	"	"	15	$\underline{1.25}$	-6				(4)(13)(11)	
							25	$\underline{4.05}$	-6					
							35	$\underline{1.25}$	-5					
							45	$\underline{3.60}$	-5	20.2				
		Ac 90	"	"	"	"	5	2.10	-6					(4)
							15	7.43	-6					
							25	2.40	-5	19.8				
		Ac 50	"	CH_3COO^-	0.147	-dA/dt	35	2.57	-7					"
							45	7.17	-7					
							55	1.98	-6	20.3				
		Ac 75	"	"	"	"	35	2.90	-7					"
							45	7.38	-7					
							55	1.87	-6	18.4				
		Ac 90	"	"	"	"	35	2.62	-7					"
							45	7.05	-7					
							55	1.85	-6	19.3				

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.13	$CH_3COC_6H_5 + Br_2$ *(continued)*	Ac 75	A = 0.1	CH_3COO^-	0.147	-dA/dt	45	8.7	-7				*	(12)
							55	2.08	-6					
							65	5.50	-6	19.4				
.14	$CH_3CO(m\text{-}C_6H_4CH_3) + Br_2$	Ac 75	"	HCl	0.5	"	15	1.49	-6				*	(13)
							25	4.95	-6					
							35	1.39	-5	20.0				
.15	$CH_3CO(m\text{-}C_6H_4NO_2) + Br_2$	Ac 75	"	"	"	"	15	5.0	-7				*	(13)
							25	1.65	-6					
							35	5.40	-6					
							45	1.59	-5	21.0				
.16	$CH_3CO(p\text{-}C_6H_4NO_2) + Br_2$	Ac 75	"	"	"	"	15	6.2	-7				*	(13)
							25	1.97	-6					
							35	6.30	-6					
							45	1.90	-5	21.0				
.17	$CH_3CO(m\text{-}C_6H_4F) + Br_2$	Ac 75	"	"	"	"	25	2.75	-6				*	(13)
							35	7.10	-6					
							45	2.57	-5	20.7				
.18	$CH_3CO(p\text{-}C_6H_4F) + Br_2$	Ac 75	"	"	"	"	25	2.99	-6				*	(13)
							35	9.60	-6					
							45	2.72	-5	20.5				
.19	$CH_3CO(m\text{-}C_6H_4Cl) + Br_2$	Ac 75	"	"	"	"	15	1.22	-6				*	(13)
							25	2.44	-6					
							35	7.90	-6					
							45	2.31	-5	20.8				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.20	$CH_3CO(m\text{-}C_6H_4Br) + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	15	1.23	-6				*	(13)
							25	2.29	-6					
							35	8.00	-6					
							45	2.34	-5	20.8				
.21	$CH_3CO(p\text{-}C_6H_4Br) + Br_2$	Ac 75	"	"	"	"	15	9.7	-7				*	(13)
							25	3.19	-6					
							35	9.50	-6					
							45	2.90	-5	20.4				
.22	$CH_3CO(m\text{-}C_6H_4I) + Br_2$	Ac 75	"	"	"	"	15	1.24	-6				*	(13)
							25	2.50	-6					
							35	1.81	-5					
							45	2.35	-5	20.7				
.23	$CH_3CO(p\text{-}C_6H_4I) + Br_2$	Ac 75	"	"	"	"	25	3.25	-6				*	(13)
							35	1.00	-5					
							45	2.93	-5	20.4				
.24	$CH_3COC_6H_5 + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	0.021	k A	25	2.60	-6				(14)	(15)
					0.716		"	9.51	-6					
					1.39		"	1.84	-5					
					3.02		"	6.56	-5					
		"	"	H_2SO_4	0.053	"	25	1.10	-6					"
					0.1618		"	3.10	-6					
					0.530		"	1.25	-5					
					1.94		"	8.70	-5					
					4.03		"	4.30	-4					

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.25	$CH_3CO(p\text{-}C_6H_4CH_3) + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	1.388	kA	25	2.17	-5					(14) (15)
.26	$CH_3CO(2,4,6\text{-}C_6H_2(CH_3)_3) + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	1.388	kA	25	2.71	-5					(14) (15)
.27	$CH_3CO(p\text{-}C_6H_4Br) + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	1.388	kA	25	1.42	-5					(14) (15)
.28	$CH_3CH_2COC_6H_5 + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	25	1.90	-6				*	(11)
							35	5.35	-6					
							45	1.87	-5	22.1				
		Ac 75	A = 0.1	CH_3COO^-	0.147	-dA/dt	45	1.33	-7				*	(12)
							55	3.70	-7					
							65	9.40	-7	19.9				
.29	$CH_3CH_2COC_6H_5 + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	1.388	kA	25	8.56	-6					(14) (15)
.30	$C_2H_5CH_2COC_6H_5 + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	25	1.20	-6				*	(11)
							35	4.07	-6					
							45	1.29	-5					
		Ac 75	A = 0.1	CH_3COO^-	0.147	-dA/dt	45	1.04	-7				*	(12)
							55	2.90	-7					
							65	7.30	-7	20.2				
.31	$C_2H_5CH_2COC_6H_5 + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	1.388	kA	25	6.97	-6					(14) (15)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.32	$(CH_3)_2CHCOC_6H_5 + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	25	3.6	-7				*	(11)
							35	1.22	-6					
							45	3.85	-6	22.1				
		Ac 75	A = 0.1	CH_3COO^-	0.147	-dA/dt	45	2.6	-8				*	(12)
							55	7.4	-8					
							65	2.0	-7	20.9				
.33	$(CH_3)_2CHCOC_6H_5 + I_2$	H_2O	$10^3A = 5 - 8$ $10^5B = 7 - 50$	$HClO_4$	1.388	k A	25	3.73	-7					(14) (15)
.34	$C_3H_7CH_2COC_6H_5 + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	25	1.42	-6				*	(11)
							35	4.73	-6					
							45	1.46	-5					
		Ac 75	A = 0.1	CH_3COO^-	0.147	-dA/dt	45	1.17	-7				*	(12)
							55	3.10	-7					
							65	8.0	-7	20.1				
.35	$(CH_3)_2CHCH_2COC_6H_5 + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	25	5.6	-7				*	(12)
							35	1.87	-6					
							45	5.80	-6	21.7				
		Ac 75	A = 0.1	CH_3COO^-	0.147	-dA/dt	45	5.1	-8				*	(12)
							55	1.42	-7					
							65	3.70	-7	20.5				
.36	$C_4H_9CH_2COC_6H_5 + Br_2$	Ac 75	A = 0.1	HCl	0.5	-dA/dt	25	1.37	-6				*	(11)
							35	4.45	-6					
							45	1.37	-5	21.4				
.37	$C_2H_5CH(CH_3)COC_6H_5 + I_2$	CH_3COOH	A = 0.9	HNO_3	1.19	k A	36.7	5.0	-4					(2)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
Nitro-compounds														
.38	$CH_3NO_2 + 3\ Br_2 \rightarrow CBr_3NO_2 + 3\ HBr$	H_2O		HBr	1	kA	35.0	1.5	-7					(16)
							49.9	8.1	-7					
							59.9	2.3	-6					
							69.8	6.0	-7					
				HCl	1	"	69.8	6.5	-7					"
		H_2O, D_2O	A = 0.15 - 0.70 B ~ 0.03	H_2SO_4 CH_3COO^- CH_2ClCOO^-	See $CH_3NO_2 + \left\{\begin{matrix} H_2O(D_2O) \\ CH_3COO^- \\ CH_2ClCOO^- \end{matrix}\right. \rightarrow CH_2:NO_2^- + \left\{\begin{matrix} H_3O^+(HD_2O^+) \\ CH_3COOH \\ CH_2ClCOOH \end{matrix}\right.$ 402.450.								*	(18) (17) (16)
.39	$CD_3NO_2 + 3\ Br_2 \rightarrow CBr_3NO_2 + 3\ DBr$	H_2O, D_2O	A = 0.15 - 0.70 B ~ 0.03	H_2SO_4 CH_3COO^- CH_2ClCOO^-	See $CD_3NO_2 + \left\{\begin{matrix} H_2O(D_2O) \\ CH_3COO^- \\ CH_2ClCOO^- \end{matrix}\right. \rightarrow CD_2:NO_2^- + \left\{\begin{matrix} H_2DO^+(D_3O^+) \\ CH_3COOD \\ CH_2ClCOOD \end{matrix}\right.$ 402.450.								*	(18)
.40	$CH_2BrNO_2 + 2\ Br_2 \rightarrow CBr_3NO_2 + 2\ HBr$	H_2O	A = 0.01 - 0.04 B = 0.02 - 0.04	HBr	1	kA	35.0	2.0	-3					(16)
.41	$CH_2BrNO_2 + Br_2 \rightarrow CHBr_2NO_2 + HBr$	H_2O	A = 0.01 - 0.04 B = 0.02 - 0.04	HBr	1	kA	35.0	3.9	-5				*	(16)
.42	$CHBr_2NO_2 + Br_2 \rightarrow CBr_3NO_2 + HBr$	H_2O	A = 0.01 - 0.02	HBr	1	kA	5.0	6.1	-5				*	(16)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.42	$CHBr_2NO_2 + Br_2 \rightarrow CBr_3No_2 + HBr$ *(continued)*		B = 0.01 - 0.04				10.0	1.16	-4					
							14.9	2.16	-4					
							35.0	(2.0)	-3					
.43	$(CH_3)_2CHNO_2 + Br_2$	H_2O		HBr	1	kA	59.9	5.0	-7					(16)

SUPPLEMENTARY TABLE

(.4) $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ (10)(6)(9)(7)

Solvent H_2O; A = 0.272; B = 0.005; Temperature 25°C.

Data of -10^6 (dA/dt) (initial rate, *M*/l per sec).

Addend =	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0
CH_3COOH	-	-	0.007	-	0.017	0.025	0.046	0.07
$CH_2ClCOOH$	0.0177	0.0276	0.0425	0.077	0.120	0.196	0.380	0.66
$CHCl_2COOH$	-	0.068	0.132	0.300	0.540	0.995	-	-
C_2H_5COOH	-	0.003	0.0045	0.0075	0.011	0.016	0.029	-
$CH_2BrCHBrCOOH$	-	0.046	0.078	0.150	0.244	0.450	-	-
CH_2ClCH_2COOH	-	0.008	0.0118	0.020	0.030	0.047	0.084	-
$COOHCH_2CH_2COOH$	-	0.0065	0.0098	0.017	0.0267	0.041	0.079	-
$CH_2OHCOOH$	-	0.0097	0.0147	0.008	0.038	0.060	0.113	-
COOHCOOH	-	0.0725	-	0.32	0.590	1.07	2.40	-

Data of rates in buffer solutions ($CH_3COOH + CH_3COONa$; COOHCOOH + COOHCOOK; $CH_2ClCOOH + CH_2ClCOONa$) see (10)(5).

SOLVENTS

Ac 25 (50, 75, 90) = $H_2O + CH_3COOH$ %.

COMMENTS

General. All reaction rates tabulated for hydrogen-halogen exchange on the aliphatic carbon in ketones and in nitroalkanes are first-order in the ketone (or nitroalkane), and independent of the concentration of the halogen. The rate determining step, in the case of the ketones, is, consequently, enolization of the ketone, and the rates and rate constants listed are, consequently, the rates and rate constants of the enolization of the ketone.

(.2) (3)(4) give initial rates, -dB/d*t* = dA/d*t*, at different concentrations of the catalyzing acid or base (CH_3COO^-). In Ac 50 as solvent, one run was observed to 2/3 completion, with the observation that the acid-catalyzed reaction is zero-order in the ketone (4). The data of (3)(4) listed in the columns *k* are initial *rates*, in M/l per sec, calculated from the original figures of fall of thiosulfate titer, i.e. decrease of the number of ml 0.02*N* $Na_2S_2O_3$ used for 20 ml of solution. The catalytic action of H^+ is representable by $kA[H^+]$ (19), whereas, according to (3), the autocatalytic effect of the HBr formed in the reaction is actually stronger than first-order, which would correspond to a rate law $k''A[H^+]\ (1 + 1.5[H^+])$. (.4) The acid-catalytic constant *k*, as defined by $kA[H^+]$, at 25°C, calculated from the data of (8)(9), is in good accord with (21), and also with the same magnitude from reaction (.2); it clearly corresponds to the rate of enolization of CH_3COCH_3 in acid solution, and is independent of the nature of the halogen (Br_2, I_2). According to (8), the initial rate of the reaction is much greater then can be accounted for on the basis of the initial acidity of the initially "neutral" solution, and corresponds to an acidity of $\sim 2 \times 10^{-5}$; however, if that amount of HCl is added from the outset, the rate corresponds to an acidity of only 3.4×10^{-5}, and with 8×10^{-5} HCl added, it corresponds to an acidity of only 8.4×10^{-5}. Addition of 4×10^{-5} NaOH leaves the apparent initial acidity of the "neutral" solution unchanged. In the presence of small amounts of CH_3COO^-, the rate remains for many hours constant at $\sim 3.5 \times 10^{-10}$ M/l per sec. According to (20)(21), addition of sucrose, glycerol, etc.; increases the rate, but nonelectrolytes up to 30 % have no effect on the temperature coefficient. **(.8) (.9) (.10) (.11) (.12)** Reactions (.8) and (.9), and (.10) and (.11), are consecutive reactions. For each single step, the rate is represented by $k_wA + k_xA[X]$, where k_w is the first-order *k* in pure H_2O (without addend). For the consecutive reaction (.8) and (.9),

COMMENTS *(continued)*

$2(r - 1)[c - (x/4)] / c = (1 - f)(2r - 1)e^{-k_8 t} - (1 - rf)e^{-k_9 t}$, where $r = k_9/k_8$, f = equilibrium fraction of enol, c = initial ketone, x = equivalents Br present at final t. The same relation holds for the consecutive reaction pair (.10) and (.11). The separate k for the two steps were evaluated from the second-step and the overall reaction. The second-step k is not evaluated for reaction (.12). In all cases, the rate is independent of $[Br_2]$. **(.13) - (.23) (.28) (.30) (.32) - (.36)** Data listed under k are *rates* -dA/dt = dB/dt in M/l per sec, calculated from original figures of fall of thiosulfate titer [see (.2)]. **(.38) (.39)** Rates of the rate determining steps, see 402.450. **(.41)** Rate-determining step → $CHBr{:}NO_2^- + H_2^+$. **(.42)** k at 35°C is extrapolated.

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EXCHANGE

of H for halogen on aromatic C

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.
*Coded solvents, Comments, Literature, at the end of the table.

Reaction type: $ArH + X_2 \longrightarrow ArX + HX$

Rate measured $- dB/dt = +\cdot dM/dt$

Note: For compounds involving more than one aromatic ring, it is understood that the substitution takes place in the ring written *last*. The position of the substituent halogen atom in the product, *if given*, is designated by a position number counted from the substituent designated in the initial reactant by the number 1.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
Unsubstituted aromatic hydrocarbons														
.1	$C_6H_6 + Cl_2$	Ac 99	A = 0.5; B = 0.05			$k\,AB$	24	1.48	-6					(3)
							34.2	3.90	-6	17				
			"	HCl	1.31	"	24	6.7	-6					
.2	$C_6H_6 + Br_2$	C_6H_6	0.25 - 1	I_2	$k'B^{3/2} = kB^{3/2}[I_2]^{5/2}$								*	(2a)(19)
							25							
					0.086		k'	7.5	-6					
					0.107			1.4	-5					
					0.143			3.1	-5					
					0.214			1.1	-4					

No.	Reaction	Solvent (Medium)	Amount of reactant	Amount of reactant	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2	$C_6H_6 + Br_2$ *(continued)*				0.086		k	3.5	-3					
					0.107			5.8	-3					
					0.143			4.0	-3					
					0.214			5.1	-3					
.3	$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$	H_2O		Br^-	0.01	$k\,AB$	25	2.8	-3				*	(21)
	$C_6H_6 + HBrO \longrightarrow C_6H_5Br + H_2O$	H_2O		$HClO_4$	0.01	$k\,AB$	25	9.5	-2				*	(21)
					0.02			2.0	-1					
					0.04			3.7	-1					
					0.06			5.4	-1					
.4	$C_{10}H_8 + Cl_2$	Ac 99	0.0125 - 0.025			$k\,AB$	15.3	6.9	-2				*	(3)
							24	1.1	-1	7.5				
.5	$C_{14}H_{10} + Br_2$	CCl_4	A = B = 0.016 - 0.064	I_2	0.002 - 0.012	$k\,AB^{3/2}\,[I_2]^{5/2}$	25	1.03	-7				*	(19)
Alkyl-substituted aromatic hydrocarbons														
.6	$C_6H_5CH_3 + Cl_2$	Ac 99	A = 0.1; B = 0.025				24	See Supplementary Table						(3)
.7	$C_6H_5CH_3 + Br_2$	Ac 85	0.05				"	"		"	"			(3)
.8	$C_6H_5C_2H_5 + Cl_2$	Ac 99	A = 0.1; B = 0.025				"	"		"	"			(3)
.9	$C_6H_5C_2H_5 + Br_2$	Ac 85	0.05				"	"		"	"			(3)
.10	$(CH_3)_2CHC_6H_5 + Cl_2$	Ac 99	A = 0.1; B = 0.025				"	"		"	"			(3)
.11	$(CH_3)_2CHC_6H_5 + Br_2$	Ac 85	0.05				"	"		"	"			(3)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.12	$(CH_3)_3CC_6H_5 + Cl_2$	Ac 99	A = 0.1; B = 0.025				24	See Supplementary Table						(3)
.13	$(CH_3)_3CC_6H_5 + Br_2$	Ac 85	0.05				"	"		"	"			(3)
.14	$1,2 - (CH_3)_2C_6H_4 + Cl_2$	Ac 99	A = 0.1; B = 0.025				"	"		"	"			(3)
.15	$1,4 - (CH_3)_2C_6H_4 + Cl_2$	Ac 99.9	A = 0.1; B = 0.025				"	"		"	"			(3)
.16	$1,2 - (CH_3)_2C_6H_4 + Br_2$	Ac 99	0.2				"	"		"	"			(3)
.17	$1,3 - (CH_3)_2C_6H_4 + Br_2$	Ac 99.9	0.0125 - 0.2				"	"		"	"			(3)
.18	$(CH_3)_3C_6H_3 + Br_2$	Ac 99.9	0.025	x =	5 %	$k\,AB^2$	"	1.45	+1				*	(20)
					15			1.56	+1					
					30			1.45	+1					
					50			1.37	+1					
Alkoxy-substituted aromatic hydrocarbons														
.19	$CH_3OC_6H_5 + Br_2$	CH_3COOH	0.0125			$k\,AB^2$	24	See Supplementary Table						(20)
.20	$p\text{-}CH_3OC_6H_4CH_3 + Br_2$	"	"			$k\,AB^2$	"	"		"	"			(20)
Amide-substituted aromatic hydrocarbons														
.21	$CH_3CONHC_6H_5 + Br_2 \rightarrow (p)$	CH_3COOH	A = B = 0.025	x =	5 %	$k\,AB^2$	24	1.48	+1				*	(20)
					15		"	1.57	+1					
					30		"	1.18	+1					
					50		"	6.2	+0					
.22	$CH_3CONHC_6H_4CH_3 + Br_2$	CH_3COOH	0.0125 - 0.1			$k\,AB^2$	"	See Supplementary Table						

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.23	$CCl_3CONHC_6H_5 + Cl_2$	Ac 99	A = 0.0075; B = 0.0025	HCl	0.0125	kAB	20	9.6	-3					(2)
							30	1.8	-2					
.24	$CCl_3CON(CH_3)C_6H_5 + Cl_2$	Ac 99	A = 0.075; B = 0.005	HCl	0.0125	kAB	20	5.6	-4					(2)
.25	$p\text{-}CH_3C_6H_4SO_2NHC_6H_5 + Cl_2$	Ac 99	A = B = 0.0025	HCl	0.0125	kAB	20	1.85	0					(2)
.26	$p\text{-}CH_3C_6H_4SO_2N(CH_3)C_6H_5 + Cl_2$	Ac 99	A = B = 0.0025	HCl	0.0125	kAB	20	4.35	-2					(2)
	Disubstituted aromatic hydrocarbons **Alkoxyl, Carboxyl**													
.27	$o\text{-}CH_3OC_6H_4COOH + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	5.8	-2					(7)
.28	$m\text{-}CH_3OC_6H_4COOH + Cl_2$	Ac 99	A = 0.01 - 0.02; B = 0.0075	HCl	0.0375	kAB	20	2.6	-2					(14)
.29	$p\text{-}CH_3OC_6H_4COOH + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	7.4	-3				(1)(2)	(7)
							30	1.48	-2					
.30	$m\text{-}C_2H_5OC_6H_4COOH + Cl_2$	Ac 99	A = 0.01 - 0.02; B = 0.0075	HCl	0.0375	kAB	20	5.5	-2					(14)
.31	$p\text{-}C_2H_5OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.46	-2					(1)
.32	$m\text{-}C_3H_7OC_6H_4COOH + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	5.8	-2					(14)
.33	$p\text{-}C_3H_7OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.6	-2					(1)
.34	$m\text{-}(CH_3)_2CHOC_6H_4COOH + Cl_2$	Ac 99	A = 0.01 - 0.02; B = 0.0075	HCl	0.0375	kAB	20	1.06	-1					(14)

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No.	Reaction	Solvent (Medium)	Amount of reactant	Adeend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.35	p-$(CH_3)_2CHOC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.3	-2					(1)
.36	m-$C_4H_9OC_6H_4COOH + Cl_2$	Ac 99	A = 0.015 - 0.0225; B = 0.0075	HCl	0.0375	kAB	20	6.0	-2					(14)
.37	p-$C_4H_9OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0025; B = 0.0075	HCl	0.0375	kAB	20	1.61	-2					(1)
.38	p-$C_2H_5CH(CH_3)OC_6H_4COOH(1) + Cl_2 \rightarrow (2)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.56	-2					(2)
.39	m-$C_5H_{11}OC_6H_4COOH + Cl_2$	Ac 99	A = 0.0225 - 0.0150; B = 0.0075	HCl	0.0375	kAB	20	5.83	-2					(14)
.40	p-$C_5H_{11}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.61	-2					(6)
.41	m-$C_6H_{13}OC_6H_4COOH + Cl_2$	Ac 99	A = 0.0150; B = 0.0075	HCl	0.0375	kAB	20	5.9	-2					(14)
.42	p-$C_6H_{13}C_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.6	-2					(6)
.43	m-$C_7H_{15}C_6H_4COOH + Cl_2$	Ac 99	A = 0.015; B = 0.0075	HCl	0.0375	kAB	20	5.75	-2					(14)
.44	p-$C_7H_{15}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.58	-2					(6)
.45	m-$C_8H_{17}OC_6H_4COOH + Cl_2$	Ac 99	A = 0.015; B = 0.0075	HCl	0.0375	kAB	20	5.8	-2					(14)
.46	p-$C_8H_{17}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.53	-2					(6)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.47	$m\text{-}C_9H_{19}OC_6H_4COOH + Cl_2$	Ac 99	A = 0.015; B = 0.0075	HCl	0.0375	kAB	20	5.75	-2					(14)
.48	$m\text{-}C_{12}H_{25}OC_6H_4COOH + Cl_2$	Ac 99	A = 0.015; B = 0.0075	HCl	0.0375	kAB	20	5.63	-2					(14)
.49	$p\text{-}C_{16}H_{33}OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0025; B = 0.0075	HCl	0.0375	kAB	20	1.86	-2					(6)
.50	$o\text{-}C_6H_5CH_2OC_6H_4COOH + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	4.5	-2					(7)
.51	$m\text{-}C_6H_5CH_2OC_6H_4COOH + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.9	-2					(14)
.52	$p\text{-}C_6H_5CH_2OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	5.23	-3				(1)	(7)
.53	$m\text{-}C_6H_5CH_2CH_2OC_6H_4COOH + Cl_2$	Ac 99	A = 0.015 - 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.8	-2					(14)
.54	$p\text{-}C_6H_5CH_2CH_2OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	8.8	-3					(6)
.55	$m\text{-}C_6H_5CH_2CH_2CH_2OC_6H_4COOH + Cl_2$	Ac 99	A = 0.015 - 0.0225; B = 0.0075	HCl	0.0375	kAB	20	4.67	-2					(14)
.56	$p\text{-}C_6H_5CH_2CH_2CH_2OC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.27	-2					(6)
.57	$o\text{-}(p\text{-}CH_3C_6H_4CH_2O)C_6H_4COOH + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	6.2	-2					(6)
.58	$p\text{-}(o\text{-}CH_3C_6H_4CH_2O)C_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	7.75	-3					(6)

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.59	p-(m-$CH_3C_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	7.6	-3					(7)
.60	p-(p-$CH_3C_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	7.35	-3					(7)
.61	o-(p-$FC_6H_4CH_2O$)C_6H_4COOH + Cl_2	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.65	-2					(7)
.62	m-(p-$FC_6H_4CH_2O$)C_6H_4COOH + Cl_2	Ac 99	A = 0.015 - 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.56	-2					(14)
.63	p-(o-$FC_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	2.67	-3					(7)
.64	p-(m-$FC_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	2.62	-3					(7)
.65	p-(p-$FC_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	4.37	-3					(6)
.66	o-(p-$ClC_6H_4CH_2O$)C_6H_4COOH + Cl_2	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.05	-2					(6)
.67	m-(p-$ClC_6H_4CH_2O$)C_6H_4COOH + Cl_2	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.20	-2					(14)
.68	p-(o-$ClC_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	2.53	-3					(6)
.69	p-(m-$ClC_6H_4CH_2O$)C_6H_4COOH(1) + Cl_2 → (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	2.55	-3					(6)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.70	$p\text{-}(p\text{-ClC}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{COOH}(1) + \text{Cl}_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.33	-3					(^{6})
.71	$o\text{-}(p\text{-BrC}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{COOH} + \text{Cl}_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.1	-2					(^{6})
.72	$m\text{-}(p\text{-BrC}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{COOH} + \text{Cl}_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.15	-2					(^{14})
.73	$p\text{-}(m\text{-BrC}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{COOH}(1) + \text{Cl}_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.65	-3					(^{6})
.74	$p\text{-}(p\text{-BrC}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{COOH}(1) + \text{Cl}_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20°	3.38	-3					(^{6})

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
	Disubstituted aromatic hydrocarbons Alkoxy, Benzoyl													
.75	p-$C_6H_5COC_6H_4OCH_3$ (1) + Cl_2 → (2)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	2.10	-2					(8)
.76	p-$C_6H_5COC_6H_4OC_2H_5$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	4.00	-2				(12)	(8)
							30	7.38	-2	10.9	6	6		
.77	p-$C_6H_5COC_6H_4OC_4H_9$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	4.37	-2					(8)
.78	p-$C_6H_5COC_6H_4OC_5H_{11}$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	4.27	-2				(12)	(8)
							35	1.08	-1	10.9	6	6		
.79	p-$C_6H_5COC_6H_4OC_7H_{15}$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	4.48	-2					(8)
.80	p-$C_6H_5COOC_6H_4OCH_3$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	1.23	-1					(12)
							35	2.88	-1	10.1	4.7	6		
.81	p-(m-$CH_3C_6H_4CO)C_6H_4OCH_3$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	2.57	-2					(8)
.82	p-(p-$CH_3C_6H_4CO)C_6H_4OCH_3$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	2.80	-2					(8)
.83	p-(p-$CH_3OC_6H_4CO)C_6H_4OCH_3$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	7.73	-2					(8)
.84	p-(p-$CH_3OC_6H_4CO)C_6H_4OC_2H_5$ (1) + Cl_2 → (2)	"	"	"	"	k AB	20	1.16	-1					(8)

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.85	$p\text{-}(p\text{-}CH_3OC_6H_4CO)C_6H_4OCH_2CH_2Cl + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	4.65	-2					(^{8})
.86	$p\text{-}(p\text{-}CH_3OC_6H_4CO)C_6H_4OC_3H_7 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.22	-1					(^{8})
.87	$p\text{-}(p\text{-}CH_3OC_6H_4CO)C_6H_4OC_4H_9 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.22	-1					(^{8})
.88	$p\text{-}(p\text{-}CH_3OC_6H_4CO)C_6H_4OC_5H_{11} (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.26	-1					(^{8})
.89	$p\text{-}(p\text{-}C_2H_5OC_6H_4CO)C_6H_4OC_2H_5 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.57	-1					(^{8})
.90	$p\text{-}(p\text{-}C_2H_5OC_6H_4CO)C_6H_4OC_4H_9 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.64	-1					(^{8})
.91	$p\text{-}(p\text{-}C_2H_5OC_6H_4CO)C_6H_4OC_5H_{11} (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.62	-1					(^{8})
.92	$p\text{-}(p\text{-}C_3H_7OC_6H_4CO)C_6H_4OC_3H_7 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.71	-1					(^{8})
.93	$p\text{-}(p\text{-}(CH_3)_2CHOC_6H_4CO)C_6H_4OCH(CH_3)_2 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	3.77	-1					(^{8})
.94	$p\text{-}(p\text{-}C_4H_9OC_6H_4CO)C_6H_4OC_4H_9 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.75	-1					(^{8})
.95	$p\text{-}(p\text{-}C_5H_{11}OC_6H_4CO)C_6H_4OC_2H_5 (1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.72	-1					(^{8})

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.96	p-(m-$NO_2C_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	7.33	-3					(8)
.97	p-(p-$NO_2C_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	6.42	-3					(8)
.98	p-(m-$NO_2C_6H_4CO)C_6H_4OC_4H_9(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.62	-2					(8)
.99	p-(o-$FC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	9.75	-3					(8)
.100	p-(m-$FC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.30	-2					(8)
.101	p-(p-$FC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.78	-2					(8)
.102	p-(o-$ClC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	7.83	-3					(8)
.103	p-(p-$ClC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.45	-2					(8)
.104	p-(p-$ClC_6H_4CO)C_6H_4OC_2H_5(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	2.67	-2				(12)	(8)
							35	6.80	-2	11.0	4.7	6		
.105	p-(o-$ClC_6H_4CO)C_6H_4OCH_2CH_2Cl(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.92	-3					(8)
.106	p-(o-$BrC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	7.67	-3					(8)
.107	p-(m-$BrC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.29	-2					(8)
.108	p-(p-$BrC_6H_4CO)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.42	-2					(8)
	Disubstituted aromatic hydrocarbons Carboxyl, Amide													
.109	p-$C_2H_5CONHC_6H_4COOH(1) + Cl_2 \rightarrow (3)$	Ac 99	B = 0.02	HCl	0.05	k AB	20							(4)
			A = 0.02					1.20	-2					
			0.1					1.48	-2					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.110	p-$C_6H_5SO_2NHC_6H_4COOH$(1) + Cl_2 → (3)	Ac 99	A = 0.06; B = 0.002	HCl	0.05	kAB	20	3.32	-3					(4)
Disubstituted aromatic hydrocarbons Hydroxyl, Aminoalkyl														
.111	p-$NH_2CH_2CH_2C_6H_4OH$ + $2I_2$ tyramine	H_2O; pH 5.23	A = 0.003; B = 0.005	I^-	0.0334	$kA[I_3^-]$	25	1.2	-4				*	(18)
					0.0408		"	7.5	-3					(17)
					0.0484		"	5.8	-3					(15)
					0.0634		"	3.3	-3					
.112	p-$(COO^-)CHNH_3^+CH_2C_6H_4OH$ + $2I_2$	"	"	I^-	0.0334	"	"	8.7	-3				*	"
					0.0408		"	6.3	-3					
					0.0484		"	4.7	-3					
					0.0634		"	2.7	-3					
.113	p-$(COO^-)CH(NHCOCH_2NH_3^+)CH_2C_6H_4OH$ + $2I_2$	"	"	I^-	0.0334	"	"	1.5	-2				*	"
					0.0408		"	1.05	-2					
					0.0484		"	7.5	-3					

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
	Disubstituted aromatic hydrocarbons Hydroxyl, Halogen													
.114	p-$ClC_6H_4OH + 2I_2$	H_2O; pH 5.23	A = 0.003; B = 0.005	I^-	0.0334	$k A [I_3^-]$	25	2.25	-3				*	(18)
					0.0408		"	1.35	-3					(17)
					0.0484		"	1.0	-3					(15)
					0.0634		"	5.5	-4					
	Disubstituted aromatic hydrocarbons Alkoxyl, Nitro													
.115	o-$NO_2C_6H_4OCH_3 + Br_2$	H_2O; pH - 2.3	A = 0.0025 - 0.005 B = 0.002 - 0.01										*	(21)
				Br^-	0.01	$k AB$	25	5.5	-2					
.116	o-$NO_2C_6H_4OCH_3 + HBrO$	H_2O; pH 2.8	"	"	"	"	"	1.7	-2				*	"
.117	m-$NO_2C_6H_4OCH_3 + Cl_2$	Ac 99	A = 0.10; B = 0.02	HCl	0.0475	$k AB$	20	8.90	-5					(5)
.118	p-$NO_2C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	A = 0.0225; B = 0.0075	"	0.0375	$k AB$	20	4.78	-5					(12)
							35	1.63	-4	14.6	4.2	6		
.119	m-$NO_2C_6H_4OC_2H_5 + Cl_2$	"	A = 0.10; B = 0.20	"	0.0475	$k AB$	20	1.77	-4					(14)
.120	p-$NO_2C_6H_4OC_2H_5(1) + Cl_2 \rightarrow (2)$	"	A = 0.0225; B = 0.0075	"	0.0375	$k AB$	20	9.8	-5				(12)	(2)
							35	3.27	-4	14.3	5.0	6		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.121	p-$NO_2C_6H_4OC_3H_7(1) + Cl_2 \rightarrow (2)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.10	-4					(1)
.122	p-$NO_2C_6H_4OCH(CH_3)_2(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	2.35	-4					(12)
							35	7.38	-4	13.8	4.7	6		
Disubstituted aromatic hydrocarbons Alkoxyl, Sulfo														
.123	p-$(p$-$CH_3OC_6H_4SO_2)C_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.83	-3					(8)
.124	p-$(p$-$C_2H_5OC_6H_4SO_2)C_6H_4OC_2H_5(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	3.72	-3					(8)
.125	p-$(p$-$C_3H_7OC_6H_4SO_2)C_6H_4OC_3H_7(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.12	-3					(8)
.126	p-$(p$-$(CH_3)_2CHOC_6H_4SO_2)C_6H_4OCH(CH_3)_2(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	8.93	-3					(8)
.127	p-$(p$-$C_4H_9OC_6H_4SO_2)C_6H_4OC_4H_9(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.12	-3					(8)
.128	p-$(p$-$C_5H_{11}OC_6H_4SO_2)C_6H_4OC_5H_{11}(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.15	-3					(8)
Disubstituted aromatic hydrocarbons Alkoxyl, Halogen														
.129	p-$FC_6H_4OCH(CH_3)_2(1) + Cl_2 \rightarrow (2)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.58	-1					(12)
							35	3.62	-1	9.9	3.7	6		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.130	$o\text{-}ClC_6H_4OCH_3 + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	7.40	-2					(7)
.131	$m\text{-}ClC_6H_4OCH_3 + Cl_2$	"	"	"	"	kAB	20	1.20	-2					(5)
.132	$p\text{-}ClC_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	B = 0.0075; A = 0.0075	HCl	0.0375	kAB	20	2.2	-2				(1)	(12)
			"		0.0600		"	2.3	-2					
			"		0.0075		"	2.0	-2					
			0.0225	HCl	0.0375	"	20	2.0	-2					"
			"		"		35	5.2	-2	11.3	6.0	6		
		Ac 98	A = B = 0.0075	HCl	0.0375	"	20	3.7	-2					
.133	$o\text{-}ClC_6H_4OC_2H_5 + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	"	0.0375	kAB	20	1.45	-1					(2)
.134	$p\text{-}ClC_6H_4OC_2H_5(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	3.88	-2					(12)
							35	9.47	-2	10.8	4.5	6		
.135	$o\text{-}ClC_6H_4OC_3H_7 + Cl_2$	"	"	"	"	kAB	20	1.68	-1					(6)
.136	$p\text{-}ClC_6H_4OC_3H_7(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	2.05	-1					(2)
.137	$o\text{-}ClC_6H_4OCH(CH_3)_2 + Cl_2$	"	"	"	"	kAB	20	2.69	-1					(6)
.138	$p\text{-}ClC_6H_4OCH(CH_3)_2(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	8.6	-2					(12)
							35	2.1	-1	10.5	6.0	6		
.139	$o\text{-}ClC_6H_4OC_4H_9 + Cl_2$	"	"	"	"	kAB	20	1.7	-1					(6)
.140	$m\text{-}ClC_6H_4OC_4H_9 + Cl_2$	"	"	"	"	kAB	20	4.53	-2					(2)
.141	$p\text{-}ClC_6H_4OCH(CH_3)(C_2H_5)(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.50	-2					(2)

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.142	$o\text{-}ClC_6H_4OC_5H_{11} + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	1.64	-1					(6)
.143	$p\text{-}ClC_6H_4OC_5H_{11}(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.60	-2					(6)
.144	$p\text{-}ClC_6H_4OC_6H_{13}(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.62	-2					(6)
.145	$p\text{-}ClC_6H_4OC_7H_{15}(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.57	-2					(6)
.146	$p\text{-}ClC_6H_4OC_{16}H_{33}(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	4.43	-2					(6)
.147	$p\text{-}ClC_6H_4OCH_2COOH(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	8.2	-4					(12)
							35	2.43	-3	12.9	3.8	6		
.148	$p\text{-}ClC_6H_4OCH_2COOCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	7.7	-4					(12)
							35	2.20	-3	13.0	5.9	6		
.149	$p\text{-}ClC_6H_4OCH_2COOC_2H_5(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	8.0	-4					(12)
							35	2.35	-3	12.8	3.2	6		

Disubstituted aromatic hydrocarbons
Arylalkoxyl, Halogen

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	k°	n	E	A°	n	Comments	Literature
.150	$o\text{-}C_6H_5CH_2OC_6H_4F + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	6.02	-2					(9)
.151	$p\text{-}C_6H_5CH_2OC_6H_4F(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	2.47	-2					(12)
							35	6.22	-2	11.0	4.3	6		
.152	$o\text{-}(p\text{-}CH_3C_6H_4CH_2O)C_6H_4F + Cl_2$	"	"	"	"	kAB	20	8.18	-2					(9)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.153	p-(p-$CH_3C_6H_4CH_2O)C_6H_4F(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	kAB	20	3.72	-2					(9)
.154	o-(p-$NO_2C_6H_4CH_2O)C_6H_4F + Cl_2$	"	"	"	"	kAB	20	1.28	-2					(9)
.155	p-(p-$NO_2C_6H_4CH_2O)C_6H_4F(1) + Cl_2 \rightarrow (2)$	"	"	"	"	kAB	20	3.63	-2					(9)
.156	p-(p-$NO_2C_6H_4CH_2O)C_6H_4F(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	5.0	-3					(12)
							35	1.35	-2	11.9	4.2	6		
.157	p-(p-$ClC_6H_4CH_2O)C_6H_4F(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	1.42	-2					(12)
							35	3.72	-2	11.4	5.0	6		
.158	o-(p-$BrC_6H_4CH_2O)C_6H_4F + Cl_2$	"	"	"	"	kAB	20	3.48	-2					(9)
.159	p-(p-$BrC_6H_4CH_2O)C_6H_4F(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	1.52	-2					(9)
.160	m-$C_6H_5CH_2OC_6H_4Cl + Cl_2$	"	"	"	"	kAB	20	8.8	-1					(14)
.161	p-$C_6H_5CH_2OC_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	1.31	-2					(12)
							35	3.40	-2	11.4	4.3	6		
.162	o-(m-$CH_3C_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	kAB	20	7.25	-2					(9)
.163	o-(p-$CH_3C_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	kAB	20	7.17	-2					(9)
.164	p-(p-$CH_3C_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	1.94	-2				(9)	(7)
.165	o-(p-$C_2H_5C_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	kAB	20	7.05	-2					(9)
.166	p-(p-$C_2H_5C_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	1.93	-2					(9)
.167	p-(p-$(CH_3)_2CHC_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	kAB	20	1.98	-2					(9)

No	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law		$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.168	o-(p-$(CH_3)_3CC_6H_4CH_2O)C_6H_4Cl + Cl_2$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	7.02	-2					(9)
.169	p-(p-$(CH_3)_3CC_6H_4CH_2O)C_6H_4Cl(1) \rightarrow (3)$	"	"	"	"	k AB	20	1.92	-2					(9)
.170	o-(o-$NO_2C_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	k AB	20	1.05	-2					(6)
.171	o-(p-$NO_2C_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	k AB	20	1.07	-2					(6)(2)
.172	p-(m-$NO_2C_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	3.00	-3					(12)(7)
							35	8.43	-3	12.3	4.7	6		
.173	p-(p-$NO_2C_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	2.62	-3					(12)
							35	7.43	-3	12.4	4.7	6		
.174	o-(m-$FC_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	k AB	20	4.13	-2					(7)
.175	p-(m-$FC_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	6.57	-3					(7)
.176	p-(p-$FC_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.12	-2					(7)
.177	o-(p-$ClC_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	k AB	20	3.10	-2					(7)
.178	p-(o-$ClC_6H_3CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	5.77	-3					(7)
.179	p-(m-$ClC_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	6.20	-3					(7)
.180	p-(p-$ClC_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	7.8	-3					(12)
							35	2.10	-2	11.9	6.0	6		
.181	o-(p-$BrC_6H_4CH_2O)C_6H_4Cl + Cl_2$	"	"	"	"	k AB	20	3.08	-2					(7)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.182	p-(m-$BrC_6H_4CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	6.28	-3					(7)
.183	p-$(1,2 - Cl_2 - C_6H_3 - 4 - CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	3.25	-2					(9)
.184	p-$(1,3 - Cl_2 - C_6H_3 - 4 - CH_2O)C_6H_4Cl(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	8.05	-2					(9)
.185	o-$BrC_6H_4OCH_3 + Cl_2$	"	"	"	"	k AB	20	9.10	-2					(7)
.186	p-$BrC_6H_4OCH_3(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	2.09	-2					(7)
.187	p-$BrC_6H_4OCH_2CH_2Br(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	4.43	-3					(7)
.188	p-$BrC_6H_4OCH_2CH_2CH_2Br(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	1.37	-2					(7)
.189	p-$BrC_6H_4OCH(CH_3)C_2H_5(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	4.57	-2					(6)
.190	p-$BrC_6H_4OC_{16}H_{33}(1) + Cl_2 \rightarrow (2)$	"	"	"	"	k AB	20	4.45	-2					(6)
.191	p-$C_6H_5CH_2OC_6H_4Br(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.42	-2					(7)
.192	p-(p-$CH_3C_6H_4CH_2O)C_6H_4Br(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.95	-2					(7)
.193	o-(o-$NO_2C_6H_4CH_2O)C_6H_4Br + Cl_2$	"	"	"	"	k AB	20	1.26	-2					(7)
.194	o-(m-$NO_2C_6H_4CH_2O)C_6H_4Br + Cl_2$	"	"	"	"	k AB	20	1.47	-2					(7)
.195	o-(p-$NO_2C_6H_4CH_2O)C_6H_4Br + Cl_2$	"	"	"	"	k AB	20	1.25	-2					(7)
.196	p-(m-$NO_2C_6H_4CH_2O)C_6H_4Br(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	3.35	-3					(7)
.197	p-(p-$NO_2C_6H_4CH_2O)C_6H_4Br(1) + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	2.95	-3					(7)
.198	o-(p-$ClC_6H_4CH_2O)C_6H_4Br + Cl_2$	"	"	"	"	k AB	20	3.60	-2					(7)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.199	$p\text{-}(p\text{-}\mathrm{ClC_6H_4CH_2O)C_6H_4Br}(1) + \mathrm{Cl_2} \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	8.68	-3					(7)
Disubstituted aromatic hydrocarbons **Amide, Halogen**														
.200	$p\text{-}\mathrm{CH_3CONHC_6H_4F}(1) + \mathrm{Cl_2} \rightarrow (3)$	Ac 99	B = 0.02; A = 0.02	HCl	0.0475	k AB	20	6.03	-3					(9)
			0.04					6.43	-3					
			0.06					6.83	-3					
.201	$p\text{-}\mathrm{C_6H_5CONHC_6H_4F}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	A = B = 0.02	"	"	k AB	20	5.40	-3					(9)
.202	$p\text{-}\mathrm{C_6H_5SO_2NHC_6H_4F}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	B = 0.02; A = 0.02	"	"	k AB	20	3.07	-3					(9)
			0.04					3.10	-3					
			0.06					3.52	-3					
.203	$p\text{-}\mathrm{CH_3CONHC_6H_4Cl}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	B = 0.02; A = 0.02	"	0.05	k AB	20	6.08	-3					(4)
			0.04					6.85	-3					
			0.06					7.75	-3					
.204	$p\text{-}\mathrm{C_2H_5CONHC_6H_4Cl}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	A = 0.10; B = 0.02	"	"	k AB	20	1.58	-2					(4)
.205	$p\text{-}\mathrm{C_6H_5CONHC_6H_4Cl}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	"	"	"	k AB	20	6.08	-3					(4)
.206	$p\text{-}\mathrm{C_6H_5SO_2NHC_6H_4Cl}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	B = 0.02; A = 0.02 - 0.06		"	k AB	20	3.41	-3					(4)
.207	$p\text{-}\mathrm{CH_3C_6H_4SO_2NHC_6H_4Cl}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	B = 0.02; A = 0.02,	"	"	k AB	20	4.73	-3					(4)
			0.10					5.18	-3					
.208	$p\text{-}\mathrm{CCl_3CONHC_6H_4Cl}(1) + \mathrm{Cl_2} \rightarrow (3)$	"	A = B = 0.02	"	"	k AB	20	1.95	-5					(4)

312.472.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.209	p-$CH_3CONHC_6H_4Br(1) + Cl_2 \rightarrow (3)$	Ac 99	B = 0.02; A = 0.02	HCl	0.05	k AB	20	6.97	-3					(^{4})
			0.10					8.80	-3					
.210	p-$C_2H_5CONHC_6H_4Br(1) + Cl_2 \rightarrow (3)$	"	A = 0.10; B = 0.02	"	"	k AB	20	1.74	-2					(^{4})
.211	p-$C_6H_5SO_2NHC_6H_4Br(1) + Cl_2 \rightarrow (3)$	"	A = 0.06; B = 0.02;	"	"	k AB	20	3.78	-3					(^{4})
Three substituents Alkyl, Alkoxy, Nitro														
.212	$1 - CH_3 - 2 - CH_3O - 3 - NO_2 - C_6H_3 + Cl_2$	Ac 99	A = 0.10; B = 0.02	HCl	0.0475	k AB	20	2.05	-4					(^{14})
.213	$1 - CH_3 - 4 - CH_3O - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$	"	A = 0.12; B = 0.04	"	0.05	k AB	20	3.67	-4					(^{10})
.214	$1 - CH_3 - 2 - C_2H_5O - 3 - NO_2 - C_6H_3 + Cl_2$	"	A = 0.10; B = 0.02	"	0.0475	k AB	20	4.67	-4					(^{14})
.215	$1 - CH_3 - 4 - C_2H_5O - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$	"	A = 0.12; B = 0.04	"	0.05	k AB	20	7.00	-4					(^{10})
.216	$1 - CH_3 - 4 - (CH_3)_2CHO - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.25	-3					(^{10})
.217	$1 - CH_3 - 4 - C_4H_9O - 5 - NO_2 - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	7.67	-4					(^{10})
Three substituents Alkyl, Alkoxy, Halogen														
.218	$1 - CH_3 - 2 - CH_3O - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	Ac 99	B = 0.0075; A = 0.0225	HCl	0.0375	k AB	20	7.27	-2					(^{10})(^{11})
			"		0.01		"	6.83	-2					
			"		"		35	1.64	-1	10.5	4.8	6		

312.472.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.218	*(continued)*		0.0075		0.0375		20	7.67	-2					
.219	$1 - CH_3 - 4 - CH_3O - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	Ac 99	A = 0.0225; B = 0.0075	HCl	"	k AB	20	1.19	-1					(^{10})
.220	$1 - CH_3 - 2 - C_2H_5O - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	"	"	"	k AB	20	1.44	-1					(^{10})
.221	$1 - CH_3 - 4 - C_2H_5O - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	"	"	"	k AB	20	2.2	-1					(^{10})
.222	$1 - CH_3 - 2 - C_3H_7O - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	"	"	"	k AB	20	1.52	-1					(^{10})
.223	$1 - CH_3 - 2 - (CH_3)_2CHO - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	"	"	"	k AB	20	2.36	-1					(^{10})
.224	$1 - CH_3 - 2 - C_5H_{11}O - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	"	"	"	k AB	20	1.54	-1					(^{10})
.225	$1 - CH_3 - 2 - C_6H_5CH_2O - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	"	"	"	k AB	20 35	3.63 8.92	-2 -2	10.7	3.8	6		(^{11})
.226	$1 - CH_3 - 2 - (p\text{-}CH_3C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	B = 0.0075; A = 0.0075 0.0225	"	"	k AB	20	5.78 5.30	-2 -2					(^{10})
.227	$1 - CH_3 - 4 - (p\text{-}CH_3C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow$ (3)	"	B = 0.0075; A = 0.0225 0.0375	"	"	k AB	20	9.12 8.63	-2 -2					(^{10})

No	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.228	$1 - CH_3 - 2 - (p\text{-}C_2H_5C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	5.30	-2					(^{10})
.229	$1 - CH_3 - 4 - (p\text{-}C_2H_5C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	B = 0.0075; A = 0.0225	"	"	k AB	20	9.08	-2					(^{10})
			0.0375					8.75	-2					
.230	$1 - CH_3 - 2 - (p\text{-}(CH_3)_3CC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	A = 0.0225; B = 0.0075	"	"	k AB	20	5.13	-2					(^{10})
.231	$1 - CH_3 - 2 - (o\text{-}NO_2C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	6.38	-3					(^{10})
.232	$1 - CH_3 - 2 - (p\text{-}NO_2C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	A = B = 0.0075	"	"	k AB	20	8.80	-3					(^{10})
.233	$1 - CH_3 - 4 - (o\text{-}NO_2C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	A = 0.0225; B = 0.0075	"	"	k AB	20	1.27	-2					(^{10})
.234	$1 - CH_3 - 4 - (m\text{-}NO_2C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.56	-2					(^{10})
.235	$1 - CH_3 - 4 - (p\text{-}NO_2C_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.35	-2					(^{10})
.236	$1 - (CH_3)_3C - 4 - (p\text{-}NO_2C_6H_4CH_2O) - 5 - Cl - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	4.85	-3					(^{13})
							35	1.35	-2	12.2	7.2	6		

312.472.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k° \times 10^n$		E	$A = A° \times 10^n$		Comments	Literature
								$k°$	n		$A°$	n		
.237	$1 - CH_3 - 2 - (m\text{-}FC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	1.82	-2					(10)
.238	$1 - CH_3 - 4 - (m\text{-}FC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	3.17	-2					(10)
.239	$1 - CH_3 - 2 - (o\text{-}ClC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.53	-2					(10)
.240	$1 - CH_3 - 2 - (m\text{-}ClC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	1.72	-2					(10)
.241	$1 - CH_3 - 2 - (p\text{-}ClC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	2.30	-2					(10)
.242	$1 - CH_3 - 4 - (o\text{-}ClC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	2.60	-2					(10)
.243	$1 - CH_3 - 4 - (p\text{-}ClC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	3.72	-2					(10)
.244	$1 - CH_3 - 2 - (p\text{-}BrC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	2.23	-2					(10)
.245	$1 - CH_3 - 4 - (p\text{-}BrC_6H_4CH_2O) - 5 - Br - C_6H_3 + Cl_2 \rightarrow (3)$	"	"	"	"	k AB	20	3.67	-2					(10)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
	Three substituents Alkoxy, Halogen, Halogen													
.246	$1-CH_3O-2,4-Cl_2-C_6H_3+Cl_2 \rightarrow (6)$	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	5.2	-5					(13)
							35	1.72	-4	14.3	2.7	6		
.247	$1-CH_3O-3,5-Cl_2-C_6H_3+Cl_2$	"	B = 0.0075; A = 0.0075 0.0225	"	"	k AB	20	1.41 1.19	-1 -1					(14)
.248	$1-C_2H_5O-2,4-Cl_2-C_6H_3+Cl_2 \rightarrow (6)$	"	A = 0.0225; B = 0.0075	"	"	k AB	20	1.06	-4					(13)
							35	3.43	-4	14.0	3.3	6		
.249	$1-C_3H_7O-2,4-Cl_2-C_6H_3+Cl_2 \rightarrow (6)$	"	"	"	"	k AB	20	1.12	-4					(13)
							35	3.60	-4	14.1	4.2	6		
.250	$1-(CH_3)_2CHO-2,4-Cl_2-C_6H_3+Cl_2 \rightarrow (6)$	"	"	"	"	k AB	20	1.58	-4					(13)
							35	4.93	-4	13.6	2.2	6		
.251	$1-C_6H_5CH_2O-2,4-Cl_2-C_6H_3+Cl_2 \rightarrow (6)$	"	A = 0.12; B = 0.04	"	0.0475	k AB	20	1.67	-5					(10)
.252	$1-C_6H_5CH_2O-2,5-Cl_2-C_6H_3+Cl_2$	"	A = 0.0225; B = 0.0075	"	0.0375	k AB	20	5.33	-3					(14)
.253	$1-(p\text{-}CH_3C_6H_4CH_2O)-2,5-Cl_2-C_6H_3+Cl_2$	"	A = 0.015; B = 0.0075	"	"	k AB	20	7.63	-3					(14)
.254	$1-(m\text{-}FC_6H_4CH_2O)-2,5-Cl_2-C_6H_3+Cl_2$	"	"	"	"	k AB	20	2.87	-3					(14)
.255	$1-(p\text{-}FC_6H_4CH_2O)-2,5-Cl_2-C_6H_3+Cl_2$	"	"	"	"	k AB	20	4.27	-3					(14)
.256	$1-(m\text{-}ClC_6H_4CH_2O)-2,4-Cl_2-C_6H_3+Cl_2 \rightarrow (6)$	"	A = 0.12; B = 0.04	"	0.0475	k AB	20	1.67	-5					(10)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.257	1 - (p-$BrC_6H_4CH_2O$) - 3,5 - Cl_2 - C_6H_4 + Cl_2	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20	6.17	-2					([14])
Four substituents														
.258	1 - $COOHCH_2O$ - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H_2 + Cl_2 → (2)	Ac 99	A = 0.0225; B = 0.0075	HCl	0.0375	k AB	20 35	1.39 3.65	-2 -2	11.5	5.3	6		([13])
Five substituents														
.259	1 - CH_3O - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - NO_2 - C_6H + Cl_2	Ac 99	A = 0.04; B = 0.02	HCl	0.0475	k AB	20	6.43	-4					([10])
.260	1 - C_2H_5O - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - NO_2 - C_6H + Cl_2		"	"	"	k AB	20	1.15	-3					([10])
.261	1 - C_3H_7O - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - NO_2 - C_6H + Cl_2		"	"	"	k AB	20	1.25	-3					([10])
.262	1 - $C_6H_5CH_2O$ - 3,5 - $(CH_3)_2$ - 4 - Cl - 6 - NO_2 - C_6H + Cl_2		"	"	"	k AB	20	1.21	-3					([10])
.263	1 - CH_3O - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2		"	"	"	k AB	20 35	2.08 4.85	-1 -1	9.9	5.2	6		([13])

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.264	1 - C_2H_5O - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2	Ac 99	A = B = 0.0075	HCl	0.0375	k AB	20	4.50	-1					([10])
.265	1 - C_3H_7O - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2	"	A = B = 0.0075	"	"	k AB	20	4.72	-1					([10])
.266	1 - $C_6H_5CH_2O$ - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2	"	A = 0.0225; B = 0.0075	"	"	k AB	20	1.19	-1					([13])
							35	2.78	-1	10.1	4.5	6		
.267	1 - (m-$FC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2		"	"	"	k AB	20	6.42	-2					([10])
.268	1 - (o-$ClC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2		"	"	"	k AB	20	2.35	-1					([10])
.269	1 - (m-$ClC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2		"	"	"	k AB	20	5.63	-2					([13])
							35	1.41	-1	10.8	6.5	6		
.270	1 - (p-$ClC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2		"	"	"	k AB	20	7.28	-2					([13])
							35	1.72	-1	10.4	4.2	6		
.271	1 - (p-$BrC_6H_4CH_2O$) - 3,5 - $(CH_3)_2$ - 4,6 - Cl_2 - C_6H + Cl_2		"	"	"	k AB	20	7.85	-2					([10])

SUPPLEMENTARY TABLES

(.6) - (.17) Time (sec) for the absorption of x % of the total initial halogen.

Reaction	x	sec
(.6)	10	1975
	15	3240
(.7)	10	39800
	15	67600
(.8)	10	2390
	15	3830
(.9)	10	51500
	15	88000
(.10)	10	3820
	15	6360
(.11)	10	92500
	15	154000

Beaction	x	sec
(.12)	10	6360
	15	10100
(.13)	10	172000
	15	298000
(.14)	20	366
(.15)	20	780
(.16)	20	16950
(.17)	20	181 (0.2)
	20	48300 (0.025)

(.19) *Relative* initial rates, R

Order of the reaction, n

% $CHCl_3$	0	50	75	90
R	*1.00*	0.30	0.12	0.08
n	3.0	2.8	3.1	3.6

Time required for absorption of 10 % of the initial Br_2,

in 0.0125 M/l, 32.4 sec
0.00625 " 125 "

(.20) The order of the reaction varies from 2.9 to 3.2 with 5 - 20 % reaction. Time required for absorption of 10 % of the initial Br_2,

in 0.025 M/l, 126 sec
0.0125 " 534 "
0.00625 " 2240 "

SUPPLEMENTARY TABLES *(continued)*

(.22) Order of the reaction, n

5 - 20 % reaction,	0.1 - 0.05 M/l,	n = 3.3
	0.05 - 0.0125	3.1

SOLVENTS

Ac 99	CH_3COOH 99 % + H_2O

COMMENTS

Classification.

(.1) - (.5)	*Unsubstituted aromatic hydrocarbons*
(.6) - (.26)	*Monosubstituted aromatic hydrocarbons:*
(.6) - (.18)	Alkyl-substituted
(.19) - (.20)	Alkoxy-substituted
(.21) - (.26)	Amide-substituted
(.27) - (.211)	*Disubstituted aromotic hydrocarbons:*
(.27) - (.74)	Alkoxy-carboxyl
(.75) - (.108)	Alkoxy-benzoyl
(.109) - (.110)	Carboxyl-amide
(.111) - (.113)	Hydroxyl-aminoalkyl
(.114)	Hydroxyl-halogen
(.115) - (.122)	Alkoxy-nitro
(.123) - (.128)	Alkoxy-sulfo
(.129) - (.149)	Alkoxy-halogen
(.150) - (.199)	Arylalkoxy-halogen
(.200) - (.211)	Amide-halogen
(.212) - (.257)	*Trisubstituted aromatic hydrocarbons:*
(.212) - (.217)	Alkyl-Alkoxy-Nitro
(.218) - (.245)	Alkyl-Alkoxy-halogen
(.246) - (.257)	Alkoxy-halogen-halogen
(.258)	*Tetrasubstituted aromatic hydrocarbons*
(.259) - (.271)	*Pentasubstituted aromatic hydrocarbons*

COMMENTS *(continued)*

Reactions. (.2) Selected points. The data of (2a) who represented them as second-order in Br_2 at constant I_2 were recalculated by (19) in terms of a rate constant 3/2 order in Br_2 and 5/2 order in I_2. The constancy of k with varying amounts of I_2 is only approximate. (.3) The rate constant can have no absolute significance, as the reaction is actually heterogeneous, and its rate depends on the total C_6H_6/H_2O interface produced by shaking. Br^+ is considered to be the brominating agent. (.4) Solvent erroneously described in original (3) as "1 % aqueous acetic acid"; must be CH_3COOH 99 % + H_2O 1 %. (.5) k does not become constant in any experiment until the equilibrium of the addition reaction $C_{14}H_{10} + Br_2 \rightarrow C_{14}H_{10}Br_2$ has been established. Units of time and temperature not clearly stated in original, are inferred from the context. (.18) k has maximum at ~ 15 % conversion. (.21) The actual total order of the reaction (at 20 % conversion) falls with increasing dilution, from 2.9 at 0.05 M/l to 2.3 at 0.00078 M/l in CH_3COOH. At constant dilution, 0.00625 M/l. dilution of the CH_3COOH solvent with CCl_4 causes the rate to fall to one third between 10 % and 60 % conversion; however, on dilution with 90 % CCl_4, the rate in this range increases by a factor of ~ 6. The decrease of the third-order k in CH_3COOH is ascribed to negative catalysis by HBr. **(.111) - (.114)** Maintained equilibria are $I_3^- \rightleftarrows I_2 + I^-$ (K_1); $I_2 + H_2O \rightleftarrows HIO + H^+ + I^-$ (K_2); ROH(= A) $\rightleftarrows RO^- + H^+$ (K_3). The rate can be represented, alternatively, by

$$k[ROH][I_3^-] = k'[ROH][HIO] + k''[RO^-][HIO],$$

with the following values of k', k'', (converted from min to sec), and K_3 (at 25°C);

Reaction	$10^7 k'$	$10^{11} k''$	$10^{11} K_3$
(.111)	1.67	9.68	1.26
(.112)	1.40	1.83	8.5
(.113)	2.00	6.67	4.0
(.114)	0.28	0.033	66

In terms of the equilibrium constants,

$$k = (K_1/[I^-]^2[H^+])(k'K_2 + k''K_2K_3/[H^+])$$

(.115) (.116) For the reaction A + HBrO, in chloroacetic acid buffers, pH 2.8, k increases with the increase of total buffer concentration, from $k = 1.7 \times 10^{-2}$ to 5.0×10^{-1}.

LITERATURE

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(21) W.J.Wilson, F.G.Soper, *CSL* **1949**, 3376.

EXCHANGE

NO_3^- for halogen

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $RNO_3 + X^- \longrightarrow RX + NO_3^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$	
						k°	n		A°	n
.1	$C_6H_5CH_2NO_3 + Br^-$	$(CH_3)_2CO$	A = 0.025 B = 0.0125	k AB	20 40	3.3 2.50	-4 -3	18.4	1.7	10
.2	p-$CH_3C_6H_4CH_2NO_3 + Br^-$	$(CH_3)_2CO$	A = 0.025 B = 0.0125	k AB	20 40	7.3 4.63	-4 -3	18.9	7.2	10
.3	p-$C_2H_5C_6H_4NO_3 + Br^-$	$(CH_3)_2CO$	A = 0.025 B = 0.0125	k AB	40	4.17	-3			
.4	p-$(CH_3)_3CC_6H_4NO_3 + Br^-$	$(CH_3)_2CO$	A = 0.025 B = 0.0125	k AB	40	3.66	-3			
.5	p-$NO_2C_6H_4NO_3 + Br^-$	$(CH_3)_2CO$	A = 0.025 B = 0.0125	k AB	20 40	9.9 9.1	-4 -3	18.9	1.2	11
.6	2, 4-$(NO_2)_2C_6H_3NO_3 + Br^-$	$(CH_3)_2CO$	A = 0.025 B = 0.0125	k AB	20 40	(7.7) (6.1)	-3 -2			

COMMENTS

(.3) (.4) (.5) k calculated from reverse reaction and equilibrium; (.5) values of k uncertain. Reverse exchange, see 332.751.

LITERATURE

J. W. Baker, W. S. Nathan, *CSL* 1936, 236.

EXCHANGE

Halogen for NO_3^-

Liquid phase

Reaction type $RX + NO_3^- \longrightarrow RNO_3 + X^-$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
							k^o	n		
.1	$CH_3I + AgNO_3$	H_2O	A = B = 0.025		k AB	24.5	2.66	-6	*	(2)
		$H_2O + C_2H_5OH$ 10 vol %			"	"	3.84	-6		"
		20				"	4.50	-6		
		40				"	6.34	-6		
		70				"	1.67	-5		
		90				"	1.54	-5		
		C_2H_5OH	"		"	"	1.64	-5		"
		CH_3OH	"		"	"	3.0	-5		"
.2	$CHI_3 + 3AgNO_3$	C_2H_5OH	A = 0.04; B = 0.04		k AB	25	2.3	-5		(3)
			0.033 0.033			"	1.9	-5		
			0.025 0.025			"	1.1	-5		
			0.025 0.033			"	1.7	-5		
			0.020 0.025			"	1.0	-5		
.3	$C_2H_5I + AgNO_3$	CH_3OH	A = B = 0.025		k AB	24.5	7.3	-5	*	(2)
		"	A = 0.025; B = 0.0125		k AB	25.0	7.5	-5	*	(4)
			0.0125 0.0125			"	9.2	-5		
			0.025 0.025			"	1.24	-4		
			0.0125 0.025			"	1.40	-4		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.3	$C_2H_5I + AgNO_3$ *(continued)*	$CH_3OH + C_2H_5OH$ 25 vol %	0.0125	0.0125		k AB	25.0	6.3	-5		(4)
							"	9.5	-5		
								1.15	-4		
		50	0.025	0.0125		"	"	5.2	-5		"
			0.0125	0.0125			"	6.3	-5		
			0.025	0.025			"	7.8	-5		
			0.0125	0.025			"	9.0	-5		
		75	0.0125	0.0125		"	"	4.0	-5		"
			0.025	0.025			"	6.5	-5		
			0.0125	0.025			"	7.6	-5		
		C_2H_5OH	0.025	0.0125		"	"	4.5	-5	*	(4)
			0.0125	0.0125			"	4.6	-5		
			0.025	0.025			"	5.7	-5		
			0.0125	0.025			"	6.3	-5		
		"	A = B = 0.025			k AB	24.5	3.7	-5	*	(2)
		CH_3CN	A = B = 0.1			k AB	25	2.7	-5		(3)
			0.05				"	1.75	-5		
			0.025				"	1.35	-5		
.3.1	$C_2H_5I + \begin{cases} NO_3^- \ (LiNO_3) \quad (B) \\ C_2H_5OH \end{cases}$ $\longrightarrow \begin{cases} C_2H_5NO_3 + I^- \quad (a) \\ (C_2H_5)_2O + H^+ + I^- \quad (b) \end{cases}$	C_2H_5OH		$(a + b) = kA = k_1A + k_2AB;\ k = k_1 + k_2B$						*	(3a)
			A = 0.01: B =				25				
			0				k	8.2	-9		
			0.06					9.8	-9		
			0.244					1.75	-8		
			0.488					2.49	-8		
							k_2	3.3	-8		

332.751.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$: k^o	n	Comments	Literature
.3.1	C_2H_5I + NO_3^- ($LINO_3$) (B)						50				
	C_2H_5OH		0				k	2.27	-7	*	(3a)
	$C_2H_5NO_3 + I^-$ *(a)*		0.06					3.00	-7		
	$(C_2H_5)_2O + H^+ + I^-$ *(b)*		0.122					3.84	-7		
	(continued)		0.224					6.67	-7		
			0.489					8.35	-7		
							k_2	1.30	-6		
		C_2H_5OH 96 % + H_2O	A = 0.01; B =			"	50				
			0				k	3.67	-7		
			0.059					4.65	-7		
			0.144					5.06	-7		
			0.380					6.89	-7		
							k_2	1.46	-6		
		C_2H_5OH 36.9 % + H_2O	A = 0.01; B =			"	50				
			0				k	2.34	-6		
			0.099					2.41	-6		
			0.248					2.70	-6		
			0.39					2.87	-6		
			0.497					3.29	-6		
							k_2	1.46	-6		
.4	$C_3H_7I + AgNO_3$	CH_3OH	A = B = 0.025			k AB	24.5	3.8	-5	*	(2)
		C_2H_5OH	"			"	"	1.6	-5		"
.5	$(CH_3)_2CHI + AgNO_3$	C_2H_5OH	A = B = 0.005			k AB	24.5	3.3	-4		(2)
.6	$C_4H_9I + AgNO_3$	CH_3OH	A = B = 0.025			k AB	24.5	2.4	-5	*	(2)
		C_2H_5OH	"			"	"	1.15	-5		"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.7	$(CH_3)_2CHCH_2I + AgNO_3$	C_2H_5OH	A = B = 0.025			k AB	24.5	2.3	-5	*	(2)
.8	$(CH_3)_2CHCH_2CH_2I + AgNO_3$	C_2H_5OH	A = B = 0.025			k AB	24.5	9.5	-6	*	(2)
.9	$2C_6H_5CH_2Cl + Hg(NO_3)_2$	60 % dioxane + H_2O	A = 0.025 B = 0.025 - 0.050	HNO_3	0.013 - 0.029	k AB	24.6	1.65	-2	*	(5)
					0.085		"	1.78	-2		
.10	p-$C_2H_5C_6H_4CH_2Br + NO_3^-$	$(CH_3)_2CO$	A = B = 0.025			k AB	40	7.1	-4	*	(1)
.11	p-$(CH_3)_3CC_6H_4CH_2Br + NO_3^-$	$(CH_3)_2CO$	A = B = 0.025			k AB	40	6.8	-4	*	(1)
.12	2, 4 - $(NO_2)_2C_6H_3CH_2Br + NO_3^-$	$(CH_3)_2CO$	A = B = 0.025			k AB	20	4.0	-4	*	(1)
							40	3.3	-3		

COMMENTS

General. The rate measured is $-dB/dt$. All reactions $RX + NO_3^- \longrightarrow RNO_3 + X^-$ in R'OH solvents are accompanied by solvolyses of RNO_3 according to $RNO_3 + R'OH \rightarrow ROR' + HNO_3$, resulting in mixed products. For reaction (.3) in C_2H_5OH, the solvolysis to $(C_2H_5)_2O$ accounts for 70 % of the reaction (4). **(.3.1)** Simultaneous exchange for NO_3^- and solvolysis by C_2H_5OH or $C_2H_5OH + H_2O$; k refers to the total rate of production of I^- by combined exchange and solvolysis, k_2 to the rate of exchange for NO_3^-. All k converted from minutes to seconds. Data on solvolysis in $C_2H_5OH + H_2O$, and in the presence of CH_3COO^- and of $(C_2H_5)_3N$, see 212.471. For reaction (.9), the fraction of $C_6H_5CH_2OH$ in the product varies, depending on the nature and amounts of nitrates added (HNO_3, KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$) in the range of 76 - 86 % of the total product. Reaction (.9) is complicated by formation of chloromercuribenzyl alcohol. $Hg(ClO_4)_2$ reacts faster than $Hg(NO_3)_2$. $HgCl_2$ accelerates the reaction in 60 % dioxane, but slows it down in 95 % dioxane. Data of (2) are valid for the given concentrations; k increases with the square root of the concentration (2).

LITERATURE

(1) J.W.Baker, W.S.Nathan, *CSL* **1936**, 236. (2) K.A.Burke, F.G.Donnan, *CSL* **1904**, 555; *ZPC* 1909, **69**, 148. (3) F.G.Donnan, H.E.Potts, *CSL* **1910**, 1882. (3a) S.Eagle, J.C.Warner, *ACS* 1939, **61**, 488. (4) J.N.Pearce, O.M.Weigle, *ACJ* 1912, **48**, 243. (5) I.Roberts, L.P.Hammett, *ACS* 1937, **59**, 1063.

EXCHANGE

Halogen for NH_2 (or NR_2) group on aliphatic C

Liquid phase

Reaction type $RX + NH_3 \longrightarrow RNH_2 + HX$

(or $RX + 2\ NH_3 \longrightarrow RNH_2 + NH_4X$)

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$ClCH_2COONH_4 + NH_3$	H_2O	A = 0.05; B = 8.6			kA	39.9	1.50	-4		*	(1)
			" 9.2			"	"	1.66	-4			
			" 9.1			"	50.0	4.0	-4			
			" 9.4			"	"	4.2	-4			
			" ~ 9			kAB	39.9	1.8	-5		*	"
.2	$ClCH_2CONHCH_2COONH_4 + NH_3$ (chloroacetylglycine)	H_2O	A = 0.05; B = 9.3			kA	20.4	3.8	-5		*	(1)
			" 9.1				23.0	5.1	-5			
			" 9.3				39.9	3.18	-4			
			" ~ 9			kAB	39.9	3.5	-5			"
.3	$ClCH_2CONHCH_2CONHCH_2COONH_4 + NH_3$ (chloroacetylglycylglycine)	H_2O	A = 0.05; B = 9.2			kA	18.1	3.6	-5		*	(1)
			" 9.4				19.1	4.3	-5			
			" 9.6				39.9	4.32	-4			
			" ~ 9			kAB	39.9	4.6	-5		*	"

332.755.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.4	$ClCH_2CO(NHCH_2COO)_2NHCH_2COONH_4 + NH_3$ (chloroacetyldiglyeylglycine)	H_2O	A = 0.05; B = 9.2			kA	19.8	4.7	-5		*	(1)
			" "				39.9	4.03	-4			
			" ~ 9			kAB	39.9	4.3	-5		*	"
.5	$BrCH_2COONH_4 + NH_3$	H_2O	A = 0.05; B = 9.0			kA	0.1	1.12	-4		*	(1)
			" 9.2				13.6	5.50	-4			
			" 9.2				15.2	6.40	-4			
			" 9.0				24.6	1.79	-3			
			" 9.2				39.9	1.04	-2			
			" ~ 9			kAB	39.9	1.1	-3		*	"
.6	*dl* - $CH_3CHBrCOONH_4 + NH_3$	H_2O	A = 0.05; B = 9.1			kA	21.0	5.0	-5		*	(1)
			" 9.0				28.2	1.07	-4			
			" 9.2				39.9	4.00	-4			
			" ~ 9			kAB	39.4	4.2	-5		*	"
.7	*dl* - $(CH_3)_2CHCH_2CHBrCOONH_4 + NH_3$	H_2O	A = 0.05; B = 8.8			kA	39.9	8.5	-5		*	(1)
			" "				50.0	2.40	-4			
			" ~ 9			kAB	39.9	9.7	-6		*	"
.8	*dl* - $(CH_3)_2CHCH_2CHBrCONHCH_2COONH_4 + NH_3$ (bromoisocaproylglycine)	H_2O	A = 0.05; B = 9.1			kA	39.9	8.0	-5		*	(1)
			" 9.0				50.0	2.12	-4			
			" ~ 9			kAB	39.9	8.6	-6		*	"
.9	*dl,dl* - $(CH_3)_2CHCH_2CHBrCONHCH(CH_3)COONH_4 + NH_3$ (bromoisocaproylalanine)	H_2O	A = 0.05; B = 8.9			kA	39.9	7.0	-5		*	(1)
			" "				50.0	2.0	-4			
			" ~ 9			kAB	39.9	8.0	-6		*	"

332.755.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	Comments	Literature
								k^{o}	n			
.10	$(C_6H_5)_3CBr + p\text{-}CH_3C_6H_4NH_2$	C_6H_6	A = 0.1; B = 0.03 - 0.2	C_5H_5N	0.1		25	very fast				(²)
.11	$(C_6H_5)_3CBr + (C_6H_5)(CH_3)NH$	C_6H_6	A = 0.1; B = 0.03 - 0.2	C_5H_5N	0.1	kAB^2	25	5.0	-4	6.6 (25 - 60°)		(²)

COMMENTS

(.1) - (.9) First-order k fairly constant owing to excess of NH_3. Second-order k at 39.9°C converted to sec^{-1} $(M/l)^{-1}$ units from original k expressed in sec^{-1} atm^{-1} units, i.e. in terms of vapor pressure of NH_3 in atm. Original data (¹) of k at 39.9°C (sec^{-1} atm^{-1}), ΔH_a and ΔS_a:

Reaction	$10^4 k$	ΔH_a	ΔS_a
(.1)	3.2	2.84	-65.5
(.2)	6.0	2.73	-64.5
(.3)	7.7	2.84	-63.8
(.4)	7.3	2.69	-64.4
(.5)	(165)	2.37	-59.2
(.6)	7.0	2.60	-65.0
(.7)	1.7	3.40	-65.0
(.8)	1.5	3.20	-66.0
(.9)	1.4	3.60	-65.0

LITERATURE

(¹) A.F.Chadwick, E.Pacsu, *ACS* 1941, **63**, 2427. (²) C.G.Swain, *ACS* 1948, **70**, 1119.

EXCHANGE

Halogen for amine on aromatic C

Liquid phase

Amounts are in M/l.

Reaction type $ArX + NHR(NH_3) \longrightarrow ArNR(ArNH_2) + HX$

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of Addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n	E	Comments	Literature
.1	$p\text{-}CH_3OOC_6H_4Br + C_6H_{10}NH$	C_6H_6	$A = 0.05;\ B = 1.5$			$k\ AB$	99	8.6	-8			(1)
.2	$p\text{-}NO_2C_6H_4Cl + C_6H_{10}NH$	C_6H_6	$A = 0.05;\ B = 1.5$			$k\ AB$	99	1.1	-6			(1)
.3	$p\text{-}NO_2C_6H_4Br + C_6H_{10}NH$	C_6H_6	$A = 0.05;\ B = 1.5$			$k\ AB$	99	6.5	-6			(1)
.4	$p\text{-}CNC_6H_4Br + C_6H_{10}NH$	C_6H_6	$A = 0.05;\ B = 1.5$			$k\ AB$	99	1.2	-7			(1)
.5	$p\text{-}CH_3SO_2C_6H_4Br + C_6H_{10}NH$	C_6H_6	$A = 0.05;\ B = 1.5$			$k\ AB$	99	3.4	-7			(1)
.6	$C_{19}H_{13}Cl + NH_3 \rightarrow C_{19}H_{13}NH_2 + HCl$	NH_3	$A = 0.075;\ M = 0 - 0.2$		$k_1A + k_2AM + k_3AX$						*	(2)
	(9-Ph-9-Cl-fluorene)						15.1					
							k_1	9.7	-6			
							k_2	1.14	-4			
							25.1					
							k_1	2.22	-5	14.3		
							k_2	2.65	-4	14.4		
				X = NaCl	0.05 - 0.2			k_3				
							15.1	6.72	-5			
							25.1	1.92	-4	17.9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.6	$C_{19}H_{13}Cl + NH_3 \rightarrow C_{19}H_{13}NH_2 + HCl$ (9-Ph-9-Cl-fluorene)			$NaNO_3$	0.05 - 0.2		15.1	1.13	-4			
							25.1	3.34	-4	15.6		
				NH_4NO_3	"		15.1	1.91	-4			
	(continued)						25.1	4.55	-4	14.8		

COMMENTS

(.6) k_3 decreases somewhat with increasing X.

LITERATURE

(1) J. F. Bunnet, A. Levitt, *ACS* 1948, 70, 2778. (2) P. M. Williamson, R. C. Anderson, G. W. Watt, *ACS* 1943, 65, 49; 1944, 66, 376.

EXCHANGE

Halogen for $S_2O_3^{--}$

Liquid phase

Reaction type $RX + S_2O_3^{--} \rightarrow RS_2O_3^{-} + X^{-}$

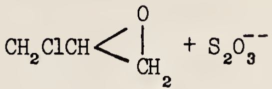
Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, see at end of the table.

In compounds with two halogen atoms, if only one is exchanged (reaction with 1 $S_2O_3^{--}$), it is the one written last. If the reaction equation involves 2 $S_2O_3^{--}$, both halogens are exchanged.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$CH_3Cl + S_2O_3^{--}$	H_2O	A ~ 0.02; B ~ 0.05	kAB	20.0	4.96	-4				*	(^{3a})
					24.9	9.09	-4					
					30.0	1.62	-3					
					40.0	4.71	-3					
					49.6	1.32	-2	20.5	1.0	12		
.2	$CH_3Br + S_2O_3^{--}$	H_2O	A ~ 0.02; B ~ 0.05	kAB	0.1	1.93	-3				*	(^{3a})
					4.8	3.36	-3					
					9.2	6.00	-3					
					15.5	1.30	-2					
					20.0	2.19	-2					
					25.1	3.77	-2	19.5	6.8	12		
.3	$CH_3I + S_2O_3^{--}$	H_2O	A ~ 0.02; B ~ 0.05	kAB	9.2	4.83	-3				*	(^{3a})
					12.9	7.56	-3					
					19.2	1.56	-2					
					25.5	3.15	-2	18.9	2.0	12		
.4	$C_2H_5Br + S_2O_3^{--}$	H_2O	0.01	kAB	25	5.2	-4					(^{4})
					50	8.3	-3					

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
						k^o	n			
.4	$C_2H_5Br + S_2O_3^{--}$ *(continued)*	Et50A	~ 0.1	kAB	12.5	2.43	-4		*	(1)
					25.0	9.53	-4			
					37.5	3.33	-3	18.5		
.5	$C_2H_5I + S_2O_3^{--}$	H_2O	0.01	kAB	25	8.3	-4		*	(4)
					35	2.8	-3			
		H_2O	0.015	kAB	25.0	1.23	-3		*	(3)
					36.2	4.25	-3			
					44.5	1.21	-2			
					51.6	2.55	-2			
					55.6	3.59	-2	21.4		
.6	$CH_2ClCH_2Br + S_2O_3^{--}$	EtW 3	B>A	kAB	40	8.3	-6			(4)
					50	2.5	-5			
.7	$CH_2ClCH_2I + S_2O_3^{--}$	EtW 3	B>A	kAB	40	2.3	-5			(4)
					50	6.7	-5			
.8	$CH_2BrCH_2Br + S_2O_3^{--}$	EtW 3	B>A	kAB	40	2.8	-3			(4)
					50	8.2	-3			
.9	$CH_2BrCH_2I + 2\ S_2O_3^{--}$	EtW 2	0.01	kAB	15	3.5	-3		*	(4)
					25	9.2	-3			
.10	$CH_2ICH_2I + 2\ S_2O_3^{--}$	EtW 2	0.01	kAB	15	5.7	-3		*	(4)
					25	1.7	-2			
.11	$C_3H_7Br + S_2O_3^{--}$	Et50A	~ 0.1	kAB	12.5	1.27	-4		*	(1)
					25.0	4.74	-4			
					37.5	1.63	-3	18.0		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
						k^o	n			
.12	$(CH_3)_2CHBr + S_2O_3^{--}$	Et50A	~ 0.1	k AB	12.5	6.77	-6		*	(1)
					25.0	2.94	-5			
					37.5	1.18	-4	20.1		
.13	$C_3H_7I + S_2O_3^{--}$	EtW 3	0.01	k AB	35	9.3	-4			(4)
.14	$(CH_3)_2CHI + S_2O_3^{--}$	EtW 3	0.01	k AB	35	5.7	-5			(4)
.15	$CH_2{:}CHCH_2I + S_2O_3^{--}$	EtW 3	0.01	k AB	15	2.3	-2			(4)
					25	6.0	-2			
.16	$(CH_3)_2CHCH_2Br + S_2O_3^{--}$	Et50	~ 0.01	k AB	12.5	4.59	-6		*	(2)
					25.0	2.02	-5			
					37.5	7.60	-5			
					50.0	2.60	-4	19.7		
Acids, Esters, Ethers										
.17	$ClCOOC_2H_5 + S_2O_3^{--}$	EtW 3	0.01	k AB	35	1.7	-2			(4)
.18	$CH_2ClCOO^- + S_2O_3^{--}$	H_2O	0.01	k AB	25	7.0	-5			(4)
					50	6.6	-4			
.19	$CH_2ClCOOCH_3 + S_2O_3^{--}$	H_2O	0.01	k AB	25	9.8	-4			(4)
					35	2.7	-3			
.20	$CH_2ClCOOC_2H_5 + S_2O_3^{--}$	H_2O	0.01	k AB	25	1.0	-3			(4)
					35	2.9	-3			
.21	$CH_2BrCOO^- + S_2O_3^{--}$	H_2O	0.01	k AB	25	5.2	-3			(4)
					35	1.1	-2			

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n	E	Comments	Literature
.22	$CH_2BrCOOCH_3 + S_2O_3^{--}$	H_2O	0.01	k AB	15 25	3.5 9.7	-2 -2			(4)
.23	$CH_2BrCOOC_2H_5 + S_2O_3^{--}$	H_2O	0.01	k AB	15 25	3.9 1.1	-2 -1			(4)
.24	$CH_2ICOOC_2H_5 + S_2O_3^{--}$	H_2O	0.01	k AB	15 25	4.25 1.2	-2 -1			(4)
.25	$CH_3CHBrCOOC_2H_5 + S_2O_3^{--}$	EtW 3	0.01	k AB	25 35	6.2 1.4	-4 -3			(4)
.26	$C_2H_5CHBrCOOC_2H_5 + S_2O_3^{--}$	EtW 3	0.01	k AB	35	3.7	-4			(4)
.27	$(CH_3)_2CBrCOOC_2H_5 + S_2O_3^{--}$	EtW 3	0.01	k AB	35	slow				(4)
.28	$CH_2ClCOCH_3 + S_2O_3^{--}$	EtW 3	0.01	k AB	25 35	6.3 1.75	-3 -2			(4)
.29	 $CH_2ClCH\langle\overset{O}{\underset{CH_2}{\vert}} + S_2O_3^{--}$	EtW 3	0.01	k AB	35	1.7	-3			
	Aryl-substituted alkyl halide									
.30	$C_6H_5CH_2Cl + S_2O_3^{--}$	EtW 3	0.01	k AB	35	2.8	-3			(4)
.31	$o\text{-}NO_2C_6H_4CH_2Cl + S_2O_3^{--}$	EtW 3	0.01	k AB	35	2.8	-3			(4)
.32	$m\text{-}NO_2C_6H_4CH_2Cl + S_2O_3^{--}$	EtW 3	0.01	k AB	35	3.2	-3			(4)
.33	$p\text{-}NO_2C_6H_4CH_2Cl + S_2O_3^{--}$	EtW 3	0.01	k AB	35	5.0	-3			(4)

SOLVENTS

EtW 2	$C_2H_5OH + H_2O$; $C_2H_5OH/H_2O = 5/2$ (vol).
EtW 3	" " " " = 5/3 "
Et50	$H_2O + C_2H_5OH$ 50 %
Et50A	$H_2 + C_2H_5OH$ 50 %; CH_3COONa 0.020 *M*.

SUPPLEMENTARY TABLE

Heat and Entropy of Activation (1)(2)

ΔH_a (kcal/mole) and ΔS_a (cal/mole/degree) referred to C_2H_5Br as zero.
For C_2H_5Br, $\Delta S_a = -12.3$.

	Reaction	Solvent	ΔH_a	ΔS_a
(.2)	$CH_3Br + S_2O_3^{--}$	Et50	- 2.9	- 0.6
(.11)	$C_3H_7Br + S_2O_3^{--}$	Et50A	- 0.5	- 3.0
(.12)	$(CH_3)_2CHBr + S_2O_3^{--}$	Et50A	1.6	- 0.9
(.16)	$(CH_3)_2CHCH_2Br + S_2O_3^{--}$	Et50	1.1	- 3.4

COMMENTS

(.1) (.2) (.3) New data of (3a) given in preference to the markedly lower, old data of k of (4). Hydrolysis of A is negligible. (.4) In Et50A (1), simultaneous solvolysis by CH_3COO^- negligible. (.5) k of (3), more reliable, are about 50 % higher than k of (4) at the same temperatures; k of (3) are initial values, the second-order k falling off somewhat with the progress of the reaction, in conformity with a true rate law $k_1A + k_2AB$, with $k_1 \ll k_2$. (.9) (.10) Original k, halved to apply to one halogen, have been doubled. (.11) Stimultaneous solvolysis by CH_3COO^- negligible (.12) Stimultaneous solvolysis *not* negligible; k corrected. At 25.0 and 37.5°C, k (solvolysis) = 3.4×10^{-7} and 1.7×10^{-6}, respectively.

LITERATURE

(1) F.J.Crowell, L.P.Hammett, *ACS* 1948, 70, 3444. (2) P.M.Dunbar, L.P.Hammett, *ACS* 1950, 72, 109. (3) E.A.Moelwyn-Hughes, *CSL* 1933, 1576. (4) A.Slator, D.F.Twiss, *CSL* 1909, 95, 93; A.Slator, *CSL*, 1904, 85, 1286.

EXCHANGE

Halogen for halogen on aliphatic carbon

Liquid phase

Reaction type $RX_1 + X_2^- \longrightarrow RX_2' + X_1^-$

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, see at the end of the table.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$CH_3Br + I^-$	H_2O	0.035-0.060	k AB	0.5	4.5	-5					(6)
					20.4	4.36	-4					
					25.0	7.02	-4					
					35.5	2.00	-3					
					50.3	7.70	-3					
					66.9	3.12	-2	18.3	1.7	10		
		CH_3OH		k AB	0.0	5.3	-5					(7)
					15.5	3.53	-4					
					24.8	9.84	-4					
					34.6	2.43	-3					
					44.6	6.35	-3	18.2	2.3	10		
.2	$CH_3I + Br^-$	CH_3OH		k AB	0.0	2.94	-6					(7)
					20.4	4.54	-5					
					30.2	1.38	-4					
					40.3	4.54	-4					
					49.1	1.21	-3	21.4	3.9	11		
.3	$C_2H_5Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	2.8	-5					(4)
					60	5.4	-5	14.2				

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No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.4	$CH_3OCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	0	~ 5.4	-5					(5)
					10	~ 1.7	-4					
.5	$CNCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	10	6.2	-4					(5)
					20	1.96	-3	18.8				
.6	$NH_2COCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	25	1.0	-4					(5)
					30	1.66	-4					
					50	1.10	-3	18.3				
.7	$C_3H_7Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.2	-5					(4)
					60	2.0	-5	18.8				
.8	$(CH_3)_2CHCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	4.1	-7					(4)
.9	$C_2H_5OOCCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	25	2.6	-5					(4) (5)
.10	$CH_3COCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	0	2.1	-3					(5)
					10	7.9	-3	19.7				
.11	$CH_3COOCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	20	1.6	-4					
					30	2.7	-4	18.3				
.12	$C_4H_9Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.1	-5					(4) (5)
					60	2.8	-5	19.7				
.13	$C_2H_5CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	6.1	-7					(4)
.14	$C_2H_5OOCCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	25	1.76	-3					(4) (5)
					30	2.90	-3	17.8				
.15	$(CH_3)_3CCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	5.0	-7					(4)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.16	$C_5H_{11}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.5	−5					(4)
					60	3.5	−5	18.3				
.17	$(CH_3)_2CHCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	1.9	−5					(4)
.18	$C_3H_7CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	1.33	−6					(4)
.19	$C_6H_{13}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.45	−5					(4)
					60	3.5	−5	18.8				
.20	$C_4H_9CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	2.1	−6					(4)
.21	$(C_3H_7)(CH_3)_2CCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	8.0	−7					(4)
.22	$C_7H_{15}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.4	−5					(4)
					60	3.4	−5	18.8				
.23	$(C_2H_5OOC)_2CHCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	0	3.6	−3					(5)
					10	6.6	−3					
.24	$C_8H_{17}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.5	−5					(4)
					60	3.7	−5	19.2				
.25	$C_6H_{13}CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	60	7.2	−7					(4)
.26	$C_{12}H_{25}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.3	−5					(4)
					60	2.8	−5	17.1				
.27	$C_{14}H_{29}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; R = 0.04	k AB	50	1.1	−5					(4)
					60	2.7	−5	19.2				

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.28	$C_{16}H_{33}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.0	−5					(4)
					60	2.5	−5	19.2				
.29	$C_{30}H_{61}Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	50	1.0	−5					(4)
					60	2.46	−5	18.8				
Aryl-substituted aliphatic halide												
.30	$C_6H_5CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	25	2.18	−4					(4)(5)
					30	3.64	−4					
					50	2.19	−3	18.3				
		An 50		k AB	0.1	3.7	−5					
					20	3.7	−4	18.3				(3)
.31	$C_6H_5CH_2CH_2Cl + I^-$	An 50		k AB	75	2.4	−4					(2)
.32	p-$CH_3OC_6H_4CH_2CH_2Cl + I^-$	An 50		k AB	75	2.9	−4					(2)
.33	$(C_6H_5)_3CCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	0	2.28	−3					(5)
.34	$C_6H_5COCl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	0	~4.4	−5					(5)
.35	$C_6H_5COCH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	− 10	1.64	−3					(4)(6)
					0	6.2	−3					
.36	$C_6H_5COCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	25	2.35	−4					(5)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.37	$C_6H_4NHC(CH_2Cl):N + I^-$	$(CH_3)_2CO$	A = 0.1; B = 0.02	k AB	25	8.2	−3				*	(8)
			0.01 0.03		"	4.15	−2					
			0.005 "		"	6.5	−2					
			" 0.01		"	7.2	−2					
			" 0.02		"	1.08	−1					
.38	$C_6H_4NHC(CH_2CH_2Cl):N + I^-$	$(CH_3)_2CO$	A = 0.05; B = 0.02	k AB	25	1.22	−2				*	(8)
			0.02 "		"	2.54	−2					
			" 0.01		"	3.80	−2					
			0.01 0.026		"	4.55	−2					
.39	$C_6H_4NHC(CH_2CH_2CH_2Cl):N + I^-$	$(CH_3)_2CO$	A = 0.03; B = 0.016	k AB	25	1.26	−2				*	(8)
			0.02 0.02		"	4.9	−2					
			0.025 0.01		"	5.7	−2					
			0.01 0.02		"	9.3	−2					
.40	$C_6H_4NHC[CH(CH_3)CH_2Cl]:N + I^-$	$(CH_3)_2CO$	A = 0.02; B = 0.02	k AB	25	6.5	−2				*	(8)
			0.025 0.01		"	2.42	−1					
			0.01 0.02		"	4.25	−1					
.41	$C_6H_4N(CH_3)C(CH_2Cl):N + I^-$	$(CH_3)_2CO$	A = 0.02; B = 0.02	k AB	25	7.0	−3				*	(8)
			0.025 0.01		"	2.50	−2					
			0.01 0.02		"	6.95	−2					
.42	$C_6H_4N(CH_3)C(CH_2CH_2Cl):N + I^-$	$(CH_3)_2CO$	A = 0.038; B = 0.02	k AB	25	1.2	−2				*	(8)
			0.029 "		"	1.65	−2					
			0.025 0.01		"	1.50	−1					
			0.005 0.02		"	2.30	−1					
.43	$o\text{-}NO_2C_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	3.6	−4					(3)
					20	3.16	−4	17.4				

332.771.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.44	m-$NO_2C_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	0.1	1.35	−4					(3)
					20	1.33	−2	18.4				
.45	p-$NO_2C_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	0.1	2.5	−4					(3)
					20	2.26	−3	17.6				
.46	p-$NO_2C_6H_4CH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	75	1.14	−3					(2)
.47	o-$FC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	1.25	−4					(3)
					20	1.08	−3	17.2				
.48	m-$FC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	5.1	−5					(3)
					20	5.12	−4					
.49	p-$FC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	5.7	−5					(3)
					20	5.3	−4	17.8				
.50	p-$FC_6H_4CH_2CH_2Cl + I^-$	An 50		k AB	75	4.3	−4					(2)
.51	o-$ClC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	1.76	−4					(3)
					20	1.45	−3	16.9				
		$(CH_3)_2CO$	A = 0.2; B = 0.04	k AB	25	7.5	−4					(4)
					30	1.22	−3	17.6				
.52	m-$ClC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	6.5	−5					(3)
					20	6.0	−4	17.7				
.53	p-$ClC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	8.1	−5					(3)
					20	7.9	−4	18.0				
.54	p-$ClC_6H_4CH_2CH_2Cl + I^-$	An 50		k AB	75	4.55	−4					(2)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.55	o-$BrC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	1.57	−4					(3)
					20	1.46	−3	17.8				
.56	m-$BrC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	7.2	−5					(3)
					20	6.85	−4	18.0				
.57	p-$BrC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	1.39	−4					(3)
					20	8.7	−4	18.7				
.58	p-$BrC_6H_4CH_2CH_2Cl + I^-$	An 50		k AB	75	4.52	−4					(2)
.59	o-$IC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	1.74	−4					(3)
					20	1.53	−3	17.4				
.60	m-$IC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	6.7	−5					(3)
					20	6.5	−4	18.1				
.61	p-$IC_6H_4CH_2Cl + I^-$	An 50		k AB	0.1	8.2	−5					(3)
					20	8.25	−4	18.4				
.62	p-$IC_6H_4CH_2CH_2Cl + I^-$	An 50		k AB	75	3.90	−4					(2)
Arylthio-substituted aliphatic halide												
.63	$C_6H_5SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	55	2.5	−5					(1)
.64	p-$CH_3C_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	55	2.1	−5					(1)
					75	1.21	−4	20.3				
.65	p-$CH_3OC_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	75	1.2	−4					(1)

332.771.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.66	p-$ClC_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	55	5.5	-5					(1)
					75	3.5	-4	21.0				
.67	2, 5-$Cl_2C_6H_3SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	55	5.2	-5					(1)
					75	3.1	-4	20.3				
.68	p-$BrC_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	55	4.2	-5					(1)
					75	2.65	-4	21.1				
.69	p-$IC_6H_4SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	55	3.2	-5					(1)
					75	2.2	-4	21.9				
.70	β-$C_{10}H_7SCH_2CH_2Cl + I^-$	$(CH_3)_2CO$		k AB	75	1.85	-4					(1)

SOLVENTS

An 50 $H_2O + (CH_3)_2CO$ 50 vol %

COMMENTS

(.37)-(.42) Selected values. Addition of H_2O or $C_6H_5NO_2$ lowers *k*, addition of C_6H_6 raises *k*.

LITERATURE

(1) G. Baddeley, G. Mc. Bennett, *CSL* 1933, 261.

(2) G. Baddeley, G. Mc. Bennett, *CSL* 1935. 1819.

(3) G. Mc. Bennett, B. Jones, *CSL* 1935, 1815.

(4) J. B. Conant, R. E. Hussey, *ACS* 1925, 47, 476.

(5) J. B. Conant, W. R. Kirner, R. E. Hussey, *ACS* 1925, 47, 488.

(6) E. A. Moelwyn-Hughes, *CSL* 1938, 779.

(7) E. A. Moelwyn-Hughes, *TFS* 1939, 35, 368.

(8) H. Skolnik, A. R. Day, J. C. Miller, *ACS* 1943, 65, 1858.

EXCHANGE

Halogen for halogen
on aromatic and hydroaromatic carbon

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $ArX + X'^- \longrightarrow ArX' + X^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
						k^o	n		A^o	n	
.1	*cyclo*-$C_6H_{11}Cl + KI$	$(CH_3)_2CO$	A = 0.2 B = 0.04	k AB	60	< 2.8	-8				(²)
.2	p-$NO_2C_6H_4Cl + LiBr$	90 % $(CH_3)_2CO$		k AB	30	1.35	-4				(¹)
					50	6.7	-4	15.6	2.5	7	
.3	p-$NO_2C_6H_4Br + LiCl$	90 % $(CH_3)_2CO$		k AB	30	2.14	-3				(¹)
					50	1.32	-2	17.9	1.6	10	

LITERATURE

(¹) T. A. Bither, J. M. Sturtevant, H. C. Thomas, *ACS* 1945, **67**, 1562.

(²) J. B. Conant, R. E. Hussey, *ACS* 1925, 47, 476.

EXCHANGE

Halogen for ClO_4^-

Liquid phase

Amounts are in M/l.
Rates in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
						k^o	n	
.1	$CH_3I + AgClO_4 \rightarrow CH_3ClO_4 + AgI$	$(C_2H_5)_2O$	$A = B \sim 0.005 - 0.2$	$k\,AB$	15	5.0	-4	
					25	9.2	-4	
		CH_3COOH	0.04 - 0.08	$k\,AB^{3/2}$	15	1.8	-4	
					25	3.8	-4	12.7
		$(CH_3)_2CO$	"	"	25	1.8	-4	
		C_2H_5OH	"	"	15	3.3	-4	
					25	7.0	-4	13.0
		$CH_3COOC_2H_5$	"	"	25	1.1	-3	
		$H_2O + CH_2OCH_2O$ 50 %	"	"	15	1.8	-4	
					25	4.0	-4	13.3
		$H_2O + C_2H_5OH$ 50 %	$A = B \sim 0.08 - 0.16$	"	15	2.5	-4	
					25	5.0	-4	11.4
		C_6H_6	"	"	25	4.1	-5	
					35	9.0	-5	13.9

COMMENTS

At low concentrations of $AgClO_4$, the $k\,AB^{3/2}$ reaction rate law becomes pseudo-bimolecular, $k'\,AB$ (k' proportional to $B^{1/2}$).

LITERATURE

M. F. Redies, T. Iredale, *JPC* 1944, 48, 224.

EXCHANGE

Halogen for hydrogen in cyanogen halide

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant		Defined mass-action law	Temperature	$k = k^o \times 10^n$	
							k^o	n
.1	$CNBr + 2\ HI \longrightarrow HCN + HBr + I_2$	CCl_4	$10^3A = 35.5$;	$10^3B = 0.3$	kAB	25	1.3	-1
	$(CNBr + HI \longrightarrow CNI + HBr)$		5.0	2.5		"	4.1	-1
			5.0	1.3		"	2.0	-1
			5.0	0.8		"	1.1	-1
			2.5	2.5		"	1.3	-1
.2	$CNI + HI \longrightarrow HCN + I_2$	CCl_4	$10^3A = 0.6$;	$10^3B = 1.7$	kAB	25	2.1	+4
			0.6	0.8		"	2.5	+4
			1.2	0.8		"	2.6	+4
			1.2	0.4		"	1.7	+4
			0.6	0.4		"	7.0	+3
			5.7	0.2		"	4.0	+3

COMMENTS

Reaction (.1) is assumed to proceed over the rate-determining slow step $CNBr + HI \longrightarrow CNI$, followed by the rapid step (.2). The scattering of the second-order k is attributed to experimental difficulties. Mean values of k are given as (.1) $k = 2.0 \times 10^{-1}$, (.2) $k = 1.6 \times 10^4$. The reaction $CNCl + HI$ is substantially slower than $CNBr + HI$.

LITERATURE

R. B. Mooney, H. G. Reid, *CSL* **1933**, 1318.

EXCHANGE

Halogen for NH_2 (or NR_2) group in cyanogen halide

Liquid phase

Reaction type $CNX + NR_3 \longrightarrow CNNR_2 + RX$

(or $CNX + 2\ NR_3 \longrightarrow CNNR_2 + NR_3RX$)

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Ionic strength μ	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
						k^o	n	
.1	$CNBr + NH_3$	H_2O	0.2	k AB	10	3.25	-3	17.5
.2	$CNBr + CH_3NH_2$	H_2O	1.0	k AB	10	2.22	0	14.5
.3	$CNBr + C_2H_5NH_2$	H_2O	1.0	k AB	10	1.08	0	14.3
.4	$CNBr + (C_2H_4OH)_3N$	H_2O	1.0	k AB	10	3.93	-2	14.9
.5	$CNI + NH_3$	H_2O	3.0	k AB	10	7.60	-6	19.6
.6	$CNI + CH_3NH_2$	H_2O	1.0	k AB	10	8.35	-3	17.1
.7	$CNI + C_2H_5NH_2$	H_2O	1.0	k AB	10	4.30	-3	17.2
.8	$CNI + (CH_3)_2NH$	H_2O	1.0	k AB	10	2.17	-1	17.0
.9	$CNI + (C_2H_5)_2NH$	H_2O	1.0	k AB	10	6.38	-2	16.4
.10	$CNI + (CH_3)_3N$	H_2O	1.0	k AB	10	2.54	-1	17.6
.11	$CNI + (C_2H_5)_3N$	H_2O	1.0	k AB	10	4.50	-2	16.7
.12	$CNI + (C_2H_4OH)_3N$	H_2O	1.0	k AB	10	4.35	-5	18.5

LITERATURE

R. O. Griffith, R. S. Jobin, A. McKeown, *TFS* 1938, 34, 316.

382.870.

COORDINATIVE EXCHANGE

Halogen - water in VIII th - group complex.

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	$k = k^o \times 10^n$		E
					k^o	n	
.1	$[Co(NH_3)_5Cl]^{++} + H_2O \rightarrow [Co(NH_3)_5(H_2O)^{+++} + Cl^-$	H_2O	0.007 - 0.015	k A	1.7	-6	23.7
.2	$[Co(NH_3)_5(H_2O)]^{+++} + Cl^- \rightarrow [Co(NH_3)_5Cl]^{++} + H_2O$	H_2O	0.007 - 0.015	k AB	7.2	-6	

COMMENTS

(.1)(.2) k identical for the chloride, nitrate, and perchlorate, depends on the anion but not on the cation; perchlorate. Salt effect, positive except for the is usually less than 1 %.

LITERATURE

F. J. Garrick, *TFS* 1937, 33, 486. A. B. Lamb, J. W. Marden, *ACS* 1911, 33, 1882.

ELIMINATION
of H^+ from a C - N bond

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$CH_3NO_2 + H_2O \rightarrow CH_2{:}NO_2^- + H_3O^+$	H_2O; buffers	~ 0.001	pH	6.1	k A	25	1.20	-4					(5) (9)
					7.0		"	1.65	-4					
					8.0		"	2.50	-4					
					8.9		"	3.00	-4					
		H_2O	A ~ 0.15 - 0.7	H_2SO_4	~ 0.15	k AB	70	1.2	-7				*	(8)
				Br_2	~ 0.03					22				(1)
.2	$CH_3NO_2 + D_2O \rightarrow CH_2{:}NO_2^- + HD_2O^+$	D_2O	A ~ 0.15 - 0.7	H_2SO_4	~ 0.15	k AB	70	7.3	-8				*	(8)
				Br_2	~ 0.03									
.3	$CD_3NO_2 + H_2O \rightarrow CH_2{:}NO_2^- + H_2DO^+$	H_2O	A ~ 0.15 - 0.7	H_2SO_4	~ 0.15	k AB	70	3.3	-8				*	(8)
				Br_2	~ 0.03									
.4	$CD_3NO_2 + D_2O \rightarrow CD_2{:}NO_2^- + D_3O^+$	D_2O	A ~ 0.15 - 0.7	H_2SO_4	~ 0.15	k AB	70	1.4	-8				*	(8)
				Br_2	~ 0.03									
.5	$CH_3NO_2 + OH^- \rightarrow CH_2{:}NO_2^- + H_2O$	H_2O	0.017 - 0.027			k AB	0	4.0	+1				*	(4)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$CH_3NO_2 + CH_3COO^- \rightarrow CH_2NO_2^- + CH_3COOH$	H_2O	A ~ 0.15 - 0.7	CH_3COOH	0.1 - 0.2	k AB	11	1.6	-5				*	(8)
			B ~ 0.1 - 0.5	Br_2	~ 0.03		25	7.7	-5					
							35	2.3	-4	20				
		D_2O	"	"	"	"	25	6.6	-5					"
.7	$CD_3NO_2 + CH_3COO^- \rightarrow CD_2{:}NO_2^- + CH_3COOD$	H_2O	A ~ 0.15 - 0.7	CH_3COOH	0.1 - 0.2	k AB	25	1.2	-5				*	(8)
			B ~ 0.1 - 0.5	Br_2	~ 0.03									
		D_2O	"	"	"	"	11	1.9	-6				*	"
							25	9.6	-6					
							35	2.4	-5	20				
.8	$CH_3NO_2 + CH_2OHCOO^- \rightarrow CH_2{:}NO_2^- +$	H_2O	A = 0.05	$CH_2OHCOOH$	~ 0.1	k AB	20	1.05	+1				*	(7)
	$CH_2OHCOOH$		B = 0.08 - 0.15	Br_2	0.002 - 0.012									
.9	$CH_3NO_2 + CH_2ClCOO^- \rightarrow CH_2{:}NO_2^- +$	H_2O	A ~ 0.15 - 0.7	$CH_2ClCOOH$	0.20 - 0.25	k AB	11	8.4	-7				*	(8)
	$CH_2ClCOOH$		B = 0.2 - 0.7	Br_2	~ 0.03		25	4.2	-6					
							35	1.3	-5	20				
		D_2O	"	"	"	"	25	3.1	-6					"
.10	$CD_3NO_2 + CH_2ClCOO^- \rightarrow CD_2{:}NO_2^- +$	H_2O	A ~ 0.15 - 0.7	$CH_2ClCOOH$	0.20 - 0.25	k AB	25	9.6	-7				*	(8)
	$CH_2ClCOOH$		B = 0.2 - 0.7	Br_2	~ 0.03		35	3.0	-6					
		D_2O	"	"	"	"	25	4.6	-7				*	"
							35	2.0	-7	21				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.11	$C_2H_5NO_2 + H_2O \rightarrow CH_3CH{:}NO_2^- + H_3O^+$	H_2O buffers	~ 0.001	pH	6.1	k A	25	1.16	-4					(5) (9)
					7.0		"	1.54	-4					
					8.0		"	3.00	-4					
					8.9		"	3.67	-4					
					10.0		"	1.13	-3					
					10.9		"	3.17	-3					
.12	$C_2H_5NO_2 + OH^- \rightarrow CH_3CH{:}NO_2^- + H_2O$	H_2O	~ 0.02 - 0.05			k AB	0	6.52	-1	12	3.2	9	*	(6) (10)
							5	9.85	-1	ΔH_a = 12.1;	ΔS_a = -15.5			(3) (4)
.13	$C_2H_5NO_2 + OD^- \rightarrow CH_3CH{:}NO_2^- + HDO$	D_2O	0.015 - 0.027			k AB	0	9.3	-1	11.5	1.26	9	*	(10)
							5	1.39	0		ΔS_a = -16.4			(3)
.14	$CH_3CHDNO_2 + OD^- \rightarrow CH_3CD{:}NO_2^- + HDO$	D_2O	0.015 - 0.027			k AB	0	(6.0)	-1				*	(10)
							"	3.5	-1	10.7	1.26	8		(3)
							5	4.6	-1		ΔS_a = 21.2			(3)
.15	$CH_3CD_2NO_2 + OD^- \rightarrow CH_3CD{:}NO_2^- + D_2O$	D_2O	A = B ~ 0.05 - 0.065			k AB	0	(~ 1.0)	-1				*	(10)
.16	$C_2H_5NO_2 + NH_3 \rightarrow CH_3CH{:}NO_2^- + NH_4^+$	H_2O	0.021			k AB	0	9.5	-4				*	(6) (4)
			0.065				"	7.8	-4					
			0.021				5.2	1.6	-3	ΔH_a = 14.9	ΔS_a = -17.9			(4)
			0.065				"	1.3	-3					
.17	$C_2H_5NO_2 + CH_3NH_2 \rightarrow CH_3CH{:}NO_2^- + CH_3NH_3^+$	H_2O	0.021			k AB	0	1.44	-2				*	(5) (4)
			0.065				"	1.30	-2					
			0.021				5.2	2.46	-2	ΔH_a = 15.0	ΔS_a = -12.0			(4)
			0.065				"	2.35	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.18	$C_2H_5NO_2 + (CH_3)_2NH \rightarrow CH_3CH{:}NO_2^- + (CH_3)_2NH_2^+$	H_2O	0.0173			k AB	0	4.34	-2				*	(6) (4)
			0.051				"	4.08	-2					
			0.024				5.2	7.58	-2	$\Delta H_a = 15.9$	ΔS_a			
			0.046				"	7.36	-2		-6.6			(4)
.19	$C_2H_5NO_2 + (CH_3)_3N \rightarrow CH_3CH{:}NO_2^- + (CH_3)_3NH^+$	H_2O	0.033			k AB	0	3.43	-2				*	(6) (4)
			0.045				"	3.41	-2					
			0.020				5.2	6.13	-2	$\Delta H_a = 15.8$				(4)
			0.045				"	6.00	-2		-7.3			
.20	$C_3H_7NO_2 + H_2O \rightarrow C_2H_5CH{:}NO_2^- + H_3O^+$	H_2O buffers	~ 0.001	pH	8.0	k A	25	1.57	-4					(5) (9)
					8.9		"	2.34	-4					
					10.0		"	7.34	-4					
.21	$C_3H_7NO_2 + OH^- \rightarrow C_2H_5CH{:}NO_2^- + H_2O$	H_2O	0.017 - 0.027			k AB	0	4.9	-1					(3) (2)
.22	$(CH_3)_2CHNO_2 + H_2O \rightarrow (CH_3)_2C{:}NO_2^- + H_3O^+$	H_2O buffers	~ 0.001	pH	8.0	k A	25	1.30	-4					(5) (9)
					8.9			1.35	-4					
					10.0			1.50	-4					
					10.9			3.17	-4					
.23	$(CH_3)_2CHNO_2 + OH^- \rightarrow (CH_3)_2C{:}NO_2^- + H_2O$	H_2O	0.017 - 0.027			k AB	0	3.5	-2					(3)
							5	5.6	-2					

COMMENTS

General. Reverse reactions of proton elimination from C – N bond, see 622.450.

Methods. (5) Reactions (.1) (.11) (.20) (.22) (.23) polarography of A. (1) (7) (8) Reactions (.1) (.2) (.3) (.4) (.6) (.7) (.8) (.9) (.10), derived from substitution reactions of the type $CH_3NO_2 + 3Br_2 \rightarrow CBr_3NO_2 + 3HBr$ (see 312.471) in the presence of the stated acid. (3) (4) (6) (10) Reactions (.5) (.12) (.13) (.14) (.15) (.16) (.17) (.18) (.19) (.21) (.23), electric conductivity measurements.

Reactions. (.10) *k* at 25° (in H_2O) extrapolated. (.12) *k* data of (6) and (10) in agreement; *k* varies slightly in the course of the reaction (10). Reverse reaction negligible except at later stages (6). (.14) Discrepancy between *k* of (10) and (3) at 0°C; value of (3) more reliable, (10) claiming no precision. Accompanying reaction $CH_3CDHNO_2 + OD^- \rightarrow CH_3CHNO_2 + D_2O$ has apparently no effect on *k*. (.15) No precision claimed; *k* decreases with time and on repeated experiments, because of the presence of some incompletely deuterated substrate. (.16) (.17) (.18) (.19) Reverse reaction negligible except at late stages.

LITERATURE

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ELIMINATION
of Hydrogen halide
Double Bond Formation

Reaction type $R_1CHXCH_2R_2 + ROH \rightarrow R_1CH{:}CHR_2 + X^- + ROH_2^+$
(A) (B) (L) (M) (N)
$R_1CHXCH_2R_2 + OR^- \rightarrow R_1CH{:}CHR_2 + X^- + ROH$

Rate measured $+\,dM/dt$

Amounts are in M/l.
Rates are in M/l per sec.
Coded solvents, see at the end of the table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$C_2H_5Br + OC_2H_5^-$	C_2H_5OH	B = 0.05			kAB	54.9	1.97	-4					(5)
			0.1					1.74	-4					
			2.0					1.19	-4					
.2	$COOHCHClCHClCOOH + H_2O$	H_2O				kA	70	5.06	-6					(14)
							80	1.11	-5					
							89	2.50	-5					
.3	$COOHCHClCHClCOOH + OH^-$	H_2O	A = 0.15			kAB	25	3.17	-6					(14)
.4	*iso*-$COOHCHClCHClCOOH + H_2O$	H_2O	A = 0.03			kA	60	3.33	-6					(14)
							70	9.08	-6					
							80	2.23	-5					
							90	6.19	-5					
.5	*iso*-$COOHCHClCHClCOOH + OH^-$	H_2O	A = B = 0.086			kAB	25	1.49	-5				*	(14)
							→	8.1	-6					
.6	$CH_2ClCH_2SO_3Na + OH^-$	H_2O				kAB	1.1	2.42	-4					(13)
							9.5	4.44	-4					
							25	1.79	-3	17.4	1.3	9		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.7	$(CH_3)_2CHCl + OH^-$	Et80				kAB	70	6.78	-6				*	(10)
							80	1.89	-5					
							90	5.06	-5	24.8	4.8	10		
.8	$(CH_3)_2CHBr + C_2H_5OH$	C_2H_5OH		H_2SO_4		kA	54.9	1.73	-7					(5)
.9	$(CH_3)_2CHBr + OC_2H_5^-$	C_2H_5OH	B = 0.05			kAB	54.9	2.01	-5					(5)
			0.1				"	2.12	-5					
			2.0				"	9.7	-6					
.10	$(CH_3)_2CHBr + OH^-$	Et60	A = 0.1; B = 0.85			kAB	45	1.57	-5				*	(7)
							60	7.52	-5					
							75	3.20	-4	22.0	2.8	10		
		Et80	"	"		kAB	50	3.89	-5				* (7)	(10)
							80	7.78	-4	22.6	8.3	10		
.11	$(CH_3)_2CHI + OH^-$	Et60				kAB	50	1.22	-4				*	(10)
							69.8	9.08	-4					
							80.0	2.31	-3	22.2	1.4	11		
.12	$(CH_3)_3CCl + H_2O$ (See Supplementary table)	Et80	A = 0.09	NaOH	0-0.1	kA	25	1.44	-6				*	(3)
.13	$(CH_3)_3CBr + C_2H_5OH$	C_2H_5OH		H_2SO_4		kA	54.9	1.98	-4					(5)
.14	$(CH_3)_3CBr + OC_2H_5^-$	C_2H_5OH	B = 0.02			k_1A + k_2AB	54.9						*	(5)
			0.05				k_1	2.33	-4					
			2.0				k_1	2.42	-4					
							k_2	5.0	-5					
.15	$(CH_3)_3CBr + H_2O$ (See Supplemertary table)	Et80	A = 0.173			kA	25	4.69	-5				*	(3)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.16	$(CH_3)_3CI + H_2O$	Et80	A = 0.173			k A	25	1.16	-4				*	(3)
	(See Supplementary table)													
.17	$(C_2H_5)(CH_3)_2CCl + H_2O$	Et60	A = 0.078			k A	25.2	1.10	-4				*	(9)
	(See Supplementary table).	Et80	A = 0.078			k A	25.2	1.00	-5				*	(9)
			0.16				"	9.41	-6					
			0.147				50.0	1.15	-4					
		Et80	A = 0.078	NaOH	0.2	k A	25.2	1.01	-5				*	(9)
.18	$(C_2H_5)(CH_3)_2CBr + H_2O$	Et80	A = 0.07			k A	25.2	4.30	-4				*	(9)
	(See Supplementary table)	"	A = 0.06	NaOH	0.12	k A	25.2	4.01	-4				*	(9)
.19	$(C_2H_5)(CH_3)_2CI + H_2O$	Et80	A = 0.13			k A	25.2	1.29	-3				*	(9)
	(See Supplementary table)	"	A = 0.12	NaOH	0.12	k A	25.2	1.34	-3				*	(9)
.20	$C_6H_{13}CH(CH_3)Cl + H_2O$	Et60				k A	100	1.05	-6				*	(8)
	(See Supplementary table)													
.21	$C_6H_{13}CH(CH_3)Br + H_2O$	Et60				k A	100	3.75	-5				*	(8)
	(See Supplementary table)													
.22	$C_6H_{13}CH(CH_3)Br + OH^-$	Et60	A = 0.057; B = 0.80			k AB	80.0	4.40						(11)
	Aryl-substituted aliphatic halide													
.23	$C_6H_5CH_2CH_2Br + C_2H_5OH$	C_2H_5OH				k A	54.9	1.92	-4				*	(5)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.24	$C_6H_5CH_2CH_2Br + OC_2H_5^-$	C_2H_5OH	B = 1.5 2.5			k AB	54.9 "	1.5 1.6	-4 -4				*	(5)
.25	$C_6H_5CH(CH_3)Br + OC_2H_5^-$	C_2H_5OH	B = 0.05 0.1			k AB	54.9 "	6.58 5.93	-4 -4					(5)
.26	$(C_6H_5)_2CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1 30.4	3.7 1.27	-4 -3	 21.3				(1)
.27	$(p\text{-}CH_3C_6H_4)_2CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1 30.4	1.1 3.7	-4 -4	 21.0				(1)
.28	$(p\text{-}CH_3OC_6H_4)_2CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1 30.4	9.2 3.0	-4 -3	 20.6				(1)
.29	$[p\text{-}(CH_3)_3CC_6H_4]_2CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1 30.4	1.1 3.4	-4 -4	 19.8				(1)
.30	$[p\text{-}NO_2C_6H_4CH_2CH_2N(CH_3)_3]Br$ $\rightarrow NO_2C_6H_4CH{:}CH_2 + N(CH_3)_3 \cdot HBr$	H_2O	0.3			k A	100	4.0	-5					(4)
.31	$[p\text{-}NO_2C_6H_4CH_2CH_2N(CH_3)_3]I$ $\rightarrow NO_2C_6H_4CH{:}CH_2 + N(CH_3)_3 \cdot HI$	H_2O	0.3 - 0.6			k A	100	4.0	-5					(4)
.32	$(p\text{-}FC_6H_4)_2CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1 30.4	3.03 9.4	-3 -3	 19.5				(1)
.33	$(p\text{-}ClC_6H_4)_2CHCH_2Cl + OH^-$	Et92.6wt				k AB	20.1 30.4	9.1 2.82	-4 -3	 19.5				(1)

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.34	$(p\text{-}ClC_6H_4)_2CHCHCl_2 + OH^-$	Et92.6wt				k AB	20.1	5.67	-3					(1)
							30.4	1.72	-2	19.1				
.35	$(p\text{-}ClC_6H_4)_2CHCCl_3 + OH^-$	$H_2O + C_2H_5OH$	76.0 wt%			k AB	20.1	1.32	-2					(1)
			87.0				"	1.89	-2					
			92.6				"	2.48	-2					
			"				30.4	7.11	-2	18.2				
.36	$(p\text{-}ClC_6H_4)(C_6H_5)CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1	3.01	-3					
							30.4	1.0	-2	19.0				(1)
.37	$(p\text{-}BrC_6H_4)_2CHCCl_3 + OH^-$	Et92.6wt				k AB	20.1	3.47	-2					(1)
							30.4	1.03	-1	18.8				
Aromatization														
.38	$\alpha\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$		See Supplementary table											
.39	$\alpha\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$	Et76	A $\sim$ 0.001; B $\sim$ 0.005			k AB	20.1	1.7	-1				*	(2)
.40	$\alpha\text{-}C_6H_6Cl_3 + 3\ C_5H_{10}NH \rightarrow C_6H_3Cl_3 + 3\ C_5H_{10}NH.HCl$	Et95	A = 0.0125; B = 0.0375			k AB	56.2	2.0	-3				*	(15)
							79.5	1.25	-2	19.5	2	10		
.41	$\beta\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$	Et76	See (.42)											(2)
.42	$\beta\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$	Et76	A $\sim$ 0.001; B $\sim$ 0.005			k AB	20.1	$\sim$ 3	-6					(2)
.43	$\gamma\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$		See Supplementary table											
.44	$\gamma\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$	Et76	A $\sim$ 0.001; B $\sim$ 0.005			k AB	20.1	4.4	-2				*	(2)

422.471.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.45	$\gamma\text{-}C_6H_6Cl_6 + 3\ C_5H_{10}NH \rightarrow C_6H_3Cl_3 + 3\ C_5H_{10}NH.HCl$	Et95	A = 0.0125; B = 0.0375			k AB	56.2	9.2	-4				*	(15)
							79.5	3.4	-3	13.8	1	6		
.46	$\delta\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$	See Supplementary table												
.47	$\delta\text{-}C_6H_6Cl_6 + OH^- \rightarrow C_6H_5Cl_5 + Cl^- + H_2O$	Et76					20.1	fast					*	(2)
.48	$C_6H_5Cl_5 + OH^- \rightarrow C_6H_4Cl_4 + Cl^- + H_2O$	Et76	A ~ 0.001; B ~ 0.005			k AB	20.1	1.1	-1				*	(2)
.49	$C_6H_4Cl_4 + OH^- \rightarrow C_6H_3Cl_3 + Cl^- + H_2O$	Et76	A ~ 0.001; B ~ 0.005				20.1	fast					*	(2)
.50	$\delta\text{-}C_6H_6Cl_6 + 3\ C_5H_{10}NH \rightarrow C_6H_3Cl_3 + 3\ C_5H_{10}NH.HCl$	Et95	A = 0.0125; B = 0.0375			k AB	56.2	1.3	-3				*	(15)
							79.5	1.19	-2	20.4	6	10		
.51	$\epsilon\text{-}C_6H_6Cl_6 + 3\ OH^- \rightarrow C_6H_3Cl_3 + 3\ Cl^- + 3\ H_2O$	See Supplementary table												

SUPPLEMENTARY TABLES

Simultaneous first-order hydrolysis and elimination.

Reactions (.12) (.15) (.16) (.17) (.18) (.19) (.20) (.21)

k_E = first-order k for the elimination reaction

k_s = first-order k for the hydrolysis

$k_t = k_E + k_s$ = first-order k for the total reaction (elimination + substitution)

k_t is the rate of formation of the carbonium ion, assumed to be the rate determining step.

	Reaction	Temperature	$10^5 k_E$	$10^5 k_s$	$10^5 k_t$	k_E/k_t
(.12)	$(CH_3)_3CCl + H_2O$	25	0.144	0.710	0.854	0.168
(.15)	$(CH_3)_3CBr + H_2O$	25	4.69	32.5	37.2	0.126
(.16)	$(CH_3)_3CI + H_2O$	25	11.6	78.5	90.1	0.129
(.17)	$(C_2H_5)(CH_3)_2CCl + H_2O$	25	1.00	0.500	1.50	0.333
(.18)	$(C_2H_5)(CH_3)_2CBr + H_2O$	25	43.0	15.3	58.3	0.262
(.19)	$(C_2H_5)(CH_3)_2CI + H_2O$	25	128.8	45.2	174	0.260
(.20)	$C_6H_{13}C(CH_3)Cl + H_2O$	100	0.105	0.700	0.805	0.13
(.21)	$C_6H_{13}C(CH_3)Br + H_2O$	100	3.75	23.0	26.8	0.14

SUPPLEMENTARY TABLES *(continued)*

Aromatization

Solvent CH_3OH . A ~ 5g/l; B = 0.1 *M* . *Temperature* 0° C (12)

Reaction	Fraction of reaction completed	Time (Hours)
(.36) $\alpha - C_6H_6Cl_6 + 3\ OH^-$	0.27	0.5
	0.049	1.0
(.40) $\gamma - C_6H_6Cl_6 + 3\ OH^-$	0.30	2.5
	0.56	5.5
(.43) $\delta - C_6H_6CL_6 + 3\ OH^-$	0.26	0.75
	0.56	2.5
(.48) $\epsilon - C_6H_6Cl_6 + 3\ OH^-$	0.28	3.0
	0.50	6.5

SOLVENTS

Et x = $H_2O + C_2H_5OH$ x % (by volume, except where noted wt).

COMMENTS

(.5) *k* falling in the course of the reaction, possibly as a result of conversion of the *iso* form into the normal form. (.7) (.10) - (.22) Concomitant solvolysis reaction, see 212.471. (.14) First order prevailing at low alkali concentrations; k_1 not corrected for the few % of simultaneously present second-order reaction. (.17) (.18) (.19) Addition of NaOH in the stated amounts is practically without effect on the rate of the first-order elimination reaction, as it is on the rate of the first-order hydrolysis, and of the total reaction. (.23) (.24) With $OC_2H_5^-$ 0.05 - 0.1, about 25 - 50 % of the reaction is second-order. (.39) - (50) Configuration of product not specified. (.39) from (.38). (.42) from (.41). (.44) from (.43). (.48) from (.46); this is the rate determining step of (.46), the remaining steps (.47) and (.49) being fast.

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ELIMINATION
Bond Unsaturation

Liquid phase

Elimination of hydrogen halide from C, N bond
(Chlorimine → Nitrile)

Reaction type $ArCH{:}NX + OR^- \longrightarrow ArCN + HOR + X^-$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		ΔS_a	Literature
					k°	n		A°	n		
.1	$C_6H_5CH{:}NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	k AB	0	1.67	-2					(1) (2)
				30	6.2	-1	19.8	1.2	14	+1.3	
.2	*o* - $CH_3C_6H_4CH{:}NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	k AB	0	4.45	-2					(1)
.3	*p* - $CH_3C_6H_4CH{:}NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	k AB	0	8.66	-3					(1)
.4	*o* - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	k AB	0	2.84	-3					(1)
.5	*m* - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	k AB	0	1.83	-2					(1)
		H_2O + dioxane 50 %	k AB	0	4.83	-3					(1)
.6	*p* - $CH_3OC_6H_4CH{:}NCl + OC_2H_5^-$	H_2O + dioxane 50 %	k AB	0	5.0	-3					(1)
		$H_2O + C_2H_5OH$ 80 %	k AB	0	4.00	-3					(1)
		92.5 %	k AB	0	4.7	-3					(1)
		95 %	k AB	0	4.7	-3					(2)
				30	1.8	-1	19.9	1.0	14	-0.6	

No.	Reaction	Solvent	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		ΔS_a	Literature
					k°	n		A°	n		
.6	*p* - $CH_3OC_6H_4CH:NCl + OC_2H_5^-$	C_2H_5OH (100%)	*k* AB	0	4.9	-3					(2)
	(continued)			30	1.5	-1	17.0	6.1	11	-6.9	
.7	*p* - $CH_3OC_6H_4CH:NCl + OCH_3^-$	$H_2O + CH_3OH$ 95 %	*k* AB	0	5.6	-4					(2)
				30	2.7	-2	21.3	4.7	14	0	
		CH_3OH (100%)	*k* AB	0	3.5	-4					(2)
				10	2.07	-3					
				30	2.27	-2	20.6	4.3	14	-2.4	
.8	3, 4 - $CH_2O_2C_6H_3CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	6.72	-3					(1) (2)
				30	2.77	-1	20.4	1.5	14	-1.6	
.9	$C_6H_5CH:CHCH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	5.8	-3					(1) (3)
				30.5	2.3	-1	20.1	1.8	14	-0.3	
.10	*o* - $C_4H_3OCH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	6.32	-1					(1)
.11	*o* - $NO_2C_6H_4CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	9.0	0					(1)
.12	*m* - $NO_2C_6H_4CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	5.27	-1					(1)
.13	*p* - $NO_2C_6H_4CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	1.30	0					(1)
.14	3 - NO_2-4-CH_3O-$C_6H_3CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	9.65	-2					(1)
.15	*o* - $ClC_6H_4CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	1.28	-1					(1)
		H_2O + dioxane 50 %	*k* AB	0	6.16	-2					(1)
.16	*m* - $ClC_6H_4CH:NCl + OC_2H_5^-$	$H_2O + C_2H_5OH$ 92.5 %	*k* AB	0	1.02	-1					(1)
.17	*p* - $ClC_6H_4CH:NCl + OC_2H_5^-$	H_2O + dioxane 50 %	*k* AB	0	2.83	-2					(1)

No.	Reaction	Solvent	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		ΔS_a	Literature
					k^o	n		A^o	n		
.17	p - $ClC_6H_4CH:NCl + OC_2H_5^-$ *(continued)*	$H_2O + C_2H_5OH$ 80 %	k AB	0	3.93	-2					(1)
		92.5	k AB	0	4.67	-2					(1)
		95	k AB	0	5.0	-2					(2)
				30	1.8	0	20.1	1.4	15	+4.6	
		C_2H_5OH (100%)	k AB	0	6.0	-2					(2)
				30	1.4	0	17.4	1	13	-4.8	
.18	p - $ClC_6H_4CH:NCl + OCH_3^-$	$H_2O + CH_3OH$ 95 %	k AB	0	5.1	-3					(2)
				10	1.82	-2					
				30	1.77	-1	20.1	1.7	14	0	
		CH_3OH (100%)	k AB	0	4.5	-3					(2)
				10	1.61	-2					
				30	1.59	-1	19.5	4.7	13	-2.3	
.19	p - $ClC_6H_4CH:NCl + (C_2H_5)_3N \longrightarrow$ p - $ClC_6H_4CN + (C_2H_5)_3N.HCl$	CH_3OH (100%)	k AB	25	4.0	-5					(2)
				40	1.7	-4	17.6	3.5	8	-22.1	
		C_6H_6	k AB	30	2.5	-5					(2)
				40	4.4	-5	11.9	1.5	4	-44.5	

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(2) W. E. Jordan, H. E. Dyas, D. G. Hill, *ACS* 1941, 63, 2383.

ELIMINATION

of halogen molecule by halogen ions, with charge exchange

Reaction type $\mathrm{RCHXCHXR'} + 2\ \mathrm{X'^-} \rightarrow \mathrm{RCH{:}CHR'} + \mathrm{X'_2} + 2\ \mathrm{X^-}$

$\quad\mathrm{(A)}\quad\mathrm{(B)}\quad\mathrm{(L)}\quad\mathrm{(M)}$

or $\mathrm{RCHXCHXR'} + 3\ \mathrm{X'^-} \rightarrow \mathrm{RCH{:}CHR'} + \mathrm{X'^-_3} + 2\ \mathrm{X^-}$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	ΔH_a	ΔS_a	Literature
						k^o	n				
.1	$CH_2BrCH_2Br + 2\ I^-$	CH_3OH 99 %	B = 0.25	k AB	59.7	8.30	-5				(2)
					74.9	3.70	-4	23.2	0	0	
.2	$CH_3CHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B = 0.25	k AB	59.7	3.13	-6				(2)
					74.9	1.61	-5	25.2	2.0	-0.5	
.3	$CH_2OHCHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B = 0.25	k AB	59.6	5.35	-6				(2)
					74.9	2.70	-5	25.2	2.0	0.4	
.4	$COOHCHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B = 0.25	k AB	44.7	2.85	-5				(2)
					59.4	1.15	-4				
					79.4	4.62	-4				
					85.4	1.10	-3	20.9	2.3	6.3	
.5	$C_2H_5CHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B = 0.25	k AB	59.7	4.12	-6				(2) (1)
					74.9	2.20	-5	25.8	2.6	1.8	
.6	*meso*-$CH_3CHBrCHBrCH_3 + 2\ I^- \rightarrow$ *trans*	CH_3OH 99 %	A = 0.033; B = 0.22	k AB	59.7	2.50	-6				(3) (1)
					74.9	1.55	-5	28.0			

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	ΔH_a	ΔS_a	Literature
						k°	n				
.7	*rac*-$CH_3CHBrCHBrCH_3 + 2\ I \rightarrow$ *cis*	CH_3OH 99 %	A = 0.025; B = 0.25	k AB	59.7	1.28	-6				(3)(1)
					74.9	8.36	-6	28.6			
.8	*meso*-$COOHCHBrCHBrCOOH + 2\ I^- \rightarrow$ *trans*	CH_3OH 99 %	A = 0.02; B = 0.24	k AB	59.5	3.27	-4				(3)
					74.5	1.28	-3				
.9	*rac*-$COOHCHBrCHBrCOOH + 2\ I^- \rightarrow$ *cis*	CH_3OH 99 %	A = 0.02; B = 0.25	k AB	59.5	6.28	-5				(3)
					75.0	3.13	-4	24.6			
.10	$C_3H_7CHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B = 0.25	k AB	59.6	5.12	-6				(2)
					74.6	2.48	-5	24.8	1.6	-0.8	
.11	*meso*-$C_2H_5CHBrCHBrCH_3 + 2\ I^- \rightarrow$ *trans*	CH_3OH 99 %	A = 0.02; B = 0.25	k AB	59.5	4.95	-6				(3)
					75.0	2.64	-5	25.7			
.12	*rac*-$C_2H_5CHBrCHBrCH_3 + 2\ I^- \rightarrow$ *cis*	CH_3OH 99 %	A = 0.02; B $\sim$ 0.2	k AB	59.5	2.82	-6				(3)
					75.0	1.58	-5	26.5			
.13	*meso*-$C_3H_7CHBrCHBrCH_3 + 2\ I^- \rightarrow$ *trans*	CH_3OH 99 %	A = 0.02; B = 0.25	k AB	59.4	8.10	-6				(3)
					75.0	3.98	-5	24.5			
.14	*rac*-$C_3H_7CHBrCHBrCH_3 + 2\ I^- \rightarrow$ *cis*	CH_3OH 99 %	A = 0.02; B = 0.26	k AB	59.4	2.60	-6				(3)
					75.0	1.39	-5	25.8			
.15	*meso*-$C_3H_7CHBrCHBrC_3H_7 + 2\ I^- \rightarrow$ *trans*	CH_3OH 99 %	A = 0.017; B = 0.25	k AB	59.6	7.68	-6				(3)
					75.0	3.78	-5	25.0			
.16	*rac*-$C_3H_7CHBrCHBrC_3H_7 + 2\ I^- \rightarrow$ *cis*	CH_3OH 99 %	A = 0.018; B = 0.24	k AB	59.5	5.70	-6				(3)
					75.0	2.99	-5	25.5			

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^{o} \times 10^{n}$		E	ΔH_a	ΔS_a	Literature
						k^{o}	n				
.17	$C_6H_5CHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B ~ 0.25	k AB	44.7	2.04	-5				(2)
					59.5	1.08	-4				
					74.5	4.48	-4				
					80.1	7.36	-4				
					85.4	1.12	-3	21.7	-1.5	-4	
.18	$C_6H_5CH_2CHBrCH_2Br + 2\ I^-$	CH_3OH 99 %	B ~ 0.25	k AB	59.6	5.06	-6				(2)
					74.9	2.54	-5	24.6	1.4	-1.5	

LITERATURE

(1) R. F. Dillon, W. G. Young, H. J. Lucas, *ACS* 1930, 52, 1953. (2) D. Pressman, W. G. Young, *ACS* 1944, 66, 705. (3) W. G. Young, D. Pressman, C. D. Coryell, *ACS* 1939, 61, 1640.

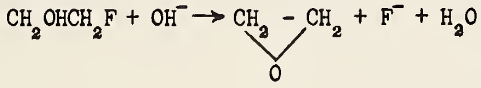
Stereochemical relations, See: S. Winstein, H. J. Lucas, *ACS* 1939, 61, 1576, 1581.

ELIMINATION

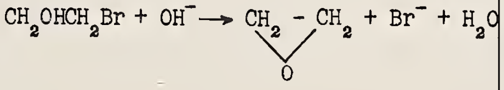
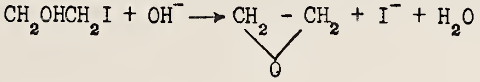
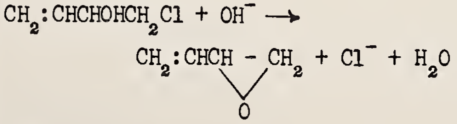
of Hydrogen halide from Halohydrins with Ring closure

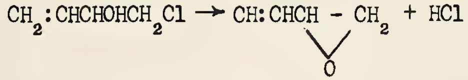
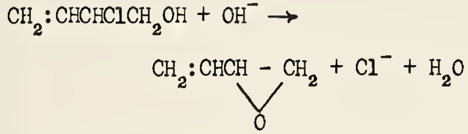
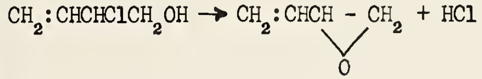
Amounts are in M/l.
Rates are in M/l per sec.

Coded solvents, see at the end of the table

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
								k^o	n		A^o	n	
.1	 $CH_2OHCH_2F + OH^- \rightarrow CH_2 - CH_2 (O) + F^- + H_2O$	H_2O	B > A			kA	30	2.5	-5				(²)(³)
							40	8.5	-5				
							60	6.2	-4	21.5	8.5	10	
		Di 55.0	"			kA	60	7.0	-4				"
		Me 55.0	"			kA	60	3.8	-4				"
.2	$CH_2OHCH_2Cl + OH^-$	H_2O	B > A			kA	0	2.8	-4				(²)(³)
							15	2.54	-3				
							25	1.0	-2				
							35	3.6	-2	23.3	1.1	15	
		H_2O	A = B = 0.091			kAB	0	2.78	-4				(⁴)
			0.073 - 0.098				15	2.57	-3				
			0.040				25	1.01	-2				
			0.042				35	3.6	-2	23.0			
		"	0.04 - 0.07	$NaNO_3$	0.0915	kAB	25	1.0	-2				

432.471.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Literature
								k°	n		A°	n	
.2	$CH_2OHCH_2Cl + OH^-$ *(continued)*	D1 64.2	B > A			kA	0	9.0	-5				(2)(3)
		D1 75	A = B = 0.071			kAB	0	4.52	-4				(4)
			0.09				15	3.33	-3				
			0.043 - 0.07				25	1.17	-2	20.9			
		Me 66.3	B > A			kA	0	7.2	-6				(2)(3)
		Et 74	A = B = 0.075			kAB	0	5.13	-4				(4)
			0.067				15	3.60	-3				
			0.040 - 0.068				25	1.18	-2	20.3			
			0.040	$NaNO_3$	0.040		25	1.19	-2				
.3	 $CH_2OHCH_2Br + OH^- \longrightarrow CH_2 - CH_2 + Br^- + H_2O$	H_2O	B > A			kA	0	1.64	-3				(2)(3)
							5	3.38	-2				
							10	6.59	-2	21.9	5.3	15	
		D1 64.2	B > A			kA	0	7.6	-2				"
		Me 66.3	B > A			kA	0	7.4	-3				"
.4	 $CH_2OHCH_2I + OH^- \longrightarrow CH_2 - CH_2 + I^- + H_2O$	H_2O	B > A			kA	0	1.50	-2				(2)(3)
							5	3.05	-2				
							10	6.40	-2	22.2	8.5	15	
		D1 64.2	B > A			kA	0	9.9	-2				"
		Me 66.3	B > A			kA	0	1.0	-2				"
.5	 $CH_2{:}CHCHOHCH_2Cl + OH^- \longrightarrow CH_2{:}CHCH - CH_2 + Cl^- + H_2O$	H_2O	A = B = 0.1			kAB	0	2.82	-2				(1)
							25	5.0	-1				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
								k^o	n		A^o	n	
.5.1	 $CH_2{:}CHCHOHCH_2Cl \rightarrow CH{:}CHCH - CH_2 + HCl$ (O)	H_2O	0.1			kA	70	9.2	-8				(1)
.6	 $CH_2{:}CHCHClCH_2OH + OH^- \rightarrow CH_2{:}CHCH - CH_2 + Cl^- + H_2O$ (O)	H_2O	A = B = 0.1			kAB	0	1.16	0				(1)
.7	 $CH_2{:}CHCHClCH_2OH \rightarrow CH_2{:}CHCH - CH_2 + HCl$ (O)	H_2O	0.1			kA	30 50 60 70	1.25 1.56 4.7 1.13	-5 -4 -4 -3				(1)

SOLVENTS

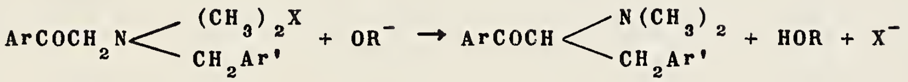
Di 55.0 (64.2) = H_2O + 1,4 - dioxane, dielectric constant = (55.0) (64.2)
Me 55.0 (66.3) = $H_2O + CH_3OH$, dielectric constant = 55.0 (66.3)
Et 74 = $H_2O + C_2H_5OH$, dielectric constant = 74

LITERATURE

(1) R. G. Kadesch, *ACS* 1946, **68**, 46. (2) C. L. McCabe, J. C. Warner, *ACS* 1948, **70**, 4031. (3) J. E. Stevens, C. L. McCabe, J. C. Warner, *ACS* 1948, **70**, 2449. (4) L. O. Winstrom, J. C. Warner, *ACS* 1939, **61**, 1205.

ELIMINATION

of Hydrogen halide from quaternary base

Reaction type 

$$ArCOCH_2N\begin{matrix}(CH_3)_2X\\CH_2Ar'\end{matrix} + OR^- \rightarrow ArCOCH\begin{matrix}N(CH_3)_2\\CH_2Ar'\end{matrix} + HOR + X^-$$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.1	$C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OH^-$	H_2O	A = 0.1; B = 0.1	k A	37.7	4.22	-6	(²)
			0.05 0.05		"	2.34	-6	
			0.05 0.1		"	4.62	-6	
.2	$C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.1; B = 0.1	k A	37.7	5.5	-5	(²)
			0.05 0.05		"	5.3	-5	
			0.05 0.1		"	7.0	-5	
			0.025 0.05		"	7.0	-5	
.3	$C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OC_2H_5^-$	C_2H_5OH	A = 0.1; B = 0.1	k A	37.7	1.65	-4	(²)
			0.5 0.1 - 0.5		37.7	1.77	-4	
.4	$C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OC_3H_7^-$	C_3H_7OH	A = 0.05; B = 0.05	k A	37.7	1.85	-4	(²)
			0.1 0.1		"	1.87	-4	
			0.05 0.1		"	2.1	-4	
.5	$C_6H_5COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH(CH_3)_2^-$	$(CH_3)_2CHOH$	A = 0.1; B = 0.1	k A	37.7	4.03	-4	(²)
			0.05 0.05		"	4.23	-4	
			0.05 0.1		"	4.58	-4	

452.471.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.6	$C_6H_5COCH_2N(m\text{-}CH_2C_6H_4OCH_3)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	6.5	-5	(2)
.7	$C_6H_5COCH_2N(p\text{-}CH_2C_6H_4OCH_3)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	5.3	-5	(2) (1)
.8	$C_6H_5COCH_2N(o\text{-}CH_2C_6H_4NO_2)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	16.4	1.78	-3	(2)
.9	$C_6H_5COCH_2N(m\text{-}CH_2C_6H_4NO_2)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	16.4	6.53	-3	(2)
.10	$C_6H_5COCH_2N(p\text{-}CH_2C_6H_4NO_2)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	16.4	1.25	-4	(2)
.11	$C_6H_5COCH_2N(o\text{-}CH_2C_6H_4Cl)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	16.4	6.12	-5	(2)
.12	$C_6H_5COCH_2N(m\text{-}CH_2C_6H_4Cl)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	1.70	-4	(2)
.13	$C_6H_5COCH_2N(p\text{-}CH_2C_6H_4Cl)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	1.94	-4	(2)
.14	$C_6H_5COCH_2N(o\text{-}CH_2C_6H_4Br)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	16.4	8.18	-5	(2)
.15	$C_6H_5COCH_2N(m\text{-}CH_2C_6H_4Br)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	1.46	-4	(2)
.16	$C_6H_5COCH_2N(p\text{-}CH_2C_6H_4Br)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	2.00	-4	(2)
.17	$C_6H_5COCH_2N(o\text{-}CH_2C_6H_4I)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	16.4	1.38	-4	(2)
.18	$C_6H_5COCH_2N(m\text{-}CH_2C_6H_4I)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	1.33	-4	(2)
.19	$C_6H_5COCH_2N(p\text{-}CH_2C_6H_4I)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	2.27	-4	(2)
.20	$p\text{-}CH_3C_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	kA	37.7	7.68	-5	(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
						k^o	n	
.21	p-$ClC_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	k A	37.7	5.65	-5	(1)
.22	m-$BrC_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	k A	37.7	1.46	-4	(2)
.23	p-$IC_6H_4COCH_2N(CH_2C_6H_5)(CH_3)_2Br + OCH_3^-$	CH_3OH	A = 0.05; B = 0.1	k A	37.7	5.46	-5	(1)

LITERATURE

(1) J. L. Dunn, T. S. Stevens, *CSL* **1932**, 1926.
(2) T. Thomson, T. S. Stevens, *CSL* **1932**, 55.

ELIMINATION

Liquid phase

CO_2 from aliphatic carboxylate

Amounts are in M/l.

Rates are in M/l per sec.

Reaction type $RCOO^- + H_2O \rightarrow RH + HCO_3^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$	
						k°	n		A°	n
.1	$CCl_3COO^- + H_2O \rightarrow CHCl_3 + HCO_3^-$	H_2O	0.5	k A	44.0	2.19	-7			
					76.4	4.19	-5			
					99.8	1.32	-3	36.6	3.6	18
.2	$CBr_3COO^- + H_2O \rightarrow CHBr_3 + HCO_3^-$	H_2O	0.5	k A	60.3	2.29	-4			
					76.4	1.16	-3	24.1	1.8	12
.3	$C_6H_5C\vdots CCOO^- + H_2O \rightarrow C_6H_5C\vdots CH + HCO_3^-$	H_2O	0.5	k A	87.0	4.7	-6			
					125.7	3.67	-4	31.5	8.5	13

COMMENTS

(.3) k at 87.0°C from initial rate; competing hydrogenation interferes at low temperatures.

LITERATURE

R. A. Fairclough, *CSL* 1938, 1186.

DISSOCIATION

N oxides

Gas phase

Amounts are in mm Hg.
Rates aee in mm Hg per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
					k^o	n	
.1	$N_2O_4 \rightarrow 2\ NO_2$	132	kA	1	4.5	+ 3	
		156		"	5.0	+ 3	
		260		"	7.0	+ 3	
		162		25	4.4	+ 4	
		260		"	4.8	+ 4	
		668		"	6.0	+ 4	
		235		30	5.5	+ 4	
		260		"	6.7	+ 4	
		342		"	7.5	+ 4	14

COMMENTS

Sound dispersion measurements. Data cover a frequency range 9 - 450 kilocycles /sec, at relatively few wave lengths, and are believed to be independent of error due to sound absorption. Data of (5) consistent with previous estimates (1,2,3). Sound dispersion due to lag in establishing thermal equilibrium between translation or rotation and vibration may modify the above interpretation (4). k falls with falling pressure especially at low pressure.

LITERATURE

(1) P.D.Brass, R.C.Tolman, *ACS* 1932, **54**, 1003.
(2) E.Grüneisen, E.Goens, Ann. Physik 1923, **72**, 193.
(3) G.B.Kistiakowsky, W.T.Richards, *ACS* 1930, **52**, 4661.
(4) H.O.Kneser, O.Gauler, *PZ* 1936, **37**, 627.
(5) W.T.Richards, J.A.Reid, *JCP* 1933, **1**, 114.

DISSOCIATION

Dicarboxylate → Anhydride + Aldehyde

Rate measured + Δp

Gas phase

Amounts are in mm Hg.

Rates are in mm Hg per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
					k^o	n		A^o	n
.1	$(CH_3COO)_2CH_2 \rightarrow (CH_3CO)_2O + HCHO$	0.34	k A	279	3.28	-4			
		0.14 - 0.52		296.5	7.14	-4			
		0.22 - 0.32		304.0	1.18	-3			
		0.22 - 0.37		312.1	1.95	-3			
		0.14 - 0.90		316.5	2.25	-3	32.9	2	10
.2	$(CH_3COO)_2CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CHO$	0.18 - 0.80	k A	236	2.3	-4			
				246	2.7	-4			
				260	1.0	-3			
				267	1.1	-3			
				278	2.5	-3			
				285	3.2	-3			
				297	7.6	-3	32.9	2	10
.3	$(CH_3COO)_2CHCl_3 \rightarrow (CH_3CO)_2O + CCl_3CHO$	263 - 547	k A	230	5.5	-5			
		200 - 281		240	1.15	-4			
		174 - 363		250	1.90	-4			
		172 - 390		260	3.50	-4			
		218 - 273		270	6.45	-4			
		50 - 362		280	1.23	-3			
		89 - 268		290	2.10	-3	33.0	1.3	10
.4	$(CH_3COO)_2CH:CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CH:CHCHO$	122 - 421	k A	219	3.5	-4			
		169 - 341		230	6.3	-4			
		264 - 341		240	1.15	-3			

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
					k^o	n		A^o	n
.4	$(CH_3COO)_2CH{:}CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CH{:}CHCHO$	197 - 251	k A	249	2.40	-3			
	(*continued*)	96 - 513		260	3.70	-3			
		106 - 235		270	6.9	-3			
		77 - 187		280	1.30	-2	33.0	1.3	11
.5	$(CH_3COO)_2CHC_3H_7 \rightarrow (CH_3CO)_2O + C_3H_7CHO$	269	k A	211.4	3.94	-5			
		128		227	1.28	-4			
		120		244.8	3.86	-4			
		213		263	1.07	-3			
		125		279	1.11	-3	32.9	3.2	10
.6	$(CH_3COO)_2CHC_6H_{13} \rightarrow (CH_3CO)_2O + C_6H_{13}CHO$	88 - 320	k A	230	1.45	-4			
		134 - 219		240	2.40	-4			
		117 - 256		250	4.89	-4			
		184 - 344		260	9.0	-4			
		130 - 271		270	1.70	-3			
		266 - 316		280	2.76	-3			
		133 - 447		290	5.20	-3	33.0	3.0	10
.7	$(CH_3COO)_2CHC_6H_5 \rightarrow (CH_3CO)_2O + C_6H_5CHO$	20 - 400	k A	220	4.0	-4			
				230	6.3	-4			
				240	1.18	-3			
				250	2.30	-3			
				260	4.40	-3			
				280	7.40	-3			
				290	9.11	-3	33.0	1.3	11
.8	$(CH_3COO)_2CH(o\text{-}C_6H_4Cl) \rightarrow (CH_3CO)_2O + o\text{-}ClC_6H_4CHO$	100 - 500	k A	230	6.6	-4			
				240	1.08	-3			
				250	1.85	-3			
				260	2.90	-3			

511.443.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$	
					k°	n		A°	n
.8	$(CH_3COO)_2CH(o\text{-}C_6H_4Cl) \longrightarrow (CH_3CO)_2O + o\text{-}ClC_6H_4CHO$	100 - 500	k A	270	6.30	-3			
	(continued)			280	1.00	-2	33.0	1.3	11
.9	$(CH_3COO)_2$:CH:CH ⟶ $(CH_3CO)_2O$ + CH:CHCHO	188 - 336	k A	220	3.0	-4			
	O< | | >O	20 - 191		230	6.0	-4			
	CH:CH CH:CH	122 - 245		240	1.05	-3			
		104 - 521		250	1.90	-3			
		162 - 330		260	3.50	-3			
		159 - 416		270	7.0	-3			
		72 - 290		280	1.20	-2	33.0	1.3	11
.10	$(CH_3COO)_2HCCH(OCOCH_3)_2 \longrightarrow 2(CH_3CO)_2O + OCHCHO$		k A	265	2.12	-4			
				275	4.5	-4			
				284	8.0	-4			
				295	1.58	-3			
				310	4.08	-3	39.2	1.8	12
.11	$(C_2H_5COO)_2CH_2 \longrightarrow (C_2H_5CO)_2O + HCHO$	50 - 2300	k A	220 - 305			33	1.7	9
.12	$(C_2H_5COO)_2CHCH_3 \longrightarrow (C_2H_5CO)_2O + CH_3CHO$	95	k A	221	7.0	-5			
		63		229.2	1.24	-4			
		155		238.4	2.19	-4			
		62		244.3	3.10	-4			
		317		254.4	5.35	-4			
		290		265	9.10	-4	32.9	2.5	10
.13	$(C_3H_7COO)_2CHCH_3 \longrightarrow (C_3H_7CO)_2O + CH_3CHO$	32 - 182	k A	222	4.5	-5			
		90		240	1.80	-4			
		105		253	4.25	-4			
		36 - 100		266	8.5	-4			
		144 - 273		290	2.6	-3	33.0	1.8	10

511.443.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$	
					k°	n		A°	n
.14	$(C_3H_7COO)_2CHCCl_3 \longrightarrow (C_3H_7CO)_2O + CCl_3CHO$	53 - 213	k A	240	1.4	-4			
		78 - 115		250	2.05	-4			
		114 - 144		260	4.25	-4			
		43 - 253		270	9.0	-4			
		156 - 221		280	1.40	-3			
		188 - 242		290	2.50	-3	33.0	1.3	10
.15	$(C_3H_7COO)_2CHC_6H_5 \longrightarrow (C_3H_7CO)_2O + C_6H_5CHO$	100 - 500	k A	230	7.0	-4			
				240	1.41	-3			
				250	2.35	-3			
				260	3.84	-3			
				270	6.40	-3			
				280	1.00	-2	33.0	1.3	11

COMMENTS

Proof of homogeneity given by packing. Final pressure change in agreement with theoretical equation.

(.11) Reversible, but secondary decomposition of HCHO precludes equilibrium determination and reduces precision of forward rates.

LITERATURE

C. C. Coffin, CJR^B 1931, 5, 636. J. R. Dacey, C. C. Coffin, CJR^B 1932, 6, 417. C. C. Coffin, W. B. Beazley, CJR^B 1937, 15, 229. C. C. Coffin, J. R. Dacey, N. A. D. Parlee, CJR^B 1937, 15, 247. N. A. D. Parlee, J. R. Dacey, C. C. Coffin, CJR^B 1937, 15, 254. J. R. Dacey, C. C. Coffin, CJR^B 1937, 15, 260. J. R. Dacey, C. C. Coffin, JCP 1939, 7, 315. N. A. D. Parlee, J. C. Arnell, C. C. Coffin, CJR^B 1940, 18, 223. J. C. Cornell, J. R. Dacey, C. C. Coffin,, CJR^B 1940, 18, 410.

DECOMPOSITION

Aldehyde hydrate

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
								k^o	n
.1	$CH_3CH(OH)_2 \rightarrow CH_3CHO + H_2O$	$(CH_3)_2CO$ 91 % + H_2O 9 %	1.3 wt %	X =		$k\,A[X]$			
				HCOOH	0 - 0.002		25	1.67	0
				CH_3COOH	0 - 0.006		"	7.37	−1
				C_2H_5COOH	0 - 0.005		"	6.91	−1
				$CH_2ClCOOH$	0 - 0.0006		"	5.60	0
				$CHCl_2COOH$	0 - 0.0002		"	2.96	+1
				C_6H_5COOH	0 - 0.001		"	2.27	0
				C_6H_5OH	0 - 2.2		"	6.95	−4
				$o\text{-}NO_2C_6H_4OH$	0 - 0.2		"	1.28	−2
				2, 4-$(NO_2)_2C_6H_3OH$	0 - 0.001		"	3.49	0
				CH_3NO_2	0 - 4.3		"	3.22	−5
				$C_2H_5NO_2$	0 - 3.3		"	1.07	−4

COMMENTS

Dilatometric measurements. X is the undissociated part of the catalyst; a correction allowing for the dissociation was deducted from the observed k', by $k = k'(-0.4K^{0.225})$.

Selected data only are tabulated; further data for a series of acids, phenols, and amides, in the original. Reverse reaction, see 612.410.

LITERATURE

R. P. Bell, W. C. E. Higginson, *PRS*^{A} 1949, 197, 141.

DECOMPOSITION

Cyanohydrins

Reaction type $ArCH(OH)CN \rightarrow ArCHO + HCN$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
							k^o	n
.1	$C_6H_5CH(OH)CN$	C_2H_5OH	$C_5H_5N.C_6H_5COOH$	0.01	kA	20	8.7	-11
.2	p-$CH_3C_6H_4CH(OH)CN$	C_2H_5OH	$C_5H_5N.C_6H_5COOH$	0.01	kA	20	8.8	-11
.3	p-$C_2H_5C_6H_4CH(OH)CN$	C_2H_5OH	$C_5H_5N.C_6H_5COOH$	0.01	kA	20	8.2	-11
.4	p-$(CH_3)_2CHC_6H_4CH(OH)CN$	C_2H_5OH	$C_5H_5N.C_6H_5COOH$	0.01	kA	20	6.8	-11
.5	p-$(CH_3)_3CC_6H_4CH(OH)CN$	C_2H_5OH	$C_5H_5N.C_6H_5COOH$	0.01	kA	20	6.8	-11

COMMENTS

Reverse reaction, see 612.415.

LITERATURE

J. W. Baker, M. L. Hemming, *CSL* **1942**, 191.

DECOMPOSITION

Liquid phase

Diacetone alcohol dissociation

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$CH_3COCH_2C(CH_3)_2OH \longrightarrow 2(CH_3)_2CO$	H_2O	~ 0.1	NaOH	0.01	kA	20	4.79	-5		*	(7)
					0.06		"	3.02	-4			
					0.10		"	5.15	-4			
					0.01		25	7.50	-5			"
					0.06		"	4.73	-4			
					0.10		"	8.06	-4			
					0.01		30	1.25	-4			"
					0.06		"	7.75	-4			
					0.10		"	1.34	-3			
					0.01		35	2.03	-4			"
					0.06		"	1.27	-3			
					0.10		"	2.17	-3	18		
		H_2O	~ 0.1	NaOH	0.05	kA						
				+ NaCl	0.05		20	2.47	-4			"
					0.55		"	2.15	-4			
					0.95		"	1.95	-4			
					0.05		25	3.84	-4			"
					0.55		"	3.29	-4			
					0.95		"	2.98	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.1	$CH_3COCH_2C(CH_3)_2OH \rightarrow 2(CH_3)_2CO$ *(continued)*				0.05		30	6.29	-4			(7)
					0.55		"	5.53	-4			
					0.95		"	5.08	-4			
					0.05		35	1.04	-3			"
					0.55		"	8.90	-4			
					0.95		"	8.01	-4			
		$H_2O + CH_3OH$ 0 %	~ 0.1	NaOH	0.10	kA	20	5.15	-4			"
		20					"	2.76	-4			
		60					"	7.97	-5			
		0		"	"		25	8.06	-4			"
		20					"	4.45	-4			
		60					"	1.49	-4			
		0		"	"		30	1.34	-3			"
		20					"	7.71	-4			
		60					"	2.44	-4			
		0		"	"		35	2.17	-3			
		20					"	1.29	-3			
		60					"	4.71	-4			
		H_2O	~ 0.1	NaOH ~	0.1	kA						
				+ NaCl	0.0		25	7.54	-4		*	(1)
					1.0		"	5.72	-4			
					3.0		"	3.86	-4			
					6.0		"	3.00	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	Comments	Literature
								k°	n			
.1	$CH_3COCH_2C(CH_3)_2OH \longrightarrow 2(CH_3)_2CO$ *(continued)*			KOH ~	0.1	kA						
				+ KCl	0.0		25	7.82	-4			(1)
					1.0		"	6.36	-4			
					3.0		"	4.84	-4			
		H_2O	0.43	NaOH	0.0023	kA	25.2	1.72	-5		*	(4)
					0.0094		"	8.50	-5			
					0.018		"	1.66	-4			
					0.045		"	4.32	-4			
					0.094		"	8.3	-4			
		H_2O		NaOH	0.090	kA	15.0	3.50	-4			(3)
		D_2O 99 %		NaOH	0.091	"	15.0	3.97	-4			"
					0.133		"	6.40	-4			
		$H_2O + C_2H_5OH$ 50 %	0.0805									
		CH_3NH_2	0.060	+ $CH_3NH_2.HCl$	0.020	kA	25	4.78	-5			(8)
			0.090		0.030		"	6.44	-5			
			0.150		0.050		"	1.03	-4			
		$H_2O + CH_3OH$ 75 %										
		CH_3NH_2	0.045	+ $CH_3NH_2.HCl$	0.135	kA	25	4.16	-5			"
			0.075		0.150		"	6.56	-5			
			0.120		0.040		"	1.01	-4			
			0.150		0.030		"	1.17	-4			

COMMENTS

Data of (7)(1)(4)(8) from dilatometric, data of (3) from viscosity measurements. The base of logarithms used is explicitly stated by (7) to be 10; consequently, these data have been converted to natural logarithms. By comparison with the converted data of (7), the data of (1) and (4) must also have been to the basis 10, and have been converted accordingly. Agreement of the converted *k* of (1) and (4) with (7) is fair. From all data, the rate appears to be very nearly proportional to $[OH^-]$ in the range investigated. Extensive data of *k* in the presence of NaOH (+ NaF, $Na_2CrO_4^-$, $NaNO_2$, $NaNO_3$, NaCl, NaBr, NaI, NaSCN, NaCN, Na_2CO_3) and KOH (+ K_2SO_4, K_2CrO_4, KNO_2, KNO_3, $KClO_3$, KCl, KBr, KI, KSCN, KCN) at close concentrations, in NaOH, KOH, and LiOH, + salts, and in the presence of KOH + KCl, NaOH + NaCl, LiOH + LiCl at equal total concentrations and varying proportions, and discussions, see original (1). Discussions of the data of (1) from the point of view of ionic strength and dielectric constant effects, see (2). Activation energy calculations on the basis of the data of (7), see (5).

LITERATURE

(1) G.Akerlöf, *ACS* 1926, **48**, 3046; 1927, **49**, 2960; 1928, **50**, 1272.
(2) E.S.Amis, G.Jaffe, R.T.Overman, *ACS* 1944, **66**, 1823.
(3) J.C.Hornel, J.A.V.Butler, *CSL* 1936, 1361.
(4) K.Koelichen, *ZPC* 1900, **33**, 129.
(5) V.K.LaMer, *JCP* 1933, **1**, 289.
(6) V.K.LaMer, M.L.Miller, *ACS* 1935, **57**, 2674.
(7) G.M.Murphy, *ACS* 1931, **53**, 977.
(8) F.H.Westheimer, W.A.Jones, *ACS* 1941, **63**, 3283.

DECOMPOSITION

Bond Unsaturation

Loss of hydrogen halide

Gas phase

Amounts are in mm Hg.
Rate constants are in sec^{-1}.

No.	Reaction	Amount of reactant	Addend (catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.1	$C_2H_5Br \rightarrow C_2H_4 + HBr$	140 - 360			kA	395	5.9	-4				*	(7)
						405	1.1	-3					
						420	2.5	-3	55	3.8	14		
		215 - 650			kA	375	3.3 - 5.5	-4				*	(5)
						388	6.6 - 11.7	-4					
						402	1.67	-3	~ 50	~ 1	13		
.1.1	$C_2H_5Br \rightarrow C_2H_4 + HBr$	190	Br_2	6.2	kA	400	1.0	-3				*	(2)
				14		"	1.6	-3					
				25		"	2.5	-3	22				
.2	$C_3H_7Br \rightarrow C_3H_6 + HBr$	54			kA	353.5	4.5	-4				*	(5)
		215				"	1.05	-3					
		274				"	9.7	-4					
.3	$(CH_3)_2CHBr \rightarrow C_3H_6 + HBr$	265			kA	335	1.35	-4				*	(6)
.4	$(CH_3)_3CCl \rightarrow C_4H_8 + HCl$	300			kA	280	8.7	-4				*	(6)
					kA	270 - 372			46.0	1.9	14		(1)
.5	$(CH_3)_3CBr \rightarrow (CH_3)_2C{:}CH_2 + HBr$	~ 100			kA	237	1.0	-4				*	(4)
						253	3.4	-4					
						267	9.4	-4					
						286	3.25	-3					
						290	4.2	-3	40.5	2	13		

521.471.

No.	Reaction	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.6	$(C_2H_5)(CH_3)_2CBr \rightarrow C_5H_{10} + HBr$				kA	270 – 372			46.0	4.5	14		(1)

COMMENTS

General. All data from manometric measurements. (.1)(.1.1) Data of (7) more accurate than (5). The reaction is largely homogeneous but certainly accompanied by wall reaction. Reaction products suppress wall catalysis. k falls at lower pressures, e.g. decreases to 50 % under 20 mm at 395°C, to 35 % at 405°C (7). Traces of Hg retard the reaction. N_2 and H_2 decrease k at low pressures (6). NO has no effect. For the Br_2-catalyzed reaction (2), roughly $k \sim [Br_2]^{1/2}$. See further (3). (.2) No evidence for first order. (.3)(.4) k calculated from half-times assuming first order. (.5) Selected points. Proof of homogeneity given. (.6) Assuming E to be the same as for reaction (.4).

LITERATURE

(1) D.Brearly, G.B.Kistiakowsky, C.H.Stauffer, *ACS* 1936, **58**, 43. (2) F.Daniels, P.L.Veltman, *JCP* 1939, **7**, 756. (3) P.Fugassi, F.Daniels, *ACS* 1938, **60**, 771. (4) G.B.Kistiakowsky, C.H.Stauffer, *ACS* 59, 165, 1937. (5) E.T.Lessig, *JPC* 1932, **36**, 2325. (6) E.L.Vernon , F.Daniels, *ACS* 1932, **54**, 2563. (7) E.L.Vernon, F.Daniels, *ACS* 1933, **55**, 922.

DECOMPOSITION

Bond Unsaturation

Gas phase

Mass-action in M/l.
Rates in M/l per sec.

Loss of halogen molecule

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments.	Literature
					k^o	n			
.1	$CH_2ClCH_2Cl \rightarrow C_2H_4 + Cl_2$	355 mm	kA	360	1.67	-4		*	(3)
.2	$CH_2BrCH_2Br \rightarrow C_2H_4 + Br_2$	355 mm	kA	360	1.15	-3		*	(3)
.3	$CH_2ICH_2I \rightarrow C_2H_4 + I_2$		$kA + k'A[I_2]^{1/2}$	205	k 9.0	-4		*	(1)
				"	k' 3.1	-2			
				220	k 2.4	-3			
				"	k' 7.4	-2			
				230	k 4.4	-3	36		
				"	k' 1.3	-1	29		
.4	2 *rac*-$(C_2H_5)(CH_3)CHI \rightarrow C_4H_{10} + C_4H_8 + I_2$	100 - 250 mm	$kA + k'A[I_2]^{1/2}$					*	(4)
				238.0	k 1.3	-5			
				"	k' 7.6	-4			
				254.0	k 4.0	-5			
				"	k' 2.12	-3			
				276.0	k 1.90	-4	39.4		
				"	k' 8.36	-3	35.2		

521.477.

COMMENTS

(.1) (.2) Manometric measurements; k calculated from half-time. (.3) k' converted from (mm Hg)$^{-1/2}$ to (M/l)$^{-1/2}$ units. Packing (at 205° and 220°) decreases k slightly, increases k' slightly, and increases slightly both E and E'. Reaction partly heterogeneous also according to (^{2}) who gives rate data at 65° and 75°C. The (manometric) rate of decomposition is said to be best represented by zero order in the initial stage, then by first order, and finally by second order (^{2}). (.4) Manometric measurements; k' converted from (M/ml)$^{-1/2}$ to (M/l)$^{-1/2}$ units. Mechanism proposed: $A \rightarrow C_4H_9 + I$ (k_1); $A + I \rightarrow C_4H_9 + I_2$ (k_2); $C_4H_9 + C_4H_9 \rightarrow C_4H_{10} + C_4H_8$ (fast); ($C_4H_9 + C_4H_9 \rightarrow C_8H_{18}$) (fast); $I_2 \rightleftarrows I + I$ (K); $k = k_1$; $k' = k_2K^{1/2}$.

LITERATURE

(^{1}) L.B.Arnold, G.B.Kistiakowsky, *JCP* 1933, 1, 166. (^{2}) T.Iredale, L.W.C.Martin, *JPC* 1934, 38, 365. (^{3}) E.T.Lessig, *JPC* 1932, 36, 2325. (^{4}) R.A.Ogg jr., M.Polanyi, *TFS* 1935, 31, 482.

DECOMPOSITION
Bond Unsaturation
Dehydration

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$CH_3CHOHCH_2CHO \rightarrow$ *trans*-$CH_3CH{:}CHCHO + H_2O$	H_2O		HNO_3	0.478	$k\,A[H^+]$	25	8.13	−6		*	(4)
					1.43		"	7.77	−6			
					1.905		"	8.28	−6			
				"	0.482		35	2.69	−5			
					0.96		"	2.83	−5			
					1.86		"	2.78	−5	23.5		
				$HClO_4$	0.569		25	6.35	−6			"
					0.949		"	6.45	−6			
					1.88		"	7.66	−6			
				"	0.373		35	2.43	−5			
					0.750		"	2.52	−5			
					1.872		"	2.90	−5	24.5		
.2	$CH_3CHOHCH_2COOH \rightarrow$ *trans*-$CH_3CH{:}CHCOOH + H_2O$	H_2O	0.01 − 0.02	$HClO_4$	1 − 2	$k\,A[H^+]$	90.0	3.89	−7		*	(3)
							111.3	2.78	−6	48.1		
.3	$(CH_3)_2COHCH_2CHO \rightarrow (CH_3)_2C{:}CHCHO + H_2O$	H_2O		HNO_3	0.5 − 1	$k\,A[H^+]$	20	5.00	−6		*	(2)
							25	8.88	−6			
							35	3.11	−5	22.4		
.4	$C_2H_5CHOHCH_2COOH \rightarrow CH_3CH{:}CHCH_2COOH + H_2O$	H_2O	1.0	NaOH	1.2	$k\,A$	100	3.5	−7		*	(1)
.5	$C_2H_5CHOHCH_2COOH \rightarrow C_2H_5CH{:}CHCOOH + H_2O$	H_2O	1.0	NaOH	1.2	$k\,A$	100	4.0	−7		*	(1)

COMMENTS

(.1) k calculated from experimental $k' = k[H^+]$; first order in $[H^+]$ appears approximate. (.2) Reverse reaction, see 622.442. (.3) KNO_3, $NaNO_3$ added to total $\mu = 0.5 - 2$. (.4) (.5) Rate constants calculated from the rate of establishment of the equilibrium

$$C_2H_5CH{:}CHCOOH \rightleftarrows CH_3CH{:}CHCH_2COOH$$
$$\searrow\!\!\nwarrow C_2H_5CHOHCH_2COOH \swarrow\!\!\nearrow$$

LITERATURE

([1]) D. J. G. Ives, R. H. Kerlogue, *CSL* 1940, 1362. ([2]) H. J. Lucas, W. T. Stewart, D. Pressman, *ACS* 1944, 66, 1818. ([3]) D. Pressman, H. J. Lucas, *ACS* 1939, 61, 2271. ([4]) S. Winstein, H. J. Lucas, *ACS* 1937, 59, 1461.

DECOMPOSITION

Bond Unsaturation

Elimination of quaternary base

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$	
						k^{o}	n
.1	$[C_6H_5CH_2CH_2N(CH_3)_3]OH \rightarrow C_6H_5CH{:}CH_2 + N(CH_3)_3HOH$	H_2O	0.165 - 0.330	kA^2	100	5.9	-4
.2	$[p - NO_2C_6H_4CH_2CH_2N(CH_3)_3]^+ \rightarrow p - NO_2C_6H_4CH{:}CH_2 + N(CH_3)_3H^+$	H_2O	0.3	kA	100	4.0	-5

COMMENTS

(.1) Second order indicates mass action of each of the two ions. (.2) Iodide and bromide both decompose following a first-order law, with the same value of k; consequently, the rate is that of the decomposition of the quaternary cation. Excess of $N(CH_3)_3HI$ or $N(CH_3)_4I$ has no effect.

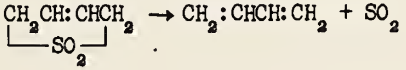
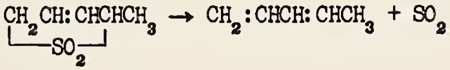
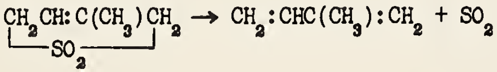
LITERATURE

E. D. Hughes, C. K. Ingold, *CSL* **1933**, 523.

DECOMPOSITION
Bond Unsaturation
Loss of SO_2 group

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Medium	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*
					k^o	n	
.1	 $\underbrace{CH_2CH{:}CHCH_2}_{SO_2} \rightarrow CH_2{:}CHCH{:}CH_2 + SO_2$	pure A	*k*A	120	2.0	-4	
				125	2.5	-4	
				135	7.0	-4	27.3
.2	 $\underbrace{CH_2CH{:}CHCHCH_3}_{SO_2} \rightarrow CH_2{:}CHCH{:}CHCH_3 + SO_2$	pure A	*k*A	85	5.5	-5	
				90	8.68	-5	
				94	1.18	-4	19.5
.3	 $\underbrace{CH_2CH{:}C(CH_3)CH_2}_{SO_2} \rightarrow CH_2{:}CHC(CH_3){:}CH_2 + SO_2$	pure A	*k*A	100	1.52	-5	
				120	1.55	-4	
				138	1.12	-3	32.9

LITERATURE

L. R. Drake, S. C. Stowe, A. M. Partansky, *ACS* 1946, 68, 2521.

REDUCTIVE DECOMPOSITION

Gas phase

Rate constants in sec^{-1}.

No.	Reaction	Wall	Amount of reactant	Carrier Gas	Surface/volume ratio (*s/v*)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
								k^o	*n*			
.1	$H_2O_2 \longrightarrow H_2 + O_2$	B_2O_3 (on pyrex)	1 - 2 mm Hg	N_2 (1 atm)	7 cm^{-1}	*k*A	467	1.8	-1		*	(^{1})
							500	5.0	-1			
							521	1.19	0	40		
				"	3 cm^{-1}	"	467	1.1	-1			"
							500	5.0	-1			
							521	1.11	0	50		
				O_2 (1 atm)	7 cm^{-1}	"	500	3.8	-1			"
							542	1.6	0	40		
				"	3 cm^{-1}	"	500	2.1	-1			"
							542	3.0	0			
.2	$H_2O_2 + H_2 \longrightarrow 2\ H_2O$	B_2O_3 (on pyrex)	A = 1 - 2 mm Hg;	N_2 ($N_2 + H_2$ = 1 atm)	3 cm^{-1}	*k*A	467	1.45	0		*	(^{2})
		B (mole fraction)	~ 0.4		"					54		
			0.074							64		
			~ 0.4		7 cm^{-1}					37		
			0.074							41		

COMMENTS

(.1) At least largely homogeneous by the slight effect of s/v between 7 and 3 cm^{-1}. $E = 40$ is by 13 kcal less than $H_2O_2 \rightarrow 2\ OH$; difference possibly attributable to some amount of wall reaction. $E = 50$ at the lower s/v is closer to $H_2O_2 \rightarrow 2\ OH$. Possibly $E = 40 - 50$ might correspond to $H_2O_2 \rightarrow H_2O + O$ (35 kcal) + excess activation. The selected data correspond to a flow rate of 0.5 l/min ; no appreciable effect of variation of flow rate.

(.2) Simplified from the expression given in the original, rate law

$$-dA/dt = k_i \frac{k_1A^2B}{k_2A + k_3B + m} \qquad (k_i = \text{initiation})$$

giving, at low H_2 ($\lesssim 0.4$ mole fraction), rate $\sim AB$, and tending, at increasingly higher H_2, towards rate $\sim A^2$.

Actual order in A, between 1 and 2; in H_2, not higher than 1, and decreasing with increasing $[H_2]$.

Surface/volume effects:

Between $s/v = 3$ and 7 cm^{-1}.

(a) at 467°, at low H_2, increase of s/v accelerates
" " " high " " " " decelerates

(b) at 480°, s/v without effect

(c) at 500°, increase of s/v decelerates at all H_2.

Mechanism:

Initiation partly homogeneous, partly at the wall; termination at the wall.

Initiation	$H_2O_2 \rightarrow 2\ OH$
	$H_2O_2 + w \rightarrow 2\ OH$
Propagation	$OH + H_2 \rightarrow H_2O + H$
	$H + H_2O_2 \rightarrow H_2O + OH$
Termination	$H + w$
	$OH + w$

COMMENTS *(continued)*

This mechanism gives the rate law schematized above. Replacement of H_2 by an equal proportion of O_2 results in from considerable reduction of the amount of H_2O_2 decomposed to suppression of decomposition and even occasional over-production of H_2O_2; attributed to initiation of the $H_2 + O_2$ reaction by H_2O_2.

LITERATURE

(1) C. K. McLane, *JCP* 1949, 17, 379.
(2) C. K. McLane, *JCP* 1950, 18, 972.

REDUCTIVE DECOMPOSITION

C oxyhalides

Gas phase

Rate measured $+\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Literature
					k°	n		A°	n	
.1	$COCl_2 \rightarrow CO + Cl_2$	0.0015 - 0.015	$k\,AM^{1/2}$	451	3.0	-1	22.9	4.18	15	(1)

COMMENTS

Reverse reaction see 641.470. The proposed mechanism, $Cl_2 \rightleftarrows 2\,Cl$; $Cl + COCl_2 \rightarrow COCl + Cl_2$; $COCl \rightleftarrows CO + Cl$, is based on analogy with photochemical reactions which seem to rule out Cl_3 as intermediate (2).

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REDUCTIVE DECOMPOSITION

N oxides

Gas phase

Rates are in "unit of amount per sec.

No.	Reaction	Method	Unit of amount	Amount of reactant	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
							k°			A°	n		
.1	$2N_2O \rightarrow 2N_2 + O_2$	p	mm Hg	80	k A	665	1.2	−4				*	(43)
				485		"	4.3	−4					
				970		"	6.5	−4					
				2000		"	1.0	−3					
				5000		"	1.4	−3					
				8000		"	1.6	−3					
				28	"	603	1.7	−5					(43)
				"		647	8.9	−5					
				"		697	3.5	−4					
				8000	"	575	8.0	−5					"
				"		620	4.0	−4	53	4.2	9		
			kg/cm^2	37.43	"	585	1.5	−4				*	(18)
				18.37		602	2.4	−4					
				24.54		615	4.2	−2					
				~ 0.1		510 - 600			64.9				(18)
				~ 0.5		630 - 695			61.0				
				~ 40		640 - 725			53.0				
			M/ml	0.4 - 40 kg/cm^2	k A$^{1/2}$	585 - 615			67	9.5	14	*	(31)

No.	Reaction	Method	Unit of amount	Amount of reactant	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
							k°	n		A°	n		
.2	$2NO \rightarrow N_2 + O_2$	flow	M/ml	A ~ 1 – 4 A/M ~ 0.1 – 1.5 A + L + M = 1 atm	$-dA/dt = A^2\{[a/(b + A/M)M^{1/2}] + [cA/M/(b + A/M)]\}$								
						906	*c* 6.0	0				*	(42)
						1252	*a* 1.15 *b* 2.0 *c* 1.35	0 −2 +3					
						1639	*a* 6.0 *b* 7.0 *c* 7.9	+2 −2 +4					
.3	$N + O_2 \rightarrow NO + O$	from .2	M/ml		k AB	1330	9.2	8	25			*	(42)
.4	$O + N_2 \rightarrow NO + N$	from .2	M/ml		k AB	1330	4.0	4	55			*	(42)
.5	$O + NO \rightarrow O_2 + N$	from .2	M/ml		k AB	1330	6.0	7	29			*	(42)
.6	$N + NO \rightarrow N_2 + O$	from .2	M/ml		k AB	1330	3.7	10	7			*	(42)
.7	$2NO \rightarrow NO_2 + N$	from .2	M/ml		k AB	1330	9.5	2	52			*	(42)
.8	$N + NO_2 \rightarrow 2NO$	from .2	M/ml		k AB	1330	4.1	10	2			*	(42)
.9	$NO_2 \rightarrow NO + O$	from .2			k A	1330	4.6	−1	78			*	(42)
.10	$O + NO \rightarrow NO_2$	from .2	M/ml		k AB	1330	8.6	7	6			*	(42)
.11	$2NO_2 \rightarrow 2NO + O_2$	*p*	M/l	10 – 40 mm Hg	$k A^2$	319 330 354 378 383	1.0 1.5 3.4 8.0 1.0	0 0 0 0 1	26.6	6	9	*	(1)

No.	Reaction	Method	Unit of amount	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.12	$2N_2O_5 \longrightarrow 4NO_2 + O_2$	$p(O_2)$	mm Hg		k A								
				0.063 - 0.081		35	1.4	-4				*	(^{24})
				0.0010 - 0.0018	"	35	3.5	-5					
						45	1.1	-4					
						55	~ 3	-4					
						65	~ 7	-4					
				30 - 700	"	0	7.9	-7				*	(^{5})
						15	1.0	-5					
						25	3.3	-5					
						35	1.3	-4					
						45	5.0	-4					
						65	4.9	-3	24.6	3.8	16	*	(^{22})

COMMENTS

(.1) Rate constants (from half-lives) given as first-order without implying an actual first order; pressure increase on completion is 46.5 %, not 50 % ([13, 43]); first-order k increase with the pressure ([18, 11]). Activation energy of 53 kcal and frequency factor of 4.2×10^9 refer to 10 atm pressure (extrapolated); the frequency factor is 100 times too small ([34]). Treatment of the data of ([18]) as of 1.5 order ([31]) gives $k = 9.5 \times 10^{14} e^{-67000/RT}$ $(M/ml)^{-1/2}$ sec^{-1} with a maximum deviation of 15 % between 0.36 and 40 kg/cm^2. The reaction is stated to be explosive under 70 atm. NO is present during the reaction ([2]) reaching a maximum at 50 % completion ([26]). Foreign gases accelerate the rate with the following activation efficiencies : H_2O 1.50, CO_2 1.32, N_2O 1.0, N_2 0.24, O_2 0.23 ([43, 14]). Under 0.1 mm Hg in quartz the reaction is heterogeneous ([8]). The reaction is catalyzed by Hg, Br_2, and I_2 vapors at rates proportional to [Hg], $[Br_2]^{1/2}$, and $[I_2]^{1/2}$ ([43]), indicating reaction over atoms Hg, Br, and I ([37]). Probable atom chain with NO participating. No decision possible between first and 1.5 order. Older reference ([19]). (.2) - (.10) The rate law ([42]) of the overall reaction (.2) is expressible by the rate constants k of the assumed constituent steps (.3) (.5) (.6) (.7) (.10) and K = dissociation constant of O_2, with $a = 2k_5K^{1/2}$: $b = k_3/k_6$; $c = 2k_7[1 + (k_5/k_{10})]$. The subscripts of k correspond to the numbers under which the constituent reactions are listed in the table. These k of these elementary steps and of the reverse reactions (.4) (.8) (.9), given under (.3) - (.10), are derived from (.2) and equilibrium data. (.11) Data, converted to M/l and sec, in agreement with the original observed k ([1]); the data tabulated in the book of Kassel ([22]) and of Schumacher are in error owing to unnecessary division by 2, whereas the original rates actually refer to one mole NO_2 and not to 2 moles. (.12) The low-pressure data are from ([24]), chosen as representative and in agreement with much of the previous work. High-pressure data are from ([5]), in very good agreement with more recent work. The low-pressure k is related to the high-pressure k_∞ by $k = k_\infty/(1 + aA)$, with $a = 0.0033$ and 0.0065 at 35° and 55°C, respectively. Data of E and the frequency factor ([22]) are weighted averages from several sources. Further literature references, and interpretations, ([3, 4, 5, 6, 7, 9, 10, 12, 15, 16, 17, 21, 23, 25, 28, 29, 30, 32, 33, 35, 36, 38, 39, 40, 41, 44]). See reaction in the liquid phase, 542.560.

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REDUCTIVE DECOMPOSITION

Ozone

Gas phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant		Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Literature
						k^o	n		
.1	$2\,O_3 \rightarrow 3\,O_2$	$10^3[O_3]$	$10^4[O_2]$	$k\,A^2$					(²)
		4.6	0.89		70	5	-3		
		6.0	1.5		80	1.4	-2		
		5.3	200		"	1.4	-2		
		6.4	5.6		90	3.5	-2		
		5.3	230		"	4.5	-2		
		3.2	5.0		100	8.6	-2	24.4	
		4.5	270		"	1.3	-1	28.5	

COMMENTS

Selected data from (²), deemed most reliable from the point of view of absence of impurities (organic matter, Hg, H_2, N_2), and in good agreement with previous work where the ranges overlap. All k are initial; k increases steadily in each run and is slightly (~ 10 %) increased by packing. Foreign gases accelerate the reaction in the order $CO_2 > N_2 > He$.

The value of $E = 24.4$ is valid for pure O_3; at high $[O_2]$ it rises to 28.5.

The chain mechanism proposed, (1) $O_3 + O_3 \rightarrow 3\,O_2^*$; (2) $O_2^* + O_3 \rightarrow 2\,O_2 + O$; (3) $O + O_3 \rightarrow 2\,O_2^{**}$; (4) $O + O_2 + M \rightarrow O_3 + M$; (5) $O_2^{**} + O_3 \rightarrow 2\,O_2 + O$; (6) $O_2^{**} + O_3 \rightarrow O_2 + O_3$; (7) $O_2^{**} + O_2 \rightarrow 2\,O_2$, gives, for $[O_2] = 0$, $-d[O_3]/dt = k_1[O_3]^2$, and for $[O_2] \gg [O_3]$, at high temperature, $-d[O_3]/dt = (k_2k_3/k_4)\,[O_3]^2/[O_2]$ (³, ⁴, ⁵, ⁷, ⁸). From the photochemical reaction (⁶), giving k_4/k_5 and $(k_6/k_5) + (k_7/k_5)$ and their temperature dependence, $k_1 = 1.7 \times 10^{13}\, e^{-24400/RT}$ and $k_2 = 1.83 \times 10^{14} e^{-28500/RT}$.

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REDUCTIVE DECOMPOSITION

Halogen oxides

Rate and rate constants are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E
					k°	n	
.1	$2\,F_2O \rightarrow 2\,F_2 + O_2$	50 - 800 mm Hg	kA^2	250	1.39	-2	
				260	2.86	-2	
				270	5.71	-2	39 ± 3

COMMENTS

Unimolecular reaction in second-order range requiring 3 oscillators and diameter 4.5×10^{-8} cm. Relative efficiencies for activation:

F_2O	F_2	O_2	N_2	SiF_4	Ar	He
1.0	1.1	1.1	1.0	0.88	0.52	0.40

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REDUCTIVE DECOMPOSITION

N oxides

Liquid phase

Rates are in M/l per sec.

No.	Reaction	Solvent (Medium)	Unit of amount	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
							k^o	n			
.1	$2 N_2O_5 \rightarrow 2 N_2O_4 + O_2$	N_2O_4	M/1	0.2	k A	15	1.6	-5		*	(1)
						20	3.4	-5	25		
		CH_3CHCl_2	"	"	"	20	3.2	-5			"
						35	2.5	-4	25		
		$CHCl_3$	"	"	"	20	2.7	-5			
						25	5.5	-5	25		"
		CH_2ClCH_2Cl	"	"	"	20	2.4	-5			
						25	4.8	-5	24		"
		CCl_4	"	0.2	"	20	2.3	-5			
				"		25	4.7	-5	24		"
		"	"	5.3	"	45	6.7	-4			"
				2.3		"	6.3	-4			
				1.4		"	6.0	-4			
		C_2H_5Cl	"	0.2	"	20	2.2	-5			"
						25	4.3	-5	25		
		Br_2	"	"	"	15	1.1	-5			"
						20	2.15	-5	24		

No.	Reaction	Solvent (Medium)	Unit of amount	Amount of reactant	Defined mass-action law	Temperature	$k' = k^\circ \times 10^n$		E	Comments	Literature
							k°	n			
.1	$2\,N_2O_5 \rightarrow 2\,N_2O_4 + O_2$	CH_3NO_2	M/1	0.2	k A	15	7.5	−5			(1)
	(continued)					45	4.3	−4	24.5		
		S = 96 % HNO_3 aq	"	A/S = 0.043	"	45	2	−5	28 (15 - 35°)		
		$CH_3CHClCH_2Cl$	"	2	"	20	2.0	−6			"
						35	2.0	−5	27		

COMMENTS

Further data (3) (5). Interpretations (4) (2). See reaction in the gas phase 541.560.

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DECOMPOSITION

Nitramide

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.1	$NH_2NO_2 \rightarrow N_2O + H_2O$	H_2O	~ 0.006		$kA = (k_0 + \kappa[X] + k'A^-)A$		25						*	(3)
	$(NH_2NO_2 = A)$						k_0	4.70	-5					
	$(NHNO_2^- = A^-)$						k'	3.68	-2					
					X =	10^4 [X]=								
					$C_6H_5NH_2$	90.7	k	4.99	-4					
							κ	4.8	-2					
					$o\text{-}ClC_6H_4NH_2$	90.1	k	6.22	-6					
							κ	1.38	-3					
					$m\text{-}ClC_6H_4NH_2$	373	k	3.38	-6					
							κ	7.70	-2					
					$p\text{-}ClC_6H_4NH_2$	17.3	k	8.10	-6					
							κ	1.60	-2					
					C_5H_5N	26.8	k	1.25	-3					
							κ	4.38	-1					
		H_2O	0.1	OH^-	0.01	kA	25	1.15	+4					(7)
		"	"	X =	[X] [HX]	kA								
				$C_6H_5O^-$	0.01 0.01–0.1		25	1.34	+2					(7)
				$2,4\text{-}Cl_2C_6H_3O^-$	0.001 0.037		"	8.9	0					
				$o\text{-}NO_2C_6H_4O^-$	0.001 0.0047		"	1.83	0					
				$2,4\text{-}(NO_2)_2C_6H_3O^-$	0.05 Sat		"	1.32	-2					
				$C_6H_5COO^-$	0.0 Sat		"	2.40	-2					
				CN^-	0.0445 0.181		"	>1.1	-1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$NH_2NO_2 \rightarrow N_2O + H_2O$					$k_oA + k'A^-A + \kappa[X]A + k''A^-$								(⁷)
	$(NH_2NO_2 = A)$						25							
	$(NHNO_2^- = A^-)$						k_o	4.70	-5					
	(continued)						k'	3.68	-2					
							k''	3.45	-4					
		H_2O		HCl	0.0057-0.057	k_oA	15	1.45	-5					(¹) (⁴)
				$HClO_4$	0.0136		25	4.68	-5					"
				$C_6H_5SO_3H$	0.05		35	1.50	-4					(¹)
							45	4.26	-4	20.7	1.9	12		"
				X =	$10^3[X]$ =	$kA = (k_o + \kappa[X])A$								
				$(CH_3)_3CCOO^-$	8.5 - 17.4	κ	15	8.22	-1					(¹)
					3.6 - 6.7		25	2.30	0					
					27 - 36		35	6.44	0	18.4	7.5	13		
				CH_3COO^-	5 - 16	κ	15	4.92	-1					(¹)
					6.4 - 8		25	1.48	0					
					3.9 - 6.6		35	4.28	0					
					2.7 - 8.2		45	1.14	+1	19.2	1.8	14		
				$C_6H_5COO^-$	14 - 37.8	κ	15	1.89	-1					(¹) (⁴)
					12.4 - 23.4		25	5.5	-1					(¹)
					8.3 - 16		35	1.57	0					"
							45	4.36	0	19.3	7.7	13		"
				$HCOO^-$	34 - 47	κ	15	8.2	-2					(¹) (⁴)
					27.4 - 50		25	2.55	-1					(¹)
					26 - 35		35	7.28	-1					"
					7.6 - 21		45	1.92	0	19.4	4.1	13		"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$NH_2NO_2 \rightarrow N_2O + H_2O$ $(NH_2NO_2 = A)$ $(NHNO_2^- = A^-)$ *(continued)*			$OHC_6H_4COO^-$	47 - 95	K	15	2.08	-2					(1) (4)
					89 - 137		25	6.65	-2					(1)
					47 - 137		35	2.05	-1					"
					24.7 - 9.7		45	5.45	-1	20.1	3.7	13		"
				CH_2ClCOO^-	65 - 176	K	25	4.65	-2					(1)
					125 - 267		35	1.33	-1					
					26 - 176		45	3.71	-1	19.9	1.9	13		
				$o\text{-}NO_2C_6H_4COO^-$	88 - 202	K	15	4.2	-3					(1)
					77 - 239		25	1.67	-2					
					88 - 202		35	5.18	-2					
					77 - 180		45	1.67	-1	22.3	3.8	14		
				$CHCl_2COO^-$	50 - 90	K	15	7.9	-4					(4)
					247 - 419		25	2.39	-3					(1)
					196 - 424		35	8.28	-3					"
					184 - 510		45	2.77	-2	23.7	5.4	14		"
				$COOHCOO^-$	14.5	K	15	0.00						(4)
				COO^-COO^-	10.4	"	"	1.04	-1					
				$COOHCH_2CH_2COO^-$	2.5 - 5.6	K	15	3.20	-1					(4)
				$COO^-CH_2CH_2COO^-$	0.07 - 0.56	"	"	1.8	0					
				$COOH(CHOH)_2COO^-$	9 - 45	K	15	3.63	-2					(4)
				$COO^-(CHOH)_2COO^-$	2.4 - 12	"	"	1.65	-1					
				$H_2PO_4^-$	58 - 84	K	15	7.85	-3					(4)
				HPO_4^{--}	0.002-0.01	"	"	8.6	+1					
				$C_6H_5NH_2$	4.03	k	15	9.75	-5					(4)
					6.44	"	"	1.47	-4					
					10.7	"	"	2.26	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$NH_2NO_2 \rightarrow N_2O + H_2O$	H_2O		HCl	0.001 - 0.03	kA	25	4.70	-5					(6)
	($NH_2NO_2 = A$)				0.615		"	5.40	-5					
	($NHNO_2^- = A^-$)				1.45		"	6.15	-5					
				HCl 0.01 + NaCl	0.05		"	4.66	-5					
	(continued)				0.48		"	4.27	-5					
					0.96		"	3.83	-5					
					2.38		"	2.73	-5					
		$H_2O + D_2O$ (atom %)				kA								(5)
		0.0					28.8	4.83	-5					
		4.69					"	4.52	-5					
		28.10					"	3.30	-5					
		45.83					"	2.54	-5					
		77.91					"	1.09	-5					
		95.40					"	1.04	-5					
		96.67					"	9.62	-6					
		(100.00)					"	(9.31)	-6					
		$C_6H_5OCH_3$	~ 0.1		$kA = (\kappa[X] + k''A^-)A =$ $k'A[X] = (\kappa + k''A^-/[X])A[X]$								*	(2)
				X =	10^3 [X] =		25							
				$(C_2H_5)_3N$	0.9 - 4.1		k'	1.96	-1					
				$(C_4H_9)_3N$	0.8 - 4.0		"	3.91	-1					
				$C_6H_5NH_2$	381 - 1023		k'	2.50	-4					
							κ	1.34	-4					
				o-$ClC_6H_4NH_2$	202 - 650		k'	9.6	-6					
							κ	8.8	-6					
				$C_6H_5NHCH_3$	270 - 730		k'	5.0	-4					
							κ	4.7	-4					
				C_5H_5N	6 - 30		k'	3.21	-2					
							κ	3.12	-2					

COMMENTS

The first-order total rate of the decomposition (rate constant k) is representable by the sum of rates of a "spontaneous" first-order decomposition of A (rate constant k_0), a first-order decomposition of A^-, a second-order decomposition proportional to $A \times A^-$, and a base-catalyzed decomposition = $\kappa A[X]$ (X = base). Plots of log κ against log K (dissociation constant of the catalyzing base) are linear.

LITERATURE

(1) E. C. Baughan, R. P. Bell, *PRS*^{A} 1937, 158, 464. (2) R. P. Bell, A. F. Trotman-Dickenson, *CSL* 1949, 1288. (3) R.P. Bell, G.L. Wilson, *TFS* 1950, 46, 407. (4) J.N. Brönsted, K.Pedersen, *ZPC* 1924, 108, 185. (5) V.K. LaMer, J.Greenspan, *TFS* 1937, 33, 1266. (6) C. A. Marlies, V. K. LaMer, *ACS* 1935, 57, 1812. (7) L. K. J. Tong, A. R. Olson, *ACS* 1941, 63, 3406.

REDUCTIVE DECOMPOSITION

Liquid phase

OZONE

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$2\,O_3 \rightarrow 3\,O_2$	CCl_4	0.00045-0.0021			kA	54.7	1.8	-5				*	(3)
							71.0	1.23	-4	26	5.82	12		
		"	0.0011-0.0034	Cl_2	0.0002-0.011	$kA^{3/2}[Cl_2]^{1/2}$	(50)	(1.45)	-2				*	(3)
							54.7	2.70	-2					
							71.0	1.93	-2	26.7	2.0	16		
.2	$2\,O_3 \rightarrow 3\,O_2$	$H_2O + H_2SO_4$ 0.005	0.00177	H_2O_2	0.00040	kA	0	3.8	-4				*	(6)
			0.00150	"	0.000785	"	"	1.1	-3					"
			0.00108	"	0.00169	"	"	2.0	-3					"
.3	$2\,O_3 \rightarrow 3\,O_2$	H_2O	Sat	OH^-	$(0.5\text{-}16) \times 10^{-13}$	$kA[OH]^{1/2}$	0	1.41	+2				*	(1)
							27	1.38	+3	9.9				
.4	$2\,O_3 \rightarrow 3\,O_2$	H_2O, pH < 1.6	Sat	Co^{++} =	$(6\text{-}36)10^{-5}$	$kA[Co^{++}]$	0	3.7	-1				*	(5)
							17.4	1.15	0		$\Delta H_a = 9.0$			
							24.1	1.97	0		$\Delta S_a = -19$			
							30.6	2.93	0	9.6				

COMMENTS

(.1) In CCl_4, without Cl_2, some $COCl_2$ is formed, as one out of 18 molecules O_3 reacts with the solvent. Extrapolated to 50°C, the rate in CCl_4, without Cl_2, is about 30 times faster than in the gas phase. The solvent supplies activation equivalent to high-pressure gas reaction (see 541.660). In CCl_4, with Cl_2, k tends to rise with the progress of the reaction. Extrapolated to 50°C, $k = 1.45 \times 10^{-2}$, is only about 50 % faster than in the gas phase, 9.50×10^{-3}. The rate law assumed in the presence of Cl_2 is the same as that obtaining in the gas phase ([3]); in the CCl_4 solution, in the presence of Cl_2, ([3]) find a rate law $kA[Cl_2]$ equally applicable. (.2) The reaction (a) $2\,O_3 \rightarrow 3\,O_2$ is accompanied by (b) $H_2O_2 + O_3 \rightarrow H_2O + O_2$, as evidenced by the concomitant decomposition of H_2O_2; in the three experiments tabulated, the ratio of decomposed O_3 to decomposed H_2O_2 is, respectively, (average) ~ 15, ~ 7, ~ 3. The ratio of the rates $(-d[O_3]/dt)/(-d[H_2O_2]/dt) = 1 + (5.2[O_3]/[H_2O_2])$. In terms of the interpretation of ([4]), rate (a) $= k_a\,[H_2O_2][O_3]$, and rate (b) $= k_b\,[H_2O_2][O_3]$; $k_a/k_b = 5.2[O_3]/[H_2O_2]$; $k_a + k_b = 1 + (5.2[O_3]/[H_2O_2])$. The interpretation assumes the mechanism $H_2O_2 + O_3 \rightarrow H_2O_3 + O_2$; $H_2O_3 + O_3 \rightarrow H_2O_2 + 2\,O_2$; $H_2O_3 + H_2O \rightarrow H_2O_2 + H_2O + O_2$. For chain mechanism, see ([7]). (.3) In solution in H_2O ([1]), the OH^- content is adjusted by $HClO_4$; k is derived from spectrophotometry which gives the rate of disappearance of O_3. By iodimetry, i.e. by the total oxidizing power, the rate is independent of $[OH^-]$ and considerably below the rate determined by spectrophotometry. The hypothetical mechanism proposed is $O_3 + H_2O \rightarrow HO_3^+ + OH^-$ (slow); $HO_3^+ + OH^- \rightleftarrows 2\,HO_2$ (maintained); $O_3 + HO_2 \rightarrow HO + 2\,O_2$ (slow); $HO + HO_2 \rightarrow O_2 + H_2O$. (.4) Iodometric determinations. In solutions acidified by $HClO_4$ or H_2SO_4, k is independent of the acidity if $pH < 1.6$. The proportionality of the rate with $[Co^{++}]$ is approximate. The hypothetical mechanism, $Co^{++} + O_3 + H_2O \rightarrow CoOH^{++} + O_2 + HO$; $HO + O_3 \rightarrow HO_2 + O_2$; $HO_2 + CoOH^{++} \rightarrow Co^{++} + H_2O + O_2$, renders the observed rate law, if $CoOH^{++}/Co^{++}$ is constant.

LITERATURE

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DECOMPOSITION
with evolution of N_2 from azo compounds

Gas phase

Amounts are in mm Hg.
Rates are in mm Hg per sec.
k is in sec^{-1}.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
					k^o	n		A^o	n
.1	$C_3H_7N{:}NC_3H_7 \rightarrow N_2 + C_6H_{14}$	4.6 - 0.26	*k* A	250	4.60	-4			
				260	1.00	-3			
				270	1.92	-3			
				280	3.90	-3			
				290	7.7	-3	40.9	5.6	13

COMMENTS

Further decomposition $C_6H_{14} \rightarrow C_3H_6 + C_3H_8$ amounts to about 15 % of the total reaction; the first-order *k* remains constant down to 0.26 mm Hg.

LITERATURE

H. C. Ramsperger, *ACS* 1928, 50, 714.

DECOMPOSITION

CO group elimination from COOH

Liquid phase

Reaction type RCOOH → ROH + CO

Rate measured CO evolved.

Amounts are in M/l.
Rates are in M/l
per sec.

No.	Reaction	Solvent	Addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
						k°	n			
.1	$HCOOH \rightarrow H_2O + CO$	$H_2O + H_2SO_4$ 97.6 %		kA	15	1.25	-3		*	(3)
		94.5			"	3.80	-4			
		91.8			"	1.27	-4			
		98.9			25	1.23	-2			
		97.6			"	4.08	-3	18.5		
		94.5			"	1.21	-3	19.7		
		91.8			"	4.03	-3	19.7		
		89.2			"	9.20	-5			
		85			"	2.88	-5			
		91.8			35	1.08	-3			
		88.9			"	4.15	-4			
		91.8			45	3.75	-3			
		88.9			"	1.19	-3			
		$(CH_3CO)_2O$	C_5H_5N 0.035	kA	50	1.7	-4		*	
			0.152		"	5.7	-4			
			0.281		"	1.08	-3			

No.	Reaction	Solvent	Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
						k^o	n			
.1	$HCOOH \rightarrow H_2O + CO$ *(continued)*	$(CH_3CO)_2O$	Strychnine 0.0019	kA	50	7.4	-5			
			0.0075		"	8.8	-4			
			0.030		"	4.2	-3			
.2	$COOHCOOH \rightarrow H_2O + CO_2 + CO$	See 562.446.								
.3	$COOHCHOHCH_2COOH \rightarrow CHOCH_2COOH + H_2O + CO$	H_2SO_4		kA	20	1.27	-4			(4)
					30	4.78	-4			
					40	1.76	-3	23.6		
		"	X =	kA $\Delta \log (10^3 k)/\Delta X =$						
			H_2O 0 - 1.25		30	-0.54				
					40	-0.61				
			M_2SO_4 0 - 0.5		40	-1.27				
			CH_3COOH 0 - 1.7		40	-0.60				
		H_2SO_4		kA	20	1.85	-4			(1a)
					25	3.96	-4			
					30	7.86	-4			
					35	1.55	-3			
		"	$(NH_4)_2SO_4$ 0.25	"	20	5.67	-5			"
					30	2.32	-4			
					40	1.01	-3			
			" 0.50		20	2.22	-5			"
					30	1.04	-4			
					40	4.60	-4			

No.	Reaction	Solvent	Addend		Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.3	$COOHCHOHCH_2COOH \rightarrow CHOCH_2COOH + H_2O + CO$ *(continued)*		H_3PO_4	0.25		20	9.3	-5			(1a)
						30	4.28	-4			
						40	1.78	-3			
			"	0.50		20	5.93	-5			"
						30	2.72	-4			
						40	1.17	-3			
.4	$(COOH)_2CH_2C(OH)COOH \rightarrow (CH_2COOH)_2CO + H_2O + CO$	H_2SO_4	H_2O	0.0	kA	15	2.55	-3			(5)
				0.10		"	3.58	-3			
				0.38		"	1.75	-3			
				1.22		"	2.07	-4			
				1.89		"	7.2	-5			
				2.80		"	2.1	-5			
			H_2O	0.0	"	25	7.3	-3			"
				0.14		"	1.33	-2			
				0.25		"	1.08	-2			
				1.04		"	1.30	-3			
				2.03		"	2.57	-4			
				3.07		"	6.9	-5			
			H_2O	0.0	"	35	2.02	-2			"
				0.22		"	3.53	-2			
				0.66		"	1.15	-2			
				1.38		"	2.62	-3			
				2.04		"	9.9	-4			
				3.03		"	2.9	-4			

No.	Reaction	Solvent	Addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
						k°	n			
.4	$(COOH)_2CH_2C(OH)COOH \rightarrow (CH_2COOH)_2CO + H_2O + CO$ *(continued)*		SO_3 0.0	kA	15	2.55	-3			(5)
			0.084		"	1.13	-3			
			SO_3 0.00	"	25	7.3	-3			"
			0.084		"	4.6	-4			
			0.15		"	1.88	-4			
			SO_3 0.00	"	35	2.02	-3			"
			0.084		"	1.57	-3			
.5	$(C_6H_5)_3CCOOH \rightarrow (C_6H_5)_3COH + CO$	$H_2SO_4 + H_2O$ 4 %		kA	12	1.02	-3			(1)
		"			22	2.08	-3			
		5			12	2.64	-4			
		"			22	5.28	-4	15.0		
		7			5	1.10	-4			
		"			22	3.07	-4			
		H_2SO_4	Na_2SO_4 12 %	kA	12	1.52	-3			
			14		12	9.10	-4			
					22	2.85	-3			
			15		22	2.07	-3			

COMMENTS

(.1) In mixtures of concentrated H_2SO_4 with CH_3COOH or with $(CH_3)_2CO$, the reaction proceeds at about the same rate as in H_2SO_4. Strong catalytic action of HCl (no numerical data). Hg_2SO_4, $CuSO_4$, K_2SO_4, H_2SO_4 have no appreciable effect on *k*. Older data of (2) are disregarded. In $(CH_3CO)_2O$, alkaloids (strychnine, brucine, nicotine, cocaine, quinine, papaverine, morphine) have an accelerating effect; data for alkaloids other than strychnine, in original (3). The relative effects of the alkaloids do not follow the order of their activities as bases. Contamination of the $(CH_3CO)_2CO$ solvent with CH_3COOH lowers *k* in the presence of the alkaloids, but not with pyridine. The data are selected.

(.3) Data of (4) and (1a) in 100 % H_2SO_4 in not very satisfactory agreement. Effects of many other addends in original (1a). (.5) *k* averaged in the 20 - 60 % reaction range. Further data on effects of K_2SO_4, CH_3COOH, C_6H_5OH, CH_3COCH_3, etc., in original (1).

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(2) J.Meyer, *ZEC* 1909, 15, 506.
(4) E.L.Whitford, *ACS* 1925, 47, 953.
(1a) H.R.Dittmar, *ACS* 1930, 52, 2746.
(3) E.R.Schierz, *ACS* 1923, 45, 447.
(5) E.O.Wiig, *ACS* 1930, 52, 4729, 4737.

DECOMPOSITION

CO_2 evolution from COOH in aliphatic monocarboxylic acids

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

Reaction type $RCOOH \rightarrow RH + CO_2$

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$CH_3COC(CH_3)_2COOH \rightarrow CH_3COCH(CH_3)_2 + CO_2$	$H_2O + CH_3OH$ 25 %	0.02 - 0.03	HCl	0.005 - 0.17	kA	25	7.1	-5		*	(5)
		50	0.02 - 0.04	"	0.005 - 0.075	"	"	7.1	-5			
		75	0.02 - 0.06	"	0.001 - 0.05	"	"	6.5	-5			
		H_2O + dioxane 50 %	0.04 - 0.06	"	0.003 - 0.01	"	"	8.0	-5			
		H_2O		"	0.01 - 0.18	"	"	6.8	-5			"
		H_2O	0.02	HCl + NaCl		"						
					0.05 - 0.10		25	6.9	-5		*	(3)
					0.2 - 0.5		"	7.0	-5			
					1.1 - 2.1		"	7.2	-5			
					0.1 - 0.2		35	1.06	-3			
		H_2O	HCl + NaCl =		0.050	"						
				HCl	0.0272		25	6.87	-5		*	(3)
					0.0169		"	6.76	-5			
					0.0053		"	6.41	-5			
		H_2O	0.015 - 0.018									
			HCl 0.175 - 0.551; NaCl 0.040			kA	18.0	2.8	-5		*	(3)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.1	$CH_3COC(CH_3)_2COOH \rightarrow CH_3COCH(CH_3)_2 + CO_2$ *(continued)*	H_2O		CH_3COOH 0.3; CH_3COONa	0.3	kA	18.0	1.7	-6		*	(3)
				0.3	0.6	"	"	9.5	-7			
				0.5	0.5		"	1.8	-6			
.2	$NO_2CH_2COOH \rightarrow NO_2CH_3 + CO_2$	H_2O	0.01	HCl 0.01; NaCl	0.09	kA	20	9.41	-4		*	(2)
				0.04	0.06		"	5.75	-4			
				0.10	0		"	3.07	-4			
				0.01	0		"	8.85	-4			
		"	"	pH 4.3 - 5.0		"	"	1.21	-3			"
.3	$CCl_3COOH \rightarrow CCl_3H + CO_2$	C_2H_5OH	0.01	X =		$kA^{1/2}X^{1/2}$					*	(4)
				o-$ClC_6H_4NH_2$	0.1		60	1.0	-7			
					"		70	4.1	-7			
				m-$ClC_6H_4NH_2$	0.1		60	2.0	-7			
					"		70	1.7	-6			
				p-$ClC_6H_4NH_2$	0.1		60	3.5	-7			
					"		70	1.2	-6			
				$C_6H_5NH_2$	0.1		60	7.8	-7			
					"		70	2.8	-6			
				p-$CH_3C_6H_4NH_2$	0.1		60	1.0	-6			
					"		70	3.8	-6			
				α-$C_{10}H_9NHC_2H_5$	0.1		60	3.2	-7			
					"		70	1.1	-6			
				$C_6H_5NHCH_3$	0.1		60	4.4	-7			
					"		70	1.6	-6			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
								k°	n			
.3	$CCl_3COOH \rightarrow CCl_3H + CO_2$ *(continued)*			o-$CH_3C_6H_4NHC_2H_5$	0.1		60	4.8	-7			
					"		70	1.8	-6			
				p-$CH_3C_6H_4NHCH_3$	0.1		60	7.8	-7			
					"		70	3.3	-6			
				$C_6H_5N(CH_3)_2$	0.1		60	4.3	-7			
					"		70	1.6	-6			
				α-$C_{10}H_9N(CH_3)_2$	0.1		60	2.4	-7			
					"		70	8.2	-7			
				$CH_3C_5H_4N$	0:1		60	3.8	-7			
					"		70	1.5	-6			
				C_5H_5N	0.1		60	4.7	-7			
					"		70	1.8	-6			
.4	$CCl_3COO^- \rightarrow CCl_3^- + CO_2$	H_2O	0.1			kA	50	6.2	-7		*	(4)(1)
							60	3.5	-6			
							70	1.7	-5			
							80	7.9	-5			
							90	3.2	-4	36		
		C_2H_5OH	0.005 - 0.1			kA	50	1.3	-5			"
							60	5.5	-5			
							70	2.2	-4	32		
		$C_6H_5NH_2$	0.2 - 0.5			kA	25	8.8	-7			"
							35	4.0	-6			
							45	1.6	-5			
							55	5.8	-5	26		

COMMENTS

(.1) Good agreement of data of (5) and (3) at 25°C. The data refer to the rate of decomposition of the undissociated acid (3). At constant (HCl + NaCl), *k* decreases slightly but distinctly with decreasing HCl acidity (3). In acetate buffers (3), the acid is partially dissociated; the data refer to the rate of decomposition of the undissociated acid. Data in glycolate buffers, in original (3).

(.2) Accelerated by KCl, K_2SO_4, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, CsCl, $CO(NH_3)_6Cl$; slowed down by LiCl, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CuSO_4$, $CuCl_2$.

(.3) *k* calculated from original data of $-1/2 \log k$. Proposed mechanism: $CCl_3COOH + X^- \rightleftarrows CCl_3COO^- + XH^+$; $CCl_3COO^- \rightarrow CCl_3^- + CO_2\ (k_1)$; $CCl_3^- + XH^+ \rightarrow CCl_3H + X$ (fast); $k = 1/2\ k_1(K_A/K_{XH})$, where K_A, K_{XH} = dissociation constants.

(.4) Reactants CCl_3COONa and $CCl_3COOH{\cdot}H_2NC_6H_5$ in H_2O and in C_2H_5OH; the latter only in $C_6H_5NH_2$; same values of *k*. Addition of HCl in equivalent amounts has no effect.

LITERATURE

(1) A.N.Kappanna, *ZPC* 1932, **158**, 355. (2) K.J.Pedersen, *TFS* 1927, **23**, 316. (3) K.J.Pedersen, *ACS* 1929, **51**, 2098; 1936, **58**, 240. (4) F.H.Verhoek, *ACS* 1934, **56**, 571; 1939, **61**, 186; 1945, **67**, 1062. (5) F.H.Westheimer, W.A.Jones, *ACS* 1941, **63**, 3283.

DECOMPOSITION

CO_2 evolution from COOH in aliphatic dicarboxylic acids

Liquid phase

Reaction type $R(COOH)_2 \rightarrow RHCOOH + CO_2$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	COOHCOOH (undissociated) $\rightarrow$ $HCOOH + CO_2$ (a) COOHCOOH (undissociated) $\rightarrow$ $H_2O + CO + CO_2$ (b)	H_2O	~ 0.4			(a + b) = kA	100	1.2	-7	42.6	1.2	18	*	$(^{5a})$
							140	3.0	-5	39.8	3.2	16		
							150	9.1	-5	37.8	2.9	15		
							160	2.5	-4	34.8	9.2	13		
							170	5.9	-4	31.0	1.2	12		
		dioxane	~ 0.4			(a) = kA	120	3.2	-5		7.5	11		"
							140	2.0	-4	29.9	7.7	11		
							150	4.6	-4	29.0	7.6	11		
.1.1	COOHCOOH (undissociated) $\longrightarrow H_2O + CO + CO_2$	H_2SO_4		H_2O	0.60 % (a)	kA	70	3.02	-4				*	$(^{11})$
					0.80 "		"	1.70	-4					
					1.20 "		"	8.18	-5					
					1.50 % (m)		"	5.34	-5					
					2.00 "		"	3.17	-5					
					3.00 "		"	1.50	-5					
					3.0 % (m)	"	98	4.0	-4					"
					6.0 % "		"	1.15	-4					
					10.0 % "		"	3.7	-5					
					20.0 % "		"	5.0	-6					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1.2	$C^{12}OOHC^{12}OOH \longrightarrow H_2O + C^{12}O + C^{12}O_2$ (*a*)	H_2SO_4				kA	100						*	(10)
	$C^{13}OOHC^{12}OOH \begin{cases} \nearrow H_2O + C^{12}O + C^{13}O_2 \text{ (b)} \\ \searrow H_2O + C^{13}O + C^{12}O_2 \text{ (c)} \end{cases}$					$k_b/k_c = 1.03$ $k_a/(k_b + k_c) = 1.03$								
.2	$CH_2(COOH)_2(A) \longrightarrow CH_3COOH + CO_2$ (*a*) $CH_2(COOH)COO^-$ (A') $\longrightarrow CH_3COO^- + CO_2$ (*b*)	H_2O	0.005 - 0.05	HCl (NaOH)	$(a+b)=k(A + A')$								*	(8)
					pH 0.42		80	2.1	-6					
					"		90	7.2	-6	31.0				
					1.18		80	2.1	-6					
							90	7.0	-6	30.7				
	[See separate reactions *a*, *b*] (.2.1) (.2.2)				1.98		80	1.9	-6					
							90	6.3	-6	30.4				
					2.40		80	1.6	-6					
							90	5.3	-6	30.2				
					3.28		80	7.2	-7					
							90	2.4	-6	30.7				
					4.02		80	4.1	-7					
							90	1.4	-6	31.1				
.2.1	$CH_2(COOH)_2 \longrightarrow CH_3COOH + CO_2$	H_2O	0.005 - 0.05			kA	80	2.1	-6				*	(8)
							90	7.1	-6	30.8				
		H_2O	~ 0.1			kA	75.0	9.3	-7				*	(2)
							88.5	5.25	-6					
							99.4	2.10	-5					
							103.6	3.00	-5					
							107.0	4.30	-5					
							110.0	5.60	-5					

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2.2	$CH_2(COOH)COO^- \longrightarrow CH_3COO^- + CO_2$	H_2O	0.5			k A	76.3	3.38	-7				*	(7) (8)
							100	5.00	-6					
							120	3.05	-5	28.1	1.48	11		
.2.3	$COOHC^{12}H_2C^{12}OOH \longrightarrow CH_3COOH + C^{12}O_2$ (*a*)	fused				k A							*	(12)
						$k_a/k_b = 1.12$								
	$COOHC^{12}H_2C^{14}OOH \longrightarrow CH_3COOH + C^{14}O_2$ (*b*)													
.3	$COOHC^{12}HBrC^{12}OOH \longrightarrow CH_2BrCOOH + C^{12}O_2$	fused				k A							*	(12)
						$k_a/k_b = 1.43$								
.4	$CBR_2(COOH) \longrightarrow CHBr_2COOH + CO_2$	H_2O	0.009–0.02	KCl 1 + HCl	0.0	k A	25.0	1.26	-4				*	(11)
					0.08		"	1.62	-4					
					0.10		"	1.74	-4					
					0.25		"	1.76	-4					
					0.50		"	1.55	-4					
					0.75		"	1.24	-4					
					1.0		"	1.08	-4					
.4.1	$CBr_2(COOH)COO^- \longrightarrow CHBrCOO^- + CO_2$	H_2O	0.009–0.2	KCl 1 + HCl	0.0 - 1.0	k A	25.0	2.18	-4	25.0	(25–35°)		*	(11)
				buffers, pH	0.9–3.7	"	"	2.18	-4					"
					4.1–4.7		"	1.8	-4					
.5	$CH_3CH(COOH)_2 \longrightarrow C_2H_5COOH + CO_2$	H_2O	~ 0.1			k A	99.6	1.66	-5					(2)
.6	$COOHC:CCOOH \longrightarrow HC:CCOOH + CO_2$	H_2O	0.027			k A	100	1.3	-6					(6)
							131.5	1.2	-5					

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6.1	$COOH⋮CCOOC_2H_5 \rightarrow HC⋮CCOOC_2H_5 + CO_2$	H_2O $C_6H_5CH_3$	0.09 0.07			kA "	100.5 "	1.1 1.8	-4 -5					(6)
.6.2	$COOHC⋮CCOOK \rightarrow HC⋮CCOOK + CO_2$	H_2O	0.06			kA	60	2.7	-5				*	(6)
.7	$C_2H_5CH(COOH)_2 \rightarrow C_3H_7COOH + CO_2$	H_2O	~ 0.1			kA	99.4	1.41	-5					(2)
.8	$(CH_3)_2C(COOH)_2 \rightarrow (CH_3)_2CHCOOH + CO_2$	H_2O	~ 0.1			kA	99.4	8.25	-6					(2)
.9	$(CH_3)(C_2H_5)C(COOH)_2 \rightarrow (CH_3)(C_2H_5)CHCOOH + CO_2$	H_2O	~ 0.1			kA	99.2	8.95	-6					(2)
.10	$CH_2:CHCH_2CH(COOH)_2 \rightarrow CH_2:CHCH_2CH_2COOH + CO_2$	H_2O	~ 0.1			kA	99.5	3.68	-5					(2)
.11	$(C_2H_5)_2C(COOH)_2 \rightarrow (C_2H_5)_2CHCOOH + CO_2$	H_2O	~ 0.1			kA	99.6	7.80	-6					(2)
.12	$(C_3H_7)_2C(COOH)_2 \rightarrow (C_3H_7)_2CHCOOH + CO_2$	H_2O	~ 0.1			kA	99.5	1.36	-5					(2)
.13	$(CH_2CH:CH_2)_2C(COOH)_2 \rightarrow (CH_2CH:CH_2)_2CHCOOH + CO_2$	H_2O	~ 0.1			kA	99.5	1.8	-5					(2)
Aryl - substituted aliphatic dicarboxylic acids														
.14	$C_6H_5CH(COOH)_2 \rightarrow C_6H_5CH_2COOH + CO_2$	H_2O	~ 0.1			kA	66 88.5	9.53 7.28	-5 -4					(2)
		A (pure liquid)				kA	125 135	1.53 4.05	-4 -4	 11.3			*	(5)
		$C_{17}H_{33}COOH$	0.1-0.3			"	125 135	1.61 3.79	-4 -4	 10.4				(5)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.14	$C_6H_5CH(COOH)_2 \rightarrow C_6H_5CH_2COOH + CO_2$	$C_{15}H_{33}COOH$	0.1-0.3			kA	135	3.72	-4					(5)
	(continued)	o-$NO_2C_6H_4Cl$	"			"	"	4.62	-4					"
		m-$NO_2C_6H_4Cl$	"			"	"	5.08	-4					"
		p-$NO_2C_6H_4Cl$	"			"	"	4.44	-4					"
		$C_6H_5N(CH_3)_2$	"			"	"	2.80	-3					"
.15	$C_6H_5CH_2CH(COOH)_2 \rightarrow C_6H_5CH_2CH_2COOH + CO_2$	H_2O	~ 0.1			kA	99.5	5.5	-5					(2)
Diazomalonates														
.16	(a) $N_2C(COO^-)_2$ (A) $+ H^+ + H_2O$	H_2O	$A + A' =$			$(a + b) = k(A + A')$							*	(9)
	(b) $N_2C(COOH)COO^-$ (A') $+ H_2O$		0.006	$HClO_4$	0.01		25	3.30	-4					
	$\rightarrow N_2 + CH_2OHCOO^- + CO_2$				0.04		"	7.70	-4					
					0.10		"	1.25	-3					
					0.20		"	1.53	-3					
						$(a) = kA[H^+]$							*	(9)
		"	"	$HClO_4$	0.01-0.20		25	3.17	-2					
.17	(a) $N_2C(COOC_2H_5)COO^-$ (A) $+ H^+ + H_2O$	H_2O	$A + A' =$			$(a + b) = k(A + A')$							*	(9)
	(b) $N_2C(COOC_2H_5)COOH$ (A') $+ H_2O$		0.006	$HClO_4$	0.01		25	4.0	-4					
	$\rightarrow N_2 + CH_2OHCOOC_2H_5 + CO_2$				0.04		"	7.9	-4					
					0.10		"	8.4	-4					
					0.20		"	8.8	-4					
					0.50		"	1.05	-3					
						$(a) = kA[H^+]$								
			"	$HClO_4$	0.01-0.50		25	1.53	-1				*	(9)

COMMENTS

(.1) Thermal decomposition in pressure bomb. In H_2O, 37 % of the decomposition follow reaction (*a*), 63% reaction (*b*); in dioxane, only reaction (*a*) occurs.

(.1.1) Decomposition through dehydration by concentrated H_2SO_4. Selected points. (a) means % based on 100 g H_2SO_4, (m) is % based on 100 g mixture. Rate constant k remains constant only as long as the amount of H_2O produced remains small as compared with that present initially. Addition of 0.1% H_2O to 100.0% H_2SO_4 lowers the rate 17 fold. Addition of 1% SO_3 makes the reaction too rapid to measure at 0°C. (.1.2) The ratio $k_a/(k_b + k_c)$ involves the relative rates of rupture of the $C^{12} - C^{12}$ and the $C^{12} - C^{13}$ bond. (.2) (.2.1) (.2.2) Reaction (.2.2) is faster than (.2.1). For (.2.2), data of (7) are obtained with a solution of $CH_2(COOH)COONa$. For (.2.1) (*a*), data of (8) derived from the overall reaction (.2) $(a + b)$ minus reaction (.2.2) (*b*), are in line with the experimental data of (2) on solutions of $CH_2(COOH)_2$ which should be partly ionized. (.2.3) (.3) The ratio k_a/k_b involves the relative rates of rupture of $C^{12} - C^{12}$ and $C^{12} - C^{14}$ bonds. See further (3). (.4) (.4.1) Reaction, (.4) actually proceeds through decomposition of the $CBr_2(COOH)COO^-$ ion, i.e. through reaction (.4.1).

The rate constant for reaction (.4.1) is won from k of reaction (.4) by division by $\alpha = [CBr_2(COOH)COO^-] / ([CBr_2(COOH)COO^-] + [CBr_2(COOH)_2])$, with α from the dissociation constant $[CBr_2(COOH)COO^-]\ [H^+]/[CBr_2(COOH)_2]$. (.6.2) First-order only at 60 °C; at 80° and 98.5°C, further reactions $HC{:}CCOOK + H_2O \longrightarrow KHCO_3 + C_2H_2$; $2\ KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$; $COOHC{:}CCOOK + KHCO_3 (K_2CO_3) \longrightarrow COOKC{:}CCOOK$, which is more stable. (.14) k calculated from original half-time data (5).

(.16) (.17) Reactants are $N_2C(COOK)_2$ in reaction (.16) and $N_2C(COOC_2H_5)COOK$ in reaction (.17). The total reactions $(a + b)$ are interpreted by the equilibria $A' \rightleftharpoons A + H^+$ (equilibrium constant K) and the rate constants are related by $k_{a+b}\ (A + A') = k_a\ A[H^+]$, hence $k_{a+b} = k_a[H^+]K/(K + [H^+])$; the rate constant k_a and the equilibrium constant K are obtained from linear plots of $k_{a+b}/[H^+]$ against k_{a+b}. For (.16) K=0.066, and for (.17), K=0.0059. CH_3COOH added to $HClO_4$ has no measurable effect, but in acetate buffers pH ~ 5, there is base catalysis by the CH_3COO^- ion, maximum at $CH_3COOH = 0.06$. At this concentration of CH_3COOH, k_{a+b} increases linearly with $[CH_3COO^-]$.

LITERATURE

(1) A. L. Bernouilli, W. Wege, *HCA* 1919, **2**, 511. (2) A. L. Bernouilli, W. Wege, *HCA* 1919, **2**, 515. (3) J. Bigeleisen, *JCP* 1949, **17**, 425. (4) G. Bredig, D. M. Lichty, *ZEC* 1906, **12**, 459. (5) R. E. Burk, W. Daus, *JPC* 1931, **35**, 1461. (5a) A. Dinglinger, E. Schroer, *ZPC*^{A} 1937, **179**, 401. (6) M.S. Dudkin, ZhOKh 1950, **20**, 1729. (7) R. A. Fairclough, *CSL* 1938, 1186. (8) G. A. Hall, Jr., *ACS* 1949, **71**, 2691. (9) C. V. King, P. Kulka, A. Mebane, *ACS*, 1950, **72**, 1906. (10) J.G. Lindsay, D.E. McElcheran, H.G. Thode, *JCP* 1949, **17**, 589. (11) J. Muus, *JPC* 1935, **39**, 343. (12) P. E. Yankwich, M. Calvin, *JCP* 1949, **17**, 109.

DECOMPOSITION
with evolution of CO_2 from aromatic carboxylic acids

Reaction type $\left.\begin{matrix}ArCOOH\\ArCOO^-\end{matrix}\right\} \rightarrow CO_2 + \left\{\begin{matrix}ArH\\Ar^-\end{matrix}\right.$

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	2, 4, 6-$(NO_2)_3C_6H_2COO^-$	C_2H_5OH	10^3A = 4.82			k A	35	7.7	-5				*	(^{2})
			9.96				"	7.0	-5					
			10.18				"	7.4	-5					
			19.88				"	6.2	-5					
			4.82			"	45	3.1	-4					
			9.96				"	2.8	-4					
			10.18				"	3.0	-4					
			19.88				"	2.4	-4	27.0				
.2	2, 4, 6-$(NO_2)_3C_6H_2COOH$	C_2H_5OH	10^3A = 4.20	X = $C_6H_5NH_2$	0.001 - 0.1	$k\ A^{1/2}\ X^{1/2}$	35	3.5	-5				*	(^{2})
							45	1.3	-4					
				o-$ClC_6H_4NH_2$	"	"	35	3.4	-6					
							45	1.3	-5					
				m-$ClC_6H_4NH_2$	"	"	35	9.8	-6					
							45	3.7	-5					
				p-$ClC_6H_4NH_2$	"	"	35	1.5	-5					
							45	5.6	-5					
				p-$CH_3C_6H_4NH_2$	"	"	35	4.7	-5					
							45	1.9	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2	2, 4, 6-$(NO_2)_3C_6H_2COOH$ *(continued)*	C_2H_5OH	$10^3A = 4.20$	$C_6H_5N(CH_3)_2$	0.001 - 0.1	$k\,A^{1/2}X^{1/2}$	35	1.2	-5					
							45	4.6	-5					
.3	2, 4, 6-$(NO_2)_3C_6H_2COOH$	H_2O				$k\,A$	60	2.3	-6				*	(1)
							70	1.1	-5					
		H_2O				$1/2\;kK[(1 + 4A/K)^{1/2} - 1]$	60	2.3	-6					"
							70	1.1	-6	36	9	18		
		H_2O + dioxane	20 %			"	60	1.5	-5					"
							70	7.0	-5					
			40 %			"	60	1.4	-4					"
							70	5.8	-4					
			60 %			"	60	9.2	-4					"
							70	3.0	-3					
			80 %				60	5.2	-3					
							70	1.5	-2	23	1	14		

COMMENTS

(.1) The data refer to the Li salt; close values for the Na salt. (.2) The order, 1/2 in A and 1/2 in X, indicates clearly that the rate of the reaction is governed by the rate of decomposition of the anion of the corresponding anilinium salt. (.3) First order in the acid holds only in H_2O and, approximately, in low-dioxane solvents. At greater dioxane concentrations, the rate $-dA/dt$ follows the order given as definition of k, involving the dissociation constant K of the acid in the given medium and indicating the decomposition of the anion as the rate-determining step. The empirical order of the reaction with respect to A falls from 1 in H_2O to about 1/2 in 90 % dioxane. In 20 %, 40 %, 60 %, 80 % dioxane, K = 0.3, 0.031, 0.002, 0.0000047. The observed rates of decomposition at an initial [A] = 0.008, are:

Solvent		H_2O	H_2O + dioxane 20 %	40 %	60 %	80 %	89 %
$-10^8 (dA/dt)$	60°C	1.8	13	90	274	98	9.5
	70°C	8.9	58	346	948	276	24.4

i.e. passing through a maximum.

LITERATURE

(1) D. Trivich, F. H. Verhoek, *ACS* 1943, 65, 1919.

(2) F. H. Verhoek, *ACS* 1939, 61, 186.

DECOMPOSITION

Evolution of N_2 from diazonium halides

Liquid phase

Reaction type $ArN_2Cl \rightarrow ArCl + N_2$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments
								k^o	n		A^o	n	
.1	$C_6H_5N_2Cl$	H_2O	0.1	HCl	pH 1.6 – 1.8	k A	5	1.5	-6				*
							25	4.10	-5				
							35.2	2.00	-4				
							50	1.40	-3	27.2	3.6	15	
			0.1	HCl	0.1	"	35.2	2.00	-4				
					5.0		"	2.35	-4				
					10.0		"	2.41	-4				
					12.0		"	2.26	-4				
.2	o-$CH_3C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	35.2	9.58	-4	26.2	3.5	15	
.3	m-$CH_3C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(10 – 35°)			25.7	1.3	15	
.4	p-$CH_3C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(25 – 55°)			27.5	7.1	14	
.5	m-$CH_3OC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(15 – 30°)			24.6	2.1	14	
.6	p-$CH_3OC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(60 – 80°)			32.5	3.9	15	
.7	o-$COOHC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(25 – 40°)			29.4	2.6	16	
.8	m-$COOHC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(30 – 40°)			27.1	1.7	15	
.9	p-$COOHC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(40 – 55°)			27.7	1.1	15	

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments
								k^o	n		A^o	n	
.10	$o\text{-}OHC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(50 - 60°)			30.4	7	15	
.11	$m\text{-}OHC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(20 - 30°)			26.0	5.5	15	
.12	$p\text{-}OHC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(50 - 60°)			23.6	3.2	11	
.13	$o\text{-}NO_2C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(60 - 80°)			26.5	5.9	11	
.14	$m\text{-}NO_2C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(60 - 80°)			33.2	7.0	16	
.15	$p\text{-}NO_2C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(60 - 80°)			29.8	1.2	15	
.16	$o\text{-}C_6H_5C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(20 - 45°)			25.5	3.2	14	
.17	$m\text{-}C_6H_5C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(15 - 35°)			22.8	5.3	12	
.18	$p\text{-}C_6H_5C_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(30 - 55°)			27.6	3.5	14	
.19	$o\text{-}SO_3HC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(40 - 50°)			30.3	7.9	16	
.20	$m\text{-}SO_3HC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(40 - 50°)			28.0	2.9	15	
.21	$p\text{-}SO_3HC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(40 - 55°)			27.4	2.9	14	
.22	$o\text{-}ClC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(60 - 90°)			30.8	2.6	14	
.23	$m\text{-}ClC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(40 - 55°)			30.2	2.1	16	
.24	$p\text{-}ClC_6H_4N_2Cl$	H_2O	0.1	HCl	0.02	k A	(60 - 80°)			31.6	1.1	16	

COMMENTS

Measurements of amount of N_2 evolved. (.1) First order over 96 % of the conversion. In dilute solution, the reaction is $A \rightarrow N_2 + C_6H_5Cl \xrightarrow{H_2O} N_2 + HCl + C_6H_5OH$, with a 95 % yield of C_6H_5OH (at $H_2O/A = 1280$); in concentrated solution, the yield of C_6H_5OH falls to 24 % (at $H_2O/A = 2.4$), and the products are C_6H_5Cl, C_6H_6, and $C_6H_5C_6H_5$. The effect of acid concentration is very slight.

LITERATURE

M. L. Crossley, R. H. Kienle, C. H. Benbrook, *ACS* 1940, 62, 1400.

PYROLYSIS
Aliphatic hydrocarbons

Gas phase

All rates are in "unit of amount" per sec.

Comments, Mechanism, Literature, at the end of the table.

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Amount of addend	Rate measured	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments Mechanism	Literature
										k^o	n		A^o	n		
.1	$CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6$	p	mm Hg	13 - 385		-	+p	k A	735	1.2	-7				*	(17)
									800	6.0	-7					"
									976	1.3	-6					"
									1008	4.3	-6					"
									1061	3.2	-5					"
									1113	1.9	-4	79	1.0	12		"
		"	"	100	-	-	"	"	850	2.8	-6				*	(13)
				200	-	-			"	3.4	-6					"
.1.1	$CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6$	"	"	100	NO	0	"	"	850	2.8	-6				*	(13)
				"		6.1			"	1.5	-6					"
				"		10			"	2.0	-6					"
				"		23			"	3.8	-6					"
				200	"	0	"	"	"	3.4	-6				*	"
				"		6.5			"	2.1	-6					"
				"		14.5			"	2.8	-6					"
				"		26			"	4.1	-6					"

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Amount of addend	Rate measured	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments Mechanism	Literature
										k^o	n		A^o	n		
.2	$CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6$	flow anal	mm Hg	760			-A	k A							*	(10)
						$100(A_o - A)/A_o$										"
						1.27			1007	4.4	-2					"
	[See Supplementary Table]					10.54			"	7.4	-2					"
						1.27			1033	5.8	-2					"
						10.88			"	1.07	-1					"
						16.91			"	1.22	-1					"
						2.29			1053	1.25	-1					"
						9.66			"	1.77	-1					"
						3.96			1075	2.50	-1					"
.3	$C_2H_6 \rightarrow C_2H_4 + H_2$	p, anal	mm Hg				+p	k A	551	2.8	-5			(+p)		(32) (18)
				100 - 1500		-A;	+M		565	6.4	-5			(+M)		(43)
							-A		572	8.9	-5			(-A)		(38) (19)
							"		580	1.2	-4					
							+p		583	1.7	-4					
							-A		595	2.8	-4					
							"		600	[7.9]	-4					
							"		607	4.6	-4					
					-	+p;	-A		614	7.6	-4					
							-A		625	1.0	-3					
					-	+p;	-A		638	1.9	-3					
							+p		663	7.4	-3	70	1	15	*	
							-A		668	[1.4]	-2					
							"		675	[2.9]	-2					
							"		700	[3.6]	-2					

No.	Reaction	Medium	Unit of amount	Amount of reactant	Addend	Amount of addend	Rate measured	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments Mechanism	Literature
										k^o	n		A^o	n		
.4	$C_2H_6 \rightarrow C_2H_4 + H_2$	p	mm Hg	150	NO	0	+p	k A	620	5.9	-4					(35)
						1.25			"	1.9	-4					"
						18.5			"	4.7	-5					"
						35.5			"	5.0	-5					"
						50.5			"	4.8	-5	74.5				"
		anal	300 - 550		NO	1%	-A	k A	565	1.3	-5					(38)
						"			607	1.2	-4					"
						"			640	7.7	-4	77.3				"
.5	$C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow CH_4, C_{>4}$ (A) (B) (C) (R)	anal	M/1	A = 0.025		-	+L	k AB	590	1.4	-2	See Supplementary Table			*	(41)
							+R	k B²	"	3.3	-2					"
.5.1	$C_2H_6 + C_2H_4 + H_2 \rightarrow CH_4, C_{>4}$	"	"	A ⇄ B + C		-	+L	k B(A + B + C)							*	(41)
			A + B = 0.025						550	1.7	-3					"
									590	5.6	-3					"
									620	1.2	-2	41				"
			"				+R	k B²	550	8.1	-3				*	"
									590	2.1	-2					"
									620	3.9	-2	35				"
			"	0.01 - 0.04		+(L + R)		k AB	550	2.3	-3				(41)	(39)
									590	1.1	-2					"
									620	3.1	-2	55			*	"
.6	$C_3H_8 \left\langle \begin{array}{ll} C_3H_6 + H_2 & (a) \\ C_2H_4 + CH_4 & (b) \end{array} \right.$	p	mm Hg	∞	-	-	+p	k A	551	1.84	-4					(37)
									572	5.24	-4					"
									602	1.85	-3	63.3	2.9	13		"
		"	"	760	-	-	"	"	625	7.2	-3					(24)
									650	2.2	-2	63	3.2	13		"

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Amount of addend	Rate measured	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments Mechanism	Literature
.6.1	$\underset{(A)}{C_3H_8} \rightarrow \underset{(B)}{C_3H_6} + \underset{(C)}{H_2} \rightarrow \underset{(L)}{CH_4}, \underset{(R)}{C_{>4}}$	anal	M/1 A + B = 0.02 C = 0.01	$A \rightleftharpoons B + C + (L + R)$				kAB	553	1.2	-2					(^{40})
.7	$C_4H_{10} \rightarrow C_3H_6 + CH_4$ (a); $C_2H_6 + C_2H_4$ (b); $C_4H_8 + H_2$ (c)	p	mm Hg	760	-	-	+p	kA	625	2.1	-2				*	(^{24})
				"	-	-	"	$k_1A^{1.5} + k_2A^2/(A_o - A)$							*	(^{4})
								k_1	480	1.1	-6					"
									500	3.0	-6					"
									535	1.4	-5	58.0				"
								k_2	480	3.0	-7	72.0				
									500	1.0	-6					
									535	7.9	-6					
.8	$(CH_3)_2CHCH_3 \rightarrow C_3H_6 + CH_4$ (a); $C_2H_6 + C_2H_4$ (b); $C_4H_8 + H_2$ (c)	p	mm Hg	760	-	-	+p	kA	600	7.7	-3					(^{24})
									625	2.9	-2					"
									650	5.0	-2					"
.9	$(CH_3)_2C{:}CH_2 \rightarrow \underset{(L)}{CH_4}, \underset{(M)}{H_2}, \underset{(N)}{CH_2{:}C{:}CH_2\ (CH{:}CCH_3)}$	anal	mm Hg	50 - 600 1.3 - 20			+(L + M)	kA	636	5.0	-4	64				(^{44})
									686	3.5	-3					"
									768	4.5	-2					"
									808	2.2	-1	67	5	12		"
.10	$(CH_3)_2C{:}CH_2 \rightarrow CH_4, H_2, CH_2{:}CHCH_3, (CH_3)_2CHCH_3$, liquid	flow anal	mm Hg	760	-	-	-A	kA	600	1.6	-3					(^{18})
									650	8.0	-3	56				"
									700	4.0	-2					"

SUPPLEMENTARY TABLES

(.2.1) $CH_4 \rightarrow H_2, C_2H_6, C_2H_4, C_2H_2, C_3H_6, CH_3C\vdots CH....$ (^{10})

Products in % in the outgoing gas

°C	$100(A_o - A)/A_o$	C_2H_4	C_2H_2	C_2H_6	C_3H_6	$CH_3C:CH$	H_2
1007	1.27	0.11	0.04	0.09	0.02	0.02	1.91
	10.54	0.87	0.39	0.10	0.07	0.05	16.56
1033	1.27	0.13	0.05	0.09	0.02	0.03	1.87
	10.88	1.08	0.62	0.10	0.08	0.10	16.35
	16.91	1.36	0.68	0.11	0.09	0.06	25.32
1053	2.29	0.031	0.08	0.12	0.03	0.07	3.15
	9.66	0.98	0.65	0.14	0.08	0.14	14.25
1075	3.96	0.049	0.25	0.15	0.03	0.11	5.67

(.5) $C_2H_6 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_4, H_2, CH_4, R$ (^{41})

Time in hours; amounts of hydrocarbons in g atom C/liter; H_2 in M/l
Temperature 590°C

Hours	$10^3C_2H_6$	$10^3C_2H_4$	10^3H_2	10^3CH_4	10^3R
0	500.00	-	-	-	-
0.5	44.18	4.16	4.66	0.95	0.71
1.0	41.76	4.52	5.42	2.21	1.51
2.0	37.38	3.54	5.96	5.43	3.64
3.0	32.78	3.34	5.44	8.46	5.42
4.0	31.54	3.16	5.99	9.54	5.76
5.0	30.16	2.86	5.84	10.75	6.23
6.5	28.80	2.62	5.94	11.94	6.64

COMMENTS

(.1) Reaction approximately 97 % homogeneous. Induction period observed (17). [See, however, (.2)] Data given for *initial* rates; *k* falls with the progress of the reaction owing to retardation by H_2 (14, 15); [See, however, (.2)] For that reason, also because of loss of H_2 by diffusion through the quartz walls, *k* is probably too low (17). Initial rates of (13) somewhat higher than those of (17), and show a pressure dependence not stated by (17). C_2H_4 is detected in products in flow with short time of contact at 900 - 1500° with N_2 as diluent (1). CH_3 radicals detected by mirror technique (26, 25) and by mass spectography but no CH_2 radicals (5). As a function of amount of NO added, *k* seems to pass through a minimum (13) (see data in table), but the quantitative effect of NO is uncertain owing to an oxidation reaction (13). Mechanism of (17), $CH_4 \rightarrow H_2 + CH_2$, is unsubstantiated. Radical mechanism (29, 18) questioned (38). Probably mixed molecular and short radical chains initiated by $CH_4 \rightarrow CH_3 + H$ (26, 25). (.2) Analytical data in flow system (porcelain tube) evaluated in terms of a first-order rate constant *k* which increases systematically with increasing degree of decomposition $100(A_o - A)/A_o$. This trend is paralleled by an increase of the amounts of C_2H_4 and C_2H_2 formed among the products, as shown in the Supplementary Table (selected data). Of these two gases, C_2H_2 has a definite catalytic effect, C_2H_4 appears to have none. The upward trend of *k* seems to level off, at 1107 and 1033°C, at around 15 % decomposition. At variance with (17), H_2 2 % increases the rate of decomposition by 20 - 30 %, and increases in particular the amounts of C_2H_2 and C_2H_4, hence no retardation effect is found; also, no induction period is observed, contrary to (17). N_2 50 % and H_2O have no effect. The data tabulated refer to a surface/volume ratio of 2.47; its increase to 9.52 increases the early rate of decomposition about 2 - 3 times; the amounts of C_2H_2 and C_2H_4 produced are increased as long as their concentrations are low, but decreased at higher concentrations, evidently owing to catalyzed decomposition at the wall. The accelerating effect of the surface disappears at 30 % decomposition. (.4) The first-order rate constants, from *initial* rates, listed in the table at close temperatures, are compiled from several sources (32, 18, 43, 38, 19) to show the degree of consistency of data of different authors, and by different manometric or analytical (-A, +M) methods; evidently, at

COMMENTS *(continued)*

the initial stage, the increase of pressure is an accurate measure of the stoichiometric change as formulated. *Very close* data of different authors have been averaged and are underlined. Data of (19) [in brackets] are systematically too high and should, roughly, be halved to fall in line with other data listed. The first order holds only in the initial stage, and the data may be in error due to back reaction (2). The reaction is very nearly homogeneous. Some CH_4 and condensate are found in addition to $C_2H_4 + H_2$ (32, 43, 3); with further progressing reaction, CH_4 + condensate become increasingly the main products: see further under (.5) and (.5.1). Mirror (27) and mass-spectrographic (5) techniques show CH_3 and C_2H_5 radicals. Para-ortho-H_2 system shows H atoms (21). The decomposition is only weakly sensitized by CH_3 radicals (34, 4). Selected data on inhibition by NO are from (35) and (38); there is evidence of oxidation by NO (12). The reaction appears to be only partly a chain process. (.5) (.5.1) The rate laws and rate constants are derived from complete analyses for C_2H_6, C_2H_4, H_2, CH_4, and condensate $R(C_{>4})$, as illustrated by the Supplementary Table for the decomposition of initially pure C_2H_6, 0.025 M/l, at 590°C. The *initial* rate constants for production of CH_4 and for production of R are derived from this table. The process is conceived as built around the "background reaction" $C_2H_6 \rightleftarrows C_2H_4 + H_2$, with the production of CH_4 and of R possibly representable by the stoichiometric equation $C_2H_6 + C_2H_4 + H_2 \rightarrow 2CH_4 + C_2H_4$, followed by polymerization of C_2H_4. Starting with pure C_2H_6 (.5), the rates are initially self-accelerating up to a breaking point lying roughly close to but not at the equilibrium composition. During the first 3 hours, k for the production of R oscillates but shows no systematic trend, whereas k for the production of CH_4 falls from 1.4×10^{-2} to 5.4×10^{-3}. Packing of the reaction vessel results in a behavior resembling the case of a near equilibrium mixture. The data under (.5.1) refer to a $C_2H_6 + C_2H_4 + H_2$ mixture initially close to the equilibrium composition. In this case, after pretreatment with H_2, increase of the surface is without effect, but some surface effect appears at high H_2 pressures. A mechanism proposed by (39) to account for the kAB law, and involving formation of an intermediate molecular compound AB as rate determining step, is unsubstantiated. (.6) Data of (37) between 550 and 600°, and data of (24) up to 650°C, are given as representative. The rate constants (37) are extrapolated from the experimental pressure range (50 - 600 mm Hg) to "infinite"

COMMENTS *(continued)*

pressure. The *k* of (22). (19), and (8) at 575°C are close to (37), and so are the arrhenian constants *E* and *A* of (19), but those of (22) are distinctly higher. Products at 10 % decomposition at 575°C under 739 mm Hg are C_3H_6 23.6, H_2 22.4, C_2H_4 23.2, CH_4 28.0, C_2H_6 2.8 % (37); analyses of (8) are in excellent agreement therewith. The change of pressure appears to be a sufficiently accurate measure of the conversion as represented by the stoichiometric formulation given, with (a) and (b) in the ratio 1:1; at later stages of the reaction, the simple stoichiometric formulation is no longer valid. The first-order *k* fell strongly in the course of a single run and with decreasing initial pressure (24, 2, 37); thus, between 760 and 2 mm Hg, *k* falls to about one-half; dilution with N_2 increases *k* only slightly (24). The reaction is essentially homogeneous (24). The reaction is sensitized by radicals from azomethane (34) and from ethylene oxide (4); it is inhibited by NO (13) and by C_3H_6 (31). CH_3 radicals detected by mirror technique (6); H atoms detected by ortho-para-H_2 conversion (20). Probably mixed molecular and short radical- chain mechanism. Further literature (23, 9, 33).

(.7) The simple first-order *k* applicable to the initial rate, is given for comparison with other hydrocarbons. At pressure reduced to 2 mm Hg, *k* falls by less than 50 %. The two-term law holds over a more extended range of the reaction. The ratio (a):(b):(c) = 3:2:1 at 25 % decomposition. The reaction is essentially homogeneous. It is sensitized by radicals from ethylene oxide (4, 36), C_3H_6 (4, 31, 36), $Hg(CH_3)_2$ (7) and azomethane (36), inhibited by NO (4, 36) but the inhibition is transitory, the rate becoming normal after about 15 % conversion (4). NO does not completely suppress chains in sensitized reaction (36). Mirror technique shows presence of CH_3 radicals (6, 30). Probably chain mechanism involving a large number of short chains (36).

(.8) Essentially homogeneous. The initial first-order *k* given fell rapidly with the progress of the reaction. At pressure reduced to 2 mm Hg, *k* falls to about 1/5 of its value under 760 mm Hg. Dilution with N_2

COMMENTS *(continued)*

increases k only very slightly. The ratio (a):(b):(c) is about 15:1:35 at the initial stage. Further literature (23, 8, 22, 37). **(.9)** Proposed mechanism:

$A \rightarrow CH_2{:}C(CH_3)CH_2 + H;$

$H + A \rightarrow CH_2{:}C(CH_3)CH_2 + H_2;$

$CH_2{:}C(CH_3)CH_2 \rightarrow CH_2{:}C{:}CH_2 + CH_3;$

$CH_3 + A \rightarrow CH_2{:}C(CH_3)CH_2 + CH_4;$

$CH_2{:}C(CH_3)CH_2 + CH_3 \rightarrow CH_2{:}C(CH_3)CHCH_3.$

Chain length about 9 (44). **(.10)** Homogeneous; k reasonably constant with variation of contact time by a factor of 2 - 3, and with variation of A (dilution by H_2 or N_2) by a factor of 2. The liquid is 20 - 60 % by weight of A decomposed.

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PYROLYSIS

Gas phase

Aromatic Hydrocarbons

Amounts are in mm Hg.
Rates are in mm Hg per sec.

No.	Reaction	Amount of reactant	Rate measured	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		*E*	$A = A^{\circ} \times 10^{n}$	
						k°	n		A°	n
.1	$o\text{-}C_6H(CH_3)_2 \longrightarrow H_2$, CH_4, C_6H_5, $o,o'\text{-}CH_3C_6H_4CH_2CH_2C_6H_4CH_3$	3 - 4	$+d(H_2 + CH_4)$	kA	730	3.8	-3			
					788	3.1	-2			
					815	7.0	-2			
					838	1.47	-1	74.8	5	13

COMMENTS

Flow system. About 10 % of A is decomposed into C_2 hydrocarbons. The products are interpreted by the reaction mechanism: $A \longrightarrow o\text{-}C_6H_4(CH_3)CH_2 + H$ (rate determining); $H + A \longrightarrow H_2 + o\text{-}C_6H_4(CH_3)CH_2$, or $H + A \longrightarrow CH_3 + C_6H_5CH_3$; $CH_3 + A \longrightarrow CH_4 + o\text{-}C_6H_4(CH_3)CH_2$; $2\ o\text{-}C_6H_4(CH_3)CH_2 \longrightarrow o,o'\text{-}CH_3C_6H_4CH_2CH_2C_6H_4CH_3$.

LITERATURE

M. Szwarc, *JCP* 1948, **16**, 128.

Homogeneous Reactions
571.413.

PYROLYSIS

Alicyclic hydrocarbons

Rate measured: $+\Delta p$

Gas phase

Amounts are in mm Hg.
Rates are in mm Hg per sec.

No.	Reaction	Method	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$cyclo\text{-}C_5H_{12} \rightarrow H_2 + cyclo\text{-}C_6H_{10} \rightarrow H_2 + C_2H_4 + C_4H_6$	p	10 - 200	k A	485 - 565			60	5	11	*	(1)
.2	$cyclo\text{-}C_6H_{10} \rightarrow C_2H_4 + C_4H_6$	p	10 - 200	k A	485	7	-4					
					485 - 565			57.5	8.9	12	*	(1)
.3	$cyclo\text{-}C_6H_9 \cdot CH_3 \rightarrow H_2 + C_2H_4 + C_4H_6$	p	10 - 150	$k\,A^{1.3}$	485 - 565			60	3.2	11	*	(1)

COMMENTS

(.1) Total pressure change 2.4. Side reaction $A \rightarrow 2C_3H_6$; no isomerization to $cyclo\text{-}C_5H_9CH_3$. Induction period not due to that isomerization, contrary to (2). H_2 has no marked effect; NO has no effect. (.2) The equation represents 80 - 90 % of the reaction. Proof of homogeneity given. H_2 has little effect, reduces the rate only in large amounts; NO has no effect. (.3) Induction period. Total pressure change 2.5.

LITERATURE

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PYROLYSIS
Aliphatic C,H,O compounds

Gas phase

Homogeneous Reactions
571.441.

Amounts are in mm Hg.
Rates are in mm Hg per sec.

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments Mechanism	Literature
											k^o	n		A^o	n		
					Aldehydes												
.1	$HCHO \longrightarrow H_2 + CO$	p	30 - 370			+p	kA^2	510			3.6	-6				*	(3)
								569			2.7	-5					
								607			9.0	-5	45				
.2	$CH_3CHO \longrightarrow CH_4 + CO$	p, anal	50 - 450			-A	$kA^2/A_o^{1/2}$									*	(17)
								450			4.8	-6					
								477			1.4	-5					
								512			4.8	-5					
								542			1.5	-4					
								577			5.0	-4	46 ±0.5	2.5	8		
.3	$CH_3CHO \longrightarrow CH_4 + CO$	p, anal	A = 37 - 172 L + M = 322 + 183			-A	$kA^{3/2}[A + b(L + M)]^{1/2}/[A + b'(L + M)]^{1/2}$									*	(17)
								577		k	5.0	-4					
										b	6.0	-2					
										b'	3.3	-1					

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments Mechanism	Literature
.4	$CH_3CHO \longrightarrow CH_4 + CO$	p, anal	75 - 225	O_2	< 0.05	-A	$k A^{3/2} + k' A^{3/2} [O_2]$										(18)
								450		k	4.8	-6					
								"		k'	7.5	-3					
								477		k	1.4	-5					
								"		k'	6.4	-3					
								512		k	4.8	-5					
								"		k'	4.3	-3					
.5	$CH_3CHO \longrightarrow CH_4 + CO$	p, (anal) (thc)	5 - 100	H_2	0 - 400		$k A^{3/2} + k' A^{1/2} [H_2]$									* (9)	(10)
						-A		556		k	3.3	-4	49.5				"
										k'	5	-5					
										(0.5)							
			17		100			556	0.04	5.2							"
			100		424			"	0.55	2.2							
			175		0			518		12.1							"
			"		400			"		9.1							
			"		800			"		7.2							
.6	$CH_3CHO \longrightarrow CH_4 + CO$	p	25 - 330	N_2O	100	+p	$k A$	480	(0.5)	155			27			*	(37)
			100	"	100	$k A^{3/2} [N_2O]^{1/2}$		460	"	2600							"
								520		335			40				
.7	$CH_3CHO \longrightarrow CH_4 + CO$	p	100	NO	100	$k A^{3/2} [NO]$		450	"	1280						*	(38)
								470		645							
								480		400							
								505		180			37.3				

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments Mechanism	Literature
											k°	n		A°	n		
										(0.5)							
.8	$CH_3CHO \rightarrow CH_4 + CO$	p	50	C_3H_6	∞	+p	$kA^{\sim 2}$	550		1400						*	$(^{28a})$
			75	"	"								48				
			200	"	0	"		550		210							"
			"		5			"		290							
			"		50			"		480							
			"		∞			"		600							
			200	"	∞	"	"	515		2300							"
			"		"			570		340			46				
			"		"												
			350	"	∞	"	"						47				"
			400	"	∞	"	"	550		350							"
.9	$CH_3CHO \rightarrow CH_4 + CO$	p				+p			$(\times 10^{3})$	(0.5)							
			50					535	1.16	670			55.2			*	$(^{28})$
			400					"	3.83	230			49.1				
			50			"		515		2135							"
			"					575		182							
	$CD_3CDO \rightarrow CD_4 + CO$	"	50			"		535	0.40	1700			56.4			*	"
			400					"	1.57	450			49.7				
			50			"		511		6065							"
			"					571		515							
.10	$CH_3CHO \rightarrow CH_4 + CO$	p	107			+p		484	0.018							*	$(^{20})$
			186					"	0.035								
			328					"	0.087								
			313					542	0.67								

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments Mechanism	Literature
											k^o	n		A^o	n		
.10	*(continued)*																
	$CD_3CDO \rightarrow CD_4 + CO$	p	293			+p		484	0.052							*	(20)
			70					542	0.057								
			210					"	0.31								
			302					"	0.56								
.11	$C_2H_5CHO \rightarrow CO, C_2H_6, H_2, CH_4, C_nH_{2n}$	p	50			+p		550	(0.5)	240			63.5			*	(28a)
			160					"		180			61	(509 - 589°)			(40a)
			300					"		150			56				
			50	C_3H_6	50	"		550		420							(28a)
			300		"			"		190							
			50		200			"		360							
			300		"			"		230							
			300	NO	1.0	"		550		200							
			"		6.0			"		250							
	$C_2H_5CHO \rightarrow CO + C_2H_6$		70 - 270	I_2	2 - 30	$kA[I_2]/(1+bA)$		336		k	7.6	-4				*	(1a)
								385			9.15	-3	33.5	1	9		
										b	7.8	-3					
.12	$CH_2{:}CHCHO \rightarrow CO + (CH_4, C_2H_6 + H_2, C_2H_4, C_4H_8)$																
		p (anal)	20			+p	$kA^{<2}$	508	(0.5)	1031						*	(35)
			100					"		408							
			300					"		167							
			30			"	"	520		690							"
			100					"		286							
			300					"		520							

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments Mechanism	Literature
											k°	n		A°	n		
.12	$CH_2{:}CHCHO \rightarrow CO + (CH_4, C_2H_6 + H_2, C_2H_4, C_4H_8)$ (*continued*)		30			+p	$kA^{<2}$	540		364			42.2				(35)
			100					"		156			40.7				
			300					"		68			36.5				
Ketones																	
.13	$CH_3COCH_3 \rightarrow CH_4 + CH_2{:}CO$	p	127			+p	kA	553			1.1	-3				*	(13)
			61					"			9.5	-3					
			6					"			5.1	-4	63	1	15		
		p	400			+p	kA	570			3.0	-3					(42)
			"					600			7.3	-3					
			"					610			1.2	-2					
			"					620			1.8	-2	68	8	14		
		p	>100			-A	kA	600			7.3	-3					
			55					"			5.3	-3					
			8					"			3.0	-3					
			2.5					"			2.3	-3					
			100	C_3H_6	100	-A	kA	570			5.3	-4				*	(29)
					"			600			1.9	-3					
					"			615			3.6	-3	62.6				
			"	"	∞	"	"	570			4.1	-4					
Ethers																	
.14	$CH_3OCH_3 \rightarrow CH_4 + HCHO \rightarrow CH_4 + H_2 + CO$	p	400 - 900			+p	kA	422			4.5	-6				*	(9)
								478			1.27	-4					(30)
								552			4.3	-3	58.5				

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k =$ $k^\circ \times 10^n$		E	$A =$ $A^\circ \times 10^n$		Comments Mechanism	Literature
											k°	n		A°	n		
.14	$CH_3OCH_3 \rightarrow CH_4 + HCHO \rightarrow CH_4 + H_2 + CO$ (*continued*)	p	400 - 900	NO	>1	+p	k A	537			2.3	-4				*	(30)
								565			9.0	-4					"
								580			1.8	-3	62				
.15	$CH_3OC_2H_5 \longrightarrow CH_4 + CH_3CHO \longrightarrow 2\ CH_4 + CO$	p	380			+p		460	(0.25)	3220						*	(34)
			720					"		2500							
			85					480		2120							
			320					"		1290							
			720					"		880							
			80					500		880							
			570					"		440							
			∞										55				
		p anal	297			+p	k A	457	(0.25)	9084						*	(36)
			"					"	(0.5)	22656	~ 3	-5					
			250					487	(0.25)	1716							
			"					"	(0.5)	4002	~ 2	-4					
			299					509	(0.25)	828							
			"						(0.5)	2058	~ 6	-4	65				
		"	270	C_2H_5I	0.6	+p	k A	480	(0.5)	550	~ 2	-3				*	(36)
			250		0			487		4002	~ 2	-4					
			241		25			"		68							
		"	50 - 300	I_2	7	+p	k A	460	(0.25)	990	1.4	-3				*	(2)
								504		230	6.1	-3					
								547		63	2.2	-2	37.5				
		"	100	NO	0	+p		560	(0.25)	65						*	(33)
					0.1			"		230							
					1			"		475							
					10			"		400							

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments Mechanism	Literature
.15	$CH_3OC_2H_5 \to CH_4 + CH_3CHO \to 2\ CH_4 + CO$ *(continued)*	p anal	400	NO	5	+p		523	(0.25)	1400						*	(33)
					"			560		270							
					"			600		48			62				
.16	$CH_3OC_3H_7 \to C_2H_6 + CH_4 + CO$	p	20 - 240			+p	k A	400	(0.5)	846	8.2	-4				*	(6)
								450		62	1.1	-2	49	1	11		
.17	$CH_3OCH(CH_3)_2$ → $CH_4 + CH_3COCH_3$ $HCHO + C_3H_8 \to$ $H_2 + CO + C_3H_8$	p	100 - 300	I_2	7	+p	k A	453			2.6	-3					(2)
								490			6.9	-3					
								518			1.4	-2	29.5				
.18	$CH_2{:}CHOC_2H_5 \to C_2H_4 + CH_3CHO$	p	50 - 190			+p	k A	389	(0.2)	265	6.0	-3				*	(39)
								412		88	1.8	-2					
								424		47	3.4	-2	44.4	4.0	11		
.19	$(CH_3)_2CHOCH(CH_3)_2 \to CH_4,\ CO,\ C_nH_{2n}$	p	30 - 330			+p	k A	551			6.3	-3				*	(7)
								566			1.3	-2	63				
.20	$(CH_3)_2CHOCH(CH_3)_2 \to C_3H_8 + CH_3COCH_3$	p	94	I_2	25	+p	k A	400			1.3	-2	29.0				(7)
	Peroxides																
.21	$(CH_3)_3COOC(CH_3)_3 \to 2\ CH_3COCH_3 + C_2H_6$	anal				+M	k A	129			2.0	-5				*	(34a)
								138			4.3	-5					
								150			1.4	-4					
								152			1.6	-4					

571.441.

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	Initial rate	Fractional time	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments Mechanism	Literature
											k°	n		A°	n		
.21	$(CH_3)_3COOC(CH_3)_3 \rightarrow 2\ CH_3COCH_3 + C_2H_6$ *(continued)*																
	$(CH_3)_3COOC(CH_3)_3 \rightarrow 2\ CH_3COCH + 2\ CH_3$; $CH_3 + C_6H_5CH_3 \rightarrow C_6H_5CH_2 + CH_4$ (M); $CH_3 + CH_3 \rightarrow C_2H_6$ (M′) $2\ C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5$	anal	10 - 40 (total)	$C_6H_5CH_3$		+(M + M')	k A	116			5.1	-6				*	(^{34a})
								125			8.5	-6					
								144			6.0	-5					
								148			9.0	-5					
								155			1.9	-4					
								167			6.1	-4	34	2	13		
.22	$(CH_3)_3COOC(CH_3)_3 \rightarrow (CH_3)_2CO,\ CH_3COC_2H_5,\ CH_4$	p anal	50 - 380	N_2	~ 5	+p	k A	147.2			1.4	-4				*	(^{21a})
								154.6			3.2	-4	39	3.2	16		
.23	$(C_2H_5)(CH_3)_2COOC(CH_3)_2(C_2H_5) \rightarrow$	p anal	70 - 150	N_2	~ 5	+p	k A	132.2			7.2	-5				*	(^{21a})
								149.7			4.8	-4	37				

COMMENTS

(.1) At higher concentrations of the products the reaction tends to become first-order; k is only approximate owing to simultaneously occurring condensation reactions.

(.2) - (.10) $CH_3CHO \rightarrow CH_4 + CO$.

(.2) - (.3) The data of Letort (.2, .3) (17, 18) valid in rigorous absence of O_2 ($<10^{-5}$ vol %) and on a surface poisoned by the decomposition products, are rated most reliable; (.1) holds in the initial stage, (.2) in the presence of considerable amounts of products. The retardation by the products, expressed by the rate law (.3), is the same whether caused by CH_4, CO, or their sum; apparent evidence to the contrary (11) is unreliable owing to disregard of sensitivity to surface treatment. The increase of the rate caused by the products (27) is for the heterogeneous reaction of condensation. The data (selected points) are recalculated to mm Hg and sec; in units of M/l and sec, the rate constant of law (.2) is $k = 7.37 \times 10^{10} e^{-46000/T}$ Analysis for CH_3CHO during a run (41) confirms the manometric data which show 96 - 98.5 % total pressure change. Large surface/volume ratio (27) or clean wall surface (17) give abnormally high rates of high apparent order and new products (CO, H_2O, propene polymer). Empirically, the order in CH_3CHO during one run, as far as it can be established, might perhaps best be approximated by 1.8, varying with the nature and condition of the surface (17, 11, 14, 10). From one run to another, the order in the initial concentration of CH_3CHO is 1.5 in the range 0.3 - 1160 mm Hg (17, 11, 14, 10). The alleged variation of E with the pressure (4) is not substantiated if E is, correctly, calculated from k instead of from the half-lives.

The empirical rate law (.3) is obtained by the following mechanism of molecular activation ⇄ deactivation and CH_3 and H radical chains (17):

(1 ⇄ 1') $A + A \rightleftarrows A^* + A$
(2 ⇄ 2') $A + L \rightleftarrows A^* + L$
(3 ⇄ 3') $A + M \rightleftarrows A^* + M$
(4) $A^* \rightarrow CH_3 + H$
(5) $CH_3 + A \rightarrow L + M + CH_3$
(6) $H + A \rightarrow M + H_2 + CH_3$
(7) $CH_3 + CH_3 \rightarrow C_2H_6$

If $k_2 = k_3$ and $k'_2 = k'_3$, one has $k = k_5 k_1 k_4 / k'_1 k_7^{1/2}$, and $b = k_2/k_1$; $b' = k'_2/k'_1$.

(.4) Selected values from (18) rated highly reliable; k and k' are calculated from *initial* rates, converted to sec; k is in complete agreement with (.2 - .3). The accelerating effect of O_2 ceases somewhat abruptly after a time and residual CH_3CHO decomposes approximately as pure CH_3CHO. The amount decomposed per O_2 varies from 1000 to 4000 as vol % O_2 decreases from 0.015 to 0.0004. The temperature coefficient of k' is negative. The first order with respect to O_2 and the independence of the rate of the surface/volume ratio are confirmed by (37). **(.5)** Selected data given as probably moderately accurate empirical material, but the original rate constants, derived from the half-lives on assumption of a rate law $kA^2 + k' A[H_2]$, evidently superseded by the work of (17) and the laws (.2 - .4) are omitted. With the rate law tentatively included in the table (by the editors), k, from *initial* rates at 556° C, is fairly consistent with the values of (17), The ratio $k'/k \sim 0.1$, as in the original. No attempt was made to derive k values from half-lives. **(.6)** Selected data given as empirical material. First order in CH_3CHO obtains in clean vessels for the *initial* rates from one run to another, but the order within one run is more nearly 1.5. The rate rises with $[N_2O]$ up to a limit for $N_2O/CH_3CHO = 2.5$. The 1.5 order in CH_3CHO and the 0.5 order in N_2O are found with wall covered with carbon. Suggested mechanism (not substantiated):

$$\begin{aligned}
&A + N_2O \longrightarrow N_2 + CH_3CO + OH\\
&OH + A \longrightarrow CH_3CO + H_2O\\
&CH_3CO \longrightarrow CH_3 + CO\\
&CH_3 + A \longrightarrow CH_4 + CH_3CO\\
&CH_3 + CH_3 \longrightarrow C_2H_6
\end{aligned}$$

(.7) Rate roughly proportional to [NO] in the presence of excess NO. Positive catalysis by NO at higher pressures but slight inhibition by small amounts of NO is also asserted by (28a). The reality of the effect, on account of possible contamination with O_2, is doubtful. The reaction is more rapid on carbon-covered surface and then increase of the surface area has little effect. **(.8)** Increasing amounts of C_3H_6 cause increasing inhibition; $C_3H_6 = \infty$ designates the amount of C_3H_6 producing extrapolated *maximum inhibition*, it being claimed that very large amounts of C_3H_6 exert positive catalysis; not substantiated. At maximum inhibition ($C_3H_6 = \infty$), it is claimed that E varies somewhat with the initial (CH_3CHO), thus, at 75, 200, and 350 mm Hg, $E = 48$, 46, and 47 kcal. Approximately second-order in CH_3CHO for the completely inhibited reaction. The maximum inhibition by C_3H_6 is interpreted as suppression of the chain part of the reaction, with only the molecular-rearrangement part subsisting (see further comment .10). **(.9)** Selected data as empirical material in view of comparison of CH_3CHO and CD_3CDO. No rate law or constants derivable. Degree of reliability from the point of view of absence of O_2 and wall condition uncertain. See the following comment (.10). **(.10)** The selected *initial* rates of (20) included in the table were obtained with CH_3CHO treated by distillation over crystals of hydroquinone to ensure removal of O_2. These are compared with initial rates calculated from data of (28) (.9) and (28a) (.8), (by assuming an 1.6 order in CH_3CHO and the corresponding k from the half-lives), and with data of (17) calculated from his Arrhenian equation (.2). It develops that the initial rates of (20) for the treated CH_3CHO, considered to be the "true" rates, are lower than the uninhibited rates of (28a), higher than the completely inhibited ($C_3H_6 = \infty$) rates, and up to 25 % lower than the initial rates of (17); this, if anything, can be taken as a confirmation of the reliability of the data of (17). With CH_3CHO not treated by distillation over hydroquinone, the rates are higher throughout, no doubt due to catalysis by traces of O_2.

Infrared analysis showed absence of formation of mixed deuteromethanes when "treated" CH_3CHO and CD_3CDO are heated together; on the assumption that CH_3 and CD_3 radicals would necessarily react according to $CH_3 + CD_3CDO \longrightarrow CH_3D + CD_3 + CO$ and $CD_3 + CH_3CHO \longrightarrow CD_3H + CH_3 + CO$, the conclusion is drawn that the pyrolysis is unimolecular and the chain part due to an impurity. For the unimolecular reaction, the ratio of the rate constants for the pyrolysis of CH_3CHO and CD_3CDO would be 1.3 - 1.4, and not ~ 2.4 as from the data of (28) (.9).

(.11) Products at 550° C, 4 mm Hg:
CO(40 %), H_2(20 %), CH_4(10 %), C_2H_6(10 %), C_nH_{2n}(20 %)
at 550°, 200 mm Hg:
CO(50 %), H_2(5 %), CH_4(10 %), C_2H_6(25 %), C_nH_{2n}(10 %); iodine-catalyzed reaction, $CO + C_2H_6$. Large relative concentrations of C_3H_6 have a catalytic effect (see half-lives for A_o = 50 mm, C_3H_6 = 50 and 200 mm.) Para-ortho hydrogen method shows presence of radicals (20a). Catalysis by iodine (1a) produced by decomposition of $(CH_3)_2CHI$; proposed mechanism $A + I_2 \longrightarrow A^*$ (k); $A^* + A \longrightarrow$ inactive products (k'); $A^* \rightarrow$ final products (k''); $b = k'/k''$; other interpretation see (26a). Further literature (12a)(29a). (.12) Products are CO(50 %), CH_4(15 %), $C_2H_6 + H_2$(15 %), C_2H_4(10 %), C_4H_8(10 %). Order between 1 and 2. Tentative rate constants at 530° C, 100 mm Hg: for kA^2, $k = 1.7 \times 10^{-5}$, and for kA, $k = 4.3 \times 10^{-5}$. Composite reaction, with several independent quasi-unimolecular processes and a superposed bimolecular one. (.13) $CH_2:CO$ decomposes further (at a 1.5-order rate (40)) to CO, H_2, C. Influence of surface/volume ratio is small. NO is said to inhibit at low and to catalyze at high concentrations. Ratio of half-lives at 60 and 75 % completion suggests an order between 1.5 and 2 (42). At 460° C, the reaction shows an induction period (1). At 800° C and ~ 1 mm Hg, CH_3 radicals are found (23). At 400° C, introduction of CH_3 radicals from $Hg(CH_3)_2$ produced $(CH_3COCH_2)_2$ and no $CH_2:CO$ (25).
Suggested chain mechanism (22):

$$A \rightarrow 2\,CH_3 + CO$$
$$CH_3 + A \longrightarrow CH_4 + CH_3COCH_2$$
$$(\longrightarrow CH_3 + CH_2:CO)$$
$$CH_3 + CH_3COCH_2 \longrightarrow C_2H_5COCH_3$$

(.14) Essentially homogeneous. First order at higher pressures. Rate falls sharply below 400 mm; maintained by H_2 but not by N_2, CO, or He. Apparent chain length 17, temperature-dependent. HCHO decomposes further to H_2 + CO. Free radicals detected by mirror technique (23). Increase of the surface/volume ratio retards the rate (21). Sensitized by radicals from photolyzing acetone (16) and by biacetyl (15); in the latter case, partly suppressed by NO. Retarded by NO (33, 15, 19) and by C_3H_6 (24). The inhibition is interrupted to indicate two processes, a decomposition by molecular rearrangement (not inhibited by NO) and a decomposition into radicals (with $E \sim 80$) with a chain of $E \sim 12$, chain length ~ 400. **(.15)** Composition of products (36): CH_4(50 %), CO(30 %), H_2(9 %), C_2H_6(5 %), C_2H_4(3 %), CO_2 (?). CH_3CHO and HCHO are found as intermediate products. The E value of (34) (55 kcal at ∞ pressure, 54 at 650 mm, from quarter-lives) is in line with the series 58, 55, 49, for CH_3OCH_3, $CH_3OC_2H_5$, $CH_3OC_3H_7$, and with the series 58, 55, 53, for CH_3OCH_3, $CH_3OC_2H_5$, $C_2H_5OC_2H_5$. For the uncatalyzed reaction in iodine-free $CH_3OC_2H_5$ (36) calculate both a first-order k in $CH_3OC_2H_5$ and a second-order k in CH_3CHO, with the reaction assumed to proceed over $CH_3OC_2H_5 \longrightarrow CH_4 + CH_3CHO$ followed by $CH_3CHO \longrightarrow CH_4 + CO$, both rates treated as comparable at 487° and 509° C. The second-order k are omitted as the derived rates compare only fairly with the directly determined rates of decomposition of CH_3CHO (see .2, .3). For the C_2H_5I — catalyzed reaction (36) give also a first-order k in CH_3CHO (omitted). In the work of (2), I_2 is supplied by decomposing $(CH_3)_2CHI$. Previous data of (6) showing obviously erroneous higher rates for the uncatalyzed as compared with the iodine-catalyzed reaction (2) are omitted, as these data have been subsequently (33) recognized to have been vitiated by traces of iodine. Both the catalyzed and uncatalyzed reactions are essentially homogeneous; first-order k first rise, then fall somewhat with the progress of the reaction. Half-lives are independent of the pressure even at low pressures if reaction products or H_2 are present. Catalysis by I_2 is proportional to its amount (2). From the inhibition by 1 mm NO (33), the chain length at 560° C under 400 mm is 7.3. **(.16)** Essentially homogeneous. Decomposition into $C_3H_6 + H_2$ + CO to the extent of about 10 % of the total reaction. Rate constants from half-lives. Inhibition by NO suggests radicals **(.17)** Essentially homogeneous. Rate is proportional to the amount of I_2. The HCHO formed decomposes further into CO + H_2. **(.18)** First order by the approximate pressure independence of fractional time. Free radicals produced in the reaction. However, NO is without effect. **(.19)** Composition of products CH_4(~ 65 %), CO(~ 20 %), C_nH_{2n}(~ 15 %). Roughly first-order from half-lives. Rate constants from half-lives. **(.20)** The iodine-catalyzed reaction seems to follow the simple stoichiometric equation, with a final pressure increase of 100 %. (.21) In the presence of excess $C_6H_5CH_3$ as carrier gas, a mixture of CH_4 and C_2H_6 is produced, with 50 - 80 % C_2H_6, and the proportion of CH_4 increasing with the excess of $C_6H_5CH_3$. The final pressure increase is 2.88. Without $C_6H_5CH_3$, the rate is about 50 % greater. The initial step is $A \rightarrow 2(CH_3)_3CO$, followed by $(CH_3)_3CO \rightarrow CH_3COCH_3 + CH_3$, followed, in the absence of carrier gas, by $CH_3 + CH_3 \rightarrow C_2H_6$, and in the presence of $C_6H_5CH_3$, by $CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2$. The activation energy $E = 34$ is identified with the bond dissociation energy $(CH_3)_3CO - OC(CH_3)_3$. (.22) First-order k falls after 30 % decomposition. Activation entropy = 14.5. Assumed 3 mole product per 1 mole A. Mechanism suggested: $A \rightarrow 2\ (CH_3)_3CO$

$$(CH_3)_3CO \rightarrow (CH_3)_2CO + CH_3$$
$$CH_3 + (CH_3)_2CO \rightarrow CH_3COC_2H_5$$
$$CH_3 + CH_3 \rightarrow C_2H_6$$

involves the same initial steps as the mechanism of (34a) (.21) for the high-temperature pyrolysis of A.

(.23) Assumed 3 moles product per 1 mole A, valid only at low pressures; 1 mole ketone yielded per mole A. At higher pressures, accompanying higher-order reaction probable.

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PYROLYSIS

Aromatic C, H, O, compounds

Gas phase

Amounts are in mm Hg.

Rates are in mm Hg/sec.

Homogeneous Reactions

571.442.

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
									k^o	n			
.1	$C_6H_5CHO \rightarrow C_6H_6 + CO$	p	14			+p	k A	550	2.3	-3		*	(1)
			58					"	4.6	-3			
			100 - 300					"	6.2	-3			
			23	NO	5	+p	k A	550	6.0	-4	63	*	"
			144					"	1.9	-3	58		
			250					"	2.8	-3	57		
											(520 - 590°)		
.2	$p - CH_3C_6H_4CHO \rightarrow C_6H_5CH_3 + CO$	p	25			+p	k A	550	2.8	-3		*	(2)
			100 - 200					"	3.9	-3			
			20	NO	5	"	"	"	5.9	-4			
			81					"	1.2	-3			
			218					"	2.4	-3			
.3	$p - ClC_6H_4CHO \rightarrow C_6H_5Cl + CO$	p	18			+p	k A	550	2.6	-3			
			63					"	4.9	-3			
			110 - 175					"	8.3	-3			

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Rate measured	Defined rate law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.3	p - $ClC_6H_4CHO \rightarrow C_6H_5Cl + CO$ *(continued)*		21	NO	5	+p	kA	550	7.0	-4			
			84					"	1.1	-3			
			166					"	2.3	-3	58 (520 - 580°)		

COMMENTS

(.1) Product composition CO (~ 50 %), C_6H_6 (~ 35 %), H_2 (~ 15 %), liquid $(C_6H_5.C_6H_5)$. First-order k calculated from half-lives but the actual order is higher. Order of inhibited reaction between 1 and 2. The inhibited reaction is interpreted as molecular rearrangement. (.2) Some amount of $(CH_3C_6H_4)_2 + H_2$ also formed. Order higher than 1. (.3) Some amount of $(ClC_6H_4)_2 + H_2$ also formed. Order higher than 1.

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PYROLYSIS

Heterocyclic C, H, O Compounds

Gas phase

Rates are in "unit of amount" per sec.

No.	Reaction	Method	Unit of amount	Amount of reactant	Defined mass action law	Temperature	Fractional time	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$C_4H_8O \longrightarrow C_2H_4$, CO, CH_4	p	mmHg	200	$kA^{3/2}$		(0.5)						*	(4)
	Furane (H_2, C_2H_6, C_3H_8...)					529.5	4020							
						550.5	1740							
						596.0	840			53	1.2	12		
.2	$C_4H_8O_2 \nearrow 2\,CO + H_2 + C_2H_6$ (a)	p	atm	70 - 700	$kA^{3/2}$	450		8.9	-5				*	(1)
	$\searrow 2\,CO + 2\,CH_4$ (b)			mmHg		498		1.1	-3				(3)	(2)
	1,4 - Dioxane					535		6.5	-3	58.5	4.5	13		

COMMENTS

(.1) Products C_2H_4 ~ 22 % , C_3H_8 up to 8 %. Slight induction period. Intermediate products CH_3CHO and HCHO. No inhibition by NO or C_3H_6. (.2) Reaction (b) to the extent of 6 - 8 % CH_4. Strong inhibition by NO, maximum with 1 - 3 % NO. Larger amounts of NO promote a first - order reaction with E = 71 kcal, $A \sim 10^{14}$ (3); 4.0 - 4.5 moles dioxane consume 1 mole NO (3). CH_3 radicals from azomethane have little effect on the decomposition; para - H_2 method shows slight effect (3). Reaction catalyzed by HCl (1).

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PYROLYSIS

Aliphatic C, H, N compounds

Gas phase

Homogeneous reactions
571.451.

All rates are in "unit of amount" per sec.

No.	Reaction	Method	Unit of Amount	Amount of reactant	Addend	Rate measured	Defined mass action law	Temperature	Fraction time	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Mechanism	Literature
										k^o	n		A^o	n			
							(a)			(a)							
.1	$CH_3NH_2 \rightarrow HCN + 2H_2$ (a)	*p*	mm Hg	30-		+*p*	*k* A	593		1.0	-3						(^{3})
				250				618		2.3	-3						
	$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$ (b)							640		5.0	-3	58	3.3	11	*	*	"
								667		1.5	-2						
.2	$2(CH_3)_2NH \rightarrow (CH_3)_3N + CH_3NH_2$							420							*	*	(^{2})
								-440									
	$CH_3NH_2 \rightarrow CH_4 + CH_3N{:}CH_2$																
.3	$(CH_3)_3N \rightarrow CH_4 + C_2H_5N^{\cdot}$	anal	M/1	0.012		+L	*k* A	380		4.0	-6						(^{2})
								400		1.9	-5						
	(H_2, C_2H_6)							420		5.9	-5				*	*	
								430		1.7	-4						
				mm Hg													
.4	$2C_2H_5NH_2 \rightarrow C_2H_5NHNHC_2H_5 + H_2$	*p*	"	224		-A	*k* A^2	482		3.0	-3						(^{12})
				33				490		2.2	-2	38			*	*	
									(0.25)								
.5	$(C_2H_5)_2NH \rightarrow NH_3, C_nH_{2n}, H_2, CH_4, C_2H_6, N_2$	"	mm Hg	44		+p		510	228								(^{13})
				419				"	90								
				37				520	138								
				437				"	58								

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Rate measured	Defined mass action law	Temperature	Fraction time	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Mechanism	Literature
										k^o	n		A^o	n			
.5	$(C_2H_5)_2NH \rightarrow NH_3, C_nH_{2n}, H_2, CH_4, C_2H_6, N_2$ *(continued)*	p	mm Hg	43		+D		530	87								
				452				"	41								
				41				540	72			49			*	*	(13)
				358				"	32								
.6	$C_3H_7NH_2 \rightarrow$?	p	"	1.40		+D	k A	500		1.55	-4						(10)
				34.7				"		3.48	-4						
				1.40				520		3.58	-4						
				34.3				"		7.96	-4						
				3.14				540		3.68	-4				*		
				36.8				"		1.72	-3						
.7	$n\text{-}C_4H_9NH_2 \rightarrow C_2H_6, H_2, CH_4, NH_3, C_2H_4, C_2H_2$, liquid (30% N)	p (anal)	"	45		+D	k A	510		2.82	-4						(1)
				217				"		4.03	-4						
				41				520		5.58	-4						
				220				"		7.66	-4						
				35				530		1.55	-4				*		
				240				"		1.66	-3						
.8	$CH_2N_2 \rightarrow N_2 + 1/2\ C_2H_4$	"	"	45		+D	k A^2	135	(0.2) 3.8×10^4								(11)
				200				"	9.4×10^3								
				45				162	1.4×10^3						*		
				155				"	3.6×10^2								
				50				217	12								
.9	$CH_3N{:}NCH_3 \rightarrow N_2, CH_4, C_2H_6, C_2H_4, H_2$, liquid	p	"	129		+D	k A	292		1.0	-4						
				191				316		7.6	-4						
				119				336		3.5	-3	52.5	3.5	16	*	*	

No.	Reaction	Method	Unit of amount	Amount of reactant	Addend	Rate measured	Defined mass action law	Temperature	Fraction time	$k = k^o \times 10^n$ k^o	$k = k^o \times 10^n$ n	E	$A = A^o \times 10^n$ A^o	$A = A^o \times 10^n$ n	Comments	Mechanism	Literature
.9	$CH_3N{:}NCH_3 \rightarrow N_2$, CH_4, C_2H_6, C_2H_4, H_2, liquid *(continued)*	anal	mm Hg	129		-A	k A	292		1.6	-4						
				191				316		1.1	-3						
				119				336		4.9	-3						
		p		248		+p	"	290		1.2	-4						(^{9})
				100				11		9.8	-5						
				12				11		4.6	-5						
		"		181		"		310		4.7	-4						
				66		"		"		3.2	-4	50.2	8	15	*		"
				0.4				"		2.0	-4	(47.7)					
.10	$CH_3N{:}NCH_3 \rightarrow N_2$	anal	mm Hg	100-	NO 200-	+L	k A	295		2.0	-4						(^{4})
				170	340	-A		320		1.1	-3						
								331		2.4	-4	52.5			*	*	(^{4})
								342		3.7	-4						

COMMENTS

(.1) Reaction (a) is homogeneous; reaction (b), heterogeneous, is treated as a side reaction. *Mechanism*: $A \rightarrow CH_3 + NH_2$; $CH_3 + A \rightarrow CH_4 + CH_3NH^{\cdot} \rightarrow CH_4 + CH_2{:}NH + H$; $NH_2 + A \rightarrow NH_3 + CH_3NH^{\cdot} \rightarrow NH_3 + CH_2{:}NH + H$; $H + A \rightarrow H_2 + CH_3NH \rightarrow H_2 + CH_2{:}NH + H$; $CH_2{:}NH \rightarrow HCN + H_2$. (.2) No rate data. (.3) Packing increases the rate; addition of He increases it slightly. *Mechanism*: $A \rightarrow CH_3 + (CH_3)_2N$; $CH_3 + A \rightarrow CH_4 + CH_2N(CH_3)_2$; $CH_2N(CH_3)_2 \rightarrow CH_3 + CH_3N{:}CH_2$. (.4) Final pressure increase is 125 - 130%. (.5) Selected points (extreme A_0). Proof of homogeneity given. (.6) Selected points. Initial rates of pressure increase. Sevenfold increase of pressure is without effect at 200 mm but the rate decreases by about 40 % below 4 mm Hg. (.7) Steady decrease of k during one run. Initial rates decrease with pressure decrease and level off at low pressures. Products taken in a flow system at 950° with a contact time of 0.1 sec : C_2H_6 (37), H_2 (22), CH_4 (17), NH_3 (13), C_2H_4 (8), C_2H_2 (3 %). Products from runs at 500°C for one hour similar.

(.8) Proof of homogeneity given. Products at 187°C: N_2 (69), C_2H_4 (29), C_nH_{2n+2} (as CH_4) (24 %). Rate constants calculated from 0.1 times. (.9) Representative data from (8) and (9). Further literature references, (10) to (13). According to (10), products at 340°C are $0.7N_2$, 0.3 C_2H_6, 0.4 - 0.7 CH_4 (depending on extent of decomposition), 0.3 liquid; extrapolated to zero decomposition, 0.5 N_2, 0.5 liquid. Mean composition of liquid H/N ~ 5, C/N ~ 2 (8). Final pressure increase 195 % (8). Analyses of (8) are in general agreement with this but give less C_2H_6 (~ 0.1), and more CH_4. Liquid is mainly $(CH_3)_2NN(CH_3)_2$. *Mechanism*: $A \rightarrow N_2 + 2CH_3$; $2CH_3 + A \rightarrow (CH_3)_2NN(CH_3)_2$ (8). (.10) Only very slight increase of pressure; hardly any hydrocarbons formed. NO/A = 2:1 reduces the rate to about one half. Product is mainly N_2 in 1:1 ratio to A decomposed. Average number of NO reacting per one A is ~ 2 (1.4 - 2.2). Some CO_2 formed, attributed to reaction of excess NO with HCHNOH. *Mechanism*: $A \rightarrow N_2 + 2CH_3$; $CH_3 + NO \rightarrow HCHNOH$ (14).

LITERATURE

(1) H.C.Beachel, H.A.Taylor, *JCP* 1942, 10, 106. (2) A.G.Carter, P.V.Bosanquet, C.G.Silcocks, M.W.Travers, A.F.Wilshire, *CSL* 1939, 495. (3) H.J.Emeleus, L.J.Jolly, *CSL* 1935, 929. (4) F.P.Jahn, H.A.Taylor, *JCP* 1939, 7, 474. (5) (L. Kassel, *JPC* 1928, 32, 225, 1065). (6) (Ramsperger, *ACS* 1927, 49, 912, 1395). (7) Riblett, Rubin, *ACS* 1937, 59, 1537. (8) (Rice, Ramsperger, *ACS* 1928, 50, 617). (9) O.K.Rice, D.V. Sickman, *JCP* 1936, 4, 239, 243, 608. (10) D.V.Sickman, O.K.Rice, *ACS* 1935, 57, 22. (H.A.Taylor, Achilles, *JCP* 1931, 35, 2658).

(11) E. W. R. Steacie, *JPC* 1931, 35, 1493. (12) H. A. Taylor, J. G. Ditman, *JCP* 1936, 4, 212. (13) H. A. Taylor, C. R. Herman, *JPC* 1935, 39, 803. (14) H. A. Taylor, F. P. Jahn, *JCP* 1939, 7, 470.

PYROLYSIS

Gas phase

Aromatic nitro compounds

Amounts are in mm Hg.
Rates in mm Hg per sec.

No.	Reaction	Amount of reactant	Rate measured	Temperature	Half-time	*E*
.1	$C_6H_5NO_2 \longrightarrow C_6H_6(\sim 40\ \%)$, $NO(\sim 30\ \%)$, $CO(\sim 15\ \%) + N_2, NO_2, H_2$, unsatd.	20	$+\Delta p$	500	190	
		85		"	150	
		~ 15		455	1420	
				470	820	
				485	360	51
.2	*m* - $NO_2C_6H_4NO_2 \longrightarrow CO(\sim 45\ \%)$, $NO(\sim 30\ \%) + C_6H_5(?)$	~ 15		440	875	
				470	235	
				500	70	48

COMMENTS

(.1) Order between 1 and 2. Half-time is increased by packing.

LITERATURE

R. E. Smith, *TFS* 1940, 36, 983.

PYROLYSIS

Aliphatic halogen compounds

Gas phase

Homogeneous Reactions
571.471.

Rate measured $+\Delta p$

Amounts are in mm Hg.
Rates are in mm Hg per sec.

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Fractional time	$k = k^o \times 10^n$		E
									k^o	n	
.1	$CCl_3CHO \rightarrow CO + CHCl_3$ ($\rightarrow CO + HCl, C_2Cl_6, C...$)	p						(0.5)			
			120			k A	400	1200			
							430	270			
							466	60			
			225			"	400	1100	6.0	-4	
							430	220	2.5	-3	
							466	50	1.26	-2	49
			50 - 300	X =							
				$(CH_3)_2CHI$	5	k $AX^{1/2}$	353	750			
							380	130			
							412	50			39
				NO	50	k AX	401	350			
					90		356	1200			
					"		401	180			
					"		421	75			
					310		401	55			37

COMMENTS

Without addend, the reaction (from the half-lives) is first-order above 20 mm Hg. Order in $(CH_3)_2CHI$ is approximately 0.5 or more complex; the catalytic effect of $(CH_3)_2CHI$ is due to I_2, formed by $(CH_3)_2CHI \rightarrow C_3H_6 + I_2$.

LITERATURE

F. H. Verhoek, C. N. Hinshelwood, *PRS*^{A} 1934, 146, 334.   F. H. Verhoek, *TFS* 1935, 31, 1521.

DECOMPOSITION

Alicyclic ring ⟶ Unsaturated compounds

Gas phase

Rate measured + Δp

Mass action is in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments
					k^o	n		A^o	n	
.1	$C_8H_{10}O \longrightarrow$ *cyclo* - $C_5H_6 + CH_2{:}CHO$ endomethylene - 2,5 - tetrahydrobenzaldehyde	A = 15 - 64 mm; L = 45 - 363 mm; B = 42 - 328 mm;	kA	192	3.5	-4				*
				206	1.0	-3				
				215	2.0	-3				
				230	5.3	-3				
				242	1.2	-2	33.6	2.2	9	

COMMENTS

Initial k. Reverse reaction, see 681.441.

LITERATURE

G. B. Kistiakowsky, J. R. Lacher, *ACS* 1936, 58,123.

ASSOCIATION

Aldehyde + Anhydride ⟶ Dicarboxylate

Gas phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Defined mass-action law	Temperature	E	$A = A^{\circ} \times 10^{n}$	
					A°	n
.1	$C_6H_5CHO + (CH_3CO)_2O \rightarrow (CH_3COO)_2CHC_6H_5$	$k\,AB$	200 - 300	22.9	5.8	7

COMMENTS

From the rate of the reverse reaction (see 511.443.) and the equilibrium constant, assumed to be the same in gas as in liquid phase.

LITERATURE

N. A. D. Parlee, J. C. Arnell, C. C. Coffin, *CJR*^{B} 1940, 18, 223.

ADDITION

Aldehyde + H_2O → Hydrate

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Defined mass-action law	Temperature	$k^o = k^o \times 10^n$	
							k^o	n
.1	$CH_3CHO + H_2O \rightarrow CH_3CH(OH)_2$	H_2O	~ 0.4		$kA = (k_o[H_2O] + k_H[H^+] + k_{OH}[OH^-])A$	0	k_o 2.96	−5
						"	k_H 1.15	+2
						"	k_{OH} 9.6	+3
				X = $m\text{-}NO_2C_6H_4COO^-$	$k'A = (k + (k_{HX} + k_X/r)[HX])A$ $r = [HX]/[X^-]$	0	k_{HX} 3.8	−3
						"	k_X 6.1	−1
				$p\text{-}NO_2C_6H_4COO^-$		0	k_{HX} 6.9	−3
						"	k_X 1.34	−1
				CH_3COO^-		0	k_{HX} 1.23	−1
						"	k_X 1.65	−2
				$C_6H_5COO^-$		0	k_{HX} 1.25	−1
						"	k_X 1.34	−2

COMMENTS

Values of k_{HX} and k_X obtained graphically by plotting $k_{HX} + k_X/r$ against $1/r$ (where $r = [HX]/[X]$), after correction of the rates for $kA = (k_o[H_2O] + k_H[H^+] + k_{OH}[OH^-])A$. Data converted to ln and sec. Acid catalysis is attributed to the rate determining step $A + H_2O + HX \rightarrow CH_3CH(OH)(OH_2^+) + X^-$, base catalysis to $A + H_2O + X^- \rightarrow CH_3CH(OH)O^- + HX$. Reverse reaction, see 612.410.

LITERATURE

R. P. Bell, B. de B. Darwent, *TFS* 1950, 46, 34.

ADDITION
HCN to carbonyl

Liquid phase

Reaction type $ArCHO + HCN \rightarrow ArCH(OH)CN$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
							k^o	n
.1	$C_6H_5CHO + HCN$	C_2H_5OH	$C_5H_5N \cdot C_6H_5COOH$	0.01	kAB	20	1.96	-8
.2	p-$CH_3C_6H_4CHO + HCN$	C_2H_5OH	$C_5H_5N \cdot C_6H_5COOH$	0.01	kAB	20	9.8	-9
.3	p-$C_2H_5C_6H_4CHO + HCN$	C_2H_5OH	$C_5H_5N \cdot C_6H_5COOH$	0.01	kAB	20	1.01	-8
.4	p-$(CH_3)_2CHC_6H_4CHO + HCN$	C_2H_5OH	$C_5H_5N \cdot C_6H_5COOH$	0.01	kAB	20	8.5	-9
.5	p-$(CH_3)_3CC_6H_4CHO + HCN$	C_2H_5OH	$C_5H_5N \cdot C_6H_5COOH$	0.01	kAB	20	9.1	-9

COMMENTS

Reverse reaction, see 512.415.

LITERATURE

J. W. Baker, M. L. Hemming, *CSL* **1942**, 191.

Hydrogenation of multiple bond

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactants	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
					k^o	n		A^o	n		
.1	$C_2H_2 + H_2 \longrightarrow C_2H_4$	A/B = 1/8; 1/16; 1/24	kAB	495	1.3	-1				*	(2)
				505	2.3	-1					
				515	3.2	-1					
				525	4.6	-1					
				535	6.4	-1	42				
.2	$C_2H_4 + H_2 \longrightarrow C_2H_6$	A = 195 (mm Hg) B = 573	kAB	475	4.7	-3				*	(2)
		196 575		500	1.14	-2					
		198 580		524	2.79	-2					
		191 562		552	7.76	-2	43.1	1.24	6		
		100 294		548	6.92	-2				*	"
		48 141		550	8.20	-2					
		A/B = 1/2; 1/1		549	5.6	-2				*	"

COMMENTS

(.1) Manometric measurements. *k* from initial rates by extrapolation to zero time, making allowance for polymerization.

(.2) *k* and *A* converted from mm^{-1} to $(M/l)^{-1}$ units. With excess of H_2, and up to 50 % conversion, *k* is not appreciably affected by reverse reaction. Increase of the surface/volume ratio by a factor of > 10 doubles the rate of disappearance of H_2 but not of C_2H_4, i.e. increase of the surface consumes H_2 through adsorption but does not affect the rate of the reaction. Side reactions are practically absent at A/B = 1:3 but at A/B = 1:2 or 1:1, some polymerization occurs, hence *k* is lowered. Combination of the data of *k* with the rate constant of Marek and McCluer, *IEC* 1931, 23, 878, for the reverse reaction (see 571.411.) gives the correct value for the equilibrium constant. Collision efficiency ~ 10 %.

LITERATURE

(1) H.A.Taylor, A.van Hook, *JPC* 1935, **39**, 811.

(2) R.N.Pease, *ACS* 1932, **54**, 1877.

ADDITION

Bond Saturation

Addition of hydrogen halide to double bond

Gas phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Defined mass-action law	Temperature	E	$A = A^\circ \times 10^n$		Comments	Literature
					A°	n		
.1	$(C_2H_4 + HF \rightarrow C_2H_5F)$	—		64.3			*	(3)
.2	$C_2H_4 + HCl \rightarrow C_2H_5Cl$	—		48.4			*	(2)
.3	$C_2H_4 + HBr \rightarrow C_2H_5Br$	—		39.0			*	
.4	$C_2H_4 + HI \rightarrow C_2H_5I$	—		31.5			*	
.5	$(CH_3)_2C{:}CH_2 + HCl \rightarrow (CH_3)_3CCl$	kAB	88 - 260	28.8 ±2.4	1	8	*	(1)
.6	$(CH_3)_2C{:}CH_2 + HBr \rightarrow (CH_3)_3CBr$	kAB	88 - 260	22.5 ±1.9	1.6	7	*	(1)

COMMENTS

(.1) (.2) (.3) (.4) *E* by quantum-mechanical calculation from Morse curves. For reaction (.1) *E* exceeds the energy of dissociation of the C – C bond, hence reaction (.1) cannot take place. (.5) (.6) Calculated from the rates of the reverse reactions (which see 521.471.) and equilibrium between 88° and 260°C. *A* converted from $(M/ml)^{-1}$ to $(M/l)^{-1}$ units. The second order is assumed.

All data are given only in the way of an order of magnitude.

LITERATURE

(1) D.Brearly, G.B.Kistiakowsky, C.H.Stauffer, *ACS* 1936, **58**, 43; G.B.Kistiakowsky, C.H.Stauffer, *ACS* 1937, **59**, 165. (2) C.E.Sun, C.Liu, *J. Chinese Chem. Soc.* 1936, **4**, 98. (3) C.E.Sun, C.H.Sze, *ibid.* 1937, **5**, 1.

BOND SATURATION

Addition of halogen to Double bond

Amounts are in mm Hg.

Rates are in mm Hg per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
					k^o	n
.1	$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$	A ~ B ~ 9	k	16	7.5	-3
			k B	16	3.1	-4
			k AB	16	2.5	-5

COMMENTS

The rate and the order of the reaction vary strongly with the nature of the wall surface. The above data are quoted only as an illustration of the orders of magnitude involved. For a given surface, lower temperature or higher pressure tend to lower the order of the reaction. H_2O vapor accelerates the rate. Wet surface, high initial $[Br_2]$, and low temperature, favor transition from second to first order. With a high surface concentration of the initial Br_2, the reaction tends to zero order. Addition of $C_2H_4Br_2$ accelerates the rate.

LITERATURE

(1) R. G. W. Norrish, *CSL* 1923, 123, 3006.

(2) R. G. W. Norrish, G. G. Jones, *CSL* 1926, 129, 55.

(3) F. F. Rust, W. E. Vaughan, *JOC* 1940, 5, 472; 1941, 6, 479.

(4) A. Sherman, O. T. Quimby, R. O. Sutherland, *JCP* 1936, 4, 732.

(5) W. E. Vaughan, F. F. Rust, *JOC* 1940, 5, 449.

(6) G. Williams, *CSL* 1932, 135, 1747.

BOND SATURATION

Addition of H_2O to C:C bond

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.1	$(CH_3)_2C{:}CH_2 + H_2O \longrightarrow (CH_3)_3CHO$	H_2O	Sat			$k\,A\,[H^+]$					*	(1)
			KNO_3,	μ = 1.0, + HNO_3	0.05		25	6.55	-4			
					0.1		"	5.85	-4			
					0.5		"	5.94	-4			
				μ = 2.0	0.1	"	"	9.08	-4			
					0.5		"	9.11	-4			
					1.0		"	8.32	-4	23.4		
.2	$(CH_3)_2C{:}CHCH_3 + H_2O \longrightarrow (CH_3)_2COHC_2H_5$	H_2O	Sat			$k\,A\,[H^+]$				(25-35°)	*	(2)
			KNO_3,	μ = 0.5, + HNO_3	0.05		25	2.14	-4	19.2		
					0.5		"	2.36	-4	(25-35°)		
				1.0	0.05 - 0.5		"	3.62	-4			
				μ = 0.1, + H_2SO_4	0.1 - 0.2	"	"	2.67	-4			
				μ = 0.1, + HCl	0.1	"	"	2.53	-4			
.3	*trans* - $CH_3CH{:}CHCHO + H_2O \rightarrow CH_3CHOHCH_2CHO$	H_2O		HNO_3	1.0	$k\,A\,[H^+]$	25	6.66	-6			(4)
					1.90		"	6.56	-6			
				"	0.48		35	1.74	-5			"
					1.86		"	1.70	-5	18.1		
				$HClO_4$	0.56	"	25	4.84	-6			"
					0.94		"	5.88	-6			
					1.86		"	5.96	-6			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$: k^0	n	E	Comments	Literature
.3	*trans* - $CH_3CH{:}CHCHO + H_2O \rightarrow CH_3CHOHCH_2CHO$ (*continued*)			$HClO_4$	0.373	$kA[H^+]$	35	1.49	-5			(^{4})
					0.75		"	1.47	-5			
					1.87		"	1.64	-5	18.2		
.4	$(CH_3)_2C{:}CHCHO + H_2O \rightarrow (CH_3)_2COHCH_2CHO$	H_2O	~ 0.02	HNO_3	0.52	$kA[H^+]$	20	2.35	-6			(^{3})
					1.04		"	2.38	-6			
				"	0.52	"	25	3.74	-6			"
					0.92		"	3.18	-6			
					1.04		"	3.61	-6			
				"	0.52	"	35	1.07	-5			"
					0.92		"	1.01	-5			
					1.04		"	1.01	-5	ΔH_a = 19.1		

COMMENTS

(.1) Rate approximately proportional to $[H^+]$ at constant ionic strength μ. Salts of heavy metals, ~ 0.015 *M*, have a negligible effect. (.2) Selected points. Data for other acids in (^{2}). (.3) Rate approximately proportional to $[H^+]$; k calculated from original rate data.

LITERATURE

(^{1}) H.J. Lucas, W.F. Eberz, *ACS* 1934, 56, 460. (^{2}) H.J. Lucas, Y.P. Liu, *ACS* 1934, 56, 2138. (^{3}) H.J. Lucas, W.T. Stuart, D. Pressman, *ACS* 1944, 66, 1818. (^{4}) S. Winstein, H.J. Lucas, *ACS* 1937, 59, 1461.

BOND SATURATION

Addition of H_2O to C : C bond

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
							k^o	n
.1	$C_2H_5OC⋮CH + H_2O \rightarrow C_6H_5OCOCH_3$	$H_2O + C_2H_5OH$ 42.7 wt %	H^+	5.85	k A	25	2.38	-4
				5.95		"	1.73	-4
		12.5	"	6.47	"	"	1.20	-4
				6.03		"	3.23	-4
				5.10		"	2.42	-3
.2	$C_4H_9OC⋮CH + H_2O \rightarrow C_4H_9OCOCH_3$	$H_2O + C_2H_5OH$ 42.7 wt %	H^+	6.27	k A	25	1.49	-4
				5.96		"	3.04	-4
.3	$C_6H_5OC⋮CH + H_2O \rightarrow C_6H_5OCOCH_3$	$H_2O + C_2H_5OH$ 42.7 wt %	H^+	2.47	k A	25	7.28	-5
				2.25		"	1.16	-4

LITERATURE

T. J. Jacobs, S. Searles, Jr., *ACS* 1944, **66**, 686.

BOND SATURATION

Proton addition to C:N bond

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		ΔH_a	ΔS_a
						k^{o}	n		
.1	$CH_3CH{:}NO_2^- + H_2O \rightarrow CH_3CH_2NO_2 + OH^-$	H_2O	~ 0.05	k AB	0	2.76	-7	24.3	+ 3.0
.2	$CH_3CH{:}NO_2^- + NH_4^+ \rightarrow CH_3CH_2NO_2 + NH_3$	H_2O	~ 0.05	k AB	0	3.17	-5	24.9	+ 14.5
.3	$CH_3CH{:}NO_2^- + CH_3NH_3^+ \rightarrow CH_3CH_2NO_2 + CH_3NH_2$	H_2O	~ 0.05	k AB	0	1.70	-5	25.5	+ 15.9
.4	$CH_3CH{:}NO_2^- + (CH_3)_2NH_2^+ \rightarrow CH_3CH_2NO_2 + (CH_3)_2NH$	H_2O	~ 0.05	k AB	0	4.57	-5	24.8	+ 14.9
.5	$CH_3CH{:}NO_2^- + (CH_3)_3NH^+ \rightarrow CH_3CH_2NO_2 + (CH_3)_3N$	H_2O	~ 0.05	k AB	0	5.74	-4	21.1	+ 6.8

COMMENTS

From reverse reaction (see 402.450).

LITERATURE

R. G. Pearson, *ACS* 1948, **70**, 204

ADDITION

Bond saturation

Addition of hydrogen halide to multiple bond

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$(CH_3)_2C{:}CH_2 + HCl$	C_7H_{16}	> 0.1		$k\,AB^3$	0	4.6	-4	*	(^{1})
		"	A = B = 0.5	H_2O	$k\,AB$	0	4.3	-5	*	"
.2	$CH_3OOCC{:}CCOOCH_3 + HBr$ → *trans* (*a*) → *cis* (*b*)	CH_3COOH		(*a* + *b*) =	$k\,AB^2$	20	3.5	-3	*	(^{2})
		C_6H_6			"	"	3.1	-2		"
		C_6H_{14}			"	0	8.7	+1		"
		CH_3COOH		LiBr	$k\,AB\,[Br^-]$	20	1.5	-2		"

COMMENTS

(.1) The fourth-order and the second-order reactions, the latter catalyzed by H_2O as an impurity, are competitive. By cooling to -80°C and warming up to 0°C, the reaction at 0°C is greatly accelerated. (.2) In CH_3COOH, C_6H_{14}, CH_3NO_2, and in pure liquid, reactions *a* and *b* occur in approximately equal amounts; in C_6H_6, reaction *b* is about 90 % of the total. Concentration and temperature have no effect on the orientation, nor have peroxides and antioxidants. Bromides shift the reaction in favor of *a*.

LITERATURE

(^{1}) F.R.Mayo, J.J.Katz, *ACS* 1947, 69, 1339.

(^{2}) I.V.Smirnov-Zamkov, E.A.Shilov, *DAN* 1949, 67, 671.

ADDITION

Bond saturation

Liquid phase

Halogen addition to multiple bond

Rate measured -dB/dt

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
								k^o	n			
.1	$C_2H_4 + Br_2$	CCl_4	0.057			k AB	0	1.8	-2		*	(4)
							25	1.7	-4			
		"	"	H_2O	0.0005		"	5.8	-4			
		"	A = 0.006 - 0.014;	B ~ 0.02			0 18	See Comments			*	(23)
.2	$CH_2{:}CHBr + Br_2$	CCl_4				k AB	15	1.18	-4		*	(11)
		CH_3COOH	B = 0.015 A = 0.13 - 0.31	LiCl	0.5	k AB[Cl$^-$]	40	5.40	-3			(15)
					0.1		"	4.57	-3			
					0.2 - 0.4		"	4.39	-3			
.3	$CH_2{:}CHCH_3 + Br_2$	CCl_4				k AB	25	3.3	-3			(4)
.4	$CH_2{:}CHCOOH + Cl_2$	CH_3COOH	A = B = 0.0125 - 0.025			k AB	25	2.8	-4			(22)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.5	$CH_2:CHCOOH + Br_2$	H_2O	A = B =			kAB	25				*	(18)
			0.0125				(0.3)	3.18	0			
			"				(0.6)	1.66	0			
			0.0062				(0.2)	4.85	0			
			"				(0.6)	3.32	0			
			0.0125	H_2SO_4	0.05	"	(0.3)	5.7	-1			"
			"		"		(0.6)	3.8	-1			
			0.0062	"	"	"	(0.3)	5.3	-1			"
			"		"		(0.6)	3.8	-1			
		$CH_3COOH + H_2O$ 25 %	0.0125	-		"	(0.3)	3.1	-3			"
							(0.6)	2.7	-3			
		50 %	"			"	(0.3)	4.8	-2			"
							(0.6)	2.2	-2			
		CH_3COOH	A = B =	HBr	HBr/Br_2	kAB	25				*	(18)
			0.0125		0.05		(0.3)	5.8	-4			
					0.125		(0.3)	2.3	-3			"
							(0.6)	2.3	-3			
					0.25		(0.3)	4.2	-3			"
							(0.6)	4.0	-3			
					0.5		(0.3)	5.1	-3			"
							(0.6)	5.3	-3			
					1.0		(0.3)	8.0	-3			"
							(0.6)	7.3	-3			
					2.0		(0.3)	9.5	-3			"
							(0.6)	7.3	-3			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	 n	E	Comments	Literature
.5	$CH_2:CHCOOH + Br_2$ *(continued)*				4.0		(0.3)	6.3	-3			$(^{18})$
							(0.6)	5.1	-3			
					5.0		(0.3)	5.7	-3			"
							(0.6)	5.3	-3			
		CH_3COOH	A = B = 0.0125	HBr	0.0125	k AB	24	7.3	-3			$(^{10})$
.6	$CH_2:CHCOOH + ICl \longrightarrow CH_2ClCHICOOH$	CH_3COOH	A = B = 0.0125 - 0.05			k AB^2	25	3.1	-1			
.7	$CH_2:CHCH_2OH + I_2$	H_2O	A = 0.1			kB = $(k_1 [I_3^-] + k_2[I_2])$A					*	$(^{3})$
			B = 0.01 - 0.04	I^-	0.05	k	0	6.1	-6			
							15	3.55	-5			
							30	1.44	-4			
			A = 0.1; B = 0.02	"	0.01	k	15	5.0	-5			"
					0.025		"	4.1	-5			
					0.05		"	3.5	-5			
					0.1		"	3.2	-5			
			"	"	0.01 - 1.0	k_1	15	3.00	-4			"
						k_2	"	1.67	-3			
		CH_3COOH	B A			k AB + k'AB^3	25.0				*	$(^{16})$
			0.023 0.283			k'	(1)	3.93	-3			
			0.027 0.577				"	6.80	-3			
			0.026 1.13				"	1.13	-2			
			0.024 2.35				"	1.72	-2			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \cdot 10^n$		E	Comments	Literature
								k^o	n			
.8	$CH_2:CHCH_2OCOCH_3 + Br_2$	CH_3COOH	A = B =			$k\,AB + k'AB^2$	25.0				*	(16)
			0.020			k	(i)	2.65	-1			
							(f)	1.30	-1			
						k'	(i)	2.23	+1			
							(f)	5.00	+1			
			0.004			k	(i)	1.13	-1			
							(f)	1.00	-1			
						k'	(i)	3.60	+1			
							(f)	1.50	+2			
							50.0					
			0.020			k	(i)	4.80	-1			
							(f)	4.50	-1			
						k'	(i)	4.60	+1			
							(f)	1.82	+2			
			0.008			k	(i)	4.13	-1			
							(f)	4.50	-1			
						k'	(i)	7.40	+1			
							(f)	3.50	+2			
			0.004			k	(i)	2.92	-1			"
							(f)	4.05	-1			
						k'	(i)	1.11	+2			
							(f)	6.80	+2			
							70.0					
			0.008			k	(i)	6.90	-1			"
							(f)	7.28	-1			
						k'	(i)	1.24	+2			
							(f)	4.63	+2			

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$ k°	n	E	Comments	Literature
.8	$CH_2:CHCH_2OCOCH_3 + Br_2$ *(continued)*		0.004			k	(1)	6.56	-1			
							(f)	1.00	0			
						k'	(1)	2.50	+2			
							(f)	6.06	+3			
			B A				25.0					(^{16})
			0.020 0.020			k	(1)	2.65	-1			
			" "			k'	"	2.15	+1			
			0.013 0.011			k	"	2.00	-1			
			" "			k'	"	2.25	+1			
			0.090 0.012			k	"	1.58	-1			
			" "			k'	"	3.05	+1			
			0.004 0.004			k	"	1.13	-1			
			" "			k'	"	3.60	+1			
		CH_3COOH	A = B = 0.0125 - 0.05			kAB^2	25	8.1	+1		*	(^{18})
							50	1.15	+2	2.7		
		CCl_4		0.0125		kAB	25					"
							(0.2)	2.3	-4			
							0					
				0.025			(0.2)	2.3	-2			
							(0.6)	3.8	-2			
							25					
							(0.2)	1.16	-2			
							(0.6)	2.50	-2			
							50					
							(0.2)	1.3	-3			
							(0.6)	8.4	-4			

No.	Reaction	Solvent	Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o = 10^n$		E	Comments	Literature
									k^o	n			
.9	$CH_2{:}CHCH_2OCOCH_3 + I_2$	CH_3COOH	B	A			$kAB + k'AB^3$	25.0				*	(^{16})
			0.016	1.48			k'	(1)	1.21	-3			
			"	"				(0.5)	1.46	-3			
			0.018	0.416			"	(1)	1.39	-3			
			"	"				(0.5)	2.62	-3			
			0.057	1.48			"	(1)	1.81	-3			
			"	"				(0.5)	3.53	-3			
			0.060	0.371			"	(1)	2.39	-3			
			"	"				(0.5)	3.33	-3			
			0.083	0.016			"	(1)	3.68	-3			
			"	"				(0.5)	2.70	-3			
		CH_3COOH	$A \sim 0.4$				kAB	25	2.57	-5			(^{15})
			$B \sim 0.018$		CH_3COONa	0.100	"	"	5.39	-5			
					LiCl	"	"	"	9.35	-5			
					HI	"	"	"	1.05	-4			
.10	$CH_2{:}CHCH_2OCOCH_3 + ICl \rightarrow CH_3COOCH_2CHICH_2Cl$ $\rightarrow CH_3COOCH_2CHClCH_2I$	CH_3COOH	A = B = 0.0125 - 0.025				kAB^2	25	7.8	-1		*	(^{22})
		"	"		HCl	HCl/ICl	kAB	25					"
						0		(0.2)	4.5	0			
								(0.6)	2.5	0			
						0.25		(0.2)	2.8	0			
								(0.6)	2.2	0			
						1.0		(0.2)	2.2	0			
								(0.6)	1.6	0			
						2.0		(0.2) - (0.6)	1.4	0			
						8.0		"	2.4	-1			
						16		"	2.1	-1			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Litera ture
.11	CH_2:$CHCH_2OCOC_6H_5 + Br_2$	C_6H_5Cl	A = B = 0.0125 - 0.1			$k AB^2$	24	1.1	0		*	(^{5})
		$CHCl_3$	0.1			$k AB^2$	24	7.4	-1		*	"
		CCl_4	A = B =			$k AB$	24					
			0.2				(0.1)	8.3	-3		*	"
							(0.4)	3.5	-3			
			0.1				(0.1)	1.5	-3		*	"
							(0.4)	8.1	-4			
		CH_3COOH	A = B = 0.0125 - 0.05			$k AB^2$	25	7.1	+1			(^{18})
							50	1.2	+2	3.9		
.12	CH_2:$CHCH_2OCOCH_2Cl + Br_2$	CH_3COOH	A = B = 0.0125 - 0.05			$k AB^2$	25	3.5	+1		*	(^{18})
							50	4.35	+1			
		CCl_4	A = B =			$k AB$	25					"
			0.05				(0.2)	2.3	-2			
			0.025				"	4.6	-3			
			0.0125				"	1.3	-4			
			0.0062				"	5.0	-5			
		"	A = B =			"	0					"
			0.025				(0.2)	5.8	-3			
							(0.6)	8.3	-3			
							25					
			"				(0.2)	4.6	-3			
							(0.6)	7.0	-3			
							50					
			"				(0.2)	4.1	-4			
							(0.6)	2.7	-4	1.6		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.12	CH_2:$CHCH_2OCOCH_2Cl + Br_2$ *(continued)*	CCl_4	A = B = 0.025	HBr	HBr/Br_2	kAB	25				*	(18)
					0.167		(0.2)	1.16	-1			
					"		(0.6)	5.0	-2			
					0.33		(0.2)	3.0	-1			
					"		(0.6)	1.16	-1			
					0.66		(0.2)	3.3	-1			
					"		(0.6)	1.0	-1			
			0.0125	"	0.33	"	(0.2)	6.7	-2			"
					"		(0.6)	3.3	-2			
					0.66		(0.2)	1.16	-1			
					"		(0.6)	5.0	-2			
					2.0		(0.2)	5.5	-1			
					"		(0.5)	1.5	-1			
					4.0		(0.2)	2.8	-1			
					"		(0.5)	1.16	-1			
			0.0062	"	2.0	"	(0.2)	1.33	-1			"
					"		(0.6)	6.6	-2			
					4.0		(0.2)	2.16	-1			
					"		(0.6)	1.33	-1			
.13	CH_2:$CHCH_2Cl + Br_2$	CCl_4				kAB	15	5.61	-4		*	(11)
		CH_3COOH	A = B = 0.008			kAB	25	2.00	-1			(15)
			"	CH_3COONa	0.100	"	"	2.75	-1			
			"	H_2SO_4	"	"	"	3.20	-1			
			"	$NaNO_3$	"	"	"	5.80	-1			
			"	LiCl	"	"	"	1.44	0			
			"	LiBr	"	"	"	6.95	-1			
			"	HBr	"	"	"	6.95	-1			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.13	CH_2:$CHCH_2Cl + Br_2$ *(continued)*	CH_3COOH	A = B =			$k\,AB + k'AB^2$	25.0				*	(16)
			0.020			k	(1)	5.5	-2			
							(f)	3.0	-2			
						k'	(1)	2.90	0			
							(f)	1.00	+1			
			0.008			k	(1)	2.0	-2			"
							(f)	2.0	-2			
						k'	(1)	2.25	0			
							(f)	1.10	+1			
							50.0					
			0.020			k	(1)	9.0	-2			"
							(f)	8.5	-2			
						k'	(1)	5.40	0			
							(f)	2.50	+1			
			0.008			k	(1)	4.3	-2			"
							(f)	5.6	-2			
						k'	(1)	7.30	0			
							(f)	5.00	+1			
							70.0					
			0.020			k	(1)	1.38	-1			"
							(f)	1.63	-1			
						k'	(1)	8.75	0			
							(f)	6.50	+1			
			0.004			k	(1)	5.6	-2			"
							(f)	3.26	-1			
						k'	(1)	1.85	+1			
							(f)	1.75	+2			

No.	Reaction	Solvent	Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
									k^o	n			
.13	$CH_2:CHCH_2Cl + Br_2$ *(continued)*		B	A				25.0					
			0.040	0.040			k'	(1)	4.58	0			(^{16})
			0.040	0.020				"	4.50	0			
			0.020	0.040				"	2.95	0			
			0.020	0.020				"	2.90	0			
			0.008	0.008				"	2.25	0			
		$CH_3COOH + H_2O$ 0.2 %	A = B = 0.008				k	25.0	2.0	-2			"
		1.0						(1)	3.2	-2			
		5.0						"	1.8	-1			
.14	$CH_2:CHCH_2Br + Br_2$	CCl_4					kAB	15	2.04	-3		*	(^{11})
.15	$CH_3CH:CHBr + Br_2$	CCl_4					kAB	15	7.68	-5		*	(^{11})
.16	$CH_3CH_2CH:CH_2 + Br_2$	CCl_4					kAB	25	3.3	-2			(^{4})
.17	$CH_3CH:CHCH_3 + Br_2$	CCl_4					kAB	25	1.0	0			(^{4})
.18	$(CH_3)_2C:CH_2 + Br_2$	CCl_4					kAB	25	1.0	0			(^{4})
.19	$CH_3CH:CHCHO + Cl_2$	CH_3COOH	A = B = 0.0125		-		kAB	25	7.0	-1			(^{22})
					HCl	0.0062		"	5.8	0			
					H_2SO_4	0.0125		"	1.0	-2			
.20	*trans* - $CH_3CH:CHCOOH + Br_2$ (crotonic acid)	CH_3COOH	A = 0.0125		HBr	HBr/Br_2	kAB					*	(^{13})
						0		24	<1.0	-4			
						0.25		"	3.0	-4			
						0.50		"	5.0	-4			
						1.0 - 4.0		"	8.5	-4			

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
								k°	n			
.20	*trans* - $CH_3CH{:}CHCOOH + Br_2$ *(continued)* (crotonic acid)	CCl_4	A = B = 0.016			kAB	15	3 - 7	-9		*	(19)
							"	1.3 - 1.7	-9		*	(20)
		"	A = B = 0.033			kAB	13				*	(24)
							(1)	1.75	-5			
							(f)	3.3	-5			
		"	"	HBr	HBr/Br_2 0.53	"	(1)	1.65	-3			"
							(f)	2.7	-4			
		"	"	H_2O	70 % sat	"	(1)	4.8	-4			"
							(f)	6.8	-4			
		CH_3COOH	A = B ~ 0.07			kAB;	$k'AB^2$				*	(1)
							35.5					
						k	(0.1)	2.7	-4			
							(0.5)	5.3	-4			
						k'	(0.1)	1.7	-2			
							(0.5)	6.3	-2			
			"	HBr	HBr/Br_2 1.05	k	(0.1)	2.8	-4			"
							(0.5)	5.6	-4			
					"	k'	(0.1)	1.8	-2			
							(0.5)	6.9	-2			
			"	"	2.10	k	(0.1)	3.2	-4			"
							(0.5)	5.8	-4			
					"	k'	(0.1)	2.0	-2			
							(0.5)	7.0	-2			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.20	*trans* - $CH_3CH:CHCOOH + Br_2$ *(continued)* (crotonic acid)		A = B = ~ 0.07	HBr	6.90	k	(0.1)	9.0	-4			(1)
							(0.5)	9.6	-4			
						k'	(0.1)	5.7	-2			
							(0.5)	1.15	-1			
				ICl	ICl/Br_2 0.95	k	(0.1)	1.8	-4			"
							(0.5)	6.3	-4			
					"	k'	(0.1)	2.1	-2			
							(0.5)	7.6	-2			
				"	7.80	k	(0.1)	8.7	-4			"
							(0.5)	9.4	-4			
						k'	(0.1)	5.5	-2			
							(0.5)	1.1	-1			
				$SbBr_3$	$SbBr_3/Br_2$ 1.0	k	(0.1)	2.3	-4			"
							(0.5)	5.0	-4			
						k'	(0.1)	1.4	-2			
							(0.5)	6.0	-2			
				"	6.40	k	(0.1)	1.7	-4			"
							(0.5)	3.2	-4			
						k'	(0.1)	1.1	-2			
							(0.5)	2.6	-2			
.21	*trans* - $CH_3CH:CHCONH(p - C_6H_4Br) + Br_2$	CH_3COOH	A = B = 0.025			k AB	25					(18)
							(0.2)	3.0	-3			
							(0.4)	4.5	-3			
							(0.6)	6.3	-3			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.21	*trans* - $CH_3CH:CHCONH(p - C_6H_4Br) + Br_2$ *(continued)*		0.0125				(0.2)	1.7	-3			
							(0.4)	2.8	-3			
							(0.6)	4.3	-3			
.22	*cis* - $COCHCH:CHCOOH + Cl_2$	H_2O	A = 0.1 - 0.6 B = 0.002 - 0.02	HCl	0.1 - 1.0	$k AB / [H^+]$	25	8.7 - 10	-4		*	(^{21})
		H_2O	A = 0.19; 10^2B =	HCl 1.0 + Fe^{++}; Fe^{++} added at rate R		$k'A^{1/2}B^{1/2}$						
			0.138		10^6R = 5.7		25	4.6	-1		*	"
			0.591		"		"	3.1	-1			
			0.096		0.55		"	1.6	-1			
		"	3.46		5.6	$k''AR^{1/2}$	25	1.45	0			
			1.41		"		"	1.25	0			
.23	*cis* - COOHCH:CHCOOH + Br ⟶ *rac*	H_2O B = 0.02	A = 0.1	KBr	1.0	$kB = (k_1A + k_2A^-)B$					*	(^{3})
	(A = COOHCH:CHCOOH					k	25	9.3	-5			
	A^- = COOHCH:CHCOO$^-$)					k_1	"	1.76	-5			
						k_2	"	2.4	-3			
		B = 0.02;	A = 0.05	HCl 1.0 + KBr 1.0		k	25	2.2	-6			"
			0.1				"	4.25	-6			
			0.2				"	8.6	-6			
		B = 0.02;	A = 0.1	HCl 0.125 +	KBr 1.0	k	25	2.34	-5			"
				0.25	"		"	1.25	-5			
				0.5	"		"	7.0	-6			
				1.0	"		"	4.25	-6			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
								k°	n			
.23	*cis* - COOHCH:CHCOOH + $Br_2 \longrightarrow$ *rac* *(continued)*		B = 0.02; A = 0.05	HCl 1.0 + KBr	0.125	k	25	5.0	-6			(3)
				"	0.25		"	3.7	-6			
				"	0.5		"	2.8	-6			
				"	1.0		"	2.2	-6			
		CH_3COOH	A = 0.13;	KBr	0.2	$kA[Br_3^-] = k'AB[Br^-]$					*	(14)
			B = 0.01			k	30	5.90	-4			
							50	3.04	-3			
							70	1.45	-2	9.0		
						k'	30	3.28	-2			
							50	8.29	-2			
							70	2.01	-1	9.3		
		CH_3COOH	A = 0.0125	HBr	HBr/Br_2	kAB					*	(13)
					1		24	4.5	-3			
					4			9.3	-3			
.24	*trans* - COOHCH:CHCOOH + $Br_2 \longrightarrow$ *meso*	H_2O	A = 0.0215			$kB = (k_1A + k_2A^-)B$					*	(3)
	(A^- = COOHCH:$CHCOO^-$		B = 0.003 - 0.012	HCl 0.2 + KBr	1.0	k	25	3.9	-6			
	A = COOHCH:CHCOOH)					k_1	"	1.55	-4			
						k_2	"	5.0	-3			
			B = 0.004; A = 0.0086	HCl 0.05 + KBr	1.0	k	25	2.0	-6			"
			0.0172				"	4.15	-6			
			B = 0.006; A = 0.0215	HCl 0.4 + KBr	1.0	k	25	3.55	-6			"
				0.2	"		"	3.84	-6			
				0.1	"		"	4.30	-6			
				0.05	"		"	5.15	-6			
				0.025	"		"	7.50	-6			

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n	E	Comments	Literature
.24	*trans* - COOHCH:CHCOOH + $Br_2 \longrightarrow$ *meso* (*continued*)		B = 0.01; A = 0.0173	HCl 1.0 + KBr	0.005	k	25	5.0	-6			(3)
				"	0.02		"	2.62	-6			
				"	0.08		"	2.42	-6			
				"	0.16		"	2.52	-6			
				"	0.32		"	2.86	-6			
				"	0.64		"	2.95	-6			
		CH_3COOH	A = 0.13; B = 0.01	$kA[Br_3^-] = k'AB[Br^-]$							*	(14)
				LiBr	0.2	k	30	1.15	-4			
							50	6.09	-4			
							70	3.06	-3	9.4		
						k'	30	6.35	-3			"
							50	1.66	-2			
							70	4.24	-2	9.8		
				HBr	0.19	k	30	8.73	-4			"
							50	5.95	-3			
							70	3.46	-2	11.8		
						k'	30	4.8	-2			"
							50	1.62	-1			
							70	4.80	-1	11.4		
		CH_3COOH	A = 0.0125	HBr	HBr/Br_2	kAB					*	(13)
					1		24	3.2	-4			
					4		"	7.8	-4			
.25	*trans* - COOHCH:$CHCOO^-$ + Br_2	H_2O	A = 0.0173; B = 0.008	KBr	1.0	kB	25	8.5	-4			(3)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.26	$CH_2:CHCH_2CH_2Cl + Br_2$	CCl_4				kAB	15	8.87	-3		*	(11)
.27	$CH_2:CHCH_2CH_2Br + Br_2$	CCl_4				kAB	15	4.02	-2		*	(11)
.28	$CH_3CH:CHCH_2Br + Br_2$	CCl_4				kAB	15	1.46	-3		*	(11)
.29	$(CH_3)_2C:CHCH_3 + Br_2$	CCl_4				kAB	25	4.1	0			(4)
.30	$CH_2:CHCH_2CH_2COOH + Br_2$	CCl_4	A = B = 0.016			kAB	15	4 - 6	-2			(19)
.31	$CH_3CH:CHCH_2COOH + Br_2$	CCl_4	A = B = 0.016			kAB	15	3 - 16	-3			(19)
.32	$C_2H_5CH:CHCOOH + Br_2$	CCl_4	A = B = 0.016			kAB	15	0.9 - 1.7	-8			(19)
.33	*cis* - $CH_3CH:C(CH_3)COOH + Br_2$ (angelic acid)	CCl_4	A = B = 0.016			kAB	15	2 - 5	-8			(19)
		CH_3COOH	See Supplementary Table									
.34	$CH_3CH:C(CH_3)COOH + Br_2$ (tiglic acid)	CCl_4	A = B = 0.016			kAB	15	0.4 - 2.8	-8			(19)
.35	$(CH_3)_2C:CHCOOH + Br_2$	CCl_4	A = B = 0.016			kAB	15	0.9 - 2	-6			(19)
		CH_3COOH	A = 0.0125	HBr	HBr/Br_2	kAB					*	(13)
					0 - 0.5		24	2.5	-3			
					1.0 - 4.0		"	3.0	-3			
.36	$COOHCH_2CH:CHCOOH + Br_2$	CH_3COOH	A = 0.0125	HBr	HBr/Br_2	kAB					*	(13)
					1		24	1.5	-3			
					4		"	7.3	-3			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.37	$COOHC(CH_3):CHCOOH + Br_2$	CH_3COOH	A = 0.0125	HBr	HBr/Br_2	$k\,AB$					*	(^{13})
	(citraconic acid)				1		24	9.0	-5			
					4		"	2.0	-4			
.38	$COOHC(CH_3):CHCOOH + Br_2$	CH_3COOH	A = 0.0125	HBr	HBr/Br_2	$k\,AB$					*	(^{13})
	(mesaconic acid)				1		24	2.3	-4			
					4		"	4.1	-4			
.39	$CH_2:CHCH_2CH_2CH_2Br + Br_2$	CCl_4				$k\,AB$	15	6.7	-1		*	(^{11})
.40	$CH_3CH:CHCH:CHCOOH + Br_2$	CCl_4				$k\,AB$	15	0.3 - 3	-5			(^{19})
.41	*allo* - $CH_3CH:CHCH:CHCOOH + Br_2$	CCl_4				$k\,AB$	15	0.8 - 1	-5			(^{19})
.42	$C_2H_5CH:CHCH_2COOH + Br_2$	CCl_4				$k\,AB$	15	0.3 - 1	-1			(^{19})
.43	$(CH_3)_2C:C(CH_3)COOH + Br_2$	CCl_4				$k\,AB$	15	3 - 6	-8			(^{19})
.44	$COOHCH_2C(CH_3):CHCOOH + Br_2$	CH_3COOH	A = 0.0125	HBr	HBr/Br_2	$k\,AB$					*	(^{13})
					1		24	2.5	-4			
					4		"	8.1	-4			
.45	$CH_2:CH(CH_2)_8COOH + Br_2$	CCl_4	A = B = 0.016			$k\,AB$	15	1.5 - 4	-4			(^{19})
.46	$CH_3CH:CH(CH_2)_7COOH + Br_2$	CCl_4	A = B = 0.0031			$k\,AB$	25	2.7	-2		*	(^{18})
							50	1.2	-2			
		CH_3COOH	"			$k\,AB^2$				3.0		"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.47	*cis* - $C_8H_{17}CH:CH(CH_2)_7COOH + Br_2$ (oleic acid)	CCl_4	A = B = 0.016			kAB	15	4 - 8	-3		*	(^{19})
		"	A = B = 0.033			kAB	13					
							(1)	2.2	+1		*	(^{24})
							(f)	2.2	-1			
.48	*trans* - $C_8H_{17}CH:CH(CH_2)_7COOH + Br_2$ (elaidic acid)	CCl_4	A = B = 0.016			kAB	15	0.8 - 3	-3		*	(^{19})
		"	A = B = 0.033			kAB	13				*	(^{24})
							(1)	2.8	+1			
							(f)	1.1	0			
.49	$C_8H_{17}CH:CH(CH_2)_{11}COOH + Br_2$ (erucic acid)	CCl_4	A = B = 0.016			kAB	15	0.8 - 3	-3			(^{19})
.50	$C_8H_{17}CH:CH(CH_2)_{11}COOH + Br_2$ (brassidic acid	CCl_4	A = B = 0.016			kAB	15	0.8 - 2	-3			(^{19})
.51	$C_{15}H_{31}CH:CHCOOH + Br_2$	CCl_4	A = B = 0.016			kAB	15	6.8	-9			(^{19})
	Aryl-substituted olefins											
.52	$C_6H_5CH:CHC_6H_5 + Br_2$	CH_3OH	A = 0.01	kAB; $k_1A[Br_3^-] + k_2AB$			0				*	(^{2})
				KBr	0		k_2	3.3	0			
				"	0.0186		k	3.95	-1			
					0.114		"	1.02	-1			
					0.205		"	7.0	-2			
					0.500		"	5.0	-2			
				"	0.02 - 0.5		k_1	3.3	-2			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.53	$C_6H_5CH:CHCHO + Cl_2$	CH_3COOH	A = B = 0.025	-		k AB	25	8.3	-2			(22)
				HCl	0.1		"	3.5	-1			
				H_2SO_4	0.1		"	3.3	-1			
.54	*cis* - $C_6H_5CH:CHCOOH + Cl_2$	CH_3COOH	A = B = 0.05 - 0.00625			k AB	25	3.5	-1			(22)
		$C_6H_5NO_2$	0.00625			"	"	1.25	0			"
		CH_3COOH 20 % + CCl_4 80 %	0.025			"	"	2.0	-3			"
.55	*trans* - $C_6H_5CH:CHCOOH + Cl_2$	CH_3COOH	A = B = 0.025			k AB	15	5.7	-2			(22)
			0.0125				"	4.5	-2			
			0.05				25	1.0	-1			
			0.025				"	9.5	-2			
			0.0125				"	8.2	-2			
			0.00625				"	7.2	-2			
		$C_6H_5NO_2$	0.025			"	15	5.8	-2			"
			0.00625				"	5.0	-2			
			0.025				25	9.0	-2			
			0.0125				"	8.2	-2			
			0.00625				"	7.7	-2			
.56	*cis* - $C_6H_5CH:CHCOOH + Br_2$	CH_3COOH	A = B = 0.0125 - 0.05			k AB^2	25	3.5	-1			(18)
							50	7.8	-1	5.8		
		"	A = B = 0.0125	HBr	HBr/Br_2	k AB	25					"
					0		(0.2)	1.08	-3			
					"		(0.5)	6.3	-4			
					0.125		(0.2)	1.08	-3			
					"		(0.5)	7.5	-4			
					0.25		(0.2)	1.1	-3			
					"		(0.5	8.2	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$ k°	n	E	Comments	Literature
.56	*cis* - $C_6H_5CH{:}CHCOOH + Br_2$ *(continued)*				0.5		(0.2)	1.1	-3			
					"		(0.5)	8.3	-4			
		$CH_3COOH + H_2O$ 10 %	A = B =			kAB	25				*	(^{11})
			0.0125	H_2SO_4	0.05		(0.2)	1.85	-1			
							(0.4)	1.4	-1			
							(0.6)	9.0	-2			
		"	0.0062	"	"	"	(0.2)	1.15	-1			"
							(0.4)	9.0	-2			
							(0.6)	8.3	-2			
		25 %	0.0125	-		"	(0.3)	2.5	0			"
							(0.4)	1.9	0			
							(0.5)	1.7	0			
		"	"	H_2SO_4	0.05	"	(0.2)	1.1	0			"
							(0.4)	1.05	0			
							(0.6)	8.3	-1			
.57	*trans* - $C_6H_5CH{:}CHCOOH + Br_2$	CH_3COOH	A = B =			kAB	25				*	(^{18})
			0.025				(0.2)	5.8	-4			
			"				(0.4)	5.8	-4			
			0.0125			"	(0.2)	2.8	-4			
			"				(0.4)	2.7	-4			
			"	HBr	HBr/Br_2 0.125	"	(0.2)	1.10	-3			
							(0.5)	7.7	-4			
			"		0.25	"	(0.2)	1.1	-3			
							(0.5)	7.5	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.57	*trans* - $C_6H_5CH:CHCOOH + Br_2$ *(continued)*	CCl_4				kAB	0	4.8 - 1.1	-5			(8)
		CCl_4				kAB	15	3 - 7	-8		*	(19)
		CCl_4	A = B = 0.033			kAB	0				*	(24)
							(1)	1.1	-5			
							(f)	2.7	-5			
							13					
							(1)	1.8	-5			"
							(f)	6.8	-5			
							25.5					
							(1)	1.2	-4			"
							(f)	1.9	-4			
		$CHCl_3$	"			"	13					
							(1)	2.2	-5			"
							(f)	2.2	-4			
		"	A = B = 0.033	HBr	HBr/Br_2	kAB	13					(24)
					0.28		(1)	5	-3			
					"		(f)	4.3	-3			
					0.53		(1)	1.6	-2			"
							(f)	2.0	-2			
					1.08		(1)	3.6	-2			"
							(f)	4.3	-2			
				HCl	HCl/Br_2							
					1.10		(1)	1.3	-4			"
							(f)	1.4	-4			
				H_2O	70 % sat		(1)	4.6	-5			"
							(f)	5.2	-5			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o = 10^n$		E	Comments	Literature
								k^o	n			
.58	*cis* - $C_6H_5CH{:}CHCOOH + BrCl \longrightarrow ?$	CH_3COOH 20 % + CCl_4 80 %				kAB					*	(^{22})
			A = 0.025; Br_2/Cl_2 =									
			20 % reaction		0.25		25	3.7	-3			
			50 "		"		"	3.2	-3			
			20 % "		1.0		"	7.0	-3			
			50 "		"		"	5.5	-3			
			20 % "		2.0		"	4.7	-3			
			50 "		"		"	3.5	-3			
.59	*trans* - $C_6H_5CH{:}CHCOOH + BrCl$	CCl_4	$Br_2 = Cl_2$				0	2.9	-2		*	(^{8})
.60	$C_6H_5CH{:}CHCOOCH_3 + Cl_2$	CH_3COOH				kAB	24	1.7	-1			(^{10})
.61	$C_6H_5CH{:}CHCOOCH_3 + Br_2$	$CHCl_3$	A = B = 0.033	HBr	0.015	kAB	24	4.5	-3			(^{10})
		CCl_4	A = B = 0.016			kAB	15	3 - 6.5	-8			(^{19})
		"	A = B = 0.033			kAB	13				*	(^{24})
							(1)	1.1	-5			
							(f)	1.75	-5			
.62	$C_6H_5CH{:}CHCOOC_2H_5 + Br_2$	CCl_4	A = B = 0.016			kAB	15	3 - 7	-8			(^{19})
.63	$C_6H_5CH{:}CHCH_2COOH + Br_2$	CCl_4	A = B = 0.016			kAB	15	7 - 17	-4			(^{19})
.64	$C_6H_5CH{:}C(CH_3)COOH + Br_2$	CCl_4	$Br_2 = Cl_2$			kAB	0	3.3	-8			(^{8})
.65	$C_6H_5CH{:}C(CH_3)COOH + BrCl$	CCl_4	$Br_2 = Cl_2$			kAB	0	7	-4			(^{8})
.66	$C_6H_5CH{:}CHCH_2CH_2COOH + Br_2$	CCl_4				kAB	15	1 - 2.3	-2			(^{19})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.67	$C_6H_5CH:CHCH:CHCOOH + Br_2$	CCl_4				kAB	15	3 - 9	-6		*	(19)
		$CHCl_3$	A = B = 0.033			kAB	13				*	(24)
							(1)	2.5	-1			
							(f)	4.9	-2			
.68	$C_6H_5CH:CHCH:CHCOOH + Br_2$	$CHCl_3$	A = B = 0.033			kAB	13					(24)
							(1)	7.1	-1			
							(f)	1.2	-1			
		CCl_4	A = B = 0.033			kAB	13					(24)
							(1)	2.7	-2			
							(f)	1.5	-3			
.69	$C_6H_5CH:C(COOH)_2 + Br_2$	CH_3COOH	A = 0.0125	$HBr/Br_2 = 1 - 4$		kAB	24	4.3	-1		*	(13)
.70	$C_6H_5C⋮C⋮COO^- + I_2$	H_2O	A = B = 0.010	KI = 4 A = 4 B		kAB					*	(12)
							15.2	4.07	-4			
							24.8	9.45	-4			
							40.3	3.34	-3			
							50.1	7.22	-3			
							59.8	1.49	-2	15.2		
			0.025	"		"	15.2	4.19	-4			"
							24.8	1.04	-3			
							40.3	3.63	-3			
							50.1	7.49	-3			
							59.8	1.58	-2	15.2		
			0.050	"		"	15.2	4.74	-4			
							24.8	1.14	-3			
							40.3	3.78	-3			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.70	$C_6H_5C\vdots C\vdots COO^- + I_2$ *(continued)*						50.1	7.92	-3			
							59.8	1.49	-2	14.5		
			0.094	KI = 4 A = 4 B		kAB	15.2	6.01	-4			(^{12})
							24.8	1.26	-3			
							40.3	4.38	-3			
							50.1	8.75	-3	14.5		
.71	*cis* - *o* - $CH_3OC_6H_4CH{:}CHCOOH + Br_2$	CCl_4	A = B = 0.033			kAB	13					(^{24})
							(l)	4.4	-1			
							(f)	3.5	-2			
		$CHCl_3$	"			"	(l)	5.1	-1			
							(f)	4.0	-1			
.72	*trans* - *o* - $CH_3OC_6H_4CH{:}CHCOOH + Br_2$	$CHCl_3$	A = B = 0.033			kAB	13					(^{24})
							(l)	3.0	-1			
							(f)	2.8	-2			
.73	*cis* - *o* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + BrCl$	CCl_4	$Br_2 = Cl_2$			kAB	0	1.4	0			(^{8})
.74	*trans* - *o* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + BrCl$	CCl_4	$Br_2 = Cl_2$			kAB	0	6.6	-1			(^{8})
.75	*m* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + BrCl$	CCl_4	$Br_2 = Cl_2$			kAB	0	5.5	-2			(^{8})
.76	*m* - $CH_3OC_6H_4CH{:}CHCOOCH_3 + Br_2$	CCl_4				kAB	0	~ 3	-4			(^{8})
.77	*o* - $NO_2C_6H_4CH{:}CHCOOH + Cl_2$	CH_3COOH	A = B = 0.05			kAB	24	1.83	-5			(^{10})
.78	*m* - $NO_2C_6H_4CH{:}CHCOOH + Cl_2$	CH_3COOH	A = B = 0.05			kAB	24	1.83	-4			(^{10})
.79	*p* - $NO_2C_6H_4CH{:}CHCOOH + Cl_2$	CH_3COOH	A = B = 0.05			kAB	24	8.2	-5			(^{10})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.80	m - $NO_2C_6H_4CH{:}CHCOOH + Br_2$	CH_3COOH	A = B = 0.0125	HBr	0.0125	kAB	24	9.5	-5			(10)
.81	p - $NO_2C_6H_4CH{:}CHCOOH + Br_2$	CH_3COOH	A = B = 0.0125	HBr	0.0125	kAB	24	5.5	-5			(10)
.82	o - $NO_2C_6H_4CH{:}CHCOOCH_3 + Br_2$	$CHCl_3$	A = B = 0.033	HBr	0.015	kAB	24	1.35	-5			(10)
.83	m - $NO_2C_6H_4CH{:}CHCOOCH_3 + Br_2$	$CHCl_3$	A = B = 0.033	HBr	0.015	kAB	24	1.28	-4			(10)
.84	p - $NO_2C_6H_4CH{:}CHCOOCH_3 + Br_2$	$CHCl_3$	A = B = 0.033	HBr	0.015	kAB	24	6.8	-5			(10)

SUPPLEMENTARY TABLES

(.33) $CH_3CH{:}C(CH_3)COOH + Br_2$. *Solvent* CH_3COOH. *Temperature* 35.5 (1)

A	B	Time(sec) for completion of 0.1 (fraction of complete reaction)	0.5
0.033	0.017	3780	24600
0.017	0.033	10700	72000
0.033	0.009	8000	25200
0.017	0.009	10500	76500

No rate law established. Induction period observed.

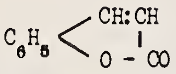
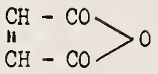
Classification of Br_2 addition reactions to a double bond (24):

(1) Rapid addition; some substitution; second-order k increases with the progress of the reaction.

Examples: Reactions (.47)(.48)(.67)(.71)(.72).

(2) Slow addition; induction period; second-order k decreases with the progress of the reaction.

Examples: (.57)(.61).

(3) No measurable addition (13°C, in CCl_4, $CHCl_3$). Example  ;  ; $C_6H_5CH:C(C_6H_5)CN$.

Induction period and *Fractional times* data in originals (24)(9). Phenanthrene derivatives + Br_2, see originals (7)(8).

COMMENTS

General. In many instances, halogen addition reactions to multiple bonds present anomalies, the rates failing to follow satisfactorily a definite kinetic order. Indications of partial heterogeneity and of chain character, evidence by induction periods and sensitivity to inhibitors, are frequent. The mass-action laws given in the tables are very often purely conventional and do not establish a valid rate law of the reaction. Trends of the k, as defined, are illustrated by a statement of the fraction of the conversion, e.g. (0.1), (0.5), etc. to which the given value of k refers, or by the symbols (i) = initial, (f) = final. The frequently observed catalysis by halogen ions X^- is interpreted by (17) as $RCH:CHR + X^- \longrightarrow RCHX - CHR$, followed by $RCHXCHR + X_2 \longrightarrow RCHXCHXR + X^-$.

References. (8) BrCl formed from equimoleculer amounts of Br_2 and Cl_2. The data of k are average values. Reactions of $o - CH_3OC_6H_4CH:CBrCOOH$ and of $m - CH_3OC_6H_4CH:CHCOOH$ with BrCl do not follow the second order. (11) Original k converted from ml of 0.0182 N $Na_2S_2O_3$ used for a 10-ml sample, and hours, to l M^{-1} sec^{-1} (GSF). For the bromides, $k_{n+1} / k_n \sim 18$, i.e. k increases in a geometrical progression with increasing number of C atoms above 2 (for $CH_2:CHBr$, $n = 0$). (13) Data of k given for 0.1 completion of the reaction. (19)(24) Unexplained serious discrepancies.

Reactions. (.1) Data of (4) refer to the lowest k observed in dry CCl_4. According to (23) the reaction is autocatalyzed; rates are not reproducible, and no rate constant can be derived. Agreement between (4) and (23)

COMMENTS *(continued)*

on the fact that at the higher temperature (18°, 25°C) the reaction is considerably slower than at 0°C. HBr exerts an accelerating influence (23), contrary to (4). Assumption of $Br_2 \cdot H_2O$ as the brominating agent (4) contradicted by (23). (.2) In the gas phase (25) at 300°C, only an initial pressure drop is observed, coming to an early halt. Consequently, no reaction occurs on simple collision between A and B. (.7) The rate in CH_3COOH is formulated by (16) $k_oA[I_3^-] + kAB + k'AB^3$, with only k'(initial) evaluated. The I^- ions forming the I_3^- are produced by a side reaction of A with the solvent (CH_3COOH). In H_2O, the formulation of the rate in the presence of I^- ions added, is (3) $k_1A[I_3^-] + k_2AB$, with the equilibrium $I_2 + I^- \rightleftarrows I_3^-$. (.8) The total rate is represented by (16) as $k_oA[Br_3^-] + kAB + k'AB^2$, with the first term assuming increasing importance at higher temperatures; k_o was not evaluated. The Br^- ions forming Br_3^- with Br_2 are produced by a side reaction of A with the solvent (CH_3COOH). Experimental evidence for acceleration by Br^- is the 2.3-fold rate increase on addition of 0.004 HBr (at A = 0.008). Both k and k' show marked trends from initial (i) to final (f) values. The data do not establish the kinetics of the reaction. The orders of magnitude of the third-order rate constants of (16) and of (18) are in fair agreement; the figure of (18) at 50°C lies between the initial and the final k' values of (16). Addition of 1 % H_2O increases the rate by 80 % (16). Oxygen and CO_2 have no effect (16). In CCl_4, the reaction is partly heterogeneous (18), assumedly governed by the formation of a film on the wall of the reaction vessel; under these conditions, the reaction is *not* actually second-order, but rather more nearly first-order at 0° and 25°C, and more nearly third-order at 50°C. This accounts for the increase of the second-order k, at 0° and 25°C, from 0.2 and 0.6 completion of the reaction, and the abnormal decrease of the second-order k with rising temperature.

(.9) The total rate in CH_3COOH is represented (16) as $k_oA[I_3^-] + kAB + k'AB^3$, with only k' evaluated. The I^- ions forming I_3^- are produced by a side reaction of A with the solvent (CH_3COOH). The data do not establish satisfactorily the kinetics of the reaction. Oxygen and CO_2 have no effect. (.11) In CCl_4, the reaction is partly heterogeneous. The data given are for N_2 atmosphere; O_2 inhibits, H_2O accelerates the homogeneous part of the reaction which becomes predominant at lower concentrations. In C_6H_5Cl and $CHCl_3$ the reaction is homogeneous; k calculated from 0.5 time and 0.2 time,

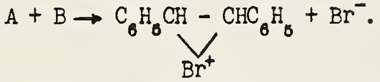
COMMENTS *(continued)*

respectively, assuming second-order. In all cases, the rate tends to second-order with decreasing concentration. (.12) Reaction partly heterogeneous in CCl_4; at 0° and 25°C showing unimolecular, at 50°C termolecular character. (.13) The total rate in CH_3COOH is represented (16) as $k_o A[Br_3^-] + kAB + k'AB^2$, with the first term small at 25°C but assuming increasing importance at higher temperatures; k_o was not evaluated. The Br^- ions forming Br_3^- are produced by a side reaction of A with the solvent (CH_3COOH). Both k and k' show marked trends from initial (i) to final (f) values. The data do not establish satisfactorily the kinetics of the reaction. (.20) In CH_3COOH, second-order constants of (13) (at 0.1 completion of the reaction) are distinctly higher than the second-order k of (1). In CCl_4, unexplained serious discrepancy between the second-order k of (19) (20) and of (24). From the marked trends of both the second and third-order k in CH_3COOH, between 0.1 and 0.5 completion of the reaction, the presence of an induction period, and the inhibition by $SbBr_3$, (1) concludes that the reaction involves a chain mechanism (no evidence for the specific mechanism proposed). (.22) The uninduced reaction (in the presence of HCl only) is unaffected by O_2. The reaction induced by Fe^{++} is inhibited by O_2 and was carried out under CO_2. The inductor, $FeCl_2$ solution, is added to the A + B solution at the stated *rate R* (M/l per sec) and the reaction is allowed to proceed as long as the Fe^{++} is being added (5 - 10 sec), then quenched immediately. The rate laws are different at low and at high B/A ratios. In the latter case, the rate depends on $R^{1/2}$. Further inductors, Ti^{++}, V^{++}, V^{+++}, Mo^{+++}, have the same effect as Fe^{++}; the reaction is also induced by Ce^{++++}. The reaction is inhibited by Mn^{++}, Mo^{+++++}, VO^{++}, Cu^{++}, Co^{++}, Ce^{+++}, Pr^{+++}, Ni^{++}, Cr^{+++}, Fe^{+++}, La^{+++}. Chain lengths, computed by $\Delta B/Rt$ (amount of Cl_2 consumed in the reaction divided by the total amount of inductor added during the same time) vary between 40 and 120. On the assumption that R is identical with the rate of the very rapid initiating reaction (1) $Fe^{++} + Cl_2 \rightarrow FeCl^{++} + Cl$, followed by (2) $A + Cl \rightarrow COOHCHCl\dot{C}HCOOH$; (3) $COOHCHCl\dot{C}HCOOH + Cl_2 \rightarrow L + Cl$; (4) $COOHCHCl\dot{C}HCOOH + Cl \rightarrow L$; (5) $Cl + Cl \rightarrow Cl_2$; $k' = (k_2 k_3 / k_4)^{1/2}$, and $k'' = k_2 / k_5^{1/2}$. (.23) (.24) In H_2O (3) the rate is $k_1 AB + k_2 A^- B$, with A = undissociated acid, A^- = anion. The decrease of the rate with increasing $[Br^-]$ is due to the slower reaction of A (or A^-) with Br_3^- as compared with the reaction with Br_2 (see .7). For the reaction in CH_3COOH (14), $k' = k/K$,

COMMENTS *(continued)*

with $K = [Br_2][Br^-]/[Br_3^-]$. Added salts exert retarding effects, in the order of decreasing effectiveness NaBr > LiBr > CH_3COONa > $LiSO_3C_2H_5$ > $LiSO_3C_6H_4CH_3$. At 50°C, 1 % H_2O lowers k by about 20 % for (.23), 75 % for (.24). (.46) Reaction partly heterogeneous in CCl_4; in CH_3COOH, only data of E. (.47) (.48) Unexplained serious discrepancy between data of ([19]) and ([24]).

(.52) Addition of Br^- converts part of the Br_2 present into Br_3^- which reacts with A much more slowly than Br_2 ($k_2 \sim 100k_1$). Consequently, k decreases with increasing $[Br^-]$. With no Br^- added in advance, some Br_3^- is formed as a by-product of a side reaction, and causes k within each single run to fall with the progress of the reaction much more rapidly than is warranted by a second-order law, on account of the progressive replacement of the more reactive Br_2 by the less reactive Br_3^-. Consequently, with no Br^- added in advance, $k = k_2$ only at the initial stages of the reaction. The observed k are rendered satisfactorily by the values of k_1, k_2, and the equilibrium constant $K = [Br_3^-]/[Br_2][Br^-] = 0.0024$. The primary step is represented as



$$A + B \rightarrow \underset{\diagdown\diagup \atop Br^+}{C_6H_5CH - CHC_6H_5} + Br^-.$$

(.58) k evaluated as second-order although the actual order is 2.9, i.e. closer to kAB^2. In CCl_4, the equilibrium $Br_2 + Cl_2 \rightleftarrows 2\ BrCl$ is 60 % BrCl.

(.57) (.62) (.67) Unexplained serious discrepancy bewteen ([19]) and ([24]). (.70) The reaction proceeds actually between A and I_3^-, as, at B > 0.005, more than 90 % of it is present in the form of I_3^- (with the stated amount of I^- added). The increase of k with the concentration of the reactants parallels the increasing stability of I_3^-. At B < 0.0025, k increases rapidly with the dilution, which indicates increasing participation of a reaction between A and HIO (produced by hydrolysis of I_2). The total rate $-dB/dt = k_1A[I_3^-] + k_2A[HIO]$; $k_1 = k(K + [I^-])/[I^-]$; $K = [I_2][I^-]/[I_3^-]$. k_2 is not evaluated.

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ADDITION

Ring opening by addition of OH^-

Liquid phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
						k^o	n		A^o	n
.1	$\underline{CH_2CH_2CH_2CO} + OH^- \longrightarrow C_3H_7COO^-$	H_2O	0.005 - 0.01	kAB	0	1.96	-1			
					15	5.82	-1	11.3	3.7	6
.2	$\underline{CH_3CH_2CH_2CH_2CO} + OH^- \longrightarrow C_4H_9COO^-$	H_2O	0.005 - 0.01	kAB	0	8.23	-2			
					15	2.40	-1			
					25	4.68	-1	11.2	1.3	6
		$H_2O + C_2H_5OH$ 21 %	"	"	0	6.31	-2			
					15	1.82	-1			
					25	3.43	-1	10.8	4.8	5
		$H_2O + C_2H_5OH$ 40 %	"	"	0	3.0	-2			
					15	1.01	-1			
					25	2.06	-1	12.6	6.2	6
		$H_2O + C_2H_5OH$ 60 %	"	"	0	1.45	-2			
					15	6.10	-2			
					25	1.38	-1	14.5	1.0	8
.3	$\underline{C_6H_4COOCH_2} + OH^- \longrightarrow C_6H_5COOCH_2O^-$	H_2O	0.005 - 0.01	kAB	0	3.92	-2			
					15	1.29	-1			
					25	2.73	-1	12.6	8.0	6

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$	
						k°	n		A°	n
.3	$\underline{C_6H_4COOCH}_2 + OH^- \rightarrow C_6H_5COOCH_2O^-$ *(continued)*	$H_2O + C_2H_5OH$ 21.5 %	0.005 - 0.01	k AB	0	2.06	-2			
					15	7.38	-2			
					25	1.57	-1	13.2	1.3	7
		$H_2O + C_2H_5OH$ 40 %	"	"	0	8.84	-3			
					15	3.78	-2			
					25	8.84	-2	14.9	1.3	8
		$H_2O + C_2H_5OH$ 60 %	"	"	0	4.32	-3			
					15	2.12	-2			
					25	5.18	-2	16.1	5.7	8
.4	$5\text{-}NH_2\underline{C_6H_3COOCH}_2 + OH^- \rightarrow NH_2C_6H_4COOCH_2O^-$	H_2O	"	"	0	2.27	-2			
					15	8.16	-2			
					25	1.76	-1	13.3	1.7	8

COMMENTS

Electric conductivity measurements.

LITERATURE

D. S. Hegan, J. H. Wolfenden, *CSL* **1939**, 508.

OXIDATIVE ADDITION

C oxide + halogen

Rate measured $-\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Literature
				k°	n		A°	n	
.1	$CO + Cl_2 \rightarrow COCl_2$	$k\,AB^{3/2}$	349	3.81	0				(¹)
			395	1.55	+ 1				
			452	7.78	+ 1	11.5	1.45	10	

COMMENTS

Reverse reaction, see 541.470. The proposed mechanism, $Cl_2 \rightleftarrows 2\ Cl$; $Cl + CO \rightleftarrows COCl$; $COCl + Cl_2 \rightarrow COCl_2 + Cl$; is based on analogy with photochemical reactions which seem to rule out Cl_3 as intermediate (²).

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OXIDATIVE ADDITION

N oxides

Rate measured $-\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
					k^o	n	
.1	$2\ NO + O_2 \longrightarrow 2\ NO_2$	$A + B = 3 \times 10^{-5} - 7 \times 10^{-4}$	$k\,A^2B$	-130	1.48	+5	(9)
				-78	2.58	+4	"
				-19	1.31	+4	"
				0	1.04	+4	"
				60	5.5	+3	(1) (4)
				141	4.0	+3	"
				241	3.0	+3	"
				340	2.8	+3	"
				389	2.5	+3	"

COMMENTS

Selected data. The rate is unaffected by added H_2O, NO_2, SO_2 (4), N_2 (10), increased surface (4), magnetic field (8). Homogeneity, confirmed by (6), contested by (12). Proposed mechanisms: (3) $2\,NO \rightleftarrows (NO)_2$; $(NO)_2 + O_2 \rightarrow 2\,NO_2$; (13) $NO + O_2 \rightleftarrows NO_3$; $NO_3 + NO \rightarrow 2\,NO_2$. The negative temperature coefficient is attributed by (7) to suppression of translation and rotation in reactants and replacement as vibration in complex, requiring no activation energy.

Reverse reaction. $2\,NO_2 \rightarrow 2\,NO + O_2$, rate = $k\,AB$; k can be calculated from the rate of the forward reaction and the equilibrium constant (2) $\log K_p = -(2891/T) + 1.75 \log T + 0.0046\,T - 8.92 \times 10^{-6} T^2 + 3.934$ (in atm.).

LITERATURE

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OXIDATIVE ADDITION

N oxide + halogen

Gas phase

Rate measured $-\Delta p$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
					k^o	n			
.1	$2\ NO + Cl_2 \rightarrow 2\ NOCl$	A = 0.001 - 0.004 B = 0.0004 - 0.005	$k A^2 B$	0	5.4	0		*	(3)
				30	1.25	+1			
				59	2.48	+1			
				150	1.05	+2			
				197	1.91	+2	4.5		
		0.01 - 0.015	$k A^2 B (1 - \sigma)$; $d\sigma/dt = k'(1 - \sigma) L$					*	(4)
			k	15	5.70	0			
			"	"	1.18*	0			
			"	25	6.90	0			
			"	"	2.59*	0			
			k_2	15 - 25	5.6	-2			
.2	$2\ NO + Br_2 \rightarrow 2\ NOBr$	0.0003 - 0.002	$k A^2 B$	-8.2	2.12	+3		*	(2)
				0	2.35	+3			
				15	2.67	+3	1.5		

COMMENTS

(.1) Data from (3), in substantial agreement with earlier data of (5). Mechanism proposed (1) $2\ NO \rightleftarrows (NO)_2$; $(NO)_2 + Cl_2 \rightarrow 2\ NOCl$; (5) $NO + Cl_2 \rightleftarrows NOCl_2$; $NOCl_2 + NO \rightarrow 2\ NOCl$; no evidence for either. Data of (4); The rate is represented by $kA^2B(1-\sigma)$, where σ = fraction of surface covered; in $d\sigma/dt = k'(1-\sigma)L$, the constant k' is independent of the temperature. Starred (*) values of k refer to rates observed on surface poisoned after many runs, when reproducible rates from run to run and concordant values within one run are found. Intense drying with P_2O_5 gave, at 15 and 25°C, k = 5.86 and 7.25; these are taken to correspond to rates on NOCl-free surface; the reaction is inhibited by adsorbed NOCl on moist surface. Data of (3), extrapolated to 15° and 25°C, give k = 8.19 and 10.9, as against (4) 5.70 (1.18*) and 6.90 (2.59*), i.e. distinctly higher than (4). (.2) Selected data. Proposed mechanisms of (1) and (5), as for reaction (.1); neither mechanism substantiated.

Reverse reaction $2\ NOBr \rightarrow 2\ NO + Br_2$, rate = kAB; k can be calculated from the forward reaction and the equilibrium constant (5) $\log K_p = (-2867/T) + 8.025$ (in atm.).

LITERATURE

(1) M. Bodenstein, *HCA* 1935, **18**, 743. (2) W. Krauss, *ZPC*^{A} 1936, **175**, 295. (3) W. Krauss, M. Saracini, *ZPC*^{A} 1937, **178**, 245. (4) E. Stoddart, *CSL* **1940**, 823; **1944**, 388. (5) M. Trautz, *ZEC* 1916, **22**, 104; M. Trautz, Dalal, *ZAC* 1918, **102**, 149; 1920, **110**, 1.

651.471.

ADDITION

Alkyl halide + aliphatic amine

Quaternary base formation

Gas phase

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Amount of reactant		Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$C_2H_5I + (C_2H_5)_3N$	100 A = 1.0 ;	100 B = 1.0	k AB	140.6	1.9	-4
		2.74	1.70		"	3.68	-4
		4.70	2.90		"	6.46	-4
		2.11	4.37		"	1.31	-3
		7.91	13.6		"	1.86	-3
		11.2	15.4		"	2.67	-3

COMMENTS

Selected figures. The second-order k increases with increasing initial amounts of reactants. The reaction is clearly partly heterogeneous, as evidenced by the strong rate-increasing effect of packing. The gas-phase reaction is ~ 5 times as fast as in C_6H_{14}, and somewhat slower than in CCl_4.

LITERATURE

E. A. Moelwyn-Hughes, C. N. Hinshelwood, *CSL* 1932, 230.

ADDITION

Aliphatic carboxylic acid ester + Amine

Quaternary base formation

Liquid phase

Reaction type $RCOOR' + NR''_3 \longrightarrow RCOO^- + NR''_3R'^+$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$CH_3COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	1.65	-6
.2	$CH_3CHOHCOOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	9.74	-6

COMMENTS

$\log k = -2.46 + 0.67 \log K$ (ionization constant of the acid).

LITERATURE

L. P. Hammett, H. L. Pfluger, *ACS* 1933, 55, 4079.

ADDITION

Aromatic carboxylic acid ester + Amine

Liquid phase

Quaternary base formation

Amounts are in M/l.
Rates are in M/l per sec.

Reaction type $ArCOOR + NR''_3 \longrightarrow ArCOO^- + NR''_3R^+$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$C_6H_5COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	4.48	-6
.2	$C_6H_4(COOCH_3)_2 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	3.45	-5
.3	*o* - $CH_3C_6H_4COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	4.62	-6
.4	*p* - $CH_3C_6H_4COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	3.41	-6
.5	*o* - $NO_2C_6H_4COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	(9.15)	-5
.6	*p* - $NO_2C_6H_4COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	3.14	-5
.7	*o* - $ClC_6H_4COOCH_3 + N(CH_3)_3$	CH_3OH	A = 0.14 - 0.62; B ~ 0.18	kAB	100	2.03	-5

COMMENTS

$\log k = -2.46 + 0.67\,K$ (ionization constant of the acid). (.5) extrapolated to zero time.

LITERATURE

L. P. Hammett, H. L. Pfluger, *ACS* 1933, 55, 4079.

ADDITION

Alkyl halide + aliphatic amine

Quaternary base formation

Liquid phase

Reaction type $RX + NR'_3 \rightarrow R'_3\ NR^+ + X^-$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$CH_3I + N(CH_3)_3$	C_6H_6	A = B = 0.1	k AB	4.4	6.0	-3					(^{3})
					16.0	1.15	-2					
					25.0	1.85	-2					
					40.1	3.71	-2	8.7				
.2	$CH_3I + N(C_2H_5)_3$	C_6H_6	A = B = 0.1	k AB	4.6	$\underline{4.4}$	-4				*	(^{2})
					14	$\underline{8.0}$	-4				(^{2a})	(^{3})
					25.0	$\underline{1.45}$	-3					
					40.0	$\underline{3.20}$	-3					
					60	$\underline{8.25}$	-3	9.7	2.1	4		(^{2a})
		$C_6H_5NO_2$ 25% + C_6H_6 75%		k AB	4.4	2.20	-3					(^{2a})
					15	4.3	-3					
					25.0	7.75	-3					
					40.0	1.55	-2	9.5	7.7	4		
		$C_6H_5NO_2$ 50% + C_6H_6 50%		k AB	4.6	4.4	-3					(^{2a})
					15	8.0	-3					
					25.0	1.48	-2					
					40.1	3.41	-2	9.8	2.4	5		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.2	$CH_3I + N(C_2H_5)_3$ *(continued)*	$C_6H_5NO_2$ 75% + C_6H_6 25%		k AB	4.7	7.0	-3					(^{2a})
					15	1.30	-2					
					25.0	2.44	-2					
					40.0	5.50	-2	10.0	5.8	5		
		$C_6H_5NO_2$ 90% + C_6H_6 10%		k AB	4	9.27	-3					(^{2a})
					15	1.79	-2					
					25	3.21	-2					
					40	7.08	-2	9.8	5.0	5		
		$C_6H_5NO_2$		k AB	4.1	9.35	-3					(^{2})
					5	1.07	-2					(^{2a})
					15.0	$\underline{1.9}$	-2				(^{2})	(^{2a})
					25.0	$\underline{3.35}$	-2				"	"
					40.0	$\underline{7.3}$	-2	9.7	4.3	5	"	"
.3	$C_2H_5Cl + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = 1.43; B = 0.14	k AB	55	4.86	-5					(^{1})
.4	$C_2H_5I + N(CH_3)_3$	C_6H_6	A = B = 0.1	k AB	25.0	2.12	-4					(^{3})
					40.1	5.26	-4					
					80.6	4.39	-3	11.4				
.5	$C_3H_7Br + N(CH_3)_3$	C_6H_6	A = B = 0.1	k AB	80.5	1.78	-4					(^{3})
					99.7	4.26	-4					
					117.6	8.76	-4					
					139.4	1.96	-3	11.7				
.6	$C_3H_7I + N(CH_3)_3$	C_6H_6	A = B = 0.1	k AB	40.0	1.20	-4					(^{3})
					80.6	9.95	-4					
					99.7	2.19	-3	11.2				

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.7	$(CH_3)_2CHI + N(C_2H_5)_3$	C_6H_6	A = B = 0.1	k AB	99.6	1.77	-6				*	(2)
					120.4	6.25	-6				(2)	(2a)
					138	1.45	-6				"	"
					153	2.9	-6	17.1	1.9	4		(2)
								16.3	7.7	3		((2a)
		$C_6H_5NO_2$ 25 % + C_6H_6 75 %		k AB	99.8	1.51	-5					(2a)
					120.6	4.59	-5					
					139.0	1.02	-4					
					153.4	2.21	-4	16.5	1.2	4		
		$C_6H_5NO_2$ 50 % + C_6H_6 50 %		k AB	80.2	1.68	-5					(2a)
					99.9	5.62	-5					
					120	1.96	-4					
					153.4	8.23	-4	16.0	1.6	5		
		$C_6H_5NO_2$ 75 % + C_6H_6 25 %		k AB	99	1.23	-4					(2a)
					121	4.17	-4					
					153	2.05	-3	16.1	3.9	5		
		$C_6H_5NO_2$	A = B = 0.1	k AB	60.1	1.95	-5					(2)
					80.0	8.22	-5				(2)	(2a)
					100	2.9	-4				"	"
					120	8.8	-4	16.0	6	5	"	"
		"	A = B = 0.04	"	79.9	9.47	-5					(2)
					100.2	3.08	-4					
					121.1	9.00	-4					
		"	A = B = 0.02	"	121.1	1.10	-3					(2)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
						k°	n		A°	n		
.8	$CH_2Cl_2 + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = 1.43; B = 0.143	k AB	55	1.01	-5					(1)
.9	$CH_2Br_2 + N(CH_3)_3$	$(CH_3)_3CO$ 90 %	A = 0.07; B = 0.15	k AB	35	7.0	-5					(1)
			1.47 0.146		45	1.23	-4					
			0.113 0.113		"	1.56	-4					
			0.141 0.141		55	3.50	-4					
.10	$CH_2ClCH_2Cl + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = 1.43; B = 0.143	k AB	55	4.65	-6					(1)
.11	$CH_2BrCH_2Br + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = 1.47; B = 0.147	k AB	35	5.80	-5					(1)
			0.087 0.087		"	9.30	-5					
			0.075 0.150		"	9.30	-5					
			1.46 0.146		45	1.30	-4					
			0.147 0.147		"	1.78	-4					
			0.229 0.114		55	3.30	-4					
			0.071 0.071		"	3.82	-4					
			1.83 0.176		"	2.18	-4					
.12	$CH_2BrCH_2CH_2Br + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = 0.12; B = 0.145	k AB	35	~ 6.5	-4					(1)
			0.23 0.115		"	4.66	-4					
			1.46 0.146		45	7.36	-4					
			0.226 0.113		"	1.00	-3					
			0.223 0.111		55	1.92	-3					
.13	$BrN(CH_3)_3CH_2Br + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = B = 0.107	k AB	55	5.3	-5					(1)
.14	$BrN(CH_3)_3CH_2CH_2Br + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = 0.085; B = 0.1	k AB	35	1.0	-5					(1)
					55	5.7	-5					
.15	$BrN(CH_3)_3CH_2CH_2CH_2Br + N(CH_3)_3$	$(CH_3)_2CO$ 90 %	A = B = 0.11	k AB	35	4.0	-4					(1)
					55	1.4	-3					

COMMENTS

(.2) Averaged close data of (2) (2a) and (3) are underlined. (.7) In C_6H_6, pronounced autocatalysis, attributed to increasing polarity of the solvent through dissolved quaternary salt.

LITERATURE

(1) W.C.Davies, E.B.Evans, F.L.Hulbert, *CSL* **1939**, 412.
(2) K. J. Laidler, C. N. Hinshelwood, *CSL* **1938**, 858.
(2a) H. C. Raine, C. N. Hinshelwood, *CSL* **1939**, 1378.
(3) C. A. Winkler, C. N. Hinshelwood, *CSL* **1935**, 1147.

ADDITION

Alkyl halide + aromatic amine

⟶ quaternary base

Reaction type $RX + ArNR'R'' \longrightarrow ArNRR'R''^{+} + X^{-}$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n	E	$A = A^{o} \times 10^{n}$ A^{o}	n	Comments	Literature
.1	$CH_3I + C_6H_5N(CH_3)_2$	CH_3OH		kAB	25	5.62	-5					(2)
					35.5	1.31	-4					
					65	1.19	-3	15.2	7.9	6		
		$C_6H_5NO_2$	A = B = 0.05	kAB	24.8	8.39	-5					(2a)
					40.1	2.10	-4					
					60.0	7.72	-4	12.8	2.2	5		
.2	$CH_3I + C_6H_5N(CH_3)(C_2H_5)$	CH_3OH		kAB	44.8	1.97	-4					(2)
					65.1	8.50	-4					
					84.2	2.90	-3	15.4	7.9	6		
.3	$CH_3I + C_6H_5N(C_2H_5)_2$	CH_3OH		kAB	65	1.24	-4					(2)
					85.5	5.69	-4					
					99.4	1.49	-3	18.0	5	7		
.4	$CH_3I + C_6H_5N(CH_3)(C_3H_7)$	CH_3OH		kAB	44.8	1.12	-4					(2)
					65.2	4.94	-4					
					84.9	1.75	-3	15.4	5	6		
.5	$CH_3I + C_6H_5N(C_2H_5)(C_3H_7)$	CH_3OH		kAB	65.0	7.75	-5				*	(2)
					84.3	3.54	-4					
					99.8	1.10	-3	19.0	1.6	8		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.6	$CH_3I + C_6H_5N(C_3H_7)_2$	CH_3OH		$k AB$	65.2	5.48	-5				*	(2)
					84.7	2.52	-4					
					100	7.72	-4	19.0	1.2	8		
.7	$CH_3I + C_6H_5N(C_4H_9)_2$	CH_3OH		$k AB$	65	6.80	-5					(2)
					85	2.83	-4					
					100	8.66	-4	19.0	1.2	8		
.8	$CH_3I + m\text{-}CH_3C_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	$k AB$	35.5	1.75	-4					(1a)
					45.0	3.74	-4					
					55.0	7.56	-4					
					65.0	1.50	-3	14.9	6.3	6		
.9	$CH_3I + p\text{-}CH_3C_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	$k AB$	25.0	1.42	-4					(1a)
					35.0	3.2	-4					
					50.0	9.4	-4					
					65.0	3.55	-3	14.5				
		$C_6H_5NO_2$	A = B = 0.05	$k AB$	24.8	2.84	-4					(2a)
					40.1	7.96	-4					
					60.0	2.53	-3	12.3	3.3	5		
.10	$CH_3I + p\text{-}CH_3OC_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	$k AB$	25.0	2.53	-5					(1a)
					35.0	5.72	-4					
					45.0	1.14	-3					
					55.0	2.34	-3	14.3	7.9	6		
		$C_6H_5NO_2$	A = B = 0.05	$k AB$	15	3.46	-4					(2a)
					24.8	7.19	-4					
					40.1	1.83	-3					
					60.0	5.60	-3	11.7	2.8	5		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.11	$CH_3I + o\text{-}C_6H_5C_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	65	3.0	-5					(1^a)
					85.9	1.99	-4					
					101	6.74	-4	21.6	3			
.11.1	$CH_3I + p\text{-}C_6H_5C_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	45	4.96	-5					(1^a)
					55	9.29	-5	15.4	5	7		
.12	$CH_3I + o\text{-}C_6H_5OC_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	35	7.14	-5					(1^a)
					45	1.60	-4					
					55	3.57	-4					
					65	7.47	-4	16.2	2.5	7		
.13	$CH_3I + o\text{-}NO_2C_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	135	2.15	-4					(1^a)
					145.1	4.01	-4	20.9	5	7		
.14	$CH_3I + o\text{-}FC_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	45	7.10	-5					(1^a)
					55	1.50	-4					
					65	3.09	-4					
					74.8	5.95	-4	16.3	1	7		
.15	$CH_3I + p\text{-}FC_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	35	1.06	-4					(1^a)
					45	2.32	-4					
					55	4.95	-4					
					65	9.63	-4	15.5	1	7		
.16	$CH_3I + o\text{-}ClC_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	75	1.02	-4					(1^a)
					85.2	2.33	-4					
					98.9	6.53	-4	19.9	3.1	8		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
						k^{o}	n		A^{o}	n		
.17	$CH_3I + p\text{-}ClC_6H_4N(CH_3)_2$	CH_3OH	A = B = 0.1	k AB	45	7.87	-5					(^{1a})
					55	1.70	-4					
					65	3.5	-4					
					75	7.2	-4	16.2	1	7		
		$C_6H_5NO_2$	A = B = 0.05	k AB	15.0	9.26	-6					(^{2a})
					24.8	2.11	-5					
					40.1	5.97	-5					
					60.0	2.56	-4	13.9	3.9	5		
.18	$CH_3I + p\text{-}BrC_6H_4N(CH_3)_2$	$C_6H_5NO_2$	A = B = 0.1	k AB	15.0	8.24	-6					(^{2a})
					24.8	1.80	-5					
					40.1	5.54	-5					
					60.1	2.13	-4	13.7	2.2	5		
Aryl - substituted alkyl halide												
.19	$C_6H_5CH_2Cl + C_6H_5NH_2$	CH_3OH	A = 0.05; B = 0.2	k AB	30	3.96	-5					(^{3})
			0.01 0.4		35	7.60	-5					
			" "		45	1.71	-4					
			0.05 0.2		50	2.20	-4					
		Et 90	A = 0.025; B = 0.25	k A	30.5	1.16	-5				*	(^{1})
.20	$C_6H_5CH_2Cl + C_6H_5NHC_2H_5$	CH_3OH	A = 0.2; B = 0.05	k AB	30	5.65	-5				*	(^{3})
			0.4 0.1		35	9.60	-5					
			" "		45	2.15	-4					
			0.2 0.05		50	2.95	-4					

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.21	$C_6H_5CH_2Cl + C_6H_5N(CH_3)_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	3.70	-5				*	(3)
			0.4 0.1		35	5.80	-5					
			" "		45	1.34	-4					
			0.2 0.05		50	1.87	-4					
.22	$C_6H_5CH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	5.80	-4				*	(1)
.23	$C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH_2$	$(CH_3)_2CO$		k AB	35	6.2	-5					(4)
					45	1.24	-4	13.6				
.24	$C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(m\text{-}C_6H_4CH_3)$	$(CH_3)_2CO$		k AB	45	1.95	-5					(4)
.25	$C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(p\text{-}C_6H_4CH_3)$	$(CH_3)_2CO$		k AB	45	2.83	-5					(4)
.26	$C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(m\text{-}C_6H_4Cl)$	$(CH_3)_2CO$		k AB	45	2.33	-6					(4)
.27	$C_6H_5CH_2Br + m\text{-}NO_2C_6H_4NH(p\text{-}C_6H_4Cl)$	$(CH_3)_2CO$		k AB	45	3.00	-6					(4)
.28	$C_6H_5CH_2Br + p\text{-}NO_2C_6H_4NH_2$	$(CH_3)_2CO$		k AB	35	6.0	-5					(4)
					45	1.22	-5	13.6				
.29	$C_6H_5CH_2Br + p\text{-}NO_2C_6H_4CH_2NHC_6H_5$	$(CH_3)_2CO$		k AB	35	1.17	-4					(4)
					45	2.33	-4					
.30	$C_6H_5CH_2Br + p\text{-}NO_2C_6H_4CH_2NH(p\text{-}C_6H_4CH_3)$	$(CH_3)_2CO$		k AB	45	~ 2.5	-5					(4)
.31	$C_6H_5CH_2Br + p\text{-}NO_2C_6H_4CH_2NH(p\text{-}C_6H_4Cl)$	$(CH_3)_2CO$		k AB	45	4.7	-6					(4)
.32	$C_6H_5CH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.01	-3				*	(1)
.33	$p\text{-}CH_3C_6H_4CH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.45	-3				*	(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.34	o-$CNC_6H_4CH_2Cl + C_6H_5NH_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	2.20	-5				*	(3)
			0.4 0.1		35	3.75	-5					
			" "		45	9.00	-5					
			0.2 0.05		50	1.16	-4					
.35	o-$CNC_6H_4CH_2Cl + C_6H_5NHC_2H_5$	CH_3OH	A = 0.2; B = 0.05	k AB	30	1.89	-5				*	(3)
			0.4 0.1		35	3.38	-5					
			" "		45	7.60	-5					
			0.2 0.05		50	9.50	-5					
.36	o-$CNC_6H_4CH_2Cl + C_6H_5N(CH_3)_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	5.30	-6				*	(3)
			0.4 0.1		35	1.05	-5					
			" "		45	2.45	-5					
			0.2 0.05		50	2.82	-5					
.37	m-$CNC_6H_4CH_2Cl + C_6H_5NH_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	2.02	-5				*	(3)
			0.4 0.1		35	3.30	-5					
			" "		45	8.00	-5					
			0.2 0.05		50	1.11	-4					
.38	m-$CNC_6H_4CH_2Cl + C_6H_5NHC_2H_5$	CH_3OH	A = 0.2; B = 0.05	k AB	30	2.09	-5				*	(3)
			0.4 0.1		35	3.55	-5					
			" "		45	7.95	-5					
			0.2 0.05		50	1.10	-4					
.39	m-$CNC_6H_4CH_2Cl + C_6H_5N(CH_3)_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	8.15	-6				*	(3)
			0.4 0.1		35	1.46	-5					
			" "		45	3.18	-5					
			0.2 0.05		50	4.50	-5					

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.40	$p\text{-CNC}_6H_4CH_2Cl + C_6H_5NH_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	1.67	-5				*	(3)
			0.4 0.1		35	2.78	-5					
			" "		45	6.80	-5					
			0.2 0.05		50	8.80	-5					
.41	$p\text{-CNC}_6H_4CH_2Cl + C_6H_5NHC_2H_5$	CH_3OH	A = 0.2; B = 0.05	k AB	30	1.63	-5				*	(3)
			0.4 0.1		35	3.02	-5					
			" "		45	6.85	-5					
			0.2 0.05		50	8.50	-5					
.42	$p\text{-CNC}_6H_4CH_2Cl + C_6H_5N(CH_3)_2$	CH_3OH	A = 0.2; B = 0.05	k AB	30	6.00	-7				*	(3)
			0.4 0.1		35	1.25	-6					
			" "		45	2.90	-6					
			0.2 0.05		50	3.36	-6					
.43	$m\text{-NO}_2C_6H_4CH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	5.06	-4				*	(1)
.44	$p\text{-NO}_2C_6H_4CH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	3.70	-4				*	(1)
.45	$m\text{-NO}_2C_6H_4CH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	7.30	-4				*	(1)
.46	$p\text{-NO}_2C_6H_4CH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	6.01	-4				*	(1)
.47	$p\text{-ClC}_6H_4CH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	7.33	-4				*	(1)
.48	$p\text{-BrC}_6H_4CH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	6.83	-4				*	(1)
.49	$p\text{-IC}_6H_4CH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	7.50	-4				*	(1)
.50	$C_6H_5COCH_2Cl + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	2.50	-6				*	(1)
.51	$C_6H_5COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	2.40	-5				*	(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.52	$C_6H_5COCH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	2.47	-4				*	(1)
.53	$C_6H_5COCH(CH_3)Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.16	-5				*	(1)
.54	p-$CH_3C_6H_4COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.90	-4				*	(1)
.55	p-$CH_3C_6H_4COCH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.83	-4				*	(1)
.56	p-$CH_3OC_6H_4COCH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.66	-4				*	(1)
.57	m-$NO_2C_6H_4COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	7.3	-4				*	(1)
.58	p-$NO_2C_6H_4COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	5.8	-4				*	(1)
.59	m-$NO_2C_6H_4COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	7.8	-4				*	(1)
.60	p-$NO_2C_6H_4COCH_2I + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	6.9	-4				*	(1)
.61	m-$NO_2C_6H_4COCH(CH_3)Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	4.3	-5				*	(1)
.62	p-$NO_2C_6H_4COCH(NO_2)\ Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	4.18	-7				*	(1)
.63	p-$ClC_6H_4COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	3.22	-4				*	(1)
.64	p-$BrC_6H_4COCH_2Br + C_6H_5NH_2$	Et 90	A = 0.025; B = 0.25	k A	30.5	3.24	-4				*	(1)

SOLVENTS

Et 90 = $H_2O + C_2H_5OH$ 90 %

COMMENTS

General. Data of (1): The first-order *k* is pseudomonomolecular, valid for the given concentrations, not independent of A/B. (.5) (.6) Slight autocatalytic effect. (.19) The reaction is formulated

$$2\ A + 2\ B \longrightarrow C_6H_5NHC_2H_5{\cdot}HCl + (C_6H_5CH_2)_2(C_6H_5)N{\cdot}HCl;$$

the rate measured is the formation of Cl^-. (.20) Formulated $2\ A + 2\ B \longrightarrow C_6H_5N(CH_3)_2{\cdot}HCl + (C_6H_5CH_2)_2(C_6H_5)N{\cdot}HCl$; rate measured is formation of Cl^-. (.34) Formulated

$$2\ A + 2\ B \longrightarrow C_6H_5NH_2{\cdot}HCl + (o\text{-}CNC_6H_4CH_2)_2(C_6H_5)N{\cdot}HCl.$$

(.35) - (.41) As (.34).

LITERATURE

(1) J. W. Baker, *CSL* **1932**, 1148, 2631; **1933**, 1128. (1a) D. P. Evans, H. B. Watson, R. Williams, *CSL* **1939**, 1345. (2) D. P. Evans, *CSL* **1944**, 422. (2a) K. J. Laidler, *CSL* **1938**, 1787. (3) D. H. Peacock, Potha, *CSL* **1937**, 955. (4) D. H. Peacock, *CSL* **1935**, 6.

ADDITION

Aromatic halide + aromatic amine

Quaternary base formation

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$	
						k°	n		A°	n
.1	2, 4-$(NO_2)_2C_6H_3Br$ + $C_6H_5NH_2$		B = 0.1; A = 0.4 - 0.8	k AB	35	1.63	-4			
			" 0.4		45	3.00	-4	11.2	1	6
.2	2, 4-$(NO_2)_2C_6H_3Br$ + *m*-$CH_3C_6H_4NH_2$		B = 0.1; A = 0.4	k AB	35	2.30	-4			
					45	4.18	-4	11.6		
.3	2, 4-$(NO_2)_2C_6H_3Br$ + *p*-$CH_3C_6H_4NH_2$		B = 0.1; A = 0.4	k AB	35	5.31	-4			
					45	9.19	-4	10.6	1	6

LITERATURE

A. Singh, D. H. Peacock, *CSL* 1936, 1410.

ADDITION

Quaternary base formation

Aromatic acyl halide + Aromatic amine

Liquid phase

Reaction type $ArCOCl + Ar'NH_2 \rightarrow (ArCO)Ar'NH_2^+ + Cl^-$

Rate measured $+ d[Cl^-]/dt$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*
						k^o	n	
.1	$C_6H_5COCl + C_6H_5NH_2$	C_6H_6	A = 0.005; B = 0.01	kAB	5.0	3.08	-2	
					25.0	7.48	-2	
					40.0	1.22	-1	
					70.0	4.17	-1	7.3
.2	C_6H_5COCl + *p*-$CH_3C_6H_4NH_2$	C_6H_6	A = 0.0025; B = 0.005	kAB	5.0	1.34	-1	
					15.0	2.07	-1	
					25.0	2.98	-1	
					40.0	5.52	-1	6.8
.3	C_6H_5COCl + *m*-$NO_2C_6H_4NH_2$	C_6H_6	A = 0.0025 - 0.01; B = 0.005 - 0.02	kAB	25.0	4.5	-4	10.5
.4	C_6H_5COCl + *p*-$NO_2C_6H_4NH_2$	C_6H_6	A = 0.2; B = 0.01	kAB	25.0	4.2	-5	
					40.0	1.1	-4	
					70.0	6.2	-4	
					100	2.5	-3	11.8

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E
						k°	n	
.5	$C_6H_5COCl + p\text{-}ClC_6H_4NH_2$	C_6H_6	A = 0.005; B = 0.01	k AB	5.0	6.8	-3	
					25.0	1.63	-2	
					40.0	2.98	-2	
					70.0	9.5	-2	7.6
.6	$p\text{-}CH_3C_6H_4COCl + C_6H_5NH_2$	C_6H_6	A = 0.0025; A = 0.005	k AB	5.0	1.64	-2	
					25.0	3.91	-2	
					40.0	7.46	-2	
					70.0	2.39	-1	7.8
.7	$p\text{-}NO_2C_6H_4COCl + C_6H_5NH_2$	C_6H_6	A = 0.005; B = 0.0025	k AB	5.0	2.86	-1	
					15.0	3.65	-1	
			0.01 0.005		25.0	6.07	-1	
			0.005 0.0025		"	5.81	-1	
			0.005 0.0025		40	8.71	-1	5.9
.8	$p\text{-}NO_2C_6H_4COCl + p\text{-}NO_2C_6H_4NH_2$	C_6H_6	A = 0.1; B = 0.005	k AB	25.0	9.7	-5	
					40.0	2.14	-4	
					70.0	9.30	-4	
					100	4.09	-3	10.4
.9	$p\text{-}ClC_6H_4COCl + C_6H_5NH_2$	C_6H_6	A = 0.005; B = 0.0025	k AB	25.0	1.05	-1	
					40.0	1.78	-1	
					70.0	5.46	-1	7.0

LITERATURE

E. G. Williams, C. N. Hinshelwood, *CSL* **1934**, 1079.

ADDITION

Alkyl halide + heterocyclic amine → Quaternary base

Reaction type $RX + C_5H_5N \longrightarrow C_5H_5NR^+ + X^-$

Rate measured $+ dX^-/dt$

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$CH_3I + C_5H_5N$	C_6H_6		k AB	40	3.6	-5					(7) (10)
					60.0	1.46	-4					(7)
					80.3	5.24	-4					(7) (10)
					99.5	1.21	-3	14.3	3.9	5		" "
					117.2	3.28	-3					
		$C_6H_5NO_2$		k AB	24.8	31.8	-4					(7)
					39.9	9.82	-4					
					60.0	3.49	-3					
					80.3	1.18	-2	13.6	3.2	6		
		AnW 40		k AB	25.0	1.76	-4					(6)
					39.9	6.20	-4					
					60.1	2.78	-3					
					80.4	9.08	-3	14.7	2	7		
		Et 55.7		k AB	25.0	5.3	-5					(6)
					39.9	2.11	-4					
					60.1	1.15	-3					
					80.4	5.95	-3	18.2	1.1	9		

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.2	$CH_3I + \alpha\text{-}CH_3C_5H_4N$	C_6H_6		kAB	80.5	1.21	-4					(10)
					99.8	3.62	-4					
					119.2	9.10	-4					
					139.4	1.57	-3	12.2				
		$C_6H_5NO_2$		kAB	15.0	7.05	-5					(7)
					24.9	1.46	-4					
					40.1	4.51	-4					
					60.0	1.77	-3	13.9	2.6	6		
.2.1	$CH_3I + C_2H_5OOCC_5H_4N$	$C_6H_5NO_2$		kAB	24.9	4.85	-5					
					40.0	1.63	-4					
					60.0	6.23	-4	14.6	2.7	6		
.3	$C_2H_5Br + C_5H_5N$	C_6H_6		kAB	80.5	7.25	-6					(10)
					99.8	2.49	-5					
					118.5	6.85	-5					
					139.4	2.10	-4	16.2				
.4	$C_2H_5I + C_5H_5N$	C_6H_6	0.4 - 0.77	kAB	25	7.8	-7					(8)
					80.5	4.17	-5					(10)
					99.7	1.38	-4					
					118.2	3.27	-4					
					139.3	1.07	-3	15.7				
		$(CH_3)_2CO$	0.7	kAB	25	1.0	-5					(8)
		C_2H_5OH	"		"	1.07	-6					
		C_4H_9OH	"		"	8.6	-7					
		$C_6H_5NO_2$	0.2 - 1.0		"	1.95	-5					
		$(CH_3)_2CHOH$	0.7		"	8.3	-7					
		$(CH_3)_3COH$	"		"	7.2	-7					

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$			Literature
						k°	n		A°	n		
.4	$C_2H_5I + C_5H_5N$ *(continued)*	$C_2H_5CH(CH_3)OH$	0.7		25	7.8	-7					
		CH_3OH	"		"	1.94	-6					
		C_3H_7OH	"		"	8.6	-7					
.5	$C_3H_7Br + C_5H_5N$	C_6H_6		k AB	80.6	2.82	-6					(10)
					99.7	1.01	-5					
					117.7	2.50	-5					
					139.4	7.82	-5	15.9				
.6	$(CH_3)_2CHBr + C_5H_5N$	C_6H_6		k AB	99.7	1.04	-5					(7)
					121.0	3.90	-5					
					138.0	1.09	-4					
					149.8	1.96	-4	18.0	4.2	5		
		$C_6H_5NO_2$		k AB	60.0	2.64	-5					(7)
					80.1	1.13	-4					
					100.2	4.28	-4					
					112.0	1.33	-3	16.7	2.7	6		
.7	$C_3H_7I + C_5H_5N$	C_6H_6		k AB	80.6	1.47	-5					(10)
					99.7	4.84	-5					
					117.7	1.23	-4					
					139.4	3.96	-4	16.1				
.8	$(CH_3)_2CHI + C_5H_5N$	C_6H_6		k AB	80.6	2.68	-6					(10)
					99.6	9.0	-6				(9)	(10)
					121	2.95	-5					(9)
					138.9	8.10	-5					"
					150.8	1.51	-4	17.9	2.8	5		"

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.8	$(CH_3)_2CHI + C_5H_5N$ *(continued)*	$C_6H_5NO_2$ 25 % + C_6H_6 75 %		k AB	60	2.83	-6					(9)
					80.2	1.21	-5					
					99.9	4.25	-5					
					121.0	1.37	-4	16.3	2.2	5		
		$C_6H_5NO_2$ 50 % + C_6H_6 50 %		k AB	60.0	8.45	-6					(9)
					80.2	3.44	-5					
					100.2	1.15	-4					
					121.0	4.14	-4	17.3	1.9	6		
		$C_6H_5NO_2$ 75 % + C_6H_6 25 %		k AB	60	1.2	-5					(9)
					80.2	9.4	-5					
					99.6	2.10	-4					
					121.0	5.71	-4	17.6	4.5	6		
		$C_6H_5NO_2$		k AB	40	4.0	-6					(9)
					60	2.21	-5					
					80	9.12	-5					
					99.3	3.10	-4	16.7	2.0	6		
Aryl - substituted alkyl halide												
.9	$C_6H_5CH_2Cl + C_5H_5N$	Et 90	A = 0.025; B = 0.25	k A	30.5	1.5	-6				*	(1)
.10	$C_6H_5CH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	k A	30.5	7.3	-5				*	(1)
		"	A = B = 0.025	k AB	20	1.29	-4					(2)
					30	3.07	-4	15.3	3.3	7		
		$(CH_3)_2CO$	A = B = 0.025	k AB	0	2.48	-5					(2) (4)
					20	1.22	-4					
					30	8.43	-4					
					40	4.82	-4	12.4	2.4	5		

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.10	$C_6H_5CH_2Br + C_5H_5N$ *(continued)*	$H_2O + (CH_3)_2CO$ 90 %	A = B = 0.025	kAB	20	2.34	-4					(2)
					40	1.05	-3	13.7	3.9	5		
.11	$C_6H_5CH_2I + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	8.5	-5				*	(1)
.12	$C_6H_5CH_2Br + \alpha\text{-}CH_3C_5H_4N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.8	-5					(2)
					30	3.6	-5					
					40	7.0	-5	12.4	2.3	5		
.13	$m\text{-}CH_3C_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.43	-4					(4)
					30	5.15	-4	11.7				
.14	$p\text{-}CH_3C_6H_4CH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.58	-4				*	(1)
		"	A = B = 0.025	kAB	20	2.84	-4					(2)
					30	7.0	-4	16.0	2.4	8		
		$(CH_3)_2CO$	A = B = 0.025	kAB	0	4.2	-5					(2)
					20	2.02	-4					(4) (2)
					30	3.90	-4					(2)
					40	7.15	-4	11.9	4.3	5		(2)
					"	7.98	-4	12.5				(3)
		$H_2O + (CH_3)_2CO$ 90 %	A = B = 0.025	kAB	20	4.20	-4					(2)
					40	1.87	-3	13.7	6.6	5		
.15	$p\text{-}CH_3C_6H_4CH_2Br + \alpha\text{-}CH_3C_5H_4N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	3.2	-5					(2)
					30	6.4	-5					
					40	1.24	-4	12.2	4	4		
.16	$p\text{-}C_2H_5C_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.81	-4					(3)
					30	3.51	-4					
					40	6.73	-4	12.3	2.2	5		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.17	2, 4-$(CH_3)_2C_6H_3CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	6.28	-4					(3)
					30	1.25	-3					
					40	2.40	-3	12.2	7.9	5		
.18	p-$(CH_3)_2CHC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.63	-4					(3)
					40	6.50	-4	12.6	3.9	5		
.19	m-$(CH_3)_3CC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.22	-4					(4)
					40	4.82	-4	12.5				
.20	p-$(CH_3)_3CC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.65	-4					(3) (4)
					30	3.35	-4					
					40	6.46	-4	12.5	3.3	5		
.21	p-$CH_3OC_6H_4CH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25		30.5	∞						(1)
.22	m-$NO_2C_6H_4CH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	2.26	-5				*	(1)
		$(CH_3)_2CO$	A = B = 0.025	kAB	20	9.9	-5					(4)
					40	3.5	-4	11.5				
.23	p-$NO_2C_6H_4CH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	2.6	-5				*	(1)
		"	A = B = 0.025	kAB	20	4.2	-5					(2)
					30	1.02	-4	15.8	2.5	8		
		$(CH_3)_2CO$	A = B = 0.025	kAB	0	2.3	-5					(2) (4)
					20	1.12	-4					
					30	2.26	-4					
					40	4.33	-4	12.3	1.7	5		
		$H_2O + (CH_3)_2CO$ 90 %	A = B = 0.025	kAB	20	1.58	-4					(2)
					40	7.16	-4	13.8	3.3	6		

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No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.24	$p\text{-}NO_2C_6H_4CH_2Br + \alpha\text{-}CH_3C_5H_4N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.2	-5					(2)
					30	2.5	-5					
					40	4.7	-5	12.1	1.3	4		
.25	$2,4\text{-}(NO_2)_2C_6H_3CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	2.28	-4					(3)
					30	4.70	-4					
					40	8.96	-4	12.4	4.0	5		
.26	$m\text{-}FC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	9.5	-5					(4)
					40	3.62	-4	12.5				
.27	$p\text{-}FC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.22	-4					(4)
					40	5.78	-4	12.5				
.28	$m\text{-}ClC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.08	-4					(4)
					40	4.07	-4	12.1				
.29	$p\text{-}ClC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.27	-4					(4)
					40	5.10	-4	12.7				
		Et 90	A = 0.025; B = 0.25	k A	30.5	5.3	-5				*	(1)
.30	$m\text{-}BrC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.07	-4					(4)
					40	3.77	-4	11.5				
.31	$p\text{-}BrC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.30	-4					(4)
					40	5.19	-4	12.6				
		Et 90	A = 0.025; B = 0.25	k A	30.5	5.0	-5				*	(1)
.32	$m\text{-}IC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	k AB	20	1.14	-4					(4)
					40	4.13	-4	11.8				

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.33	p-$IC_6H_4CH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	1.48	-4					(4)
					40	5.43	-4	11.9				
		Et 90	A = 0.025; B = 0.25	kA	30.5	5.5	-5				*	(1)
Benzoyl - substituted alkyl halide												
.34	$C_6H_5COCH_2Cl + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.83	-6				*	(1)
.35	$C_6H_5COCH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.08	-4				*	(1)
		$(CH_3)_2CO$	A = B = 0.025	kAB	20	7.9	-4					(5)
					40	2.83	-3	11.7				
.36	$C_6H_5COCH_2I + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	8.3	-5				*	(1)
.37	o-$CH_3C_6H_4COCH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	5.5	-4					(5)
.38	p-$CH_3C_6H_4COCH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	7.4	-4					(5)
					40	2.62	-3	11.6				
		EtOH	A = 0.025; B = 0.25	kA	30.5	9.2	-5				*	(1)
.39	2, 4-$(CH_3)_2C_6H_3COCH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	5.0	-4					(5)
					40	1.82	-3	11.8				
.40	p-$(CH_3)_3CC_6H_4COCH_2Br + C_5H_5N$	$(CH_3)_2CO$	A = B = 0.025	kAB	20	5.7	-4					(5)
					40	2.0	-3	11.5				
.41	m-$NO_2C_6H_4COCH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.88	-4				*	(1)
.42	p-$NO_2C_6H_4COCH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.73	-4				*	(1)

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No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
						k°	n		A°	n		
.43	p-$ClC_6H_4COCH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.20	-4				*	(1)
.44	p-$BrC_6H_4COCH_2Br + C_5H_5N$	Et 90	A = 0.025; B = 0.25	kA	30.5	1.20	-4				*	(1)

SOLVENTS

An W 40 = H_2O 40 g + $(CH_3)_2CO$ 100 ml

Et 55.7 = $H_2O + C_2H_5OH$ 55.7 vol %

Et 90 = $H_2O + C_2H_5OH$ 90 vol %

COMMENTS

Data of (1) : the pseudomonomolecular k is not independent of A/B.

LITERATURE

(1) J. W. Baker, *CSL* **1933**, 1128; **1932**, 2631. (2) J.W. Baker, W. S. Nathan, *CSL* **1935**, 519. (3) J.W.Baker, W.S. Nathan, *CSL* **1935**, 1840. (4) J.W.Baker, *CSL* **1936**, 1449. (5) J. W. Baker, *CSL* **1938**, 445. (6) R.A. Fairclough, C. N. Hinshelwood, *CSL* **1937**, 538. (7) K. J. Laidler, C. N. Hinshelwood, *CSL* **1938**, 858. (7a) K. J. Laidler, *CSL* **1938**, 1787. (8) J.F. Norris, S. W. Prentiss, *ACS* 1928, **50**, 3042. (9) H. C. Raine, C. N. Hinshelwood, *CSL* **1939**, 1378. (10) C.A. Winkler, C. N. Hinshelwood, *CSL* **1935**, 1147.

ADDITION

SO_3 to aromatic hydrocarbons

Sulfonic acid formation

Liquid phase

Reaction type $ArH + SO_3 \longrightarrow ArSO_3H$

(A) (B) (L)

Rate measured $-dB/dt$

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Literature
						k^o	n		
.1	$C_6H_6 + SO_3$	$C_6H_5NO_2$	A = 0.05	$k\,AB^2$	3.1	1.72	+1		(1)
					40.1	4.88	+1	4.8	
.2	$C_6H_5NO_2 + SO_3$	$C_6H_5NO_2$	A = 10.85 B = 0.3 - 1.0	$k\,AB^2$	25	2.77	-6		(1)(2)
					40.0	7.85	-6		
					60.0	2.49	-5		
					80.0	4.98	-5		
					100.4	1.52	-4	11.4	
.3	$p - CH_3C_6H_4NO_2 + SO_3$	$C_6H_5NO_2$	A = 1.5 B = 0.1 - 0.6	$k\,AB^2$	0.0	6.14	-5		(1)(3)
					14.9	2.12	-4		
					24.9	4.16	-4		
					39.9	9.53	-4		
					60.0	2.36	-3	11.0	

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Literature
						k°	n		
.4	p - $CH_3OC_6H_4NO_2 + SO_3$	$C_6H_5NO_2$	A = 0.10	$k\,AB^2$	2.0	2.41	0		(1)
					40.1	6.29	0	4.3	
.5	$C_6H_5Cl + SO_3$	$C_6H_5NO_2$	A = 0.4	$k\,AB^2$	0.0	4.04	-1		(1)(3)
					14.9	8.63	-1		
					24.9	1.47	0		
					39.9	2.40	0	7.7	
.6	m - $C_6H_4Cl_2 + SO_3$	$C_6H_5NO_2$	A = 0.5	$k\,AB^2$	1.9	5.50	-3		(1)
					40.1	4.36	-2	9.2	
.7	$C_6H_5Br + SO_3$	$C_6H_5NO_2$	A = 0.25	$k\,AB^2$	3.1	3.88	-1		(1)
					40.1	2.12	0	7.8	
.8	α - $C_{10}H_7NO_2 + SO_3$	$C_6H_5NO_2$	A = 0.25	$k\,AB^2$	3.3	5.88	-1		(1)
					25.1	1.30	0	7.9	
					40.1	3.27	0		

COMMENTS

The rate laws are primarily given in the form $k'B^2$, and some data only in the from $k\,AB^2$. In the table, all data have been made uniform by dividing the original k' by [A] (occasionally inferred from the conversion of k' to k), and tabulation of values of k.

LITERATURE

(1) E. Dresel, C. N. Hinshelwood, *CSL* **1944**, 649.
(2) D. R. Vicary, C. N. Hinshelwood, *CSL* **1939**, 1374.
(3) K. D. Wadsworth, C. N. Hinshelwood. *CSL* **1944**, 469.

ASSOCIATION

Unsaturated compounds → Alicyclic ring

Gas phase

Rate measured $-\Delta p$

Mass action is in M/l.

Rates are in M/l per sec.

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments
					k°	n		A°	n	
.1	$CH_2{:}CHCH{:}CH_2 + CH_2{:}CHCHO \rightarrow C_7H_{10}O$ tetrahydrobenzaldehyde	A = 43 - 365 mm; B = 99 - 473 mm	k AB	155	1.37	-4				*
				208	1.58	-3				
				245	6.9	-3				
				291	3.4	-2				
				296	4.0	-2				
				328	9.1	-2				
				331	9.5	-2	19.7	1.46	6	
.2	$CH_2{:}CHCH{:}CH_2 + CH_3CH{:}CHCHO \rightarrow C_8H_{12}O$ methyl-6-Δ^3-tetrahydrobenzaldehyde	A = 92 - 224 mm; B = 393 - 440 mm	k AB	242	3.8	-4				*
				250	5.5	-4				
				277	1.55	-3				
				296	3.1	-3	22.0	9.0	5	
.3	*cyclo*-$C_5H_6 + CH_2{:}CHO \rightarrow C_8H_{10}O$ endomethylene-2, 5-tetrahydrobenzaldehyde	A = 45 - 363 mm; B = 42 - 328 mm; L = 15 - 64 mm	k AB	78	9.9	-4				*
				93	1.4	-3				
				108	3.1	-3				
				120	5.4	-3				
				144	1.55	-2				
				167	3.9	-2				
				184	7.25	-2				
				205	1.54	-1				
				210	2.03	-1	15.2	1.5	6	

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments
					k°	n		A°	n	
.4	$CH_2:CHC(CH_3):CH_2 + CH_2CHO \longrightarrow C_8H_{12}O$ methyl-3-Δ^3-tetrahydrobenzaldehyde	A = 39 - 340 mm; B = 50 - 432 mm	k AB	219	5.7	-3				*
				247	1.55	-2				
				292	6.6	-2				
				299	8.2	-2				
				332	2.0	-1	18.7	1.02	6	
.5	$2\ CH_2:CHCH:CH_2 \longrightarrow C_8H_{12}$ (dimer)		$k\ A^2$	282	2.56	-3				*
				291	3.37	-3				
.6	$2\ CH_2:CHC(CH_3):CH_2 \longrightarrow C_{10}H_{16}$ (dimer)		$k\ A^2$	245	6.5	-4				*

COMMENTS

(.1) (.2) (.3) (.4) Association through Diels-Alder reaction. A small correction, averaging 3 %, was applied to allow for polymerization of A. Packing seems to have no effect. Reaction begins to reverse itself at higher temperatures. Data converted from $(M/ml)^{-1}\ sec^{-1}$ to $(M/l)^{-1}\ sec^{-1}$ units.

(.3) Initial k. Reverse reaction, see 581.441. (.5) k at about 6 % reaction. (.6) The exptl. values are about 3/2 of those calculated from the collision theory.

LITERATURE

G. B. Kistiakowsky, J. R. Lacher, *ACS* 1936, 58, 123.

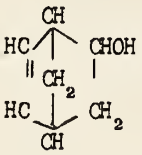
ASSOCIATION

Unsaturated compound + Alicyclic ring

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*
					k^o	n	
.1	$CH_2:CHCHO + \underline{CH:CHCH:CHCH_2} \rightarrow$ 	C_6H_6	k AB	40	3.3	-4	13.7

COMMENTS

Colorimetric determination.

LITERATURE

A. Wassermann, *CSL* 1936, 1028.

OXIDATION-REDUCTION

Dismutation

VI th group elements

Liquid phase

Amounts are in M/l.

Rates in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$2\ S_2O_4^{--} + H_2O \rightarrow 2\ HSO_3^- + S_2O_3^{--}$	H_2O	A ~ 0.3; L = 1.47			$k\,A^2$	0	4.0	−6				*	(2)
							10	6.5	−6					
							20	1.05	−5					
							30	1.8	−5					
			A ~ 0.3; L = 0.98			"	18	2.0	−6					
			1.47				"	8.8	−6					
			2.64				"	1.8	−5					
			3.24				"	3.1	−5					
.2	$S_2O_6^{--} + H_2O \rightarrow SO_3^{--} + SO_4^{--}$	H_2O	0.05 − 1.0			$k\,A$	140	7	−8					
		"	"	H^+	1.3	$k\,A[H^+]$	50	1.2	−6				*	(4)
					0.4		80	4.6	−5					
					0.8		85	1.1	−4	29.8	1.6	14		
		"	"	OH^-	0.20	$k\,A[OH^-]$	110	1.9	−5					"
					0.16		140	1.0	−4					
					"		160	4.0	−4					
					"		180	1.45	−3	25	1.6	8		
.3	$UO_2^+ \rightarrow U^{VI} + U^{IV}$	H_2O	$A = 10^{-5} - 10^{-3}$	$HClO_4$		$k\,A^2(H^+)$	25	1.3	2				*	(3)
			$\mu = 0.4;\ (H^+) = 0.02 - 0.3$											

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.3	$UO_2^+ \rightarrow U^{VI} + U^{IV}$	H_2O		$HClO_4 + NaClO_4$	(0.1)									(3)
	(continued)		μ = 0.119; (H^+) = 0.02 - 0.16			$k A^2 (H^+)$	25	7.8	1					
			0.156				"	8.0	1					
			0.192				"	9.7	1					
			0.4				"	1.3	2					

COMMENTS

(.1) Recalculated from min., g/100 ml. The rate is approximately proportional to $[HSO_3^-]^2$. This is accounted for by (1) through evidence of two isomeric dithionous acids, reacting to form the observed products HOSOSOOH + $(HO)_2SSO_2 \rightleftarrows H_2S_2O_3 + H_2S_2O_5$; both isomers are stabilized by HSO_3^-, according to HOSOSOOH + $H_2O \rightleftarrows S(OH)_2 + H_2SO_3$; $S(OH)_2 + SO_2 \rightleftarrows (HO)_2SSO_2$. (.2) Evidence of partial reaction $S_2O_6^{--} \rightarrow 2\ SO_3^-$. The rate is not affected by SO_3^{--}, SO_4^{--}, CrO_4^{--}, or BrO_3^-, in neutral, acid, or alkaline solution. (.3) Polarography. (H^+) is the activity of H^+ (quinhydrone electrode). Proposed mechanism $UO_2^+ + H^+ \rightarrow UOOH^{++}$; $UO^+ + UOOH^{++} \rightarrow UO_2^{++} + UOOH^+$ (k'); $UOOH^+ \rightarrow U^{IV}$ (stable); $k = k'/K$, where K = dissociation constant of $UOOH^+$. From the fact that the U^V/U^{VI} potential is independent of (H^+) even in 0.5 M $HClO_4$, k' must be > 1300.

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Homogeneous Reactions
712.770.

OXIDATION - REDUCTION

Liquid phase

Dismutation

VII th group element

Amounts are in M/l.
Rates are in M/l.per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$3\ Cl_2 + 3\ H_2O \longrightarrow 6\ H^+ + 5\ Cl^- + ClO_3^-$	H_2O				$+\ dN/dt = kA^3/L^4M^3$	25	2	-29				*	(40)
.2	$Cl_2 + OH^- \longrightarrow HOCl + Cl_3^-$	H_2O				kAB	1.2 17.0	~ 8 "	+12 "	 0	ΔS_a = 12.4		*	(28)
.3	$ClO^- + 2\ HClO \longrightarrow 2\ H^+ + 2\ Cl^- + ClO_3^-$	H_2O	A = 0.005; B = 0.005			kA	25	6.5	-7				*(a)	(45)
			0.01 0.005				"	7.1	-7					
			0.01 0.01				"	2.8	-6					
			0.01 0.02				"	1.0	-5					
		"	0.01 0.01	$NaNO_3$	0.2	"	"	3.0	-6					"
			" "	NaCl	0.2		"	4.6	-6					
		"	A = 1; B = 0.02 - 0.08			kAB^2	15 25	1.9 2.7	-2 -2				*(b)	(10)
		"	buffered solution			$-d(A + B)/dt = k'K[H^+]/([H^+] + K) = k(A + B)^3$		k (max)						
			B = 2A; $10^7[H^+]$ = 0.8 - 2.0				25	3.8	-3				*(c)	(40,41)
		"	$[H^+] \ll 3.6 \times 10^{-8}$ $B \ll A$			$-dB/dt = k[H^+]^2A^3/K$	25	2.6	-2				*(d)	"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.3	$ClO^- + 2\,HClO$ $\longrightarrow 2\,H^+ + 2\,Cl^- + ClO_3^-$ *(continued)*	H_2O	$[H^+] \gg 3.6 \times 10^{-8}$ $B \gg A$			$-dA/dt = k\,K\,A^3/[H^+]$	25	2.7	-2				*(e)	(40,41)
		"				$-dB/dt = B^3[H^+][Cl^-]/(k_1[H^+][Cl^-] + k_2B)$	25						*(f)	"
							k_1	4.6	-4					
							k_2	1.75	-8					
		"	$[H^+]^2[Cl^-] \gg k_2B$			$-dB/dt = kB^3/[H^+]$	25	9.7	-10				*(g)	"
		"	$k_2B \gg k_1[H^+]^2[Cl^-]$			$-dB/dt = kB^2[H^+]\,[Cl^-]$	25	5.7	-11				*(h)	"
.4	$3\,ClO^- \longrightarrow ClO_3^- + 2\,Cl^-$	H_2O		OH^-	0.1	kA^2	25	2.5	-8				*	(11,49,18,26)
					0.5		"	2.7	-8					
					2.0		"	(3.3)	-7					
					0.1		50	5.3	-7				*	"
					0.5		"	5.8	-7					
					2.0		"	(9.2)	-7					
					0.1		90	(5.5)	-5	25	1	12	*	"
		"		ClO_2^-		$k_1A^2 + k_2A[ClO_2^-]$	25						*	"
							k_1	2.8	-8					
							k_2	9.7	-7					
							50							
							k_1	5.3	-7					
							k_2	1.4	-6					
.4.1	$2\,ClO^- \longrightarrow 2\,Cl^- + O_2$	H_2O	$A = 2.3$	OH^-	0.1	$+d(1/2\,O_2)/dt = kA^2$	30	6.7	-8				*	(16)
			$A = 1$	$NaCl = 2;\ \mu \sim 3$			45	3.8	-7					(48)
.5	$6\,ClO + 3\,H_2O$ $\longrightarrow 5\,ClO_3^- + Cl^- + 6\,H^+$	H_2O		HCl	0.006 - 0.0115	$kA^2[Cl^-] + k'A^2[Cl^-][H^+]$							*	(4,5)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.5.1	$2\ ClO_2 + Cl^- + H_2O$ $\longrightarrow HClO_2 + ClO_2^- + HClO$	H_2O	$[H^+] = 0.006 - 0.0115$			$kA^2[Cl^-]$	60	9.3	-4				*	(4,5)
.6	$2\ ClO_2 + 2\ OH^-$ $\longrightarrow ClO_2^- + ClO_3^- + H_2O$	H_2O				kA^2B	0	5	0				*	(4)
							19	1.6	+1					
.7	$BrO^- + 2\ HBrO$ $\longrightarrow 2\ H^+ + 2\ Br^- + BrO_3^-$ $(3\ HBrO + OH^- \longrightarrow$ $2\ H^+ + 2\ Br^- + BrO_3^- + H_2O)$ $(3\ Br_3^- + 6\ OH^- \longrightarrow$ $8\ Br^- + BrO_3^- + 3\ H_2O)$ (In not strongly alkaline solution)	H_2O	$-d([Br_2] + [HBrO])/dt =$			$k_a[Br_3^-]^3[OH^-]^4/[Br^-]^6$	25	4.0	21				$*_a$	*
						$k_b[HBrO]^3[OH^-]$	25	1.3	8				$*_b$	*
						$k_c[HBrO]^2[BrO^-]$	25	6.7	4				$*_c$	*
						$k_d[OH^-][Br_3^-]^2/[Br^-]^3$	25	1.1	3				$*_d$	*
.7.1	$(BrO^- + 2\ HBrO \longrightarrow$ $2\ H^+ + 2\ Br^- + BrO_3^-)$	H_2O				kAB^2	0	(1.2)	(-1)				*	(19,26)
							25	(1.7)	(0)					
.7.2	$3\ BrO^- \longrightarrow BrO_3^- + 2\ Br^-$ (In strongly alkaline solution)	H_2O		OH^-	1.89	kA^2	80	9.3	-4	25	1.7	12	*	(19,26)
.7.3	$2\ BrO^- \longrightarrow BrO_2^- + Br^-$	H_2O		OH	1.89	kA^2	80	9.3	-4	25	1.7	12	*	"

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.8	$3\ I_2 + 6\ OH^-$	H_2O	$[OH^-] > [I^-]$			$k[OH^-][I_3^-]^2/[I^-]^3$	25	3.3	-2				$*_a$	(31) (32)
	$\longrightarrow IO_3^- + 5\ I^- + 3\ H_2O$		$[OH^-] < [I^-]$			$k[OH^-]^4[I_2]^3/[I^-]^6$	25	1.7	17				$*_b$	(44)
	$(3\ I_3^- + 6\ OH^-$		$[OH^-] \ll [I^-]$			$k[OH^-]^4[I_3^-]^3/[I^-]^6$	25	3.3	9				$*_c$	(31) (32)
	$\longrightarrow IO_3^- + 8\ I^- + 3\ H_2O)$													
.9	$I_2 + H_2O \longrightarrow HIO + I^- + H^+$	H_2O				kA	25	(~ 4)	(-3)				*	(1)
.10	$3\ HIO + 3\ OH^-$	H_2O	$[OH^-] > [I_2]$			$kA^2[I^-]/[OH^-]$	25	4.8	-1				*	*
	$\longrightarrow IO_3^- + 2\ I^- + 3\ H_2O$						35	1.0	0					
.11	$3\ IO^- \longrightarrow IO_3^- + 2\ I^-$	H_2O	strongly alkaline, low $[I^-]$			$kA^2/[OH^-]$	25	3.3	-2					(32) (44a)
							35	8.4	-2					(40)
			" " , high $[I^-]$			$kA^2[I^-]/[OH^-]$	25	1.45	0					"
							35	3.0	0					

COMMENTS

(.1) Calculation. The reaction is characteristic of solutions of high HCl concentration, where ClO^- is negligible and HClO very small. $k = k'KK_h^3/3$; $k' = 0.027$ = third-order rate constant for $2\ HClO + ClO^- \longrightarrow ClO_3^- + 2\ H^+ + 2\ Cl^-$; $K = [H^+][ClO^-]/[HClO] = 3.6 \times 10^{-8}$; $K_h = 1.01 \times 10^{-14}/3.6 \times 10^{-8}$. (.2) Calculated from data of Shilov and Solodushenkov, *C.R.Acad. Sci. USSR* 1936, 3, No. 1, p. 17. (.3) *(a)* k over the first 50 % of the reaction; increases by about 25 % over the second half of the reaction. *(b)* Valid at low $[H^+]$ and very low $[Cl^-]$: HClO regenerated as fast as expanded. k increases slightly with increasing μ. (49) writes $-dA/dt = k'f^2AB^2$, with $\log f = 0.0289\ \mu$. *(c)* Low $[Cl^-]$. K = ionization constant of HClO = 3.6×10^{-8}; k is a function of $[H^+]$ and goes

COMMENTS *(continued)*

through a maximum at the stated concentrations. *(d)* Low $[Cl^-]$. Low $[H^+]$. All hypochlorite practically A. $K = 3.6 \times 10^{-8}$; $k/K = 2 \times 10^{13}$. *(e)* Low $[Cl^-]$. High $[H^+]$. All hypochlorite practically B. $K = 3.6 \times 10^{-8}$; $kK = 9.7 \times 10^{-10}$. *(f)* Sufficiently high $[Cl^-]$; general rate law. *(g)* Special case of *(f)*; this case goes over into *(b)* by substituting $1/[H^+] = A/KB$, where $K = 3.6 \times 10^{-8}$. *(h)* Special case of *(f)*; cannot be realized experimentally, since even in solutions poor in $[H^+]$, $k_1[H^+]^2[Cl^-]$ is not negligible compared with k_2B; the value of k is extrapolated. Mechanisms: (11, 12) (49) $2\ H^+ + 2\ A \rightleftarrows 2\ B \rightleftarrows Cl_2O + H_2O$ (very fast); $(Cl_2 + H_2O) + A \rightarrow 2\ H^+ + 2\ Cl^- + ClO_3^-$ (rate determining). Mechanism of (33):

$2\ Cl_2 + H_2O \rightleftarrows HCl_3O + H^+ + Cl$; $HCl_2O + H_2O \rightleftarrows 2\ H^+ + 2\ Cl^- + HClO_2$; $HClO + HClO_2 \rightleftarrows H_2Cl_2O_3$; $Cl_2 + HClO_2 \rightleftarrows H^+ + Cl_3O_2^-$; $Cl_3O_2^- \rightleftarrows Cl_2O_2 + Cl^-$ (rate determining); $Cl_2O_2 + H_2O \rightleftarrows H_2Cl_2O_3$; $H_2Cl_2O_3 \rightleftarrows 2\ H^+ + Cl^- + ClO_3^-$. Pertinent literature: (7) (9) (10) (11) (13) (15) (27) (33) (38) (39) (40) (43) (45) (49) (50)

(.4) The side reaction (.4.1) $2\ ClO^- \longrightarrow Cl^- + O_2$ is generally negligible except at $OH^- > 0.5$ to above 50°C; data of k in parentheses refer to experiments where evolution of O_2 was not negligible. In $OH^- = 2.0$, k approached first order *(?)*. Mechanism of the reaction in alkaline solution:

$2\ ClO^- \rightarrow ClO_2^- + Cl^-$ (rate determining); $ClO^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$ (faster). (18) writes for the rate determining step $HClO + ClO^- \rightarrow ClO_2^- + H^+ + Cl^-$, so that $-d[ClO^-]/dt = (k'/[OH^-])[ClO^-]^2$. (.4.1) For the total reaction $-dA/dt = k_F K A^3/[OH^-]^2 + kA^2$, where k_F = Foerster's (10) rate constant (see reaction .3, *b*). The tabulated second-order k for evolution of O_2 is constant up to 50 %. In $OH^- = 0.94$, the entire reaction is second-order. In terms of μ, in solutions $A = 1.0$, linearity between log k and $\sqrt{\mu}$ holds up to $\mu = 4$; with further increasing μ, the observed k falls short of the predicted. (.5) (.5.1) In sealed tube. ClO_3^- and Cl^- produced in the ratio 5:1. Reaction (4.1) is the primary step of (.4); ten-degree temperature coefficient ~ 2.2 (0° - 60°C); k' is not evaluated. With increasing $[H^+]$, the rate increases somewhat, but not in proportion to $[H^+]$. If ClO_2 is continuously blown out with air, the reaction

$3\ ClO_2^- + 2\ HClO \rightarrow ClO_3^- + 2\ Cl^- + 2\ ClO_2 + H_2O$ was found to occur (11). (.6) Initial k, increasing with time. With excess OH^-, the rate becomes second-order in ClO_2. Addition of Cl^- or Cl_2, or of $Cl^- + ClO_3^-$, has little effect on k. Assumed rate determining step $2\ ClO_2 + OH^- \rightarrow ClO_3^- + HClO_2$, followed by $HClO_2 + OH^- \rightarrow ClO_2^- + H_2O$, fast. (.7) Reaction in not very strongly alkaline solution. Rate laws *a*, *b*, *c*, are interconvertible with the aid of the

COMMENTS *(continued)*

equilibrium constants, $[Br_3^-][OH^-]/[HBrO][Br^-] = 3.2 \times 10^{-5}$; $[H^+][BrO^-]/[HBrO] = 2 \times 10^{-11}$; $K = [Br_2][Br^-]/[Br_3^-] = 0.067$; $K_h = [HBrO][Br^-][H^+]/[Br_2] = 5.8 \times 10^{-9}$; $[HBrO][Br^-]^2/[Br_3^-][OH^-] = (3.1 \times 10^4)^3$; $[HBrO][OH^-]/[BrO^-] = 0.5 \times 10^{-3}$. Rate law *d* was considered (47) to represent a "rapid" reaction $2\ HBrO \longrightarrow BrO_3^- + 2\ Br_2 + H^+ + 2\ H_2O$, other than the "slow" reaction (.7); however, according to (26), solutions of HBrO are more stable than implied by this reaction, and the data of (47) can be equally well interpreted by rate law *d*, analogous to F. Foerster's law of ClO_3^- formation (see .3, *b*). Literature (14) (19) (31,32) (46,47) (29) (24) (25) (26) (41) (45) (30) (7). (.7.1) Older data of (19), recalculated by (26), and showing, for a rate law entirely identical with, (.7, *c*), a very considerable divergence of the numerical values of *k*; illustrating the wide spread of the experimental data; probably superseded by the value of (26) under (.7, *c*). (.7.2) (.7.3) In strongly alkaline solution; calculated by (26) from data of (19). Reaction (.7.3) taken to be the rate determining step of (.7.2). (.8) Slightly alkaline solutions, iodine in excess (colored solutions). Direct reaction, not through IO^-. Rate law *(b)* can be derived from $d[IO_3^-]/dt = [HIO_3]^3/[H^+]$ by successively substituting $HI_3O = K[I_2]/[H^+][I^-]$ and $[H^+] = 10^{-14}/[OH^-]$. Rate law *(c)* is then obtained by substituting $[I_2] = K'[I_3^-]/[I^-]$. Mechanisms proposed (31) (32) (6) (33) (34): $2\ I_3^- + OH^- \rightleftarrows HI_3O + 3\ I^-$, fast (or $I_2 + HIO \rightleftarrows HI_3O$, fast); $HI_3O + H_2O \longrightarrow 2\ H^+ + 2\ I^- + HIO_2$, rate determining; *or*, $3\ I_3^- + 4\ OH^- \rightleftarrows 6\ I^- + I_3O_2^- + 2\ H_2O$, fast; $I_3O_2^- \longrightarrow I_2O_2 + I^-$, rate determining; HI_3O and $I_3O_2^-$ are supposed to be in equilibrium throughout the process. (.9) From rate calculations involving H_2O_2, I^-, and I_2; according to (22,23,24) *k* is much greater than the value estimated by (1).

(.10) Colorless solution. Mechanism (31,32) (6) (33,34) $I_2 + OH^- \rightleftarrows HIO + I^-$ (fast, far to the right); $2\ HIO + I^- \rightleftarrows HI_3O + OH^-$, fast; $HI_3O + H_2O \longrightarrow 2\ H^+ + 2\ I^- + HIO_2$, rate determining. Literature (10a) (12a) (5) (32) (26a) (6) (33).

(.11) Colorless solutions. Low $[I^-]$ obtained by solid AgI and Ag_2O. The two rate laws cannot be superposed (44a).

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OXIDATION - REDUCTION

of compounds of the same element

V th group element

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$	
							k°	n
.1	$NH_4^+ + NO_2^- \longrightarrow N_2 + H_2O$	H_2O	A = 0.05 - 1.0	H^+ = 0.2; μ = 0.5	$k\,K\,AB^2/[H^+]$	25	1.7	-2
	$(NH_4NO_2 \longrightarrow N_2 + H_2O)$		B = 0.005 - 0.187	0.6 1.6		"	2.5	-2
	$(NH_4^+ + HNO_2 + OH^- \longrightarrow N_2 + 2\,H_2O)$			0.6 2.5		"	3.2	-2

COMMENTS

Maintained equilibria, $HNO_2 \rightleftarrows HNO_3$, NO; $HNO_2 \rightleftarrows H^+ + NO_2^-$ ($K = 5.6 \times 10^{-4}$).

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OXIDATION-REDUCTION
of compounds of the same element
VI th group element

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
								k^o	n	
.1	$2\ S_2O_3^{--} + S_2O_8^{--} \rightarrow 2\ SO_4^{--} + S_4O_6^{--}$	H_2O	A = 0.02; B = 0.01		μ = 0.09	kB	25	3.2	-6	(¹)
					0.11		"	4.7	-6	
					0.15		"	7.5	-6	
		"	"	$10^5\ [Cu^{++}] = 0.0125–2.5$	μ = 0.09	kB $[Cu^{++}]$	25	7.6	0	(²)
					0.11		"	8.8	0	
					0.15		"	1.2	+1	
		"	"	KI	μ = 0.11	kB $[I^-]$	25	2.8	-3	(²)

COMMENTS

For the uncatalyzed reaction, $\Delta \log k / \Delta\sqrt{\mu} \sim 4$. Authors conclude that the salt effect indicates the rate determining step to be A + B ; the rate, however, is nearly independent of B. The kinetics of the Cu^{++} – catalyzed reaction is consistent with the hypothesis that the rate determining step is between two negative ions, one of which is a complex cupro-thiosulfate ion. For the KI-catalyzed reaction, $2\ I^- + S_2O_8^{--} \rightarrow I_2 + 2\ SO_4^{--}$.

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OXIDATION - REDUCTION
of compounds of the same elements

Liquid phase

VIIth group

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$Cl^- + 6\ HClO \rightarrow 3\ Cl_2 + ClO_3^- + 3\ H_2O$ (Williamson's reaction)	H_2O	See Comments			$k\ A^4B/L$	25	1.1	-3		*	(36)
.1.1	$Cl^- + HClO \rightarrow Cl_2 + OH^-$	H_2O				$k\ AB$	1.2 17.6	6.7 1.4	1 2		*	(29a) (36a) (25)
.2	$2\ Cl^- + 2\ ClO_3^- + 4\ H^+ \rightarrow 2\ ClO_2 + Cl_2 + 2\ H_2O$	H_2O	A = 0.02 - 0.04 B = 1.5 - 2.0 H^+ = 1.5 - 2.0			$k\ A^2B^2[H^+]^4$	50	1.7	-5		*	(24) (37)
		H_2O		HI		$k\ AB\ [H^+]^2$	30 38.6	3.0 6.0	-6 -6		*	(9) (12)
.3	$5\ Cl^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Cl_2 + 3\ H_2O$	H_2O	HCl = 0.5 - 1.0			$k\ AB^2[H^+]^2$	70	2.5	-5		*	(26)
.3.1	$5\ Cl^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Cl_2 + 3\ H_2O$	H_2O		H_3AsO_3		$k\ AB[H^+]^2$	25 55	7.5 4.2	-7 -5		*	(19) (37)
.4	$5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$	H_2O	$10^3[H^+]$ = 9.2;	$\sqrt{\mu}$ = 0.463		$k\ AB[H^+]^2$	25	2.7	0		*	(38)
			125	0.395			"	3.1	0			
			29	0.212			"	6.0	0			
				→ 0			"	9.0	0			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	Comments	Literature
								k°	n			
.4	$5\,Br^- + BrO_3^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$ *(continued)*	H_2O	216	0.506		$k\,AB[H^+]^2$	25	6.0	0		*	(14)
			67	0.303			"	3.7	0			
				→ 0			"	9.0	0	15.8		
										(25 – 65°; $\mu = 0.1$)		
		"		$\sqrt{\mu} = 0.9$		"	25	2.4	0		*	(29)
				0.5			"	2.9	0			
				0.2			"	4.6	0			
				→ 0			"	9.5	0	13.6		
										(0 – 32°C; $\mu = 0.1$)		
.5	$I^- + HIO + H^+ \rightarrow I_2 + H_2O$	H_2O				$k\,AB[H^+] - k'L$	25				*	(1)
							k	1.3	10			
							k'	~ 4	-3			
.6	$5\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$	H_2O	$A > 10^{-4}$			$k\,A^2B[H^+]^2 f$	25	1.3	9		*	(8)
							35	1.7	9			
							25	5.2	8		*	(3)
		"	"	I_2	sat	$k\,AB[I_3^-][H^+]^2 f^4$						(8)
							25	9.2	8		*	
							35	1.2	9			
		"	"	I_2	sat	$AB[H^+]^2(k'A + k''[I_3^-])E$					*	(6)
							25					
							k'	1.2	9			
							k''	1.0	9			
							50					
							k'	2.0	9			
							k''	1.6	9			
		"	$A < 10^{-8}$			$k\,AB[H^+]^2$	25	4	2		**	"

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.6	$5\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$	H_2O	$10^{-8} < A < 10^{-4}$			$AB[H^+](kf^2 + k'AF' + k''[I_3^-]F')$					***	(^{13})
	(continued)						25					
							k	4	2			
							k'	1.3	8			
							k''	9.1	8			
		D_2O	$A < 10^{-8}$			$k\,A^2B[H^+]^2f$	25	5.1	9		*	
.7	$7\,I^- + IO_4^- + 8\,H^+ \rightarrow 4\,I_2 + 4\,H_2O$	H_2O	See reactions (.7.1)(.7.2)									
.7.1	$2\,I^- + IO_4^- + 2\,H^+ \rightarrow I_2 + IO_3^- + H_2O$	H_2O		H_2SO_4		$AB(k'F + k''F'[H^+]^2)$					*	(^{4})(^{7})
							25					
							k'	2.2	1			
							k''	2.3	5			
.7.2	$2\,I^- + IO_4^- + 2\,H^+ \rightarrow I_2 + IO_3^- + H_2O$		$CH_3COOH + CH_3COO^-$ buffer			$k\,AB$					*	(^{4})
			$CH_3COO^- = 0$				25	6.3	0			
			$CH_3COO^- = 0.1$				"	9.1	0			
			$CH_3COOH = 0.1,\ CH_3COO^- = 0.4$				"	1.2	+			

COMMENTS

(.1) Williamson's reaction (40, 17, 30, 34) occurs when the alkaline reserve of an unbuffered NaClO solution has been depleted so that HClO, HCl, and Cl_2, are greatly in excess of over ClO^-. *k* calculated from the reactions (1) $3\ HClO \rightarrow 3\ H^+ + 2\ Cl^- + ClO_3^-$, (2) $3\ Cl_2 + 3\ H_2O \rightarrow 6\ H^+ + 5\ Cl^- + ClO_3^-$, (3) $H^+ + Cl^- + HClO \rightleftarrows H_2O + Cl_2$, occurring with NaCl and enough H_2SO_4 added to NaClO to convert ClO^- entirely to HClO; the amount of Cl^- was such that after conversion of ClO^- to ClO_3^-, $HClO/Cl^- = 6:1$. Williamson's reaction is composed of (1) and (3); $k = k_F K/K_H$, where k_F = Foerster's rate constant for $ClO^- + 2\ HClO \rightarrow ClO_3^- + 2\ Cl^- + 2\ H^+ = 2.7 \times 10^{-2}$ (see 712.770), $K\ (HClO) = 3.6 \times 10^{-8}$, $K_H = 1.01 \times 10^{-14}/3.6 \times 10^{-8}$. Substantial evidence in support of the above calculation (36). (.1.1) Derived from the reverse reaction and equilibrium. (.2) ClO_2 and Cl_2 continuously blown out by a stream of air. The $k\ A^2B^2[H^+]$ - order reaction is more nearly $k\ A^{1.65}B^{1.9}[H^+]^{3.9}$. This approximately eighth order is considered real by F. Foerster, *ZEC* 1917, 23, 137; J. Hirade, *Bull. Chem. Soc. Japan* 1935, 10, 109, holds the findings to be vitiated by salt effects. Mechanisms proposed: (12) $Cl^- + ClO_3^- + 2\ H^+ \rightarrow HClO + HClO_2$, rate determining; $HClO_2 + HClO \rightarrow ClO_2 + 1/2\ Cl_2 + H_2O$, fast; (24) $2\ Cl^- + 2\ ClO_3^- + 4\ H^+ \rightleftarrows H_2ClO_3 + Cl_2$; $H_2ClO_3 \rightarrow ClO_2 + H_2O$; $4\ H^+ + 4\ Cl^- + H_2ClO_3 \rightarrow 5/2\ Cl_2 + 3\ H_2O$; (37) for the eighth-order reaction, $HCl + HClO_3 \rightleftarrows H_2Cl_2O_3$; $H_2Cl_2O_3 \rightleftarrows Cl_2O_2 + H_2O$; $2\ Cl_2O_2 \rightleftarrows Cl_4O_4$; $Cl_4O_4 \rightleftarrows Cl_2 + Cl_2O_4$; $Cl_2O_4 \rightleftarrows 2\ ClO_2$; (37) for the fourth-order reaction, $HCl + HClO_3 \rightleftarrows H_2Cl_2O_3$ (rapid); $H_2Cl_2O_3 \rightleftarrows HClO_2 + HClO$ (rate determining); $HCl + HClO \rightleftarrows H_2O + Cl_2$; $HClO_2 + HClO_3 \rightleftarrows H_2Cl_2O_5$; $H_2Cl_2O_5 \rightleftarrows H_2O + Cl_2O_4$; $Cl_2O_4 \rightleftarrows 2\ ClO_2$; the eighth order results when the products of $H_2Cl_2O_3 \rightarrow HClO_2 + HClO$ are not rapidly removed and the mobile equilibrium $H_2Cl_2O_3 \rightleftarrows Cl_2O_2 + H_2O$ can be established. (.3) Mechanism proposed $2\ Cl^- + ClO_3^- + 2\ H^+ \rightarrow ClO^- + 2\ HClO$; $ClO^- + 2\ Cl^- + 2\ H^+ \rightarrow Cl_2 + H_2O$; $HClO + H^+ + Cl^- \rightarrow Cl_2 + H_2O$. This mechanism is the reverse of the hypochlorite formation from Cl_2. However, (12) claims that recalculation of the data of (26) shows fourth order; (24) opposes the disregard of ClO_2 in the scheme of (26). Reaction between $NaClO_3$ and concentrated HCl in a sealed tube at 60°C gave (11) ClO_2/Cl_2 = 1/2000. The rate law $k\ AB[H^+]^2$, established by (12) for dilute HCl in the presence of I^-, is held by (37) to be valid in highly concentrated HCl which acts as depolarizer (.3.1) Derived from $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$, in the presence of HCl. In concentrated HCl, order higher than $[H^+]^2$. (.4) Data of (38): direct measurements; data of (14) derived from $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ catalyzed by $Br_2 + Br^-$; data of (29) with allyl alcohol used to remove HBrO. *k* extrapolated to $\mu = 0$ in good agreement. Assumed mechanism, $Br^- + BrO_3^- + 2\ H^+ \rightarrow HBrO_2 + HBrO$ (or $H_2Br_2O_3$), rate determining, followed by rapid reactions of HBr with

COMMENTS (continued)

HBrO and $HBrO_2$. A fifth-order reaction $5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$ was expected by (33) at very high Br^-; (15) found no evidence therefor at $\mu < 0.7$ and HBr up to 0.1; however, with $Br^- = 4.2$ and $[H^+] = 0.009$, the fourth-order *k* increased, indicating a possible higher-order reaction. (.5) Calculated (1) from data on rates involving H_2O_2, I^-, I_2, and the hydrolysis constant of $I_2 = 3 \times 10^{-13}$; *k'* is for the reverse reaction $I_2 + H_2O$. However, (21,22,23) concludes that *k'* must be considerably greater than 4×10^{-3}, hence *k* considerably less than 1.3×10^{10}. (.6) *Notation:* f = activity coefficient of univalent ion; $\log F = -4\ \mu \sqrt{j} + 0.90\ j$; $\log F' = -2.20 \sqrt{j}$; $j = \Sigma\ c_1 z_1^2$. Reactions without I_2: iodine shaken out with CCl_4 as soon as formed; otherwise saturated with I_2. ** Solutions in equilibrium with solid $AgIO_3$ and AgI; in the presence of H_2SO_4; effects of electrolytes negligible. *** includes the effects of electrolytes; when I^- is very small, I_3^- has no effect on the rate. Reaction in D_2O: measured in 91 % D_2O, extrapolated to 100 %. Mechanisms proposed: * for $I^- > 10^{-4}$: (31, 13) $I^- + IO_3^- + 2\ H^+ \rightleftarrows H_2I_2O_3 \rightleftarrows I_2O_3 + H_2O$, fast; $I_2O_3 + I^- \rightarrow I_3O_2^-$, rate determining; $I_2O_3^- + 6\ I^- + 4\ H^+ \rightarrow 3\ I_3^- + 2\ H_2O$ (succession of fast steps); similar more elaborate mechanisms, (33). (2) $2\ I^- + IO_3^- + 2\ H^+ \rightarrow IO^- + 2\ HIO$, slow; $I^- + I_3^- + IO_3^- + 2\ H^+ \rightarrow 2\ HIO + I_3O^-$, slow; $I^- + IO_3^- + 2\ H^+ \rightarrow HIO_2 + HIO$, slow; fast reactions $HI + HIO_2 \rightarrow 2\ HIO$; $HI + HIO \rightarrow I_2 + H_2O$. ** and ***, for $I^- < 10^{-4}$: (5, 2) $I^- + IO_3 + 2\ H^+ \rightarrow HIO_2 + HIO$, rate determining; fast reactions $HI + HIO \rightarrow I_2 + H_2O$; $3\ HI + HIO_2 \rightarrow 2\ I_2 + 2\ H_2O$. (13, 20) $I^- + IO_3^- + 2\ H^+ \rightarrow H_2I_2O_3$; $H_2I_2O_3 \rightarrow HIO_2 + HIO$, rate determining. The kinetic improbability of rapid reactions of high order was argued by (39). (33) defended rapid equilibria of high order, but regarded them as built up by a succession of reactions very fast in comparison with the rate determining step. (.7) (.7.1) Reaction (.7) is composed of (.7.1), followed by reaction (.6). In strongly acid solutions low in A and high in B, only reaction (.7.1) occurs. $\log F = 0.71 \sqrt{j}$; $\log F' = -2.20 \sqrt{j}$; $j = \Sigma\ c_1 z_1^2$. (.7.2) In acetate buffer, mechanism proposed (4) $I^- + IO_4^- \rightarrow IO_3^- + IO^-$, rate determining; $I^- + IO^- + 2\ H^+ \rightarrow I_2 + H_2O$, fast.

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OXIDATION-REDUCTION

of compounds of different elements

Liquid phase

Reductant: H_2O_2

Oxidant: **VII group element**

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$H_2O_2 + Br_2 \rightarrow 2\ Br^- + 2\ H^+ + O_2$	H_2O	HBr = 0.01 - 0.38	k AB/LM	0	1.0	-5	*	(3) (4) (5)
					25	3.0	-4		
					35	7.1	-4		
.2	$H_2O_2 + I_2 \rightarrow 2\ H^+ + 2\ I^- + O_2$	H_2O		$k_1AB/L^2M + k_2AB/LM$	25			*	(1) (6) (7) (8) (10) (11)
					k_1	2.0	-14		
					k_2	1.1	-11		
.2.1	$H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$	H_2O		k'_1AB	25	3.3	+9	*	"
.2.2	$H_2O_2 + HIO \rightarrow H_2O + H^+ + I^- + O_2$	H_2O		k'_2AB	25	3.7	+1	*	"
.2.3	$H_2O_2 + H^+ + I^- \rightarrow H_2O + HIO$	H_2O		k ABC	25	1.6	-1	*	(11)
.3	$H_2O_2 + IO_4^- \rightarrow H_2O + IO_3^- + O_2$	H_2O	A = 0.01 - 0.02 10^3B = 0.25 = 2.0 H_2SO_4 = 0.005	k AB	0	~ 4.5	-1	*	(2)
			10^3A = 0.1 B = 1 × 10^{-5} H_2SO_4 = 0.0025	k B	25	~ 2.5	-7	*	(2)

COMMENTS

(.1) Derived from the reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$, catalyzed by $Br_2 + Br^-$. Mass-action expressed in activities of H^+ and Br^-. Assumed mechanism $Br_2 + H_2O \rightarrow HBrO + H^+ + Br^-$, followed by the rate determining step $H_2O_2 + HBrO \rightarrow H^+ + Br^- + H_2O + O_2$. (.2) Derived from the reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$, catalyzed by $I_2 + I^-$. (.2.1) (.2.2) are component steps of reaction (.2); $k_1' = k_1/K_1$, where $K_1 = [HIO][H^+]^2/[I_2] = 6 \times 10^{-24}$; $k_2' = k_2/K_2$, where $K_2 = [IO^-][H^+]^2[I]/[I_2] = 3 \times 10^{-13}$. (.2.3) Derived from $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ catalyzed by $I_2 + I^-$, and from $H_2O_2 + 2\ H^+ + 3\ I^- \rightarrow 2\ H_2O + I_3^-$. (.3) Initial rates only; k falls with progressing reaction. No satisfactory general equation evolved.

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OXIDATION - REDUCTION
by ions of different elements

Liquid phase

Reductant: I st group element

Oxidant: VI th " "

Rates in M/l per sec.

No.	Reaction	Solvent	Defined rate law	Temperature	log *k*
.1	$Ag^{+} + S_2O_8^{--} \longrightarrow Ag^{+++} + 2\ SO_4^{--}$	H_2O	kAB	25	$-1.93 - 0.38\sqrt{\mu}$

COMMENTS

The formula for log *k* obtained by graphic treatment, is the mean from the five Ag^{+} - catalyzed reactions between $S_2O_8^{--}$ and Cr^{+++}, VO^{++}, Mn^{++}, $N_2H_5^{++}$, Ce^{+++}, for which this step is considered to be rate determining. The wide scattering of the experimental points around the Brönsted slope, and the presence of higher oxide of Ag as a solid phase, suggest that this rate determining step may have been oversimplified. For possible complexities, see (³) (GSF).

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OXIDATION-REDUCTION

of compounds of different elements

Liquid phase

Reductant: IV th group element

Oxidant: VIII th " "

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$: k^o	n	Comments	Literature
.1	$Sn^{++} + 2\ Fe^{+++} \rightarrow Sn^{++++} + 2\ Fe^{++}$ (perchlorates)	H_2O	A = 0.002–0.005 B = 0.004–0.05	$HClO_4$ $[H^+]=0.10$;	$\sqrt{\mu} = 0.64–0.43$	$k\,AB/[H^+]^2$	70	6.0	-4	*	(²)
				0.05	0.28		"	8.3	-4		
		H_2O			$\mu \rightarrow 0$	"	55	4.3	-5		
							70	1.1	-3		
.1.1	$Sn^{++} + 2\ Fe(OH)_2^+ \rightarrow Sn^{++++} + 2\ Fe(OH)_2$	H_2O	"		$\mu \rightarrow 0$	$k'AB$	55	3.35	-2	*	(²)
							70	1.55	-1		

COMMENTS

Reaction (.1) assumed to proceed over $Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^+(K_1)$; $FeOH^{++} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+(K_2)$; $Sn^{++} + 2\ Fe(OH)_2^+ \rightarrow Sn^{++++} + 2\ Fe(OH)_2(k')$, i.e. (.1.1) is the rate determining step of (.1); $k = 2\,k'K_1K_2$; at 55° and 70°C, $K_1 = 0.0106$ and 0.025; $K_1K_2 = 6.5 \times 10^{-4}$ and 35.2×10^{-4}.

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732.500.

OXIDATION - REDUCTION

of compounds of different elements

Reductant: V th group element

Oxidant: O_2

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E
								k^{o}	n	
.1	$4\ V^{+++} + O_2 + 2\ H_2O \longrightarrow 4\ VO^{++} + 4\ H^{+}$	H_2O	$A = 0.008 - 0.08$ $HClO_4 = 0.02 - 0.09$ $O_2 = 0.2 - 1$ atm.	Cu^{++}	$10^{5}[Cu^{++}]$	$kA/[H^{+}]$				
					1		25	3.7	-4	
					2		"	4.5	-4	
					3		"	1.15	-3	
					10		"	1.8	-3	17.2

COMMENTS

The rate is independent of $[O_2]$ if $[Cu^{++}] \geqslant 10^{-5}$. With $Cu^{++} \sim 10^{-7}$, the rate law of the nearly uncatalyzed reaction approaches the order $k'\ AB/[H^{+}]$; with $k' = 8.3 \times 10^{-6}$ at 25°C.

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OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: V th group element

Oxidant: I st " "

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$H_3PO_2 + 2\,Ag^+ + H_2O \longrightarrow H_3PO_3 + 2\,Ag + 2\,H^+$	H_2O	$\left.\begin{matrix} A = 0.055 - 0.13 \\ B = 0.05 - 1 \\ H^+ = 0.035 - 0.07 \end{matrix}\right\}$	kA	25	2.2	-5
.1.1	$n - H_3PO_2 \longrightarrow a - H_3PO_2$	H_2O	as (.1)	kA	25	2.2	-5
.2	$H_3PO_2 + 2\,Cu^{++} + H_2O \longrightarrow H_3PO_3 + 2\,Cu^+ + 2\,H^+$	H_2O	See reactions (.1.1) and (.2.1)				
.2.1	$n - H_3PO_2 \longrightarrow a - H_3PO_2$	H_2O	$A = 0.01$ $Cu^{++} = 0.25 - 0.5$ $H^+ = 0.06$	kA	25	1.8	-6
.2.2	$a - H_3PO_2 + 2\,Cu^{++} + H_2O \longrightarrow H_3PO_3 + 2\,Cu^+ + 2\,H^+$	H_2O	$A = 0.02 - 0.075$ $B = 0.0035 - 0.025$ $H^+ = 0.04\ ;\ 0.28$	$kAB^2/[H^+]^2$	25	~ 5	-6

COMMENTS

(.1) (.1.1) Reaction (.1.1) is the rate determining step of (.1); n = normal, a = active. The following step, $a - H_3PO_2 + 2\ Ag^+ + 2\ H_2O \longrightarrow H_3PO_3 + 2\ Ag^+ + 2\ H^+$, is so rapid that the rate of the tautomeric change (.1.1) can be fully isolated. (.2) (.2.1) (.2.2) The rate of reaction (.2) is determined by the rate of (.2.1) at very high $[Cu^{++}]$, but by the rate of (.2.2) at $[Cu^{++}] \ll H_3PO_2$, when the rate-determining importance of $a - H_3PO_2 + 2\ Cu^{++} + H_2O \longrightarrow H_3PO_3 + 2\ Cu^+ + 2\ H^+$ becomes predominant over the rate of the tautomerization $n \longrightarrow a$. The value of k for (.2.1) agrees closely with k for oxidation of H_3PO_2 in the presence of excess I_2 and $HgCl_2$.

LITERATURE

(1) A.D.Mitchell, *CSL* 1920, **117**, 1322.

(2) A.D.Mitchell, *CSL* 1921, **119**, 1266.

(3) A.D.Mitchell, *CSL* 1922, **121**, 1624.

(4) A.D.Mitchell, *CSL* 1923, **123**, 629.

OXIDATION-REDUCTION
of compounds of different elements

Liquid phase

Reductant: V^{th} **group element**

Oxidant: II^{nd} **group element**

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
							k^o	n		
.1	$H_3PO_2 + 2\ Hg^{++} + H_2O \rightarrow H_3PO_3 + Hg_2^{++} + 2\ H^+$	H_2O	A = 0.01 - 0.10 B = 0.012 - 0.18		k A	15 25	7.0 2.2	-6 -5	*	(3)
.2	$H_3PO_3 + 2\ Hg^{++} + H_2O \rightarrow H_3PO_4 + Hg_2^{++} + 2\ H^+$	H_2O	A = 0.9 B = 0.0045 - 0.16 H^+ = 0.12 - 0.44	NaCl 0.0 - 0.45	$k\ A[H^+]/(1 + k'[H^+]/B)$	25	$k \sim 2$ $k' \sim 1$	-5 -5	*	(6)

COMMENTS

(.1) k is weighted average from the complete rate expression $([H^+] + m\ A)(1 - a)\ kt = \ln (A_o/A) + \ln ([H^+]_o/[H^+])$, where a = degree of dissociation of H_3PO_2 at half-time, $m \sim 1.6$. The tautomerization $n - H_3PO_2 \rightarrow a - H_3PO_2$ (normal → active) is rate determining at the higher concentrations; the subsequent step $a - H_3PO_2 + Hg^{++}$ is to a minor extent rate determining at lower concentrations. See further (2)(4)(5). (.2) k corrected for half-time dissociation of H_3PO_3; k and k' correspond to the steps: $n - H_3PO_3 \rightarrow a - H_3PO_3$ (k'); $a - H_3PO_3 \rightarrow n - H_3PO_3$ (k_2); $a - H_3PO_3 + 2\ Hg^{++} + H_2O \rightarrow H_3PO_4 + Hg_2^{++} + 2\ H^+$ (k_3); $k = k_1$; $k' = k_2/k_3$. In an acetate buffer (pH ~ 6) the rates were 160 times as fast as at pH ~ 1. See further (1).

LITERATURE

(1) R.D.Griffith, A.McKeown, *TFS* 1940, **36**, 766. (2) A.D.Mitchell, *CSL* 1920, **117**, 1322. (3) A.D.Mitchell, *CSL* 1921, **119**, 1266. (4) A.D.Mitchell, *CSL* 1922, **121**, 1624. (5) A.D.Mitchell, *CSL* 1923, **123**, 629. (6) A.D.Mitchell, *CSL* 1924, **125**, 1013.

OXIDATION - REDUCTION
of compounds of different elements

Liquid phase

Reductant: V th group element
Oxidant: " " " "

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
						k^o	n
.1	$3\ H_3AsO_3 + 2\ HNO_3 \longrightarrow 3\ H_3AsO_4 + 2\ NO + H_2O$	H_2O	A = 0.01 - 0.125 B = 0.30 - 3.0 NO, p = 0.98 atm	$k\ \alpha\ [H^+]^{2/3}[NO_3^-]^{2/3}\ (p_{NO})^{4/3}$ $\alpha = [f^2/(46 + 22\ \mu)]^{2/3}$	25	k = 1.3	-4

COMMENTS

This rate law applies only to a system in which the quasi-stationery equilibrium $HNO_3 + 2\ NO + H_2O \rightleftarrows 3\ HNO_2$ is maintained at constant p_{NO} which is usually 0.96 atm; f = activity coefficient of HNO_3. Assumed rate determining step, $H_3AsO_3 + N_2O_3 \longrightarrow H_3AsO_4 + 2\ NO + H_2O$.

LITERATURE

E. Abel, H. Schmid, J. Weiss, *ZPC* 1930, **147**, 69.

OXIDATION-REDUCTION

of compounds of different elements

Reductant: V th group element

Oxidant: VI th " "

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
							k^o	n		
.1	$NH_4 + 4\ S_2O_8^{--} + 3\ H_2O \rightarrow NO_3^- + 8\ SO_4^{--} + 10\ H^+$	H_2O	$(A + B) = 0.002$	Ag^+	$k\ B[Ag^+]$	25	2.7	-2	*	(²)
			0.5			"	4.5	-3		
			1.0			"	3.7	-3		
.2	$3\ H_3PO_2 + H_2Cr_2O_7 + 6\ H^+ \rightarrow 3\ H_3PO_3 + 2\ Cr^{+++} + 4\ H_2O$	H_2O	$A = 0.05 - 0.2;\ B = 0.001 - 0.15;\ H^+ = 0.07 - 4$		$k\ AB$	25	8.0	-6	*	(³)
							1.4	-5		

COMMENTS

(.1) Rate determining step, $S_2O_8^{--} + Ag^+ \rightarrow 2\ SO_4^{--} + Ag^{+++}$, followed by $n\ Ag^{+++} + NH_4^+ \rightarrow NO_3^-,\ H^+$. See further (¹).

(.2) Mechanism assumes equilibrium between $n - H_3PO_2$ (normal) and $a - H_3PO_2$ (active); the acid-catalyzed reaction $n - H_3PO_2 \rightarrow a - H_3PO_2$ (k_1) and the reverse reaction (k_2) is rapid, and the rate determining step is $a - H_3PO_2 + Cr_2O_7^{--} \rightarrow H_3PO_3 + Cr_2O_6^{--}$ (k_2), followed by the rapid reaction $2\ H_3PO_2 + Cr_2O_6^{--} + 8\ H^+ \rightarrow 2\ H_3PO_3 + 2\ Cr^{+++} + 4\ H_2O$; $k \sim 3\ k_1 k_3 / k_2$.

LITERATURE

(¹) C. V. King, *ACS* 1928, 50, 2080. (²) Marshall, Inglis, *PRS Edinburgh* 1900, 23, 163. (³) A. D. Mitchell, *CSL* 1924, 125, 564.

OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: V^{th} group element

Oxidant: VII^{th} group element

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$NO_2^- + I_2 + H_2O \rightarrow NO_3^- + 2\ I^- + 2\ H^+$	H_2O	buffers; pH = 6 (low $[I^-]$, or pH = 7 (high $[I^-]$;			$k\ AB/(K + M)[(aM/A) + 1]$							*	(3)
							40							
					$\mu = 2.7$		k	4.9	−7					
							50							
					0.7		k	4.7	−6					
							a	1.53	+2					
					2.7		k	2.3	−6					
							a	1.61	+2					
							60							
					0.7		k	1.9	−5					
							a	1.46	+2					
					2.7		k	9.4	−6					
							a	1.40	+2					
.2	$2\ N_3^- + I_2 \rightarrow 2\ N_2 + 2\ I^-$	H_2O	A = 0.005; B = 0.0001	$NaClO_4$	0.01	$k\ A[CS_2]$							*	(8)
				KI	0.004									
				CS_2	0.009		0.4	6.25	−3					
					0.008		10	2.34	−2					
					0.007		12.5	3.03	−2					
					0.0004		15	3.9	−2					
					0.0002		20	7.5	−2	20	5.7	13		

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of Addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.3	$3\ H_3PO_2 + IO_3^- \rightarrow 3\ H_3PO_3 + I^-$	H_2O	A = 0.05 - 0.01 B = 0.01 - 0.14	H^+	0.017 - 0.037	$k\,A[H^+]/(1 + k'[H^+]/B)$							*	(7)
							20.3							
							k	1.0	-3					
							k'	3.5	-1					
							30.1							
							k	2.7	-3	17				
							k'	4.4	-1	4.5				
.4	$H_3PO_2 + I_2 + H_2O \rightarrow H_3PO_3 + 2\ I^- + 2\ H^+$	H_2O			See Comments								*	(6)
			pH > 6	$2\ k_1B[H_2PO_3^-]K/(K + [I^-])$									*	(6)
.4.1	$H_2PO_2^- + I_2 + H_2O \rightarrow H_2PO_2^- + 2\ I^- + 2\ H^+$	H_2O	pH > 6		μ = 2.05	k_1AB	30	2.7	-4					
					"		50	4.7	-3					
					"		60	1.5	-2	25.2				
					1.1		"	1.2	-2					
.4.2	$H_3PO_2 + I_2 + H_2O \rightarrow H_3PO_3 + 2\ I^- + 2\ H^+$	H_2O	$[I^-]$ = 0.002 - 0.2		μ = 0.25	k_2AB	30	1.3	0	18			*	(6)
.4.3	$H_3PO_2 + I_3^- + H_2O \rightarrow H_3PO_3 + 3\ I^- + 2\ H^+$	H_2O	"		"	k_3AB	30	3.8	-1	18			*	(6)
.5	$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2\ I^- + 2\ H^+$	H_2O	HCO_3^-/CO_3^{--}		μ =	$k\,AB$							*	(8)
			0.014/0.118		0.60		0.1	2.2	-2					
			" "		"		10.0	1.2	-1					
			0.10/0.10		"		20.0	5.6	-1					
			0.014/0.118		0.80		"	2.8	-1	22				
			$HPO_4^{--}/H_2PO_4^-$											
			0.013/0.120		0.60		0.1	2.1	-2				*	"
			0.30/0.10		0.80		10.0	4.5	-2					
			0.014/0.12		0.60		"	1.15	-1					
			0.10/0.033		0.40		20.0	2.40	-1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.5.1	$n - H_3PO_3 + H^+ \rightarrow H_3PO_3 \cdot H^+$	H_2O	pH < 1	HX =	μ =	$k_1A[HX]$							*	(5)
				H_3O^+	0.5 - 0.6		45	1.65	-4					
				H_3PO_3	"		"	1.05	-4					
				H_3PO_4	"		"	1.2	-4					
				HSO_4^-	"		"	9.35	-5					
				CH_3COOH	"		"	5,2	-6					
				$CH_2ClCOOH$	"		"	1.6	-5					
				$CH_2OHCOOH$	"		"	1.0	-5	22.5				
.5.2	$HPO_3^{--} + I_2 + H_2O \rightarrow HPO_4^{--} + 2\ I^- + 2\ H^+$	H_2O	2 < pH < 9		μ = 0.4 - 1.15	k_2AB	20	9.5	+1				*	(5)
					0.4		30	3.3	+2	22.0				
					0.56		45	1.6	+3					
.5.3	$H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2\ I^- + 2\ H^+$	H_2O				k_3AB	45	1.35	-2				*	(5)
.5.4	$H_3PO_3 + I_3^- + H_2O \rightarrow H_3PO_4 + 3\ I^- + 2\ H^+$	H_2O				k_4AB	35	1.1	-3					
							45	3.5	-3	21.4				
.6	$3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$	H_2O		HCl		$k\ B[H^+]^2[Cl^-]$	25	7.5	-7				*	(9) (20)
							55	3.8	-5					
				HBr		$k\ B[H^+]^2[Br^-] + k'L$	25						*	"
							k	1.55	-6					
							k'	5.15	-7					
				HI		$k\ B[H^+]^2[I^-] + k'L$	25						*	"
							k	3.3	-5					
							k'	3.5	-6					
.7	$3\ H_3AsO_3 + BrO_3^- \rightarrow 3\ H_3AsO_4 + Br^-$	H_2O		$HCl + HClO_4$		$k\ B[H^+][Cl^-]$	25	1.5	-3				*	(20)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.8	$H_3AsO_3 + I_3^- + H_2O \rightarrow H_3AsO_4 + 2\ I^- + 2\ H^+$	H_2O	A = 0.022 - 0.044 B = 0.005 H^+ = 0.16; I^- = 0.16	$HClO_4$		$k\ AB/[H^+][I^-]^2$	0	1.1	-5				*	(10)(12)
							4.6	1.8	-5					
							10.4	3.6	-5					
							15.0	6.0	-5					
							20.0	9.7	-5	17.0				
.8.1	$H_3AsO_3 + HIO \rightarrow H_3AsO_4 + I^- + H^+$	H_2O	"	"		$k\ AB$	0	2.3	-1	~ 0			*	"
.9	$3\ AsO_3^{---} + IO_3^- \rightarrow 3\ AsO_4^{---} + I^-$	H_2O	B = 0.001 I^- = 0.02 - 0.04	$10^5[H^+] = 2 - 4$		$k\ B[H^+]^2[I^-]^2$							*	(9)(21)
							25	1.7	9					
.10	$AsO_2^- + IO_4^- \rightarrow AsO_3^- + IO_3^-$	H_2O	$CH_3COOH + CH_3COO^-$ buffer			$k\ AB$	25	9.2	-2					(1)

COMMENTS

(.1) Assumed mechanism $NO_2^- + I_2 \rightarrow NO_2 + I^- + I$ (k_1); $NO_2 + I^- + I \rightarrow NO_2^- + I_2$ (k_2); $NO_2 + I \rightarrow NO_2 + I^-$ (k_3); $NO_2 + I^- \rightarrow NO_2 + I$ (k_4); $2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ (k_5); $K = [I^-][I_2]/[I_3^-]$ = 0.00225 at 50° and 0.0026 at 60°C; $k = k_1K$; $a = k_2k_4/k_3k_5$. (.2) Proposed mechanism $N_3^- + CS_2 \rightarrow SCSN_3^-$ (rate determining); $2\ SCSN_3^- + I_2 \rightarrow (SCSN_3)_2 + 2\ I^-$; $(SCSN_3)_2 + 2\ N_3^- \rightarrow 2\ CS_2 + 2\ N_3^- + 3\ N_2$. (.3) Propanol (up to 7 %) added to inhibit the reaction between HIO_3 and HI; AgCl added to eliminate I^-. Mechanism assumed $n - H_3PO_2 \rightarrow a - H_3PO_2$ (normal → active) (k_1); $a - H_2PO_2 \rightarrow n - H_3PO_2$ (k_2); $a - H_3PO_2 + IO_3^- \rightarrow$ products (k_3); $k = k_1$; $k' = k_2/k_3$. Reaction 3 is about 1/35 as fast as oxidation of $a - H_3PO_2$ by halogens or by Hg^{++}. Reactions 1, 2, are acid-catalyzed. See further (14)(5)(6). (.4)(.4.1)(.4.2)(.4.3) Reaction (.4.1) is predominant in (.4) at pH > 6, or at or above 50°C; the rate of (.4) is then represented by the equation given under (.4), in terms of the rate constant k_1, of (.4.1) and of $K = [I^-][I_2]/[I_3^-]$ = 0.00155 at 30°C. The acid-catalyzed reaction $H_2PO_2^- + H^+ \rightarrow a - H_3PO_2$ (active) is negligible at

COMMENTS *(continued)*

pH < 3.4. The acid-catalyzed reaction $n-H_3PO_2$ (normal) $+ H^+ \rightarrow H_3PO_2 \cdot H^+$ is favored at high $[H^+]$. At pH >> 3.4, the follow-up reaction is (.4.2) or (.4.3); the second-order rate constants for the reactions $a-H_3PO_2 + I_2 + H_2O$ and $a-H_3PO_2 + I_3^-$ are, respectively, k_2/K and k_3/K, where $K = a-H_3PO_2/n-H_3PO_2$. (.5) (.5.1) (.5.2) (.5.3) (.5.4) Selected empirical data; further data in acetate and chloroacetate buffers, see original (5). Significant steps of the overall reaction are, (.5.1), acid-catalyzed, and followed by $H_3PO_3 \cdot H^+ + \text{base} \rightarrow a-H_3PO_3$ (active); this is followed by $a-H_3PO_3 + I_2 + H_2O$ (.5.3) or $a-H_3PO_3 + I_3^- + H_2O$ (.5.4). The rate constants of the reactions $a-H_3PO_3 + I_2 + H_2O$ and $a-H_3PO_3 + I_3^- + H_2O$ are, respectively, k_3/K and k_4/K [see comment (.4)]. At higher pH, the significant step is (.5.2), whereas $H_2PO_3^- + I_2 + H_2O$ is negligible. (.6) In concentrated HCl, the order is higher than $[H^+]^2$. The rates are independent of H_3AsO_3 which acts only to eliminate the products. The rate determining steps are $X^- + XO_3^- + 6\,H^+ \rightarrow 3\,X_2 + 3\,H_2O$ (see 722.770); X = Cl, Br, I. The acceleration by H_3AsO_4 (with Br, I) is interpreted by $2\,X^- + 2\,H^+ + H_3AsO_4 \rightleftarrows X_2 + H_3AsO_3$; $X_2 + 2\,ClO_3^- \rightarrow Cl_2 + 2\,XO_3^-$; $H_3AsO_3 + Cl_2 + H_2O \rightarrow H_3AsO_4 + 2\,Cl^- + 2\,H^+$; $3\,H_3AsO_3 + XO_3^- \rightarrow 2\,H_3AsO_4 + X^-$. (.7) Rate independent of H_3AsO_3, as above (.6). Rate determining step, $5\,Cl^- + BrO_3^- + 6\,H^+ \rightarrow 2\,Cl_2 + BrCl + 3\,H_2O$ (see 722.770). (.8) Mechanism (10)(15)(11)(2) $I_2 + H_2O \rightleftarrows HIO + I^- + H^+$, fast; $H_3AsO_3 + HIO \rightleftarrows H_4AsIO_4$, fast; $H_4AsIO_4 \rightarrow H_3AsO_4 + I^- + H^+$. (.8.1) Derived from (.8); $[I_3^-]/[I_2][I^-] = 1/7.2 \times 10^{-4}$ and $[I_2] = [H^+][I^-][HIO]/9 \times 10^{-5}$. (.9) The fifth-order Dushman reaction goes over partly into a fourth-order reaction $A[H^+]^2[I^-]$ with decreasing $[I^-]$, and consequently k decreases. If I^- is added at the start, the reaction $5\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$ is followed by $AsO_3^{---} + I_2 + H_2O \rightarrow AsO_4^{---} + 2\,I^- + 2\,H^+$, rapid until equilibrium is approached. See further (18) (criticism), (3) (16).

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OXIDATION-REDUCTION

of compounds of different elements

Reductant: V th group element

Oxidant: VIII th group (or rare earth) element

Liquid phase

Rates are in units of amounts per sec.

No.	Reaction	Solvent	Unit of amount	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		Comments	Literature
									k°	n		
.1	$NO_2^- + Fe^{+++} \rightarrow NO_2 + Fe^{++}$	H_2O	M/l				$k\,AB$	25	1.0	0	*	(1)
.2	$AsO_3^{---} + 2\,Ce^{++++} + H_2O \rightarrow$	H_2O	equiv/l	A = 0.025; B = 0.05	H_2SO_4	1	$k\,AB^2$	30	3.1	-1	*	(2, 3)
	$AsO_4^{---} + 2\,Ce^{+++} + 2\,H^+$			" 0.025				"	4.4	-1		
				" 0.125				"	5.1	-1		
				0.0125 0.05				"	3.0	-1		
				" 0.025				"	4.3	-1		
				0.00625 0.05				"	1.1	-1		

COMMENTS

(.1) Derived from the reaction $Fe^{++} + HNO_2 + H^+ \rightarrow Fe^{+++} + NO + H_2O$. Since NO reacts by $NO + NO_2 + H_2O \rightarrow 2\,HNO_2$, this reaction is virtually the reverse of $Fe^{++} + HNO_2 + H^+ \rightarrow Fe^{+++} + NO + H_2O$. (.2) The third-order k increases with decreasing B and with increasing A; k increases on addition of H_2SO_4, HNO_3, $HClO_4$, in that order. The mechanism of (3) $AsO_2^- + Ce^{++++} \rightarrow Ce^{+++} + AsO_2$ is criticized by (2) as calling for second order (not verified) and postulating AsO_2. Activation energies (2), in A = 0.025, B = 0.05, H_2SO_4 = 1.0, E = 21; in A = 0.00625, B = 0.05, H_2SO_4 = 2.0, E = 17; according to (3), E varies from 9.5 in $HClO_4$ to 17.0 in H_2SO_4.

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OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: VI th group

Oxidant: " " "

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Ionic Strength	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*
							k^o	n	
.1	$Cr^{+++} + S_2O_8^{--} + 7\ H_2O \rightarrow Cr_2O_7^{--} + 6\ SO_4^{--} + 14\ H^+$	H_2O	$\mu = 0.234$	Ag^+	$kB[Ag^+]$	25	5.7	-3	15
						35	1.3	-2	
			0.485	"	"	25	5.3	-3	

COMMENTS

The rate is independent of $[Cr^{+++}]$. Rate determining step $Ag^+ + S_2O_8^{--} \longrightarrow Ag^{+++} + 2\ SO_4^{--}$, followed by $3\ Ag^{+++} + 2\ Cr^{+++} + 7\ H_2O \longrightarrow 3\ Ag^+ + Cr_2O_7^{--} + 14\ H^+$, fast.

LITERATURE

D.M. Yost, *ACS* 1926, 48, 152.

OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: VI th group element
Oxidant: VII th " "

Amounts are in M/l.
Rates in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Completion time	$k = k^o \times 10^n$		E	Comments	Literature
									k^o	n			
.1	$SO_3^{--} + I_2 + H_2O \longrightarrow SO_4^{--} + 2\,I^- + 2\,H^+$	H_2O	A = B = 0.09	HCl	1		0	20				*	(8)(3)
							~ 20	4					
					2		0	360					
							~ 20	15					
				H_2SO_4	0.5		0	18					
							~ 20	4					
					1		0	420					
							~ 20	14					
.2	$3\,SO_3^{--} + IO_3^- \longrightarrow 2\,SO_4^{--} + I^-$	H_2O	B = 0.003 - 0.02;	kA; $k = k_1B[HSO_3^-][H^+] + k_2A^2B[H^+]^2$								*	(7)
			A = 3B; pH = 7 - 9				25	k_2	1.1	+15			
.2.1	$2\,HSO_3^- + IO_3^- + CH_3COO^- \longrightarrow 3\,SO_4^{--} + I^- + 3\,CH_3COOH$	H_2O	$10^3A = 1.5 - 9$ $10^4B = 5 - 10$ pH = 4 - 5			$k_1AB[H^+]$	25	k_1	8.8	+3		*	"
.3	$6\,S_2O_3^{--} + IO_3^- + 6\,H^+ \longrightarrow 3\,S_4O_6^{--} + I^- + 3\,H_2O$	H_2O	$10^2A = 1 - 6$ $10^3B = 2 - 15$ $10^6[H^+] = 2$			$kA^2B[H^+]^2$	24(34?)		5.0	8	4.7	*	(4)(1)

COMMENTS

(.1) The retardation at high $[H^+]$ suggests that OH^- is involved. (.2) (.2.1) The main reaction (.2), with the rate constant k_2, is isolated only between pH 7 and 9, and when $[SO_3^{--}]$ is relatively large or $[I^-]$ very small (as in the presence of AgCl). The special case (.2.1), with the rate constant k_1, is isolated between pH 4 and 5 only. At pH 13, the reaction is too slow to measure. When $[H^+] \geqq 0.01$, HIO_3 reacts so fast that the iodine-sulfite reaction becomes rate determining. If I^- is added at the start, the reaction $IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$ becomes rate determining. (.3) The rate equation corresponds to Dushman's fifth-order reaction $5\ I^- + IO_3^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$ (rate determining), followed by the rapid reaction $2\ S_2O_3^{--} + I_2 = S_4O_6^{--} + 2\ I^-$. The rate of the Dushman reaction is increased in the presence of $S_2O_3^{--}$. The temperature coefficient agrees with the Dushman reaction (A.Skrabal, *Gmelin Handbuch*, 8th edition, System-number 8, p. 569). See further (4) (5).

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OXIDATION-REDUCTION

Liquid phase

of compounds of different elements

Reductant: VII th group element

Oxidant: H_2O_2

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Addend (catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$: k^o	n	E	$A = A^o \times 10^n$: A^o	n	Comments	Literature
.1	$2H_2O_2 \rightarrow 2H_2O + O_2$	H_2O	HBr	0.01 - 0.38	$A(k_1[H^+][Br^-] + k_2[Br_2]/[H^+][Br^-])$							*	*
			See reactions (.1.1), (.1.2)										
.1.1	$Br^- + H_2O_2 + H^+ \rightarrow HBrO + H_2O$	H_2O	HBr	0.01 - 0.38	k_1ABC	25	3.6	-4				*	*
.1.2	$HBrO + H_2O_2 \rightarrow Br^- + H^+ + H_2O$	H_2O	HBr	0.01 - 0.38	$k_2A[Br_2]/[H^+][Br^-]$								
						0	1.03	-5				*	*
						25	3.0	-4					
						35	7.1	-4					
.2	$2H_2O_2 \rightarrow 2H_2O + O_2$	H_2O	HI	See reactions (.1.1) (.2.2)								*	*
.2.1	$3I^- + H_2O_2 + 2H^+ \rightarrow I_3^- + 2H_2O$	H_2O			$k_1AB + k'_1AB[H^+]$	25						*	*
						k_1	1.15	-2	13.4	8.2	7		
						k'	1.75	-1	10.4	7.6	6		
.2.1[a]	$I^- + H_2O_2 \rightarrow IO^- + H_2O$	H_2O			k_1AB	25	1.15	-2	13.4	8.2	7	*	*
.2.1[b]	$I^- + H_2O_2 + H^+ \rightarrow HIO + H_2O$	H_2O			$k'_1AB[H^+]$	25	1.75	-1	10.4	7.6	6	*	*
.2.2	$H_2O_2 + I_2 \rightarrow 2H^+ + 2I^- + O_2$	H_2O			$AB(k_2/[I^-][H^+]^2 + k'_2/[I^-][H^+])$							*	*
						25							
						k_2	2.0	-14					
						k'_2	1.1	-11					

No.	Reaction	Solvent	Addend (catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.2.2[a]	$H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$	H_2O			$k_{2a}AB$	25	3.3	+9				*	*
.2.2[b]	$H_2O_2 + HIO \rightarrow H_2O + H^+ + I^- + O_2$	H_2O			$k_{2b}AB$	25	3.7	+1				*	*
.3	$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$	H_2O	NaI	0.0205	$k\,A$	25	5.0	-4					(4)
		$H_2O + CH_3OH$ 24 %	"	"		"	2.7	-4					
		46		"		"	1.7	-4					
		93.5		"		"	9.5	-5					
		$H_2O + C_2H_5OH$ 32.6 %	"	"	"	25	2.1	-4					
		56		"		"	1.7	-4					
		93.4		"		"	1.7	-4					
		$H_2O + C_3H_7OH$ 28.3 %	"	"	"	25	3.0	-4					
		93.9				"	5.5	-4					
		$H_2O + i\text{-}C_4H_9OH$ 93.4 %	"	"		25	1.5	-3					
		$H_2O + C_5H_{11}OH$ 93.5	"	"		25	2.1	-3					
		$H_2O + C_3H_5(OH)_3$ 95.7	"	"		"	1.4	-3					
		$H_2O + C_5H_5N$ 33.5 %	"	0.1026		"	1.1	-3					
		67.1		"		"	2.8	-4					
		81.7		"		"	1.5	-4					
		94.7		"		"	2.7	-4					
.4	$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$	H_2O	KI	0.02	$k\,A\,[I^-]$	15	1.0	-2				*	(10) (23)
						25	2.3	-2					
						35	4.7	-2					
						45	9.6	-2	13.8				

No.	Reaction	Solvent	Addend (catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.4	$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$ *(continued)*	$H_2O + CH_3OH$ 25.5 %	KI	0.02	$k\,A[I^-]$	15	5.3	-3					(10) (23)
		" "				25	1.2	-2					
		" "				35	2.7	-2					
		" "				45	6.0	-2	15.1				
		" 54.4	"	"	"	15	2.8	-3					"
		" "				25	7.0	-3					
		" "				35	3.3	-2					
		" "				45	3.8	-2	15.8				
		CH_3OH 100 %	"	"	"	15	1.6	-3					"
						25	4.4	-3					
						35	1.1	-2					
		H_2O	KI 0.02	+ NaCl 1	"	15	1.2	-2					
						25	2.7	-2					
						35	5.6	-2					
						45	1.15	-1	13.7				
.5	$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$	H_2O	CdI_2	0.005 - 0.5	$A(k_1[I^-] + k_2[CdI^+] + k_3[CdI_3^-])$							*	(9)
						25							
						k_1	2.6	-2					
						k_2	~ 1.0	-2					
						k_3	~ 1.3	-2					
		"	KI	0.005 - 0.1	$k\,A[I]$	25	2.4	-2					

COMMENTS

(.1) (.1.1) (.1.2) Reaction (.1), catalyzed by the Br^- + Br_2 couple, proceeds over the steps (.1.1) and (.1.2). The data of k_1 and k_2 refer to mass action expressed in activities, i.e. $k_1 = k'_1 / f^2$ and $k_2 = k'_2 / f^2$, where k'_1 and k'_2 are the concentrational rate constants, f = activity coefficient of HBr. The concentration of HBrO in the overall reaction is stationary. Literature (19) (1) (5) (12) (13) (14) (16) (2)

(.2) (.2.1) (.2.2) Reaction (.2), catalyzed by the I^- + I_2 couple, proceeds over the steps (.2.1) [which proceeds over (.2.1^a) and (.2.1^b)]; k_2 and k'_2 are with $[H^+]$ expressed in activities. The relations between the constants are, $k_{2a} = k_2 / K_a$, where $K_a = [HIO][H^+][I^-] / [I_2] = 6 \times 10^{-24}$; $k_{2b} = k'_2 / K_b$, where $K_b = [IO^-][H^+]^2 [I^-] / [I_2] = 3 \times 10^{-13}$. Literature (3) (6) (7) (17) (18) (15) (20) (8)

(.3) (.4) (.5) Reactions catalyzed by the I^- + I_2 couple. Catalytic constant defined by $k A [I^-]$, at 25°C, in fairly good agreement $\sim 2.4 \times 10^{-2}$. (.4) Data on further salt effects, KBr, K_2SO_4, $MgSO_4$, $BaCl_2$, in original (10). Calculations based on triple collisions predict k values in fair agreement with the experiment. (.5) Only I^-, CdI^+, and CdI_3^- have a catalytic effect; Cd^{++} has none. Addition of I_2 to CdI_2 0.125 - 0.250 has little effect, but I_2 added to $CdI_2 < 0.0075$ decreases k rapidly. See further (21) (22) (11).

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Homogeneous Reactions

732.703.

OXIDATION-REDUCTION

of compounds of different elements

Liquid phase

Reductant: **VIIth group element**

Oxidant: **ozone**

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	$2\,Cl^- + O_3 + 2\,H^+ \rightarrow Cl_2 + O_2 + H_2O$	H_2O	A = 0.02 - 0.1 B = 0.0004 - 0.004	Co^{++} = 0.00011 - 0.00044	$k_1AB + k_2AB[H^+] + k_3B[Co^{++}]$	0					
						k_1	2.1	-4	17.6	2.3	10
						k_2	2.1	-3	17.5	2.0	11
						k_3	6.6	-1	(0-9.5°C)		

COMMENTS

Spontaneous decomposition of O_3 slight; Cu^{++} and Fe^{+++} are without measurable effect. Mechanism for k_1, $Cl^- + O_3 \rightarrow ClO^- + O_2$, rate determining; $ClO^- + Cl^- + 2\,H^+ \rightarrow Cl_2 + H_2O$, fast. For k_3, $Co^{++} + O_3 + H_2O \rightarrow CoOH^+ + O_2 + OH$, rate determining.

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OXIDATION-REDUCTION
of compounds of different elements

Liquid phase

Reductant: VII th group element
Oxidant: V th " "

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
					k^o	n			
.1	$3 I^- + H_3AsO_4 + 2 H^+ \rightarrow I_3^- + H_3AsO_3 + H_2O$	H_2O	k ABC	0	1.05	-4		*	(1) (2) (4) (5)
				25	1.2	-3	14.1		
.2	$3 I^- + 2 V(OH)_4^+ + 4 H^+ \rightarrow I_3^- + 2 VO^{++} + 6 H_2O$	H_2O	k ABC^2	25	1.3	-1		*	(3)

COMMENTS

(.1) Calculated (5) from exchange of radioactive As^{76} between AsO_3^{---} and AsO_4^{---} in the presence of I_3^- and I^- (no exchange in their absence). Mechanism represented as $A + B + C \rightarrow H_4AsIO_4$, fast; $H_4AsIO_4 \rightarrow I_3^- + HIO$, rate determining; $HIO + 2 I^- + 2 H^+ \rightarrow I_3^- + H_2O$, fast. (.2) The plot of $-d\ln B/dt$ against $k AC^2$ is linear.

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OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: VII th group element

Oxidant: VI th " "

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$2\ I^- + S_2O_8^{--} \rightarrow I_2 + 2\ SO_4^{--}$ $2\ I_3^- + S_2O_8^{--} \rightarrow 3\ I_2 + 2\ SO_4^{--}$	H_2O	$I^- = 0.01$ $B = 0.005$ $\mu = 0.025$	$-dB/dt = k_1[I^-]B + k_2[I_3^-]B$			25				(²)
							k_1	2.1	-3		
							k_2	1.07	-3		
		"	$I^- = 0.025$; $B = 0.0125$	X =	0.0001 - 0.0005	$k[I^-]B + k'B[X]$	25			*	(⁴)
				Fe^{++}			k'	9.1	0		
				Cu^{++}	0.0001	"	k'	7.8	0		
					0.0002			5.8	0		
					0.0005			4.6	0		
.2	$6\ I^- + Cr_2O_7^{--} + 14\ H^+ \longrightarrow 3\ I_2 + 2\ Cr^{+++} + 7\ H_2O$	H_2O	$10^4A = 68 - 277$; $10^4B = 2.0$ $10^4[H^+] = 176 - 531$	NaCl	1.5	kB; $k = aA[H^+] + bA^2[H^+]$	25			*	(¹)
							a	2.4	-1		
							b	8.9	+2		

COMMENTS

(.1) The mechanisms of the catalyzed reaction are formulated $Fe^{++} + S_2O_8^{--} \longrightarrow FeS_2O_8$ (rate determining); $FeS_2O_8 \longrightarrow 2\ Fe^{+++} + 2\ SO_4^{--}$, fast; $2\ Cu^{++} + 2\ I^- \longrightarrow 2\ Cu^+ + I_2$, fast; $Cu^+ + S_2O_8^{--} \longrightarrow CuS_2O_8^-$, rate determining ($k'$); $Cu^+ + CuS_2O_8^- \longrightarrow 2\ Cu^{++} + 2\ SO_4^{--}$, fast. (.2) The rate law holds only at the given concentrations; otherwise the rate is $kABC$ or kAB^2C^2; k passes through a minimum at $\mu = 0.5$, and is about equal at $\mu = 0.04$ and $\mu = 1.5$.

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OXIDATION-REDUCTION

of compounds of different elements

Reductant: VII^th group element

Oxidant: VII^th group element

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
						k^o	n		
.1	$5\ Cl^- + BrO_3^- + 6\ H^+ \rightarrow 2\ Cl_2 + BrCl + 3\ H_2O$	H_2O	H_3AsO_3	$k\ ABC^2$	25	1.5	-3	*	(⁶)
.1.1	$5\ Cl^- + BrO_3^- + 6\ H^+ \rightarrow 2\ Cl_2 + BrCl + 3\ H_2O$	H_2O		$k\ ABC^2$	25	5.3	-1	*	(¹)(⁸)
		D_2O		"	"	1.9	0		"
.2	$6\ Br^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + Cl^- + 3\ H_2O$	H_2O	HNO_3	$k\ ABC^2$	40	1.0	-5	*	(⁴)
.2.1	$6\ Br^- + ClO_3^- + 6\ H^+ \rightarrow 3\ Br_2 + Cl^- + 3\ H_2O$	H_2O	H_3AsO_3	$k\ ABC^2$	25	1.5	-6	*	(⁷)
.3	$6\ I^- + ClO_3^- + 6\ H^+ \rightarrow 3\ I_2 + Cl^- + 3\ H_2O$	H_2O		$k\ ABC^2$	30	1.8	-5	*	(²)(³)
.3.1	$6\ I^- + ClO_3^- + 6\ H^+ \rightarrow 3\ I_2 + Cl^- + 3\ H_2O$	H_2O	H_3AsO_3	$k\ ABC^2$	25	3.3	-5	*	(⁷)

COMMENTS

(.1) Derived from $3\ H_3AsO_3 + BrO_3^- \rightarrow 3\ H_3AsO_4 + Br^-$, in the presence of HCl. (.1.1) Measured in 91 % D_2O, extrapolated to 100 % D_2O. (.2) (⁵) predicted $k = 8.2 \times 10^{-6}$ at 25°C. (.2.1) Derived from $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$, in the presence of HBr. (.3) Ten-degree temperature coefficient = 2.6. (.3.1) Derived from $3\ H_3AsO_3 + ClO_3^- \rightarrow 3\ H_3AsO_4 + Cl^-$, in the presence of HI.

LITERATURE

(1) E. Abel, F. Fabian, *MHC* 1938, 71, 153. (2) W. C. Bray, *JPC* 1903, 7, 92. (3) W. C. Bray, *ZPC* 1906, 54, 463. (4) J. Hirada, *Bull. Chem. Soc. Japan* 1935, 10, 97. (5) A. Skrabal, R. Rieder, *ZEC* 1924, 30, 109. (6) A. Skrabal, H. Schreiner, *MHC* 1922, 43, 439. (7) A. Skrabal, H. Schreiner, *MHC* 1935, 65, 213. (8) A. Skrabal, S. R. Weberitsch, *MHC* 1915, 36, 211.

OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: VII th group element

Oxidant: VIII th " "

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$2I + 2Fe^{+++} \longrightarrow I + 2Fe^{++}$	H_2O	$\mu =$	$-dB/dt = r_1 + r_2$	25			*	(2)(3)
	(nitrates)		0.09	$r_1 = k_1A^2B/\{1 + M/B(m_4 + m_6A)\}$	k_1	8.7	+1		(4)(10)
					m_4	1.8	-2		
					m_6	2.0	+1		
			0		k_1	8.1	+2		
					m_4	2.8	-1		
					m_6	7.5	+1		
				$r_2 = k_1'AB/(1 + M[H^+]/Bm')$					
			0.09		k'	1.2	-2		
					m'	1.4	-3		
			0		k'	4.3	-2		
					m'	3.4	-3		

732.780.

COMMENTS

Reverse reaction, see 732.870. The forward and the reverse reactions are interpreted by a scheme (one variant):

$Fe^{+++} + I^- \rightleftharpoons FeI^{++}$ (fast, K_2); $FeI^{++} + I^- \longrightarrow Fe^{++} + I_2^-$ ($1/2k_1/K_2$); $Fe^{++} + I_2^- \longrightarrow FeI^{++} + I^-$ (k_2);

$Fe^{+++} + I_2^- \longrightarrow Fe^{++} + I_2$ (k_3); $Fe^{++} + I_2 \longrightarrow Fe^{+++} + I_2^-$ ($1/2k_4$); $FeI^{++} + I_2^- \longrightarrow Fe^{++} + I_3^-$ (k_5/K_2);

$Fe^{++} + I_3^- \longrightarrow FeI^{++} + I_2^-$ ($1/2k_6$); $Fe^{++} + H_2O \longrightarrow Fe^{++} + IOH^- + H^+$ ($1/2k_1/K_2$); $Fe^{++} + IOH^- + H^+ \longrightarrow$

$Fe^{++} + H_2O$ (k_2'); $Fe^{+++} + IOH^- \longrightarrow Fe^{++} + IOH$ (k_3'); $Fe^{++} + IOH \longrightarrow Fe^{+++} + IOH^-$ ($1/2k_4'/K_3$);

$IOH + I^- + H^+ \rightleftharpoons I_2 + H_2O$ (fast, $1/K_3$); $m_4 = k_3/k_2$; $m_6 = k_5/k_4$; $m' = k_3'/k_2'$;

$K = [Fe^{++}]^2[I_2]/[Fe^{+++}]^2[I^-]^2$. Further literature references (1)(5)(6)(7)(8)(9).

LITERATURE

(1) R.C.Banerji, N.R.Dhar, *ZAC* 1924, **134**, 172.

(2) W.C.Bray, M.H.Gorin, *ACS* 1932, **54**, 2124.

(3) A.V.Hershey, W.C.Bray, *ACS* 1936, **58**, 1760.

(4) N.Sasaki, *ZAC* 1924, **137**, 181. 291.

(5) K.Tominaga, S.Toraiski, *C.A.* 1931, **25**, 5613.

(6) A.von Kiss, *C.A.* 1931, **25**, 2631.

(7) A.von Kiss, *ZAC* 1931, **198**, 102.

(8) A.von Kiss, I.Bossanyi, *ZAC* 1930, **191**, 289.

(9) A.von Kiss, I.Bossanyi, *C.A.* 1931, **25**, 5071.

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OXIDATION-REDUCTION
of compounds of different elements

Liquid phase

Reductant: Rare earth element
Oxidant: VI th group element

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Ionic strength	Addend (catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E
							k^o	n	
.1	$2\ Ce^{+++} + S_2O_8^{--} \rightarrow 2\ Ce^{++++} + 2\ SO_4^{--}$	H_2O	$\mu = 1.25$	Ag^+	$k B [Ag^+]$	25	4.9	-3	
			2.95			"	4.3	-3	
			1.5	"	"	35	7.5	-3	
			3			"	7.6	-3	~ 10

COMMENTS

Rate determining step $Ag^+ + S_2O_8^{--} \rightarrow Ag^{+++} + 2\ SO_4^{--}$, see 732.160.

LITERATURE

W. H. Cone, *ACS* 1945, 67, 78.

OXIDATION-REDUCTION

Liquid phase

of compounds of different elements

Reductant: VIII th group element
Oxidant: VII th " "

Amounts are in M/l.
Rates are in M/l per sec.

No.	Reaction	Solvent	Ionic strength	Defined mass - action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
						k^o	n		
.1	$2\ Fe^{++} + I_2 \rightarrow 2\ Fe^{+++} + 2\ I^-$ (nitrates)	H_2O		$-dA/dt = r_1 + r_2$ $r_1 = (k_4AB + k_6A[I_3^-])/[1 + L\ (m_4 + m_6M)/A]$				See 732.780	
			$\mu =$ 0.09		25	k_4 1.5	−4		
						k_6 2.4	−4		
						m_4 1.8	−2		
						m_6 2.0	+1		
			0			k_4 2.4	−4		
						k_6 5.8	−4		
						m_4 2.8	−1		
						m_6 7.5	+1		
				$r_2 = (k'_4AB/M[H^+])/(1 + Lm'/A[H^+])$					
			0.09			k'_4 1.7	−9		
						m' 1.4	−3		
						K ~ 1	+4		
			0			k'_4 1.1	−9		
						$m',$ 3.4	−3		
						K ~ 1.5	+5		
	(at low $[I^-]$, buffer, $[H^+] = 0.02 - 0.0025$)		0.055	$-dA/dt = (k'_4AB/M[H^+])/(1+m\ A/M[H^+])$ (initial rate)		k'_4 1.3	−9		
						m 2.8	−9		

COMMENTS

Notation, Mechanism, see reverse reaction 732.780.

LITERATURE

See 732.780.

OXIDATION-REDUCTION

of compounds of different elements

Reductant: Organic compound

Oxidant: ozone

Liquid phase

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
									k^o	n
.1	$HCOOH + O_3 \rightarrow CO_2 + O_2 + H_2O$	H_2O	10^4 A =	10^4 B =	$HClO_4$	0.1	$-dA/dt=kAB$			
			25.6	16.3	μ =	0.1		0	1.3	−1
			8.2	5.6				"	1.2	−1
			2.05	14.4				"	9.0	−2
			0.99	16.3				"	5.3	−2
					$HClO_4$	0.03	"			
			2.93	18.4	μ =	0.1		"	3.4	−1
			"	19.8	+ Cl^-	1.8×10^{-5}		"	2.0	−1
			"	18.9	"	3.6×10^{-5}		"	2.0	−1
			"	19.4	"	3.0×10^{-3}		"	1.75	−1
			"	20.4	CH_3COOH	4.0×10^{-4}		"	2.2	−1
			"	18.2	"	8.0×10^{-4}		"	1.9	−1
			"	15.5	"	1.0×10^{-2}		"	1.6	−1
					$HClO_4$	0.01				
					μ =	0.1				
			2.10	17.4	+ Cl^-	$1. \times 10^{-4}$		"	5.3	−1
			4.2	17.5	"	1×10^{-3}		"	5.3	−1
			2.1	16.4	CH_3COOH	8.0×10^{-4}		"	5.3	−1
			4.2	15.7	"	1.0×10^{-2}		"	4.5	−1

742.403.

No.	Reaction	Solvent	Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
									k^o	n
.1.1	$2\,O_3 \rightarrow 3\,O_2$	H_2O	10^4A =	10^4 [HCOOH]			$-dA/dt=kA^2$			
					$HClO_4$	0.1				
			16.3	25.6	μ =	0.1		0	1.2	-1
			5.6	8.2				"	1.05	-1
			14.4	2.05				"	5.9	-2
			16.3	0.99				"	4.5	-2
			15.7	0.05				"	1.4	-2
			14.3	0.025				"	9.0	-3
					$HClO_4$	0.03				
			18.4	2.93	μ =	0.1		"	2.3	-1
			19.8	"	+ Cl^-	1.8×10^{-5}		"	5.5	-2
			18.9	"	"	3.6×10^{-5}		"	3.1	-2
			20.4	"	CH_3COOH	4.0×10^{-4}		"	7.0	-2
			18.2	"	"	8.0×10^{-4}		"	4.0	-2

COMMENTS

Reaction (.1.1) accompanies the main reaction (.1). The mechanism is represented as $HCOOH \rightarrow HCOO^- + H^+$; $HCOO^- + O_3 \rightarrow OH + CO_2^- + H_2O$; $OH + O_3 \rightarrow HO_2 + O_2$; $HO_2 + O_3 \rightarrow OH + 2\,O_2$; the inhibition, $OH + CH_3COOH \rightarrow H_2O + CH_3COO$, and $H^+ + Cl^- + OH \rightarrow H_2O + Cl$.

LITERATURE

H. Taube, *ACS* 1941, 63, 2453.

OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: **Aliphatic organic compound**

Oxidant: **VI th group element**

Amounts are in /M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$2\ CH_3OH + 2\ S_2O_8^{--} \rightarrow 2\ HCHO + 4\ HSO_4^-$	H_2O	A = 0.5 - 1.5 B = 0.015			$k A^{1/2} B^{3/2}$	79.8	1.4	-2	*	(¹)
.2	$COOHCOOH + S_2O_8^{--} \rightarrow 2\ CO_2 + 2\ H^+ + 2\ SO_4^{--}$	H_2O	A = 0.01; B = 0.005	Ag^+	2×10^{-6}	$k B [Ag^+]$	25	~ 4	0	*	(²)
.3	$3\ (CH_3)_2CHOH + 2\ CrO_3 + 6\ H^+$	H_2O	A = 0.21; 10^3B = 5.5;	$[H^+] \cdot =$	0.31	$k AB [H^+]$	40	3.4	-2	*	(³·⁴)
	$\rightarrow 3\ (CH_3)_2CO + Cr^{+++} + 6\ H_2O$		" 1.1		"		"	3.8	-2		
			0.03 5.5		"		"	2.9	-2		
			0.21 "		0.11		"	4.6	-2		
.3.1	$3\ [(CH_3)_2CDOH(55\ \%) + (CH_3)_2CHOH(45\ \%)]$	H_2O	A = 0.21; 10^3B = 5.5;	$[H^+] =$	0.31	"	"	1.8	-2	*	"
	$+ CrO_3 + 6\ H^+$		" 1.1		"		"	2.0	-2		
			0.03 5.5		"		"	1.5	-2		
			0.21 "		0.11		"	2.45	-2		

COMMENTS

(.1) The reaction 2 $S_2O_8^{--} + H_2O \rightarrow 4\ HSO_4^- + O_2$ could be disregarded. Mechanism proposed: $S_2O_8^{--} + CH_3OH \rightarrow HSO_4^- + SO_4^{\cdot -} + CH_2OH^{\cdot}$; $SO_4^{\cdot -} + CH_3OH \rightarrow HSO_4^- + CH_2OH^{\cdot}$; $CH_2OH^{\cdot} + S_2O_8^{--} \rightarrow HSO_4^- + SO_4^{\cdot -} + HCHO$; 2 $CH_2OH^{\cdot} \rightarrow CH_3OH +$ HCHO. (.2) k about 500 times as great as in other Ag^+- catalyzed oxidations by $S_2O_8^{--}$. (.3) (.3.1) The ratio of the k for the *pure* $(CH_3)_2CDOH$ and $(CH_3)_2CHOH$ is calculated to $k(.3.1)/k(.3) = 0.17 \pm 0.05$.

LITERATURE

(1) P.D.Bartlett, J.D.Cotman, Jr., *ACS* 1949, **71**, 1419. (2) C.V.King, *ACS* 1928, **50**, 2089. (3) F.H.Westheimer, N.Nicolaides, *ACS* 1949, **71**, 25.
(4) F.H.Westheimer, A.Novick, *JCP* 1943, **11**, 506.

OXIDATION - REDUCTION

of compounds of different elements

Liquid phase

Reductant: Aliphatic organic compound

Oxidant: VII th group element

Amounts are in M/l.

Rates are in M/l per sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.1	$5\ HCOOH + 2\ HIO_3 \rightarrow 5\ CO_2 + I_2 + 6\ H_2O$	H_2O	A = 0.1 - 0.3	H_2SO_4	0.01 - 0.3	See reaction (.1.1)					*	(2)
.1.1	$HCOOH + I_2 \rightarrow CO_2 + HI$	"	A = 0.1 - 0.3; I^- = 0.001 - 0.3	H_2SO_4	0.01 - 0.3	$k_1 B[HCOO^-] = k_1' BA/[H^+] f^2$					*a	
							60					
							k_1	1.7	0			
							k_1'	2.5	-4			
		"	"	"	"	$(k_2/f)[AB[IO_3^-][H^+](1 + aA)]$					*b	
							60					
							k_2	3.3	-4			
							a	5.7	0			
.2	$COOHCOOH + Cl_2 \rightarrow 2\ CO_2 + 2\ Cl^- + 2\ H^+$	H_2O	A = 0.01 - 0.05; HCl = 0.1 - 0.5;			$kK[COOHCOO^-]B/[H^+][Cl^-]$					*	(7)
					μ =		10					
					0.25 - 0.5		k	4.2	0			
					"		kK	1.85	-3			

742.471.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.2	$COOHCOOH + Cl_2$				$\mu =$		15					
	$\rightarrow 2 CO_2 + 2 Cl^- + 2 H^+$				0.25 - 0.5		k	6.55	0			
	(continued)				"		kK	3.7	-3			
					2		k	7.3	0			
					"		kK	4.0	-3			
							20					
					0.25 - 0.5		k	1.05	+1			
							kK	7.35	-3			
					0.7		k	1.15	+1			
							kK	7.7	-3	15		
.2.1	$COOHCOO^- + HClO$	H_2O	as (.2)				as (.2)				*	(7)
	$\rightarrow 2 CO_2 + Cl^- + H_2O$											
.3	$COOHCOOH + Cl_2$	H_2O	$HCl = 2$; $[Mn^{++}] = 0.01$	Mn^{+++}	$10^4[Mn^{+++}]$	$k\,[Mn^{+++}]$					*	(17)
	$\rightarrow 2 CO_2 + 2 Cl^- + 2 H^+$		$10^2B \sim 0.6 - 0.7$; $10^2A = 0.5 - 1$		0.27 - 0.6		25.2	1.4	-1			
			0.16		0.27		"	1.2	-1			
			0.10		"		"	9.7	-2			
			0.03		"		"	4.8	-2			
			0.016		"		"	2.7	-2			
			$\sim 0.5 - 1.0$; 0.8 - 8.0		0.11 - 0.27		34.7	3.7	-1			
			0.42; 0.16		0.11		"	2.9	-1			
			0.47; 0.03		"		"	1.4	-1			
.3.1	$MnC_2O_4^+ \rightarrow Mn^{++} + C_2O_4^-$		See (.5.2)									

No.	Reaction	Solvent	Amount of reactant		Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$ k^{o}	n	E	Comments	Literature
.4	$COOHCOOH + Cl_2 \rightarrow$	H_2O	A =	$;10^2$B =	Fe^{+++}; $+ d[Fe^{+++}]/dt = R$							*	(^{16})
	$2\ CO_2 + 2\ Cl^- + 2\ H^+$		0.2	1.7		$R = 6.7 \times 10^{-6}$	$kAR^{1/2}$	25	5.2	-2			
			"	0.7		5.1×10^{-5}		"	3.1	-2			
			"	"		9.2×10^{-9}		"	5.2	-2			
			0.02	"		1.6×10^{-7}		"	5.0	-2			
			0.007	0.14		6.0×10^{-8}		"	5.2	-2			
			0.39	0.11		1.85×10^{-7}	$k'(ABR)^{1/2}$	25	7.15	-1			"
			"	0.06		"		"	7.15	-1			
			0.2	0.05		3.7×10^{-8}		"	7.3	-1			
.5	$COOHCOOH + 2\ Mn^{+++} \rightarrow$	H_2O					kB; $k = k_1 + (k_2[H^+]/A)$						(^{6})
	$2\ CO_2 + 2\ Mn^{++} + 2\ H^+$							14					
								k_1	4.0	-4			
								k_2	~ 8	-4			
								20					"
								k_1	8.5	-4	25		
								k_2	~ 1.4	-3			
.5.1	$COOHCOOH + 2\ Mn^{+++} \rightarrow$	H_2O			kB; $k = [2\ k_1/(1 + b + c)] + 2\ k_2/(1 + b + c)] + [2\ k_3c/(1 + b + c)]$								
	$2\ CO_2 + 2\ Mn^{++} + 2\ H^+$		$(COOH)_2 = 0.05 - 0.15$					25.2				*	(^{18})
			$[C_2O_4^{--}] = 0.02 - 0.08$		$\mu = 2$			k_1	1.95	-1	18.3		
			$HCl = 0.1 - 0.4$					k_2	7.7	-4			
			$(COOH)_2 = 0.02 - 0.44$					k_3	3.3	-4	22.2		
			$[C_2O_4^{--}] = 0.08 - 0.2$		$\mu = 0.65$						(18 - 36°C)		
			$Mn^{++} = 0.05$				$b = 4.02 \times 10^{6}[C_2O_4^{--}]$						
							$c = 2.87 \times 10^{9}[C_2O_4^{--}]^2$						

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.5.2	$MnC_2O_4^+ \rightarrow Mn^{++} + C_2O_4^-$	H_2O				k_1A	15.0 25.2 34.7	5.85 1.95 4.80	-2 -1 -1	 18.3	*	(17) (18)
.5.3	$Mn(C_2O_4)_2^-$ $\rightarrow Mn^{++} + C_2O_4^- + 2\ C_2O_4^{--}$	H_2O				k_2A	25.2	7.7	-4		*	(18)
.5.4	$Mn(C_2O_4)_3^{---}$ $\rightarrow Mn^{++} + C_2O_4^- + 2\ C_2O_4^{--}$	H_2O				k_3A	25.2	3.3	-4	22.2	*	(18)
.6	$5\ C_2O_4^{--} + 2\ MnO_4^- + 16\ H^+$ $\rightarrow 10\ CO_2 + 2\ Mn^{++} + 8\ H_2O$	H_2O	See Comments									

COMMENTS

(.1) (.1.1) Reaction (.1) proceeds over (.2.1), followed by $5\ HI + HIO_3 \rightarrow 3\ I_2 + 3\ H_2O$ (see 722.770). Reaction (.1.1) may proceed over two paths. For the direct path *(a)*, $k_1 = k_1'/K$, where $K = [HCOO^-][H^+]/[HCOOH] \doteq 1.55 \times 10^{-4}$ at 60°C; temperature coefficient near 55°C, 2.78. The indirect path *(b)* is $I_2 + H_2O \rightleftarrows HIO + HI$; $HCOOH + HIO \rightarrow CO_2 + HI + CO_2$; the total rate approaches *(b)* when $[IO_3^-]$ and $[H^+]$ are large and $[I_2]$ is small; f = activity coefficient of HCOOH. **(.2) (.2.1)** Reaction (.2) proceeds over the equilibrium $Cl_2 + H_2O \rightleftarrows HClO + H^+ + Cl^-$ (at $\mu = 0$, $10^4K = 2.58, 3.28, 4.06$, at 10°, 15°, 20°C), followed by the rate determining step (.2.1). $[COOHCOO^-]$ from the first dissociation constant $\log K_1 = \bar{2}.756 + 0.42\mu^{1/2} - 0.275\mu$. **(.3) (.3.1)** The mechanism of the reaction is represented as

COMMENTS *(continued)*

COOHCOOH + $Mn^{+++} \rightleftarrows MnC_2O_4^+ + 2\ H^+$; COOHCOOH + $MnC_2O_4^+ \rightleftarrows Mn(C_2O_4)^- + 2\ H^+$; (.3.1) $MnC_2O_4^+ \rightarrow Mn^{++} + C_2O_4^-$, rate determining, which see under (.5.2). (.4) Fe^{+++} is added at the rate R (M/l per sec, converted from M/l per min). The rate constants k and k' (converted from min to sec) are, with respect to time, obviously of the dimension $(\text{time})^{-1/2}$. The reaction is represented as a chain reaction, following a scheme COOHCOOH $\rightleftarrows HC_2O_4^- + H^+$ (K); $Fe^{++} + Cl_2 \rightarrow FeCl^{++} + Cl$ (k_1); $HC_2O_4^- + Cl \rightarrow H^+ + Cl^- + C_2H_4^-$ (k_2); $C_2O_4^- + Cl_2 \rightarrow Cl + Cl^- + 2\ CO_2$ (k_3); $Cl + C_2O_4^- \rightarrow Cl^- + 2\ CO_2$ (k_4); $Cl + Cl \rightarrow Cl_2$ (k_5); $k = k_2K/k_5^{1/2}([H^+] + K)$; $k' = (k_2k_3/2\ k_4)^{1/2}(K/(K + [H^+]))^{1/2}$. The reaction is inhibited by NH^+, NO^{++}, Mn^{++}, Ce^{+++}. Further data, and chain length computations, see original (16).

(.5.1) (.5.2) (.5.3) (.5.4) For empirical first-order constants (kB) of reaction (.5.1), see original (15). This reaction is representable by the succession of reactions (.5.2) (.5.3) (.5.4), followed by the rapid step $Mn^{+++} + C_2O_4^- \rightarrow Mn^{++} + 2\ CO_2$. The coefficients of b and c are ratios of equilibrium constants (see in original). Reaction (.5.2) is also the rate determining step for (.3). (.6) No single rate equation possible. For proposed mechanisms, including the the steps of (.5.1) [(.5.2) (.5.3) (.5.4)] see (15) (10) (8) (9) (5) (3) (17) (18) (6) (11). Newer mechanism proposed by (1).

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