SUPPLEMENT 1 TO 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 issued 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.

This supplement includes additional tables, additions to tables already printed, and revised sheets canceling and replacing parts of the present tables. Further supplementary installments will be issued at future dates as new or revised data material warrants it.

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NATIONAL BUREAU OF STANDARDS, A. V. Astin, Director

Tables of Chemical Kinetics

Homogeneous Reactions

National Bureau of Standards

A. V. Astin, Director

National Research Council, Committee on Tables of Constants
Subcommittee on Chemical Kinetics

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Supplement 1 to National Bureau of Standards Circular 510

Issued November 14, 1956

Foreword

This volume is the first supplement to Tables of Chemical Kinetics, Homogeneous Reactions, issued as NBS Circular 510 in 1951. The original project was supported jointly by the National Bureau of Standards and the National Research Council in cooperation with Princeton University. The financial support for the present supplement was provided by the Office of Ordnance Research, Department of the Army. However, the National Bureau of Standards and the National Research Council through the NRC Committee on Tables of Constants assumed the initial responsibility and, for the most part, the same supervision over this compilation as before. It is therefore appropriate for the Bureau to publish this first supplement, thus maintaining, at this time, the continuity and availability of the tables for the convenience of their many users in scientific and industrial work.

The project is continuing under the direction of Prof. C. H. Stauffer at Worcester Polytechnic Institute with general supervision by the Subcommittee on Kinetics of Chemical Reactions, NRC Division of Chemistry and Chemical Technology, and with the financial sponsorship of the Office of Ordnance Research. Inquiries concerning the status of the continuing work should be sent to Prof. Stauffer.

A. V. Astin, *Director.*

Contents

CORRECTIONS TO 1951 VOLUME

Page XV - First line should be *ACA*, American Chemical Abstracts not *ACJ*, American Chemical Journal.

Page 9 - **103.000** LITERATURE, second reference should be E. Cremer, M. Polanyi, *ZPC*^{B} 1933, **21**, 459.

Page 17 - **112.440** LITERATURE, reference ([7]) should be G. C. Wilkes not G. V.

Page 28 - **122.440** LITERATURE, ([1]) should be *JCC* 1930 not *JCP* 1937; ([3]) should be K. Nozaki, not R.

Page 55 - **172.441** (.1), third addend should be $C_6H_5CH_2N(C_2H_5)_2$ not $C_6H_5CON(C_2H_5)_2$. For fourth addend k' should be 2.42 and -4 not -3 for power of ten.

Page 80 - **202.441** COMMENTS, column 1 line 3, the Goldschmidt equation should be: $k = \frac{1}{t[H^+]r}\left[(a + r)\ln\frac{a}{a-x} - x\right]$.

Page 81 - **202.441** LITERATURE, reference ([3]) *ZPC* should be in italics, not bold.

Page 100 - **212.441** (.9), k^o and n should be 1.09 and -4 not 4.8 and -5. To literature column add ([4a]).

Page 115 - **212.441** SOLVENTS, fifth line should be 65 wt % $(CH_3)_2CO$ not 56 wt %.

Page 116 - **212.441** LITERATURE, reference ([2]) insert *ACS* after V. K. LaMer; insert ([4a]) H. M. Dawson, W. Lowson, *CSL* **1928**, 2146; ([7]) should be H. B. Watson not H. W. ([22]) should be 62 not 52.

Page 120 - **212.442** (.21), Reaction column should be $2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3COOCH_3 + OH^-$.

Page 124 - **212.442** (.42), Reaction column should be $o\text{-}NO_2C_6H_4COOC_2H_5$ not $o\text{-}FC_6H_4COOC_2H_5$. Literature column should be ([1]) not ([5]).

Page 124 - **212.442** (.44), Reaction column should be $p\text{-}FC_6H_4COOC_2H_5$ not $p\text{-}C_6H_4COOC_2H_5$.

Page 132 - **212.443** LITERATURE, ([1]) should be E. Tommila not E. Tomila.

Page 137 - **212.461** LITERATURE, should be L. H. Cretcher not L. M. Fletcher.

Page 155 - **212.471** (.54), Reaction column should be $CH_2(COO^-)Cl + H_2O \longrightarrow CH(COO^-)(OH_3^+) + Cl^-$ not Br^-.

Page 181 - **212.473** LITERATURE, should be J. F. Bunnett not T. F. Bunnet.

Page 249 - **242.453** LITERATURE, ([13])([14]) add year 1942.

Page 292 - **311.700** LITERATURE, ([13]) should be H. A. Taylor not A. H. ([14]) should be *JPC* not *JCP*.

Page 317 - **312.471** LITERATURE, ([17]) should be Medd not Medt.

Page 364 - **332.756** LITERATURE, ([1]) should be J. F. Bunnett not J. F. Bunnet.

Page 371 - **332.771** (.1), solvent = H_2O amount of reactant column should be A = 0-0.06; B = 0-0.15; L = 0-0.06; M = 0-0.1 not 0.035-0.060; $k = k^o \times 10^n$ column temp = 20.4 k^o should be 4.26 not 4.36; A^o column should be 1.8 not 1.7; comments column add *.

Page 379 - **332.771** COMMENTS, add: (.1) measured in competition with hydrolysis reactions $CH_3Br + H_2O \longrightarrow$ and $CH_3I + H_2O \longrightarrow$ and calculation dependent on specific rate constants for these reactions, see 212.471 (.2) (.3). Oxidation of I^- also occurs to slight extent.

Pages 429-432 - **511.443** Add literature column (.1), ([1])([7]); (.2), ([1])([7]); (.3), ([9]); (.4), ([6]); (.5), ([5]); (.6), ([3]); (.7), ([8]); (.8), ([8]); (.9), ([6]); (.10), ([4]); (.11), ([2]); (.12), ([5]); (.13), ([3]); (.14), ([9]); (.15), ([8]).

CORRECTIONS TO 1951 VOLUME *(continued)*

Page 432 - 511.443 LITERATURE should be: ([1]) C.C. Coffin, *CJR* 1931, **5B**, 636. ([2]) C.C. Coffin, W.B. Beazley, *CJR* 1937, **15B**, 229. ([3]) C.C. Coffin, J.R. Dacey, N.A.D. Parlee, *CJR* 1937, **15B**, 247. ([4]) J.C. Cornell, J.R. Dacey, C.C. Coffin, *CJR* 1940, **18B**, 410. ([5]) J.R. Dacey, C.C. Coffin, *CJR* 1932, **6B**, 417. ([6]) J.R. Dacey, C.C. Coffin, *CJR* 1937, **15B**, 260. ([7]) J.R. Dacey, C.C. Coffin, *JCP* 1939, **7**, 315. ([8]) N.A.D. Parlee, J.C. Arnell, C.C. Coffin, *CJR* 1940, **18B**, 223. ([9]) N.A.D. Parlee, J.R. Dacey, C.C. Coffin, *CJR* 1937, **15B**, 254.

Page 442 - 521.471 (.6) Reaction column should be: $(C_2H_5)(CH_3)_2CCl \longrightarrow C_5H_{10} + HCl$ not Br. Temperature column should be 270-327 not 372.

Page 443 - 521.477 (.1) Products not determined by ([3]) and are probably CH_2CHCl and HCl, see 521.471. (.2) Products not determined by ([3]) and are probably CH_2CHBr and HBr, see 521.471.

Page 536 - 571.441 LITERATURE, ([6]) should be C.N. Hinshelwood, not F.N., ([14]) should be *JPC* not *JCP*.

Page 561 - 621.411 Upper right hand corner should be gas phase not liquid phase. Reaction (.2) E column should be 43 not 43.1, A^o column should be 1.3 not 1.24, n column should be 10 not 6; LITERATURE column add ([3]).

Page 562 - 621.411 LITERATURE, add ([3]) A. Wheeler, R.N. Pease, *ACS* 1936, **58**, 1665.

Page 604 - 622.477 LITERATURE, ([11]) should be *BDC* not *Ber.* ([25]) should be G. Williams not D.M.

Page 605 - 632.441 (.1) Reaction column should be $\underbrace{CH_2CH_2CH_2COO}^{-} + OH^- \longrightarrow HOCH_2CH_2CH_2COO^-$. (.2) Reaction column should be $CH_3\underbrace{CHCH_2CH_2COO}^{-} + OH^- \longrightarrow CH_3CH(OH)CH_2CH_2COO^-$. (.3) Reaction column should be $o\text{-}\underbrace{C_6H_4COOCH_2}^{-} + OH^- \longrightarrow o\text{-}HOCH_2C_6H_4COO^-$.

Page 606 - 632.441 (.3) Reaction column product should be $o\text{-}HOCH_2C_6H_4COO^-$ not $C_6H_5COOCH_2O^-$. (.4) Reaction column product should be $5\text{-}NH_2\text{-}2\text{-}HOCH_2C_6H_3COO^-$ not $NH_2C_6H_4COOCH_2O^-$.

Page 657 - 712.770 (.2) Reaction column should be $Cl_2 + OH^- \longrightarrow HOCl + Cl^-$ not Cl_3^-.

Page 667 - 722.660 (.1) Defined mass action column add = dB/dt. COMMENTS third line should begin, of A, not of B.

Page 674 - 722.770 LITERATURE, ([10]) should be W.C. Bray, *ZAC* 1906, **48**, 217 which is also ([11]). ([30]) should be A. Skrabal, *MHC* 1907, **28**, 319.

Page 679 - 732.480 (.1)(.1.1) Defined mass action law column add = $-dA/dt$.

Page 694 - 732.570 (.8) LITERATURE column add ([2a])([15]).

Page 696 - 732.570 LITERATURE, ([2]) should be W.C. Bray not N.C. Add ([2a]) W.C. Bray, *JPC* 1905, **9**, 578.

Page 707 - 732.701 LITERATURE, ([18]) should be R.S. Livingston, *ACS* 1926, **48**, 53.

Page 711 - 732.750 (.1) LITERATURE column add ([1a]). Literature add ([1a]) W.C. Bray, *JPC* 1905, **9**, 578.

Page 717 - 732.780 (.1) Reaction column should be $2I^- + 2Fe^{+++} \longrightarrow I_2 + 2Fe^{++}$.

Page 728 - 742.471 (.3) LITERATURE column should be ([16]) not ([17]).

Page 729 - 742.471 (.5.1) LITERATURE column should be ([17]) not ([18]).

Page 730 - 742.471 (.5.2)(.5.3)(.5.4) LITERATURE column should be ([17]) not ([18]).

Page 731 - 742.471 COMMENTS, last line take out ([18]) put in ([16]).

SUPPLEMENT TO TABLES OF CHEMICAL KINETICS HOMOGENEOUS REACTIONS

PREFACE

A description of these Tables and definition of the terms and abbreviations used may be found in the introduction to the 1951 publication. An attempt has been made in preparing this Supplement to give a complete yet critical coverage of recent work in the portion of chemical kinetics involving, Rearrangement or Isomerization, Condensation and Solvolysis. The other classifications of the 1951 Tables and some new sections are in preparation for future publication. Values of the rate constants which have been tabulated vary greatly in the probable accuracy of the individual values. For each reaction, what has been considered to be the best value has been listed with superfluous figures rounded off. Where two investigators have obtained significantly different values and there is insufficient evidence to favor one, both values have been listed.

Method. In compiling this Supplement, a search has been made of the chief American and British periodicals for the period from the closing date of the 1951 edition to December 1953 or later if indicated at the lower right hand corner of any table. Any article cited as a reference in these primary sources was also investigated if it had not been included in the 1951 Tables. References mentioned in these secondary articles were also investigated if they had not been included in the previous work. More than half of the articles included in this supplement were published prior to 1951. Although this method cannot give an absolutely complete coverage of valuable data, a more complete literature search on one section of the Tables uncovered only 7 pertinent references in addition to the 83 which had been included. This is not intended to indicate that the Supplement has a 92 % coverage, but to give some indication of the limitations of these tables. Anyone knowing of significant material which has not been included will be doing a service by notifying Dr. Charles H. Stauffer, Project Director, Dept. of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts.

Acknowledgments. The Director and his associates gratefully acknowledge the financial assistance provided by the Office of Ordnance Research, Department of the Army which made this supplement possible. The Director of the Project gratefully acknowledges the able assistance of

his associates and collaborators, the help of the National Bureau of Standards, the National Academy of Sciences, the Committee on Tables of Constants, and its chairman, Dr. A.V. Astin, the Subcommittee on Chemical Kinetics and its chairman, Prof. L.P. Hammett, and Dean H.S. Taylor of Princeton University whose encouragement and assistance were so helpful in continuing the project after the unfortunate death of Dr. N. Thon, Editor of the 1951 edition.

C.H. Stauffer

SUBJECT INDEX

1oo REARRANGEMENT - ISOMERIZATION

SUBJECT INDEX *(continued)*

SUBJECT INDEX *(continued)*

SUBJECT INDEX *(continued)*

SUBJECT INDEX *(continued)*

ALPHABETICAL INDEX

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.

ALPHABETICAL INDEX *(continued)*

ALPHABETICAL INDEX *(continued)*

Tables of Chemical Kinetics

Homogeneous Reactions

Homogeneous Reactions

102.000

ORTHO-PARA CONVERSION

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Refer to 1950 No.	Reaction	Medium (Solvent)	Method	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
.9	.2	$o\text{-}H_2 \rightleftarrows p\text{-}H_2$	H_2O	thc	sat. .25-1 atm.	X = KOH	.045-0.88	$k(A-A_e)X$	80	1.4	-3				*	(3)
									100	9.3	-3					
									110	2.0	-2	24	4.7	13		
			NH_3	thc	sat . 50-60 cm.	X = KNH_2	.026 - .00035	$k(A-A_e)X$	-50	1.3	+2				*	(2)
			quinoline	thc	sat. 50 cm.	X = CH_3COOCu	.01-.06	$k(A-A_e)X^2$	60	3.4	-1				*	(1)
									80	1.2	0					
									100	4.4	0	16	1.1	10		
.10	.3	$o\text{-}H_2 \longrightarrow p\text{-}H_2$	H_2O	from .9	sat. .25-1 atm.	X = KOH	.045-0.88	k_1AX	80	3.6	-4				*	(3)
									100	2.3	-3					
									110	5.0	-3	24	1.2	13		
			NH_3	from .9	sat. 50-60 cm.	X = KNH_2	.026 - .00035	k_1AX	-50	3.3	+1				*	(2)
			quinoline	from .9	sat. 50 cm.	X = CH_3COOCu	.01-.06	k_1AX^2	60	8.5	-2				*	(1)
									80	3.0	-1					
									100	1.1	0	16	2.8	9		

No.	Refer to 1950 No.	Reaction	Medium (Solvent)	Method	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	.4	$p\text{-}H_2 \longrightarrow o\text{-}H_2$	H_2O	from .9	sat. .25-1 atm.	X = KOH	.045-0.88	k_2AX	80	1.0	-3				*	(3)
									100	7.0	-3					
									110	1.5	-2	24	3.5	13		
			NH_3	from .9	sat. 50-60 cm.	X = KNH_2	.026 - .00035	k_2AX	-50	1.0	+2				*	(2)
			quinoline	from .9	sat. 50 cm.	X = CH_3COOCu	.01-.06	k_2AX^2	60	2.6	-1				*	(1)
									80	9.0	-1					
									100	3.3	0	16	8.2	9		

COMMENTS

Reaction: **(.9)** Pseudo first order rate constants measured as function of distance from equilibrium by Pirani gage technique. Observed rate constants corrected for volumes of liquid and gas phase. Solubility determined for each temperature. Tabulated rate constants obtained from slope of straight line plot of corrected first order constants against catalyst concentration (3) (2), and against square of catalyst concentration (1). Reaction shown to be homogeneous by increasing S/V with ground glass and non-photochemical (3). Second order rate constants of (2) show considerable scatter but no apparent drift. Plot of pseudo first order rate against $[NH_2^-]$ calculated from dissociation constant at -33° gives straight line going through origin. Indicating negligible catalysis by solvent. **(.10)** **(.11)** See comments under (.2) (.3) (.4) "Tables" 1950. E_1 assumed equal to E_2 since k_1/k_2 is essentially independent of temperature above -40°C.

LITERATURE

(1) W.K. Wilmarth, M.K. Barsh, *ACS* 1953, 75, 2237. (2) W.K. Wilmarth, J.C. Dayton, *ACS* 1953, 75, 4553. (3) W.K. Wilmarth, J.C. Dayton, J.M. Flournoy, *ACS* 1953, 75, 4549.

RACEMIZATION

Sterically hindered optical isomers

Gas phase

Amounts in mm of Hg.
Rates are in sec.

No.	Optical Isomer	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	ΔH_a	ΔS_a	Literature
	Substituted diphenyls											
.1	l-2,2'-$(NH_2)_2$-6,6'-$(CH_3)_2C_6H_3C_6H_3$	50-150	k A	342 355 387	2.4 4.6 3.4	-6 -6 -5	45.1	2.3	10	45.6	-11.5	(2) (1) (2)

COMMENTS

Rate of inversion tabulated equals one half rate of racemization. For rate of liquid phase reaction see 112.443.18. Enthalpy and entropy of activation calculated by (1).

LITERATURE

(1) F.W. Cagle, H. Eyring, *ACS* 1951, **73**, 5628. (2) G.B. Kistiakowsky, W.R. Smith, *ACS* 1936, **58**, 1043.

RACEMIZATION
C, H, O compounds

Method: polarimetry

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend = X (Acid Catalyst)	Amount of Addend = X	Addend = Y (Base Catalyst)	Amount of Addend = Y	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
.16	d-$C_2H_5CH(CH_3)CH_2CH_2CH_3$	pure liquid		H_2SO_4	saturated with 95.3 wt %			kA	60	1.5	-5				*	(2)
.16.1	d-$C_2H_5CH(CH_3)CH_2CH_2CH_3$	pure liquid		$3H_2SO_4$: $1D_2SO_4$	saturated with 95 %			kA	44 55 66	9 1.5 2.8	-6 -5 -5	11	4	2	*	(2)
.16.2	d-$C_2H_5CH(CH_3)CH_2CH_2CH_3$	pure liquid		D_2SO_4	saturated with 95 %			kA	60	1.3	-5				*	(2)
.17	d-$C_2H_5CH(CH_3)(CH_2)_3CH_3$	pure liquid		HSO_3Cl and DSO_3Cl	saturated			kA	-78 -50	1 2	-4 -4				*	(2)
.17.1	d-$C_2H_5CH(CH_3)(CH_2)_3CH_3$	pure liquid		$C_2H_5SO_3H$ and $C_2H_5SO_3D$	saturated			kA	60 100	<1 10	-7 -7				*	(2)
.18	d-$C_2H_5CH(CH_3)(CH_2)_7CH_3$	pure liquid		$3H_2SO_4$: $1D_2SO_4$	saturated with 95 %			kA	60	3	-7				*	(2)

SUPPLEMENT 1953

No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend = X (Acid Catalyst)	Amount of Addend = X	Addend = Y (Base Catalyst)	Amount of Addend = Y	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.19	α-d-$(CH_3)_4C_6H_8O_6$ (tetra methyl glucose)	H_2O		H_2O		OH^-		k AXY	25	4.0	0		(4)
		"		"		C_5H_5N		"	25	1	-4		
		"		"		H_2O		"	25	1	-8		
		"		H_3O^+		"		"	25	2	-4		
		acetone				hydroxy quinoline		k AY^2	25	2.7	-4		(4)
		C_6H_6	.09					k A	25	1.3	-6	*	(4)
				C_6H_5OH	0-0.1			k AX^2	25	8.1	-3		
				C_6H_5OH	0-0.1	$2\text{-}CH_3OC_5H_4N$		k AXY	25	1	-3		
				C_6H_5OH	0-0.1	$2\text{-}CH_3C_5H_4N$		k AXY	25	1	-2		
				C_6H_5OH	0-0.1	C_5H_5N	0-0.18	k AXY	25	2.1	-2		
		C_6H_6	.09			C_5H_5N	0-0.18	k A^2Y	25	5	-4		
		"				$4\text{-}NH_2C_5H_4N$		k A^2Y	25	2.7	-1		
		"				$(C_2H_5)_3N$		k A^2Y	25	4	-2		
		C_6H_6	.09	$p\text{-}NO_2C_6H_4OH$	.05	C_5H_5N	0-0.18	k AXY	25	1.1	0		
		"		$2,4\text{-}(NO_2)_2C_6H_3OH$	.05	C_5H_5N	0-0.18	k AXY	25	5	-2		
.20	α-1,2,3,4,6-$(CH_3COO)_5C_6H_7O$ ($\rightleftarrows$ β-) (glucose penta acetate)	CH_3COOH		H_2SO_4	.177			k $(A-A_\infty)X$	25	6.2	-5	*	(3)
					.354				25	7.1	-5		
					.708				25	4.5	-5		
		CH_3COOH		$HClO_4$	.03-.36			k $(A-A_\infty)X$	25	1.0	-3		

No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend = X (Acid Catalyst)	Amount of Addend = X	Addend = Y (Base Catalyst)	Amount of Addend = Y	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
.20	α-1,2,3,4,6-$(CH_3COO)_5C_6H_7O$ ($\rightleftarrows$ β-) (glucose penta acetate) *(continued)*	AA50*	.05-.2	H_2SO_4	.05-1.0			$k(A-A_\infty)X$	0	4.1	-5				*	(1)
									18	5.1	-4					
									25	1.1	-3					(1) (3)
									33	2.8	-3	20	5	11		
					$10^4X =$											
		AA*	.05-.2	$HClO_4$	17.8			$k(A-A_\infty)X$	25	6.2	-1					(3)
					14.2					6.9	-1					
					8.9					6.9	-1					
					5.3					6.4	-1					
					1.8					6.2	-1					
		AB*	.05-.2	H_2SO_4	.2-.5			$k(A-A_\infty)X$	25	1.7	-2				*	(1)
.21	α-1,2,3,4,6-$(CH_3COO)_5C_6H_7O$ ($\rightarrow$ β)	AA50*	.05-.2	H_2SO_4	.05-1.0			k_1AX	0	5.9	-6				*	(1)
									18	8.4	-5					
									25	1.9	-4					
									33	5.2	-4	22.5	5.9	12		
.22	β-1,2,3,4,6-$(CH_3COO)_5C_6H_7O$ ($\rightarrow$ α)	AA50*	.05-.2	H_2SO_4	.05-1.0			k_2AX	0	3.5	-5				*	(1)
									18	4.3	-4					
									25	9.0	-4					
									33	2.3	-3	21	2.7	12		
.23	*l*-$C_6H_5CH(CH_3)CH(CH_3)O$-*p*-$SO_2C_6H_4CH_3$	C_2H_5OH	0.12					kA	75	6.1	-5				*	(6)
		CH_3COOH	0.1						50	1.11	-5					
									75	2.3	-4	26				
				H_2O	0.3				50	1.8	-5					
						CH_3COONa	0.12		75	3.3	-4					
						NaOTs*	0.09		75	2.5	-4					

No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend = X (Acid Catalyst)	Amount of Addend = X	Addend = Y (Base Catalyst)	Amount of Addend = Y	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
.23	l-$C_6H_5CH(CH_3)CH(CH_3)O$-p-$SO_2C_6H_4CH_3$ *(continued)*	HCOOH	0.1					k A	25	2.6	-4					(6)
.24	d-*trans*-2-$CH_3COC_6H_{10}OSO_2C_6H_4CH_3$ (2-acetoxy cyclohexyl tosylate)	CH_3COOH	0.06			CH_3COOK	0.07	k A	75	1.34	-5				*	(5)
.25	d-endonorbornyl p-brombenzenesulfonate	C_2H_5OH	0.2-0.3					k A	75	6.0	-5				*	(7)
		Ac75*	0.2-0.3						75	2.3	-4					
		CH_3COOH	0.2-0.3						75	1.6	-4					
.26	d-exonorbornyl p-brombenzenesulfonate	C_2H_5OH	0.2						25	7.8	-5				*	(7)
		Ac75*	0.2						25	7.6	-4					
		CH_3COOH	0.2			CH_3COOK	0.25		25	4.2	-4					

SOLVENTS

AA50* 50:50 mixture of acetic acid and acetic anhydride, mol-ratio = 1.8.

AA* Acetic anhydride 10.15 M/l and acetic acid 0.36 M/l.

AB* Acetic anhydride + (0 - 50 % Benzene).

Ac75* Acetone 75 vol % + water.

COMMENTS

Reactions: (.16) (.16.1) (.16.2) (.17) (.17.1) (.18) Rate constants calculated on basis of first order equation from a few scattered points of fractional loss of activity. Rate law not confirmed over course of reaction and probably falls off with time due to dilution of catalyst. No apparent drift in rate constant after 50 hours when acid solution replaced four times during reaction. Rate of deuteruim exchange parallels but exceeds racemization. Rate of exchange sufficient to replace all hydrogen per molecule racemized except (.18). See 302.401. (.19) Pseudo first order constants measured over course at constant pH and converted to third order constants in terms of acid and base catalyst concentrations. Observed pseudo first order constant is the sum of all acid-base combinations in reaction system, $k_o = \sum_{x,y} k_{xy} XY$. (.20) Pseudo first order constant measured in terms of distance from equilibrium which was approached from each side $\alpha \longrightarrow \beta$, $\beta \longrightarrow \alpha$, converted to second order constants in terms of acid catalyst. ([3]) shows that reaction involves inversion of terminal carbon only. In 50 vol % acetic acid, acetic anhydride ([1]) shows that addition of up to 1.0 M/l of $LiSO_4$ has no effect upon rate constant. ([3]) gives much additional data upon solvent ratio effect on rate constants. At low acetic acid concentration in acetic anhydride, reaction appears to be higher than first order in H_2SO_4. At high acetic acid concentration rate appears to be less than first order in H_2SO_4. Concentration of acetic anhydride has no measurable effect upon rate constant demonstrated by dilution with benzene up to 50 vol %. Rate constants decreased markedly by, butyl ether, and dioxane. Slow side reaction between acetic anhydride and sulfuric acid decreases catalyst activity unless solutions are freshly prepared. (.21) (.22) Rate constants determined from (.20) which is sum of rate constants for forward and reverse reactions, $k = k_1 + k_2$, and equilibrium constant. Second order rate constant obtained by dividing by 0.5 M/l as concentration of H_2SO_4 instead of 0.1 as listed by ([1]), correction confirmed by author. (.23) Racemization and solvolysis proceed simultaneously, see 212.461, but ratio of rate of racemization to solvolysis is solvent dependent and greater than one, for example, 1.18 in HCOOH to ~5 in CH_3COOH. (.24) (.25) Racemization and solvolysis rates identical within experimental error. (.26) Racemization rate greater than solvolysis rate by solvent dependent factor as in (.23).

LITERATURE

(1) W.A. Bonner, *ACS* 1951, 73, 2659. (2) G.S. Gordon, R.L. Burwell, *ACS* 1949, 71, 2355. (3) E.P. Painter, *ACS* 1953, 75, 1137. (4) C.G. Swain, J.F. Brown, *ACS* 1952, 74, 2536. (5) S. Winstein, R. Heck, *ACS* 1952, 74, 5584. (6) S. Winstein, K.C. Schreiber, *ACS* 1952, 74, 2165. (7) S. Winstein, D. Trifan, *ACS* 1952, 74, 1147.

RACEMIZATION

Sterically hindered optical isomers

Liquid phase

Amounts are in M/l. Rate constants are in sec.

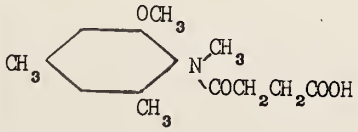
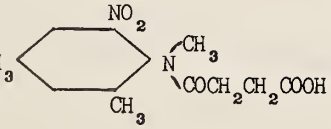
No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	ΔH_a	ΔS_a	Comments	Literature
Substituted benzene with ethylenic side chain																
.1	*l*-2,4,6-$(CH_3)_3$-5-BrC_6HCl:CHCOOH	B*	0.012			*k* A	118	2.9	-5							(2)
.2	*l*-2,4,6-$(CH_3)_3$-5-BrC_6HCl:$CHCONHCH_2COOH$	B*	0.013			*k* A	118	4.8	-5							(2)
Substituted napthalene with ethylenic side chain in α-position																
.3	*d*-1-HOOCCH:CCl-2-$CH_3C_{10}H_6$	B*	0.016-0.027			*k* A	118	8.6	-5							(3)
.4	1-$HOOCC(CH_3)$:CCl-2-$CH_3C_{10}H_6$	B*	0.015			*k* A	118	1.4	-6							(3)
Substituted diphenyls																
.5	2-NO_2-2'-CH_3-6-$HOOCC_6H_3C_6H_4$	A*				*k* A	118	3.2	-5							(9)
.6	2-NO_2-2'-CH_3O-6-$HOOCC_6H_3C_6H_4$	E*	0.025-0.044			*k* A	0	1.7	-5						*	(13)
							19	2.0	-4							
							26	6.1	-4							(18)
							35	1.4	-3	20			19.3	-9.2	(13)	(10)
		M*	~.02				24	3.6	-4							(13)
		AT*					24	4.0	-4							

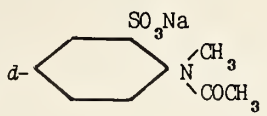
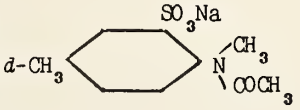
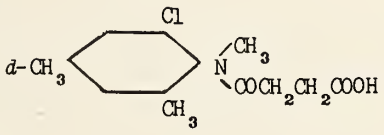
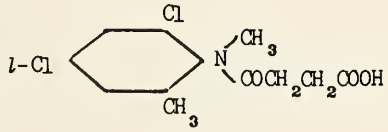
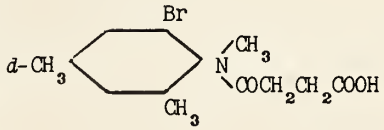
No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of Addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	ΔH_a	ΔS_a	Comments	Literature
.6	2-NO_2-2'-CH_3O-6-$HOOCC_6H_3C_6H_4$ *(continued)*	A*				k A	25	3.7	-4							
		EA*					25	3.0	-4							
		D*					25	2.5	-4							
		P*					25	4.0	-4							
.7	2-NO_2-2'-CH_3O-6-(^-OOC)$C_6H_3C_6H_4$	H_2O	~.02	NaOH	0.026		26	2.2	-4						*	(13)
		E*		$NaOC_2H_5$	0.04		26	1.3	-3							
.8	*l*-2-NO_2-2'-C_2H_5O-6-$HOOCC_6H_3C_6H_4$	M*	~0.01			k A	25	6.8	-5						*	(13)
		E*				k A	0	3.2	-6							
							18	4.2	-5							
							24	7.6	-5							
							36	2.8	-4	20			20.1	-9.4	(10)	(13)
		A*				k A	25	6.7	-5							(13)
		AT*				k A	25	7.7	-5							
		EA*				k A	25	6.5	-5							
		D*				k A	25	5.4	-5							
		P*				k A	25	8.1	-5							

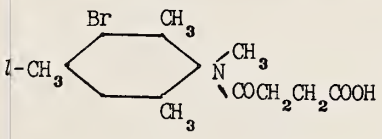
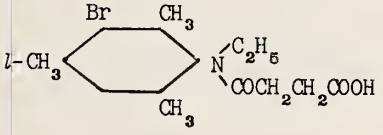
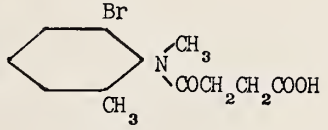
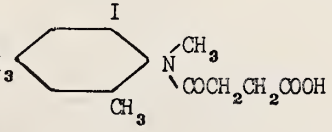
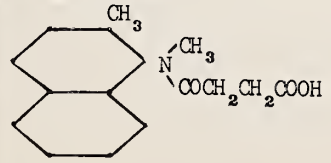
No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	ΔH_a	ΔS_a	Comments	Literature
.9	l-2-NO_2-2'-C_2H_5O-6-(^-OOC)$C_6H_3C_6H_4$	H_2O	~0.02	NaOH	0.026	k A	25	4.7	-5						*	(13)
		E*		$NaOC_2H_5$	0.04	k A	25	2.9	-4							
.10	l-2-NO_2-2'-C_3H_7O-6-$HOOCC_6H_3C_6H_4$	M*	~0.01			k A	25	4.5	-5						*	(13)
		E*				k A	0	2.4	-6						*	
							18	2.3	-5							
							25	5.6	-5							
							35	1.8	-4	20			20.0	-10.5		(10) (13)
		A*				k A	25	4.7	-5							(13)
		AT*				k A	25	5.8	-5							
		EA*				k A	25	4.4	-5							
		D*				k A	25	3.6	-5							
		P*				k A	25	5.9	-5							
.11	l-2-NO_2-2'-C_3H_7O-6-(^-OOC)$C_6H_3C_6H_4$	H_2O	~0.02	NaOH	0.026	k A	25	3.8	-5						*	(13)
		E*		$NaOC_2H_5$	0.04	k A	25	2.2	-4							
.12	2-NO_2-2',6-$(HOOC)_2C_6H_3C_6H_4$	A*				k A	118	6.4	-5							(9)
.13	2,2'-$(NO_2)_2$-6-$HOOCC_6H_3C_6H_4$	A*				k A	118	4.6	-5							(9)

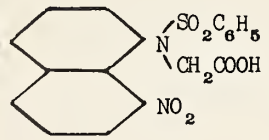
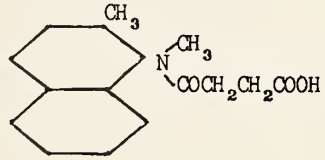
No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	ΔH_a	ΔS_a	Comments	Literature
.14	*d*-2,2'-$(CH_3O)_2$-6,6'-$(HOOC)_2C_6H_3C_6H_3$	H_2O	0.017	NaOH	0.1	*k* A	100	1.2	-5							(17)
		E*	0.011	$NaOC_2H_5$	0.2	*k* A	78	8.7	-6							
		E95*	0.015		0	*k* A	78	1.6	-6							
		A*	0.011			*k* A	118	7.8	-5							
.15	*d*-2,2'-$(CH_3O)_2$-6,6'-$(CH_3OOC)_2C_6H_3C_6H_3$	A*	0.008			*k* A	118	6.6	-5							(17)
.16	*l*-5,5'-$O(CH_2)_8O$-2,2' $(HOOC)_2C_6H_3C_6H_3$	H_2O	0.014	NaOH	0.48	*k* A	34	3.0	-4							(6)
		D*	0.016			*k* A	23	3.0	-6							
							43	3.4	-5	23			22.1	-9.2		(6) (10)
.17	*d*-5,5'-$O(CH_2)_{10}O$-2,2' $(HOOC)_2C_6H_3C_6H_3$	H_2O	0.015	NaOH	0.48	*k* A	34	2.6	-4							
		D*	0.02			*k* A	23	3.9	-6							
							43	4.8	-5	23			22.8	-6.3		(6) (10)
.18	*l*-2,2'-$(NH_2)_2$-6,6'-$(CH_3)_2C_6H_3C_6H_3$	DPE*	0.02-0.1			*k* A	307	9.0	-7							(11)
							344	9.1	-6							
							357	1.45	-5							
							385	1.00	-4	45.1	8.3	10	44.1	-11.5		(10) (11)
.19	*l*-2,2'-$(NH_2CO)_2$-6,6'-$(CH_3O)_2C_6H_3C_6H_3$	A*	0.01			*k* A	118	2.4	-5							(17)
.20	2-NO_2-2'-CH_3O-5'-CH_3-6-$HOOCC_6H_3C_6H_3$	E*				*k* A	26	5.0	-4						*	(9)

No.	Initial active compound	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	ΔH_a	ΔS_a	Comments	Literature
.21	*l*-2-NO_2-2',5'-$(CH_3O)_2$-6-HOOCC$_6H_3$C$_6H_3$	H_2O	0.013	NaOH	0.1	*k* A	26	2.1	-4						*	(19)
		E*	0.01-0.06			*k* A	0	2.1	-5							
							28	5.3	-4	19	3	10				
				$NaOC_2H_5$	0.04	*k* A	27	1.6	-3							
		A*	0.011			*k* A	26	6.7	-4							
		AT*	0.011			*k* A		4.2	-4							
.22	2,5'-$(NO_2)_2$-2'-CH_3O-6-HOOCC$_6H_3$C$_6H_3$	E*				*k* A	26	1.6	-4						*	(9)
.23	*l*-2,4'-$(NO_2)_2$-6,2'(HOOC)$_2$C$_6H_3$C$_6H_3$	H_2O	~0.05	Na_2CO_3	1	*k* A	74	2.5	-5							(12)
							98	3.5	-4	26	8	11	25.7	-4.2	(10)	(12)
.24	*l*-2-NO_2-2'-Cl-5'-CH_3-6-HOOCC$_6H_3$C$_6H_3$	H_2O	0.015-0.022	NaOH	0.1	*k* A	80	2.3	-6							(18)
							100	2.6	-5	32	1.4	14				
		E*	0.021	$NaOC_2H_5$	0.5	*k* A	78	3.3	-6							
		A*	0.032			*k* A	118	3.7	-5							
		B*	0.026			*k* A	117	4.1	-5							
.25	2-NO_2-2'-CH_3O-5'-Cl-6-HOOCC$_6H_3$C$_6H_3$	E*				*k* A	26	1.9	-4							(9)
.26	*l*-2-NO_2-2'-Br-5'-CH_3-6-HOOCC$_6H_3$C$_6H_3$	H_2O	0.021	NaOH	0.1	*k* A	100	1.6	-6							(18)
		E*	0.013	$NaOC_2H_5$	0.5	*k* A	78	2.5	-6							

No.	Initial active compound	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	ΔH_a	ΔS_a	Comments	Literature
.26	*l*-2-NO_2-2'-Br-5'-CH_3-6-$HOOCC_6H_3C_6H_3$ *(continued)*	A*	0.017			*k A*	118	1.8	-6							
		B*	0.031			*k A*	117	1.3	-6							
.27	3-NO_2-2'-CH_3O-5'Br-6-$HOOCC_6H_3C_6H_3$	E*				*k A*	26	1.8	-4							(9)
.28	*d*-2,2'-I_2-4,4'-$(HOOC)_2C_6H_3C_6H_3$ *or*	H_2O	0.013	NaOH	0.1	*k A*	25	4.0	-5							(16)
	l-2,2'-I_2-4,4'-$(HOOC)_2C_6H_3C_6H_3$	EA*	0.02			*k A*	25	4.6	-5							
		D*	0.008-0.02			*k A*	25	6.3	-5							
.29	*l*-2,2'-$(HOOC)_2$-4,6,4'-$(NO_2)_3C_6H_2C_6H_3$	H_2O	0.03-0.045	Na_2CO_3	2	*k A*	75	1.4	-5							(12)
							99	1.15	-4	22.4	8.3	8	21.2	-18.5	(10)	(12)
Sterically hindered C- and N-substituted anilines																
.30		MA*				*k A*	56	3.6	-5							(7)
.31		MA*	0.06			*k A*	57	1.8	-4							(8)

No.	Initial active compound	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	ΔH_a	ΔS_a	Comments	Literature
.32		H_2O	1.8-1.9			kA	17	1.8	-5							(15)
							24	4.6	-5							
							35	1.8	-4	22.6	2.3	12				
.33		H_2O	1.8-1.9			kA	17	3.7	-5							(15)
							24	9.2	-5							
							35	3.7	-4	22.6	4.7	12	22.8	-1.6	(10)	(15)
		$CHCl_3$				kA	17	6.8	-5							(15)
.34		MA*	0.043			kA	57	1.5	-6							(5)
		B*				kA	118	1.7	-4	~20			19	-27	* (5)	(10)
.35		MA*	0.08			kA	57	5.6	-6						*	(5)
.36		B*	0.02-0.03			kA	118	3.7	-5							(8)

No.	Initial active compound	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	ΔH_a	ΔS_a	Comments	Literature
.37		B*	0.0061			k A	118	1.07	-5						*	(4)'
.38		B*	0.04-0.06			k A	118	3.4	-6							(7)
.39		B*	0.12			k A	118	9.7	-5							(8)
.40		B*	0.05-0.08			k A	118	5.3	-6							(8)
Sterically hindered C- and N-substituted α-napthylamines																
.41		B*	0.02-0.03			k A	118	1.7	-5							(1)

No.	Initial active compound	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	ΔH_a	ΔS_a	Comments	Literature
.42	*l*- 	$CHCl_3$	0.02			kA	15	4	-4						*	(14)
.43	*d*-Cl- 	B*	0.02			kA	118	2.3	-5							(1)

SOLVENTS

B*	*n*-butanol	D*	dioxane
A*	acetic acid	P*	pyridine
AT*	acetone	DPE*	diphenyl ether
E*	ethanol	E95*	95 % ethanol + water
M*	methanol	MA*	methyl acetate
EA*	ethyl acetate		

COMMENTS

General: All rate constants listed are for rates of inversion which is equal to ½ rate of racemization. Where authors gave racemization rates these were converted to rate of inversion. In many cases pseudo first order rate constants arbitrarily calculated from half life in minutes or hours without verification of first order rate law. General order of classification follows increasing complexity of substituents with fifth group substituents preceding sixth group, preceding the halogens, and the halogens in order of increasing atomic weight.

Literature: (4) (5) (13) (14) (18) contain also rates of mutarotation of salts with optically active base, brucine and others. (9) gives complete list of all sterically hindered compounds which had been resolved to date with literature references. (10) calculated activation entropy and enthalpy.

LITERATURE

(1) R. Adams, A.A. Albert, *ACS* 1942, **64**, 1475. (2) R. Adams, A.W. Anderson, M.W. Miller, *ACS* 1941, **63**, 1589. (3) R. Adams, L.O. Binder, *ACS* 1941, **63**, 2773. (4) R. Adams, L.J. Dankert, *ACS* 1940, **62**, 2191. (5) R. Adams, J.R. Gordon, *ACS* 1950, **72**, 2454. (6) R. Adams, N. Kornblum, *ACS* 1941, **63**, 188. (7) R. Adams, H.W. Stewart, *ACS* 1941, **63**, 2859. (8) R. Adams, N.K. Sundholm, *ACS* 1948, **70**, 2867. (9) R. Adams, H.C. Yuan, *CRV* 1933, **12**, 261. (10) F.W. Cagle, H. Eyring, *ACS* 1951, **73**, 5628. (11) G.B. Kistiakowsky, W.R. Smith, *ACS* 1936, **58**, 1043. (12) R. Kuhn, O. Albrecht, *Ann.* 1927, **455**, 272. (13) C.C. Li, R. Adams, *ACS* 1935, **57**, 1565. (14) W.H. Mills, K.A. Elliott, *CSL* **1928**. 1291. (15) W.H. Mills, R.M. Kelham, *CSL* **1937**, 274. (16) N.E. Searles, R. Adams, *ACS* 1933, **55**, 1649. (17) W.M. Stanley, E. McMahon, R. Adams, *ACS* 1933, **55**, 706. (18) R.W. Stoughton, R. Adams, *ACS* 1932, **54**, 4426. (19) H.C. Yuan, R. Adams, *ACS* 1932, **54**, 2966.

RACEMIZATION
Alkyl sulfate

Liquid phase

Amounts are in M/l.
Rate constants are per sec.

No.	Reaction	Medium (Solvent)	% H_2SO_4	Amount of reactant	Acidity function H_0	Defined mass-action law	Temperature	$k = k^0 \times 10^n$. k^0	n
.1	*d*-$(C_2H_5)(CH_3)CHOSO_3H$	$H_2O + H_2SO_4$	45	A ~ 0.2	-2.09	*k* A	25	2.9	-6
			55		-3.24		25	3.0	-5
			57.7		-3.55		25	6.4	-5
			65		-4.33		25	4.6	-4

LITERATURE

N. C. Deno, M. S. Newman, *ACS* 1951, **73**, 1920.

RACEMIZATION

Organic halogen compounds

Method: polarimetry

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Initial active compounds	Medium	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.5	(+) - $CH_3CHBrCH_2COOCH_3$	pure liquid	kA	110	4.3	-7			
				131	3.0	-6			
				140	7.3	-6	29	1	10
.6	(-) - $CH_3OOCCH_2CHBrCOOCH_3$	"	"	100	3.2	-6			
				110	6.0	-6			
				131	2.7	-5	21	1	7

COMMENTS

Racemization proceeds along with loss of HBr (see 522.471) .

LITERATURE

L. J. Andrews, J. E. Hardwicke, *ACS* 1952, **74**, 3582.

RACEMIZATION

Organic-metal complex ion

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Initial active compound	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of Addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ 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	Literature
.1	d-$(C_2O_4)_2Cr^-$ (bis-oxalato-chromium III)	H_2O	~0.02			kA	0	4.2	-4				*	(3)
							10	1.1	-3					
							20	3.0	-3	16	8	8		
				KCl	0-0.5			1.04	-3					
				$K_2C_2O_4$	1.5			1.08	-3					
				$CaCl_2$	0.01			2.0	-3					
				$MnCl_2$	0.01			1.5	-3					
				$CuSO_4$	0.01			3.2	-3					
				$ZnSO_4$	0.01			2.4	-3					
				$HgCl_2$	0.01			9.4	-4					
				$La(NO_3)_3$	0.001			1.8	-3					
				$Ce(NO_3)_3$	0.001			2.1	-3					
				$Co(NH_3)_6Cl_3$	0.01			1.2	-3					
				$Co(C_2O_4)_3Cl_3$	0.01			1.2	-3					
				$Cr(C_2O_4)_3Cl_3$	0.01			1.2	-3					
.2	d-$(C_2O_4)_3Cr^{---}$ (tris-oxalato-chromium III)	H_2O	0.0008-0.0016			kA	0	5.6	-5				*	(3)
							10	3.5	-4					(3)
							25	7.2	-4					(10)
							35	1.4	-3	12.8	2	6		(10)
							50	5.0	-3	15.8				(3)

No.	Initial active compound	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
.2	d-$(C_2O_4)_3Cr^{---}$ (tris-oxalato-chromium III) *(continued)*	M40*	0.0008–0.0016			k A	25	4.6	-5					(10)
							35	1.3	-4					
		M80*					25	2.0	-5					
							35	4.6	-5					
		E10*					25	1.4	-4					(10)
							35	3.5	-4					
		E20*					25	8.2	-5					
		E30*					25	6.4	-5					
							35	6.5	-4					
		E40*					25	5.2	-5					
		NP10*					25	2.3	-4					(10)
							35	1.4	-3					
		NP30*					25	1.5	-4					
							35	1.4	-3					
		NP50*					25	1.3	-4					
		IP20*	0.0008–0.0016			k A	25	5.2	-4					(10)
		IP40*					25	4.1	-4					
		A10*					25	4.6	-4					(10)
		A30*					25	1.4	-4					
		A50*					25	8	-5					
		D5*					25	5.8	-4					(10)
		D10*					25	4.4	-4					
		D15*					25	3.6	-4					

No.	Initial active compound	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
.3	d-$(C_2O_4)_3Co^{---}$ (tris-oxalato-cobalt III)	H_2O	~.02			k A	0	1.0	-6				*	(3)
							20	2.0	-4					
							40	4.4	-4					
							50	1.7	-3	26	3	14		
				$K_2C_2O_4$	0		38	3.5	-4					
					0.5		38	5.4	-4					
					1.5		38	8.6	-4					
				K_2SO_4	0.5		38	5.8	-4					
				$CaCl_2$	0.01		38	4.4	-4					
				$MnCl_2$	0.01		38	4.2	-4					
				$Ni(NO_3)_2$	0.01		38	4.2	-4					
				$CuSO_4$	0.01		38	5.6	-4					
				$ZnSO_4$	0.01		38	4.4	-4					
				$La(NO_3)_3$	0.001		38	3.8	-4					
				$Ce(NO_3)_3$	0.001		38	4.4	-4					
.4	d-$[2,2'-(C_5H_4N)_2]_3Ni^{++}$ (tris-dipyridyl-nickel II)	H_2O	.004-.013			k A	16	7.6	-4					(9)
							20	1.18	-3					(2) (5) (6) (7) (9)
							30	4.1	-3					(9)
							40	1.3	-2	21.9	2.6	13		(1) (9)
				HCl	0.02		20	2.5	-3					(9)
					0.10		20	3.4	-3					(9)
					0.50		20	4.1	-3					(1)
				HCl }	1.0		20							
				LiCl }	1.0		20	4.8	-3					(1)
				HCl	5.0		20	8.5	-3					(1)
				NaOH	0.02		20	3.0	-3					(9)
					0.10		20	3.9	-3					(9)

No.	Initial active compound	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
.4	d-$[2,2'$-$(C_5H_4N)_2]_3Ni^{++}$ (tris-dipyridyl-nickel II) *(continued)*	H_2O	.004-.013	$(NH_4)NO_3$	3.5	k A	20	1.2	-3					(5)
				$(NH_4)_2SO_4$	1.0		20	1.2	-3					
				NH_4Cl	3.0		20	1.6	-3					
				LiCl	2.0		20	1.3	-3					
				NaCl	2.5		20	1.6	-3					
				KF	1.5		20	1.5	-3					
		M30*					18	3.2	-4					(9)
		M75*					18	2.5	-4					
		M100*					18	1.4	-4	22				
		E20*					18	2.7	-4					
		E40*					18	3.8	-4					
		E60*					18	3.6	-4					
		E100*					18	4.1	-4	22				
		A30*					18	3.4	-4					
		A40*					18	3.9	-4					
		A70*					18	4.4	-4					
		D10*					18	4.1	-4					
		D20*					18	3.7	-4					
		D35*					18	4.9	-4	22				
.5	d-$(1,10$-$C_{12}H_8N_2)_3Ni^{++}$ (tris-1,10-phenanthroline-nickel II)	H_2O	0.0003-0.0012			k A	12	1.73	-6				*	(4)
							25	1.10	-5					
							35	5.1	-5	25.0	2.5	13		(1) (4)
				HCl	1-2		25	1.1	-5					(1) (4)
				HCl	5		25	7.8	-6					(1)

No.	Initial active compound	Solvent (Medium)	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
.5	d-$(1,10\text{-}C_{12}H_8N_2)_3Ni^{++}$ (tris-1,10-phenanthroline-nickel II) *(continued)*	H_2O	0.0003-0.0012	$HClO_4$	5	kA	25	1.1	-5					(4)
				H_2SO_4	0.5		25	1.1	-5					(1)
				$(NH_4)_2SO_4$	0.5-2.5		25	9.1	-6					(4)
				LiCl	2-3		25	1.1	-5					(1)
				$La(NO_3)_3$	0.05		25	1.1	-5					
				$Ni(NH_4)_2(SO_4)_2$	0.025		25	1.1	-5					
				$C_{12}H_8N_2$	sat.		25	1.1	-5					
				KOH	1		25	1.35	-5					

SOLVENTS

MX*	X mol % methanol	(100-X) mol % water
EX*	X mol % ethanol	(100-X) mol % water
NPX*	X mol % *n*-propanol	(100-X) mol % water
IPX*	X mol % *i*-propanol	(100-X) mol % water
AX*	X mol % acetone	(100-X) mol % water
DX*	X mol % dioxane	(100-X) mol % water

COMMENTS

Classification. The complex ions or molecules undergoing racemization are grouped in order of increasing complexity of the organic complexing agent. In each group using the same complexing agent the order is in increasing number of complexing groups. In each group using the same complexing agent the metal complexes are arranged in order of increasing atomic number of the metal.

Reactions General. All reaction rate constants tabulated are rates of racemization or decrease in activity and not rate of inversion k_1, $d \xrightarrow{k_1} l$, $l \xrightarrow{k_2} d$ and $k_1 = k_2 = \frac{1}{2}k$ since $k = k_1 + k_2$. Where authors have calculated data in terms of rate of inversion it has been converted to rate of racemization. If activated complex is optically inactive rate of racemization should parallel other reactions involving same activated complex. If however activated complex leads to direct inversion other reactions involving same activated complex should parallel rate of inversion or one half rate of racemization.

Comments by Reaction. (.1) Rate of racemization converted from rate of inversion listed by authors. First order kinetics over course confirmed. (.2) Rates listed by ([3]) are rates of inversion while ([10]) list half times in min. ([10]) claim to have used data of ([3]), ([8]) ([10]) to evaluate activation energy but temperature range covered by ([3]) very much greater so both values listed. Extensive solvent concentration effects studied by ([10]) at two temperatures but no activation energies calculated as they appear to be solvent composition dependent. (.3) Rates tabulated have been converted from rates of inversion. (.4) (.5) Rate constants converted from min. to sec. Rates of racemization are found to be equal to rates of decomposition, see 592.481.

LITERATURE

([1]) F. Basolo, J.C. Hayes, H.M. Neuman, *ACS* 1953, 75, 5102. ([2]) N.W.D. Beese, C.H. Johnson, *TFS* 1935, 31, 1633. ([3]) E. Bushra, C.H. Johnson, *CSL* 1939, 1937. ([4]) N.R. Davies, F.P. Dwyer, *TFS* 1952, 48, 244. ([5]) N.R. Davies, F.P. Dwyer, *TFS* 1953, 49, 180. ([6]) F.M. Jaeger, J.A. van Dyke, *ZAC* 1936, 227, 304. ([7]) G.T. Morgan, F.H. Burstall, *CSL* 1931, 2213. ([8]) E.K. Rideal, W. Thomas, *CSL* 1922, 121, 196. ([9]) G.K. Schweitzer, J.M. Lee, *JPC* 1952, 56, 195. ([10]) G.K. Schweitzer, J.L. Rose, *JPC* 1952, 56, 428.

CIS-TRANS ISOMERIZATION

C, H, D compounds

Gas phase

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

No.	Initial isomer	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
.1	*cis* - CHD:CHD (⟶ *trans*)	infra-red absorption	9 - 310	k A	450 500 550	9 2 1.5	-7 -5 -4	61	3	12	*	(1)
.2	*trans* - CHD:CHD (⟶ *cis*)	"	"	"	"	"	"	"	"	"	"	"

COMMENTS

(.1) (.2) Rate constants taken as equal since equilibrium constant for the rearrangement observed to be nearly unity by authors. Values of rate constant calculated from A and E. Apparent decrease in A and E occurs at higher pressures but complications due to polymerization obscure isomerization reaction. Rate in packed vessel indicated negligible heterogeneous contribution.

LITERATURE

(1) B.S. Rabinovitch, J.E. Douglas, F.S. Looney, *JCP* 1952, **20**, 1807.

CIS-TRANS ISOMERIZATION
Organic halogen compounds

Gas phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Supplementing 1951 No.	Initial isomer (⟶ final)	Method	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
.4		*cis*-ClCH:CHCl (⟶ *trans*)	Dielec.	0.037	I_2	1.62×10^{-4}	kA	185	3.9	-6				*
						1.48×10^{-4}	kA	185	3.5	-6				
						$(1.5\text{-}1.6)\,10^{-4}$	$kA[I_2]^{\frac{1}{2}}$	185	2.9	-4	31	1.9	11	
.5	.1	*trans*-ClCH:CHCl (⟶ *cis*)	Dielec.	0.038	I_2	1.62×10^{-4}	kA	185	6.8	-6				*
						1.48×10^{-4}	kA	184	6.1	-6				
						$(1.5\text{-}1.6)\,10^{-4}$	$kA[I_2]^{\frac{1}{2}}$	185	5.0	-4	30	1.6	11	

COMMENTS

(.4) (.5) Dielectric constant measurements for determination of equilibrium gave several results satisfactory for determining specific reaction rate constants for forward and reverse reaction. Equilibrium constant at 185°C, trans/cis = 0.577 and ΔH° for the reaction cis ⟶ trans is -720 cals/mol. Activation energy for (.4) assumed to be same as in liquid phase as data of J.L. Jones and R.L. Taylor, *ACS* 1940, 62, 3480 for reaction in decalin gives good agreement on extrapolation to 185°C and conversion of units, see 122.470. (.5) Activation energy obtained by adding ΔH° to E for (.4). Catalysis I_2 assumed to follow same rate law as in liquid phase. Homogeneity of reactions not verified.

LITERATURE

R.E. Wood, D.P. Stevenson, *ACS* 1941, 63, 1650.

CIS-TRANS ISOMERIZATION

Cis-trans isomers of cyclic compounds

Methods of analysis: refractive index, infrared spectrometer, fractionation

Liquid phase

Amounts are in wt %.

Rate constants are in sec^{-1}

No.	Initial isomer (→ final)	Solvent (Medium)	Addend (Catalyst)	Amount of Addend	Time interval	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	*cis-cyclo*-1,2-$(CH_3)_2C_6H_{10}$ (→ *trans*)	pure liquid	H_2SO_4	sat. with 99.8 %	0-3600	*k* A	25	6.1	-5	*	
.2	*trans-cyclo*-1,2-$(CH_3)_2C_6H_{10}$ (→ *cis*)	pure liquid	H_2SO_4	sat. with 99.8 %	0-3600	*k* A	25	6	-8	*	
.3	*cis-cyclo*-1,3-$(CH_3)_2C_6H_{10}$ (→ *trans*)	pure liquid	H_2SO_4	sat. with 99.8 %	0-3600	*k* A	25	1.7	-5	*	
.4	*cis-cyclo*-1,4-$(CH_3)_2C_6H_{10}$ (→ *trans*)	pure liquid	H_2SO_4	sat. with 99.8 %	0-3600	*k* A	25	4.2	-4	*	
.5	*trans-cyclo*-1,4-$(CH_3)_2C_6H_{10}$ (→ *cis*)	pure liquid	H_2SO_4	sat. with 99.8 %	0-3600	*k* A	25	2.2	-5	*	

COMMENTS

General: Rate constants arbitrarily calculated from integrated first order equation over interval of first hour of reaction. Rate constants fall off with time due to dilution of acid catalyst. Maximum rate at 99.8 % H_2SO_4 decreasing by 60 fold at 95.5 %. Rate also falls off at higher H_2SO_4 concentrations. Simultaneous migration of methyl groups about ring observed. (.3) Migration gives 1,2 and 1,4 isomers. See 142.402.

LITERATURE

A.K. Roebuck, B.L. Evering, *ACS* 1953, 75, 1631.

CIS-TRANS ISOMERIZATION

Organic halogen compounds

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Initial isomer ⟶ final	Solvent (Medium)	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
.4	*cis*-BrCH:CHBr ⟶ *trans*	CCl_4	0.24 - 0.51	Br_2	0.007 - 0.013	$k A (Br_2)^{1/2}$	38.9	1.08	-5			
							49.0	3.1	-5			
							58.8	9.5	-5	21.7	1.7	10
.5	*trans*-BrCH:CHBr ⟶ *cis*	CCl_4	0.0 - 0.27	Br_2	0.007 - 0.01	$k A (Br_2)^{1/2}$	38.9	1.58	-5			
							49.0	4.0	-5			
							58.8	1.08	-4	19.9	1.1	9

COMMENTS

Infrared analysis. (.4) Rate law holds to equilibrium which is about 44% *trans*; consistent with mechanism involving addition of Br atoms ⟶ *cis*-$BrCHCHBr_2$, with subsequent inversion and elimination of Br atoms. Accompanying addition of Br_2, see 622.477.86; accompanying exchange, see 302.477. (.5) Rate calculated from equilibrium and reverse reaction (.4).

LITERATURE

H. Steinmetz, R. M. Noyes, *ACS* 1952, 74, 4141.

CIS-TRANS ISOMERIZATION

Organic group VIII metal complex

Liquid phase

Amounts are in M/l.
Rate constants are in $sec.^{-1}$.

No.	Initial isomer (⟶ final)	Solvent (Medium)	Amount of reactant	Addend	Ionic strength	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments
.1	*trans*-$(C_2O_4)_2(H_2O)_2Cr^-$ (⟶ cis) (trans-dioxalatodiaquochromate III)	H_2O	~0.008	$NaNO_3$	0.00825	4.45	*k* A	17	1.83	-4			*
					0.00825	4.48		29	6.43	-4			
					0.00825	4.47		36	1.25	-3	17.5	-15.3	
					0.00825	4.38		25	4.23	-4			
					0.00925	2.96		25	4.17	-4			
					0.0102	2.63		25	4.20	-4			
					0.018	1.85		25	4.19	-4			
					0.0132			29	6.48	-4			
					0.117			29	6.77	-4			
					0.235			29	7.50	-4			
					0.352			29	7.94	-4			

COMMENTS

(.1) Rate constants calculated by method of Guggenheim as modified by E.L. King, *ACS* 1952, 74, 563 using comparative adsorption at 415 mμ of two solutions started at different times. Equilibrium distribution has not been quantitatively established but the cis-isomer is the main species present in solution. Dependence of rate constant upon ionic strength may be represented by the expression $k = 6.41 \times 10^{-4} + 4.31 \times 10^{-4}\mu$ at 29.3°C.

LITERATURE

R.E. Hamm, *ACS* 1953, 75, 609.

CIS-TRANS ISOMERIZATION

Azo compounds

Liquid phase

Amounts are in M/l.
Rate constants are in $sec.^{-1}$

No.	Initial isomer (⟶ final)	Solvent	Method	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	Literature
.1	*cis* - $C_6H_5N{:}NC_6H_5$ (⟶ *trans*)	pure	sprmt*				*k* A	77	6.1	-4				(1)
								100	6.4	-3	26	1.1	13	
		H_2O	sprmt*	0.008			*k* A	25	3.2	-7				(1)
					NaCl	1.0		"	3.2	-7				
					NaOH	1.0		"	2.2	-7				
					HCl	0.26		"	2.6	-6				
					"	0.56		"	5.5	-6				
					"	0.96		"	1.2	-5				
					"	4.16		"	2.8	-5				
					$HClO_4$	0.23		"	2.4	-6				
					"	0.53		"	6.4	-6				
					H_2SO_4	0.13		"	2.0	-6				
					"	0.27		"	3.2	-6				
					CH_3COOH	50 %		"	5.3	-7				
		cyclo-C_6H_{12}	dltc*				*k* A	25	2.1	-6				(2) (3)
								45	2.4	-5	23	1.5	11	

No.	Initial isomer (→ final)	Solvent	Method	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	Literature
.1	*cis* - $C_6H_5N{:}NC_6H_5$ (→ *trans*) *(continued)*	C_6H_6	sprmt*	.008			*k A*	25	1.6	-6				(1) (2) (3)
			dltc*					45	2.0	-5				(2) (3)
			sprmt*					56	7.7	-5				(1)
			"					77	5.5	-4	23.4	2.5	11	(1)
		CH_3COCH_3	sprmt*	.008			*k A*	25	9.7	-7				(1)
		cyclo-hexanone	dltc*				*k A*	45	8.4	-6				(2) (3)
								70	2.0	-4	27	5.6	13	
		CH_3COOH	sprmt*	.008			*k A*	25	1.0	-6				
								56	4.6	-5				
								77	3.2	-4	23	8.5	10	(1)
		$CHCl_3$	dltc*				*k A*	25	2.0	-6				
								45	2.5	-5	24	7	11	(2) (3)
		CCl_4	sprmt*	.008			*k A*	25	2.1	-6				(1) (2) (3)
			dltc*					45	2.5	-5				(2) (3)
			sprmt*					56	8.4	-5				(1)
			"					77	6.7	-4	23.1	1.8	11	(1)
		C_6H_5Cl	dltc*				*k A*	25	2.1	-6				(2) (3)
								45	3.1	-5	25	5	12	
		o-$C_6H_4Cl_2$	dltc*				*k A*	25	1.3	-6				(2) (3)
								45	2.3	-5				
								70	5.5	-4	27	1.5	14	

No.	Initial isomer (⟶ final)	Solvent	Method	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	Literature
.2	*cis* - $CH_3C_6H_4N{:}NC_6H_5$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	4.4	-6				(2) (3)
								45	6.0	-5	24	5	12	
.3	*cis* -*p*-$CH_3OC_6H_4N{:}NC_6H_5$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	6.5	-6				(2) (3)
								45	6.9	-5	22	1.3	11	
.4	*cis* -*p*-$NO_2C_6H_4N{:}NC_6H_5$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	1.0	-6				(2) (3)
								45	1.2	-5				
								70	1.8	-4	23	1.0	11	
.5	*cis* -*p*-$ClC_6H_4N{:}NC_6H_5$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	3.0	-6				(2) (3)
								45	3.2	-5	22	8	10	
.6	*cis* -*p*-$BrC_6H_4N{:}NC_6H_5$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	2.8	-6				(2) (3)
								45	3.4	-5	23	1.2	11	
	Diazo nitriles													
.7	*cis* - $C_6H_5N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	15	4.0	-4				(2)
								25	1.5	-3	23	1	14	
.8	*cis* -*p*-$CH_3C_6H_4N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	15	2.9	-4				(2)
								25	1.1	-3	23	1	14	
.9	*cis* -α-$C_{10}H_7N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	6.2	-5				(2)
								45	7.1	-4	23	4	12	
.10	*cis* -β-$C_{10}H_7N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	4.6	-5				(2)
								45	5.4	-4	23	4	12	

No.	Initial isomer (⟶ final)	Solvent	Method	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	Literature
.12	*cis* -*p*-$NO_2C_6H_4N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	7.2	-6				(2)
								45	7.5	-5	22	1	11	
.13	*cis* -*p*-$ClC_6H_4N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	1.8	-5				(2)
								45	1.7	-4	21	1	11	
		cyclo-C_6H_{12}	dltc*				*k* A	25	2.3	-5				(2)
								45	2.4	-4	21	1	11	
		C_5H_5N	dltc*				*k* A	25	8.1	-6				(2)
								45	1.3	-4	26	1	14	
		$CHCl_3$	dltc*				*k* A	25	2.1	-5				(2)
								45	2.0	-4	21	1	11	
		CCl_4	dltc*				*k* A	25	2.0	-5				(2)
								45	2.1	-4	22	6	11	
		C_6H_5Cl	dltc*				*k* A	25	2.2	-5				(2)
								45	2.8	-4	24	7	12	
		o-$C_6H_4Cl_2$	dltc*				*k* A	25	1.1	-5				(2)
								45	1.6	-4	25	2	13	
.14	*cis* -*o*-$BrC_6H_4N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	7.8	-6				(2)
.15	*cis* -*p*-$BrC_6H_4N{:}NCN$ (⟶ *trans*)	C_6H_6	dltc*				*k* A	25	1.6	-5				(2)
								58	5.8	-4	22	1	11	

No.	Initial isomer (⟶ final)	Solvent	Method	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	Literature
.16	*cis* - 2,4,6-$Cl_3C_6H_2N$:NCN (⟶ *trans*)	C_6H_6	dltc*				*k* A	58 70	3.1 1.1	-5 -4	23	6	10	(2)

METHOD

sprmt* Spectrometric method, absorption by A at 400-480 mμ.

dltc* Dielectric constant measurements.

COMMENTS

General: All investigators report the cis ⟶ trans conversion goes practically to completion so that rate of trans ⟶ cis rearrangement is negligible. Data of (1) converted from time in hours. Values underlined calculated by combining data of all investigators.

LITERATURE

(1) G.S. Hartley, *CSL* **1938**, 633. (2) R.J.W. Le Fèvre, J. Northcott, *CSL* **1949**, 944. (3) R.J.W. Le Fèvre, J. Northcott, *CSL* **1953**, 867.

BRANCHING ISOMERIZATION

Hydrocarbons (Alkanes)

Liquid phase

Amounts are in wt %.
Rate constants are in $sec.^{-1}$.

No.	Reaction	Medium	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.3	$n\text{-}C_6H_{14} \longrightarrow$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	<6	-8	*	(2)
.4	$n\text{-}C_6H_{14} \longrightarrow (CH_3)_2CHCH_2CH_2CH_3, CH_3CH_2CH(CH_3)CH_2CH_3$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	5.0	-4	*	(1)
.5	$(CH_3)_2CHCH_2CH_2CH_3 \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_3$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	3.9	-5		(2)
.6	$(CH_3)_2CHCH_2CH_2CH_3 \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_3$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	4.2	-2		(1)
.7	$(CH_3)_2CHCH_2CH_2CH_3 \longrightarrow n\text{-}C_6H_{14}$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	1.9	-4		(1)
.8	$(CH_3)_2CHCH_2CH_2CH_3 \longrightarrow (CH_3)_2CHCH(CH_3)_2$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	1.7	-3		(1)
.9	$CH_3CH_2CH(CH_3)CH_2CH_3 \longrightarrow (CH_3)_2CHCH_2CH_2CH_3$	pure liquid	saturated with 96 % H_2SO_4	kA	25	6	-6	*	(2)
			" " 98 % H_2SO_4		25	3	-5		
			" " 99.8 % H_2SO_4		25	1.36	-4		
			" " 101 % H_2SO_4		25	7	-5		
			" " 102 % H_2SO_4		25	6	-5		
.10	$CH_3CH_2CH(CH_3)CH_2CH_3 \longrightarrow (CH_3)_2CHCH_2CH_2CH_3$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	1.8	-2		(1)
.11	$(CH_3)_2CHCH(CH_3)_2 \longrightarrow$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	<6	-8	*	(2)

No.	Reaction	Medium	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.12	$(CH_3)_2CHCH(CH_3)_2 \longrightarrow (CH_3)_2CHCH_2CH_2CH_3$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	1.1	-3		(1)
.13	$(CH_3)_2CHCH(CH_3)_2 \longrightarrow (CH_3)_3CCH_2CH_3$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	2.2	-4		(1)
.14	$(CH_3)_3CCH_2CH_3 \longrightarrow (CH_3)_2CHCH(CH_3)_2$	pure liquid	$AlCl_3$ = 11 % HCl = 3 %	kA	100	1	-6		(1)
.15	$(CH_3)_2CHCH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH(CH_3)CH_2CH_2CH_3$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	5.0	-5		(2)
.16	$CH_3CH_2CH(CH_3)CH_2CH_2CH_3 \longrightarrow (CH_3)_2CHCH_2CH_2CH_2CH_3$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	4.7	-5		(2)
.17	$(CH_3)_2CHCH(CH_3)CH_2CH_3 \longrightarrow (CH_3)_2CHCH_2CH(CH_3)_2$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	4.2	-5	*	(2)
.18	$(CH_3)_2CHCH_2CH(CH_3)_2 \longrightarrow (CH_3)_2CHCH(CH_3)CH_2CH_3$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	1.4	-5		(2)
.19	$(CH_3)CH_2CH(CH_3)CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH_3$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	5.0	-5	*	(2)
.20	$(CH_3)_2CHCH_2CH(CH_3)CH_2CH_3 \longrightarrow (CH_3)_2CHCH_2CH_2CH(CH_3)_2$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	1.5	-4	*	(2)

COMMENTS

Literature Reference: (1) All determinations made in bomb under hydrogen pressure of 1000 lbs./sq.in., analysis of product by fractionation in 100 plate column and characterization by boiling point and specific volume. Mass spectrograph used for determination of small conversion to other homologues. Rate law used without verification over course of reaction and rate constants drifted over course in cases checked. Rate constants tabulated were based on initial rate. (2) Used vigorous agitation of two liquid mixture during reaction to avoid rate limitation by diffusion at interface. Product

COMMENTS *(continued)*

analysis made using fractionation and characterization by refractive index and infrared spectrometer. First order rate law arbitrarily used and rate constants fall off as much as 50 % in four hours. This is assumed due to dilution of catalyst by products of side reactions. Equilibrium approached from each direction and rate of approach to equilibrium used to determine rate constants which were calculated in terms of distance from equilibrium at one hour.

Reactions: **(.1) (.11)** Rate law estimated to be less than value tabulated as no isomerization could be detected after 150 hours by refractive index measurement. **(.9)** Activation energy of 6.4 k. cals. determined from rates of isomerization from 10-50°C. Value probably has little significance as increase in temperature also increases side reactions which dilute catalyst. **(.17)** Activation energy of 4.9 k. cals. determined from rates of isomerization from 10-50°C. Value probably has little significance as increase in temperature also increases side reactions which dilute catalyst. **(.19) (.20)** Accuracy of hydrocarbon analysis of octanes not determined.

LITERATURE

(1) B.L. Evering, R.C. Waugh, *IEC* 1951, 43, 1820; (2) A.K. Roebuck, B.L. Evering, *ACS* 1953, 75, 1631.

BRANCHING ISOMERIZATION

Hydrocarbons (Cyclo alkanes)

Liquid phase

Amounts are in wt. %.
Rate constants are in sec^{-1}.

No.	Reaction	Medium	Addend (Catalyst)	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
.1	$CH_3C_5H_9 \rightarrow$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	<6	-8	*
.2	$C_6H_{12} \rightarrow$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	<6	-8	*
.3	*cis*-1,2-$(CH_3)_2C_6H_{10} \rightarrow$ *cis*-1,3-$(CH_3)_2C_6H_{10}$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	2.5	-5	*
.4	*trans*-1,2-$(CH_3)_2C_6H_{10} \rightarrow$ *cis*-1,3-$(CH_3)_2C_6H_{10}$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	6	-6	*
.5	*cis*-1,3-$(CH_3)_2C_6H_{10} \rightarrow$ *trans*-1,2-$(CH_3)_2C_6H_{10}$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	2.5	-6	*
.6	*cis*-1,3-$(CH_3)_2C_6H_{10} \rightarrow$ *trans*-1,4-$(CH_3)_2C_6H_{10}$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	1.1	-5	*
.7	*cis*-1,4-$(CH_3)_2C_6H_{10} \rightarrow$ *cis*-1,3-$(CH_3)_2C_6H_{10}$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	3.3	-5	*
.8	*trans*-1,4-$(CH_3)_2C_6H_{10} \rightarrow$ *cis*-1,3-$(CH_3)_2C_6H_{10}$	pure liquid	saturated with 99.8 % H_2SO_4	kA	25	2.5	-5	*

COMMENTS

General. Rate constants fall with time, assumed due to dilution of catalyst by products of a side reaction. First order rate constant arbitrarily calculated for first hour interval from rate of approach to equilibrium curve.

Reactions. (.1) (.2) Rate estimated to be less than value given since no isomerization detectable after 150 hours by refractive index measurement. (.3) occurs simultaneously with cis ⟶ trans isomerization see 122.441. (.4) occurs simultaneously with trans ⟶ cis isomerization see 122.441. (.5) occurs simultaneously with 1,3 to 1,4 shift as well as with cis ⟶ trans isomerization see 122.441. (.6) occurs simultaneously with reverse reaction, and 1,3 to 1,2 shift as well as with cis ⟶ trans isomerization see 122.441.

LITERATURE

A.K. Roebuck, B.L. Evering, *ACS* 1953, 75, 1631.

BRANCHING ISOMERIZATION

Group migration in substituted alkyl sulfonates

Liquid phase

Amounts are in M/l.
Rate constants are in sec^{-1}.

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
.1	$p\text{-}BrC_6H_4SO_3CH_2CH(CH_3)C_6H_5 \longrightarrow C_6H_5CH_2CH(CH_3)SO_3C_6H_4Br$	CH_3COOH	0.025-0.041			kA	75	8.1	-6				*
							100	8.5	-5	24	1.0	10	
				CH_3COONa	0.04		75	6.8	-6				
					0.04		100	8.3	-5	26	1.2	11	
				DPGHOBs*	0.04		75	8.7	-6				
				$LiClO_4$	0.03		75	9.0	-6				
				H_2O	0.3		75	9.4	-6				

ADDEND

DPGHOBs* Diphenylguanidinium-*p*-bromobenzenesulfonate

COMMENTS

(.1) Rate of rearrangement calculated from kinetic analysis of rates of solvolysis of A, L and mixtures of A and L with infrared analysis of partially solvolized mixtures. See 212.461. Authors postulate the rearrangement follows an internal mechanism because of lack of influence of DPGHOBs* upon rate. Solvolysis of L does not involve rearrangement to A.

LITERATURE

S. Winstein, K.C. Schreiber, *ACS* 1952, 74, 2171.

ISOMERIZATION
Hydrogen migration with Double bond shift

Liquid phase

Amounts are in M/l. Rate constants are in M/l and 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	Comments	Literature
.4	$p\text{-}(CH_3)_2CHC_6H_4CH{:}NCH_2C_6H_5 \rightleftarrows p\text{-}(CH_3)_2CHC_6H_4CH_2N{:}CHC_6H_5$	C_2H_5OH	A + L = 0.145	$NaOC_2H_5$	0.145	$k(A-A_e)$	82	1.30	-4	*	(1)
.5	$p\text{-}(CH_3)_2CHC_6H_4CH{:}NCH_2C_6H_5 \longrightarrow p\text{-}(CH_3)_2CHC_6H_4CH_2N{:}CHC_6H_5$	C_2H_5OH	from (.4)	$NaOC_2H_5$	0.145	k_1A	82	5.8	-5	*	(1)
.6	$p\text{-}(CH_3)_2CHC_6H_4CH_2N{:}CHC_6H_5 \longrightarrow p\text{-}(CH_3)_2CHC_6H_4CH{:}NCH_2C_6H_5$	C_2H_5OH	from (.4)	$NaOC_2H_5$	0.145	k_2A	82	7.2	-5	*	(1)
.7	$p\text{-}C_2H_5(CH_3)CHC_6H_4CH{:}NCH_2C_6H_5 \rightleftarrows p\text{-}C_2H_5(CH_3)CHC_6H_4CH_2N{:}CHC_6H_5$	C_2H_5OH	A+L = 0.145	$NaOC_2H_5$	0.145	$k(A-A_e)$	82	1.67	-4	*	(1)
.8	$p\text{-}C_2H_5(CH_3)CHC_6H_4CH{:}NCH_2C_6H_5 \longrightarrow p\text{-}C_2H_5(CH_3)CHC_6H_4CH_2N{:}CHC_6H_5$	C_2H_5OH	from (.7)	$NaOC_2H_5$	0.145	k_1A	82	6.7	-5	*	(1)
.9	$p\text{-}C_2H_5(CH_3)CHC_6H_4CH_2N{:}CHC_6H_5 \longrightarrow p\text{-}C_2H_5(CH_3)CHC_6H_4CH{:}NCH_2C_6H_5$	C_2H_5OH	from (.7)	$NaOC_2H_5$	0.145	k_2A	82	1.00	-4	*	(1)
.10	$C_2H_4NO_2H \longrightarrow C_2H_5NO_2$	H_2O	0.008-0.01	$C_2H_4NO_2^-$	0.005-0.007	$kA[C_2H_4NO_2^-]^0$		8	-2		(2)

COMMENTS

Reactions: (.4) First order with respect to A over course but order with respect to catalyst, $NaOC_2H_5$, not determined. (.5) (.6) Specific reaction rate constants for the opposing reactions of (.4) $k = k_1 + k_2$. (.7) First order with

COMMENTS *(continued)*

respect to A over course but order with respect to catalyst, $NaOC_2H_5$, not determined. (.8) (.9) Specific reaction rate constants for the opposing reactions of (.7) $k = k_1 + k_2$.

LITERATURE

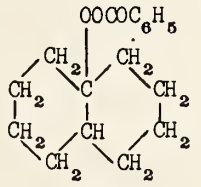
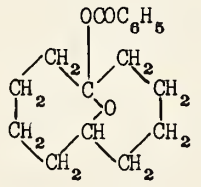
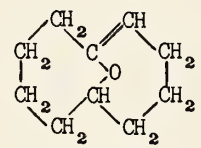
(1) J.W. Baker, W.S. Nathan, C.W. Shoppee, *CSL* **1935**, 1847. (2) R.G. Pearson, R.L. Dillon, *ACS* 1950, **72**, 3576.

ISOMERIZATION

Group migration in bicyclic ring system

Liquid phase

Amounts are in M/l.
Rate constants are in sec^{-1}.

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	E	$A = A^o \times 10^n$ A^o	n	Literature
Trans-9-decalyl perbenzoates													
.1	 $(C_{10}H_{17}OOOC_6H_5)$  $(C_{10}H_{17}OOOOC_6H_5)$ (L)  $+ C_6H_5COOH$ (M') (L') $(C_{10}H_{16}O)$	CH_3OH	0.01-0.15		$d(L+L')/dt = k\,A$		0	1.0	-6				(1) (3)
							20	2.4	-5				
							30	8.0	-5	22.7	2.0	12	(1)
							50	9.4	-4				(3)
								k_1					
					$dL/dt = k_1A$		0	8.6	-7				(3)
							20	2.0	-5				
							30	6.6	-5				
							50	7.6	-4				
								k_2					
					$dL'/dt = k_2A$		0	1.4	-7				(3)
							20	3.8	-6				
							30	1.4	-5				
							50	1.8	-4				
								k					
				L1Cl	μ=0.2								
				HCl	0.0	$k\,A$	25	5.7	-5				(1)
					0.10			7.1	-5				
					0.20			8.4	-5				
		M75*	0.01		$d(L+L')/dt = k\,A$		20	1.8	-4				(3)

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	E	$A = A^o \times 10^n$ A^o	n	Literature
.2	$C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4CH_3 \rightarrow$ $C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4CH_3$ (L); $C_{10}H_{16}O$ (L') + $p\text{-}CH_3C_6H_4COOH$ (M')	CH_3OH	0.06			kA	25	3.2	-5				(1)
.3	$C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4OCH_3 \rightarrow$ $C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4OCH_3$ (L); $C_{10}H_{16}O$ (L') + $p\text{-}CH_3OC_6H_4COOH$ (M')	CH_3OH	0.06			kA	25	2.3	-5				(1)
.4	$C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4NO_2 \rightarrow$ $C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4NO_2$ (L); $C_{10}H_{16}O$ (L') + $p\text{-}NO_2C_6H_4COOH$ (M')	CH_3OH	0.003-0.004			kA	25	5.5	-4				(1)
.5	$C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4Br \rightarrow$ $C_{10}H_{17}OCO\text{-}p\text{-}C_6H_4Br$ (L); $C_{10}H_{16}O$ (L') + $p\text{-}BrC_6H_4COOH$ (M')	CH_3OH	0.03			kA	25	1.3	-4				(1)

SOLVENTS

M75* = 75 % CH_3OH + 25 % H_2O

COMMENTS

Literature references: (1) follow rate of loss of A by iodometric titration of per acid and measure $k = k_1 + k_2$ directly with first order behavior to about 90 % reaction. (2) study rearrangement of decalin peroxy benzoate and plot two graphs of % rearrangement versus time but give no kinetic calculations. (3) follow rate of formation of M' by acidimetric titration and thus measure k_2 directly. They determine k_1 and k by determining ratio of L to L' in product. First order constant observed to about 90 % reaction inspite of gradual increase of infinity titer of acid due to competing reaction. This increase however amounted to only 5 % during forty half-life periods of main reaction. Both (1) and (3) check the ionic nature of reaction intermediate and show catalysis of polarizing solvents. Addition of large quantities of p-$NO_2C_6H_4COOLi$ to reaction mixture gave no exchange thus demonstrating an intramolecular rearrangement mechanism. Substituent effect on perbenzoate is accounted for by Hammett relation with $\rho = 1.34$.

LITERATURE

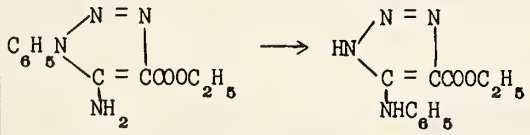
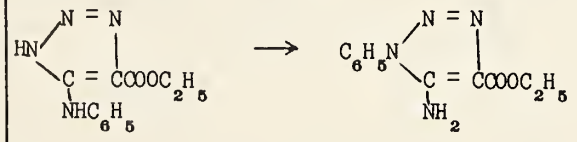
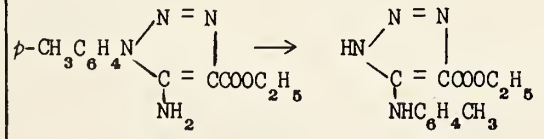
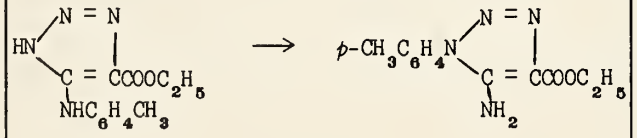
(1) P.D. Bartlett, J.L. Kice, *ACS* 1953, **75**, 5591. (2) R. Criegee, R. Kaspar, *Ann.* 1948, **560**, 127. (3) H.L. Goering, A.C. Olson, *ACS* 1953, **75**, 5853.

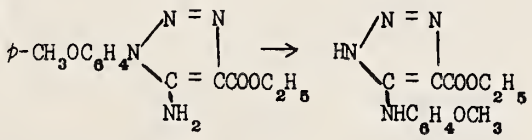
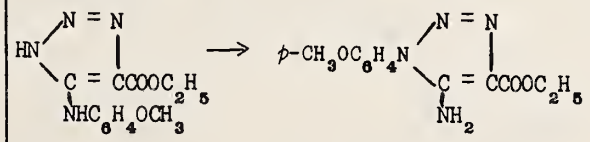
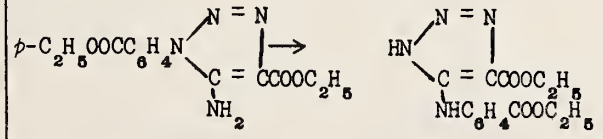
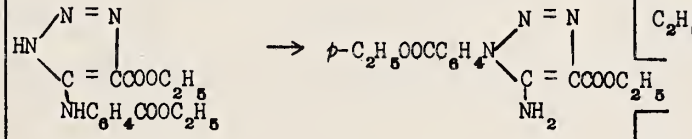
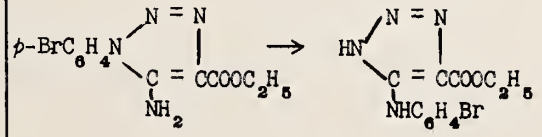
ISOMERIZATION

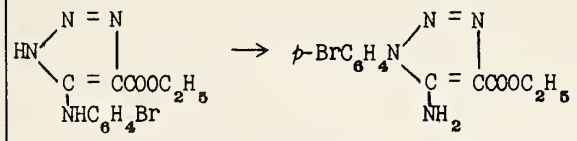
Group migration on heterocyclic ring

Liquid phase

Amounts are in M/l.
Rate constants are in sec^{-1}

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	E	$A = A^o \times 10^n$ A^o	n
.1		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	1.12 3.75	-5 -5	22.5	3	16
.2		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	3.8 8.5	-6 -6	17	1	6
.3		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	5.7 2.27	-6 -5	29	2	14
.4		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	5.4 1.43	-6 -5	21	8	8

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	$A = A^\circ \times 10^n$ A°	n
.5		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	3.3 1.15	-6 -5	27	5	12
.6		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	6.5 1.75	-6 -5	21	1	9
.7		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	5.7 1.88	-5 -4	26	2	13
.8		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	1.0 2.3	-6 -6	18	1	6
.9		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	2.1 6.9	-5 -5	26	7	12

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	E	$A = A^o \times 10^n$ A^o	n
.10		C_2H_5OH	~0.04	picric acid or $HClO_4$	0.0001-0.038 0.0001-0.0029	kA	50 60	1.5 2.6	-6 -6	12	2	2

COMMENTS

Rate constants calculated from experimental distance from equilibrium rate, (sum of rate of forward and reverse reaction) and equilibrium constant. Rates uneffected by added salts and independent of acid concentration at $[H^+]$ greater than 10^{-4}. Below 10^{-4}, $-dA/dt = k'A[H^+]$ and (.1) (.3) (.5) (.7) (.9) are observed to be autocatalytic due to acidity of L. Authors suggest mechanism involving addition of proton and opening of heterocyclic ring with bond shifting to other nitrogen atom.

LITERATURE

B.R. Brown, D.Ll. Hammick, S.G. Heritage, *CSL* **1953**, 3820.

ISOMERIZATION

OH group migration with Double bond shift

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	% H_2O in solvent	Amount of reaotant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments
.2	$(CH_3)_2C{:}CHC(OH)(CH_3)C{:}OCH_3 \longrightarrow (CH_3)_2C(OH)CH{:}C(CH_3)C{:}OCH_3$	dioxane + H_2O	40	0.13-1.3	HCl	0.1	kA	75	2.8	-5		*
			40					80	4.0	-5		
			40					85	5.8	-5		
			40					90	8.7	-5		
			40					95	9.7	-5	19	
			60					75	4.6	-5		
			60					80	7.7	-5		
			60					85	1.24	-4		
			60					90	1.88	-4		
			60					95	2.50	-4	25	

COMMENTS

(.2) Mass action law not complete rate law, initial rate only and influence of catalyst not investigated. Values of rate constant obtained by extrapolation of drifting constants to zero time since L is removed by a consecutive reaction forming the cyclic oxide, $(CH_3)_2CCH{:}C(CH_3)C(CH_3)OH$, see 172.441. Reaction followed by absorption of L at 2290 Å.

LITERATURE

E. A. Braude, C.J. Timmons, *CSL* **1953**, 3138.

ISOMERIZATION

Halogen migration with Double bond shift

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$ k^0	n	Comments
.1	$CH_2{:}CHC(CH_3)_2Cl \longrightarrow ClCH_2CH{:}C(CH_3)_2$	CH_3COOH	0.01-0.1	CH_3COOK	0.05	kA	25	3.6	-5	*
				CH_3COOLi	0.096		25	4.4	-5	
				CH_3COOK + KCl	0.036 0.012		25	3.4	-5	

COMMENTS

(.1) Rate constants calculated by kinetic analysis of solvolysis of A which simultaneously undergoes rearrangement. This calculation is possible since solvolysis of L proceeds at a different rate from solvolysis of A. Solvolysis of L proceeds with no rearrangement see 212.471.

LITERATURE

W.G. Young, S. Winstein, H.L. Goering, *ACS* 1951, 73, 1958.

ISOMERIZATION

H Substitution by NH_2 from side chain in aromatic ring

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of Addend	Ionic strength	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
.2	$C_6H_5NHNHC_6H_5 \rightarrow 4,4'-(NH_2)_2C_6H_4C_6H_4$ (L)	Et95*	~.001	HCl	.05-0.1	0.10	$-dA/dt = k A [H^+]^2$	0	2.4	-3					(2)
								15	1.6	-2					
								25	5.6	-2	21	7	13	*	
	$\rightarrow 2,4'-(NH_2)_2C_6H_4C_6H_4$ (L')	Et90*	~.005	HCl	.067	.067	$-dA/dt = k A [H^+]^2$	0	1.47	-3					(4)
								9	4.63	-3					
								25	2.96	-2	19	2	12	*	
		Et80*	~.005	HCl	.093	.093	$-dA/dt = k A [H^+]^2$	0	2.52	-3					(4)
								25	3.42	-2					
		Et75*	.005-.01	HCl	.09-.4	.39	"	0	1.1	-2					(5)
			~.005	HCl	.093	.093	"	25	4.0	-2					(4)
		Et70*	~.005	HCl	.093	.093	"	25	4.85	-2					(4)
					.084	.093			5.15	-2					
					.052	.093			5.37	-2					
					.026	.093			6.72	-2					
					.093	.093		0	3.05	-3					
					.093	.093		25	4.78	-2	18	5	11		(4)

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of Addend	Ionic strength	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
		Et50*		*See Supplementary Table											
.3	$2,2'\text{-}(CH_3)_2C_6H_4NHNHC_6H_4 \longrightarrow 2,2'\text{-}(CH_3)_2\text{-}NH_2C_6H_3C_6H_3NH_2$	Et90*	.005	HCl	.067	.067	$k\,A[HCl]^2$	0	1.35	-2					(4)
								9	3.97	-2					
								25	2.62	-1	19	2	13		
.4	$3,3'\text{-}(CH_3)_2C_6H_4NHNHC_6H_4 \longrightarrow 3,3'\text{-}(CH_3)_2\text{-}NH_2C_6H_3C_6H_3NH_2$	Et90*	.005	HCl	.067	.067	$k\,A[HCl]^2$	9	5.36	-2					(4)
								25	3.10	-1	18	5	12		
.5	$4,4'\text{-}(CH_3)_2C_6H_4NHNHC_6H_4 \longrightarrow 3\text{-}NH_2,4\text{-}CH_3C_6H_3NHC_6H_4CH_3$	H_2O	~.0025	HCl	.092	.092	$k\,A$	18	1.25	-3				*	(1)
					.092	.192		18	1.22	-3					
					.192	.192		18	1.7	-3					
					.088	.088		25	4.0	-3					
.6	$2,2',3,3'\text{-}(CH_3)_4C_6H_3NHNHC_6H_3 \longrightarrow 2,2',3,3'\text{-}(CH_3)_4\text{-}NH_2C_6H_2C_6H_2NH_2$	Et90*	.005	HCl	.067	.067	$k\,A[HCl]^2$	0	3.10	-1					(4)
								9	8.25	-1	17	7	12		
.7	$2\text{-}CH_3OC_6H_4NHNHC_6H_5 \longrightarrow 2\text{-}CH_3O,NH_2C_6H_3C_6H_4NH_2$	Et90*	.005	HCl	.067	.067	$k\,A[HCl]^2$	-5	2.37	-1					(4)
								0	3.39	-1					
								9	6.74	-1	10	3	7		
.8	$2\text{-}C_2H_5OC_6H_4NHNHC_6H_5 \longrightarrow 2\text{-}C_2H_5O,NH_2C_6H_3C_6H_4NH_2$	Et90*	.005	HCl	.067	.067	$k\,A[HCl]^2$	0	3.93	-1					(4)
								9	7.90	-1	12	2	9		
.9	$3,3'\text{-}(CH_3O)_2C_6H_4NHNHC_6H_4 \longrightarrow 3,3'\text{-}(CH_3O)_2,NH_2C_6H_3C_6H_3NH_2$	Et90*	.005	HCl	.067	.067	$k\,A[HCl]^2$	9	1.41	-2					(4)
								25	9.8	-2	20	5	13		

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of Addend	Ionic strength	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
.10	$4,4'-(NH_2)_2C_6H_4NHNHC_6H_4 \longrightarrow (NH_2)_2C_6H_3C_6H_3(NH_2)_2$	H_2O	.0024	HCl*	.091	.091	k A	18	4.7	-6				*	(1)
					.091	.091		37	3.6	-5	19	9	8		
					.091	.591		37	4.8	-5					
					.591	.591		37	1.02	-4					

SUPPLEMENTARY TABLE

(.2) Et50*

Addend (Catalyst)	Amount of Addend Acid*	Ionic strength	Defined mass-action law	Temperature	$k' = k^o \times 10^n$ k^o	n	Comments	Literature
HCOOH	0-2	.05	$1.1\,A\,[H^+]^2 + k'\,A\,[H^+]\,[acid]$*	55	9.6	-3	*	(3)
glycolic acid	0-2	.05	"	"	2.9	-2	*	(3)
$CH_2ClCOOH$	0-1.5	.05	"	"	4.7	-2	*	(3)
salicylic acid	0-1	.05	"	"	5.7	-2	*	(3)
$CH_2CNCOOH$	0-0.4	.05	"	"	1.3	-1	*	(3)

SOLVENTS

Et95*	95 % ethanol and water	Et70*	70 wt % ethanol, 30 wt % water
Et90*	90 wt % ethanol, 10 wt % water	Et60*	60 wt % ethanol, 40 wt % water
Et80*	80 wt % ethanol, 20 wt % water	Et50*	50 wt % ethanol, 50 wt % water
Et75*	75 wt % ethanol, 25 wt % water		

COMMENTS

Literature references: (1) follows reaction potentiometrically using azo, hydrogen ion, hydrazo equilibrium for electrode reaction. (2) follow concentrations of A, L, and L' spectrophotometrically. (3) (4) (5) follow reaction by oxidation of A with Bindschedler's green and back titrating with titanous chloride. (4) gives data for additional solvent conditions.

Reactions: (.2) Rearrangement produces two products, L and L', in constant ratio 70 % L and 30 % L' both produced with pseudo first order kinetics in solution at constant ionic strength and acid concentration demonstrated by (2). Ionic strength maintained constant under varying acid concentrations by addition of LiCl (2); $NaClO_4$ (5); KCl (3). Catalysis by other acids than solvated hydrogen ion demonstrated by (3) who show that at constant ionic strength and constant pH the pseudo first order rate constant is dependent upon the concentration of added acid as is required by the equation:

$$-dA/dt = 1.1\,A\,[H^+]^2 + k\,A[H^+]\,[Acid].$$

Dependence of log k upon square root of ionic strength shown by (4), who determine slope of straight line plot to be +1.19, thus indicating by the Brönsted-Bjerrum equation a charge product in reaction species of approximately +1. Same authors show that log k versus dielectric constant gives non-linear plot with negative slope. The negative slope increases in magnitude as dielectric constant increases. Negative slope is in agreement with reaction between ions of like charge but Brönsted-Christiansen-Scatchard equation predicts linear plot (.3) (.4) (.6) (.7) (.8) (.9) Pseudo first order rate constants observed for at least 60 % of reaction in solution of constant HCl concentration. (.5) (.10) Water solution in which reaction followed contained azo as well as hydrazo compound, and reaction followed by change in electrode potential due to change in azo-hydrazo ratio as hydrazo compound rearranged. Acid concentrations tabulated were corrected for reaction with A.

LITERATURE

([1]) E. Billman, J.H. Blom, *CSL* 1924, **125**[2], 1719. ([2]) R.B. Carlin, R.C. Nelb, R.C. Odioso, *ACS* 1951, **73**, 1002. ([3]) M.D. Cohen, G.S. Hammond, *ACS* 1953, **75**, 880. ([4]) L.J. Croce, J.D. Gettler, *ACS* 1953, **75**, 874. ([5]) G.D. Hammond, H.J. Shine, *ACS* 1950, **72**, 220.

ISOMERIZATION
Double bond to Closed ring

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	% H_2O in Solvent	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
.2		$(CH_3)_2C(OH)CH{:}C(CH_3)C{:}OCH_3 \longrightarrow$ $(CH_3)_2CCH{:}C(CH_3)C(CH_3)OH$ (O ring)	Dioxane + H_2O	40	0.0043	HCl	0.1	kA	75	1.13	-4		*	(2)
				40					80	1.92	-4			
				40					85	2.84	-4			
				40					90	3.92	-4	23		
				40					95	4.26	-4			
				60					75	2.8	-5			
				60					80	5.0	-5			
				60					85	8.5	-5			
				60					90	1.61	-4	30		
				60					95	1.75	-4			
.3		$(CH_3)_2C{:}CHC(OH)(CH_3)C{:}OCH_3 \longrightarrow$ $(CH_3)_2CCH{:}C(CH_3)C(CH_3)OH$ (O ring)		See 152.461 and comments (.2)									*	(2)
.4	.1	$(CH_3)_2C{:}CHC{:}OCH{:}C(OH)COOCH_3 \longrightarrow$ $(CH_3)_2CCH_2C{:}OCH{:}CCOOCH_3$ (O ring)	C_6H_5Cl		0.01-0.02	X = $(C_2H_5)_3N$	10^4X = 32-944	kA; $k = k_c k'X/(k' + k_cX)$	99	k_c = 2.37	-3		*	(2)
	.1									k' = 1.67	-4			
						$(CH_3)_3N$	92-1830		99	k_c = 3.44	-3			
										k' = 2.92	-4			
						$C_6H_5CH_2N(C_2H_5)_2$	48-343		99	k_c = 1.97	-4			
										k' = 1.12	-4			
						nicotine	46-137		99	k_c = 1.32	-4			
										k' = 1.67	-4			

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	% H_2O in Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$ k^k	n	Eq	Comments	Literature
.4	.1	$(CH_3)_2C{:}CHC{:}OCH{:}C(OH)COOCH_3 \longrightarrow$ $(CH_3)_2CCH_2C{:}OCH{:}CCOOCH_3$ (cont.)	C_6H_5Cl		0.01-0.02	X =	10^4X =	kA;	$k = k_c k'X/(k' + k_cX)$					
						o-$NO_2C_6H_4COOH$	135-802		99	k_c = 1.92	-1			
										k' = 2.38	-4			
						m-$NO_2C_6H_4COOH$	20.5-495		99	k_c = 1.19	-1			
										k' = 2.08	-4			
						C_6H_5COOH	34-1806		99	k_c = 4.19	-2			
										k' = 2.30	-4			
						p-$CH_3C_6H_4COOH$	33-720		99	k_c = 4.07	-2			
										k' = 2.08	-4			
						CH_3COOH	34-1735		99	k_c = 1.78	-2			
										k' = 2.22	-4			
						$(CH_3)_3CCOOH$	34-1885		99	k_c = 3.59	-2			
										k' = 2.20	-4			
								$k = [k_c k'X/(k' + k_cX)] + aX$						
						$CHCl_2COOH$	7.2-1823		99	k_c = 4.2	-1			
										k' = 2.42	-4			
										a = 1.2	-3			
						$CH_2ClCOOH$	16.1-1804		99	k_c = 1.31	-1			
										k' = 2.08	-4			
										a = 4.5	-5			

COMMENTS

Reactions: (.2) Pseudo first order rate law holds over course of reaction but order with respect to catalyst not investigated. Values of constants at 95°C deviate on log k vs. 1/T plot. "A" is shown to be an intermediate in the cyclization of (.3). For initial step see (.2) under 152.461. (.3) Reaction proceeds by two consecutive reactions. For the initial step see (.2) under 152.461. For second step see (.2) above. (.4) Reaction followed up to about 60% of change. At equilibrium about 3 to 8 % of A remains. No catalytic effect observed with up to 9.95 M/l of H_2O, $(C_2H_5)_2NH$ or $C_6H_5CH_2NH_2$. With basic catalysts, rate constants corrected for heterogeneous catalysis by glass; with acid catalysts k's are corrected for heterogeneous inhibition by glass.

LITERATURE

([1]) R.P. Bell, S.M. Rybicka, *CSL* **1947**, 25. ([2]) E.A. Braude, C.J. Timmons, *CSL* **1953**, 3138.

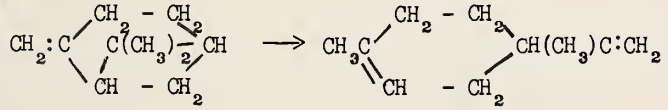
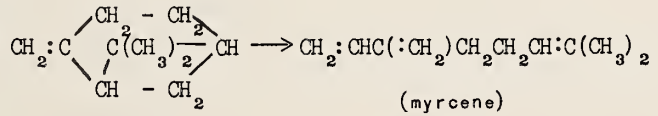
ISOMERIZATION

Ring opening to Double bond

Gas phase

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

No.	Reaction	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	$CH_2 - CH_2 \rightarrow CH_3CH{:}CH_2$ (cyclopropane)	600			k A	440	1.5	-5				*	(1) (2)
		"				460	5.6	-5					
		"				480	1.9	-4					
		"				500	5.6	-4					(1) (2) (3)
		"				520	1.7	-3	65.0	1.5	15		
		910			k A	500	5.7	-4					(2)
		700				"	5.9	-4					(1) (2)
		600				"	5.6	-4					(2)
		375				"	5.7	-4					(1) (2)
		194				"	5.5	-4					
		105				"	5.1	-4					
		54				"	4.7	-4					
		25				"	4.1	-4					
		13				"	3.8	-4					(1) (2) (3)
		3.3				"	2.7	-4				*	(3)
		1.37				"	2.1	-4					
		0.63				"	1.5	-4					
		0.36				"	1.1	-4					
		0.17				"	8.0	-5					
		0.13				"	6.9	-5					
		0.067				"	5.0	-5					
		"	He	1080		"	5.0	-4				*	
		"	Argon	1220		"	5.0	-4					
		"	H_2	270		"	5.0	-4					

No.	Reaction	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
.1	$CH_2 - CH_2 \rightarrow CH_3CH:CH_2$ *(continued)*	0.067	N_2	1080	k A	500	5.0	-4					
		"	CO	900		"	5.0	-4					
		"	CH_4	240		"	5.0	-4					
		"	H_2O	82		"	5.0	-4					
		"	$C_6H_3F_3$	59		"	5.0	-4					
		"	$CH_3C_6H_5$	41		"	5.0	-4					
		"	$(CH_3)_3C_6H_3$	45		"	5.0	-4					
.2	 (l-β-pinene) (l-limonene)	20-80			k A	350	5.7	-3				*	(2a)
						365	1.31	-2					
						379	2.83	-2					
						395	6.60	-2					
						409	1.23	-1	45.1	3	13		
.3	 (l-β-pinene) (myrcene)	20-80			k A	350	2.78	-2				*	(2a)
						365	6.9	-2					
						379	1.61	-1					
						395	4.10	-1					
						409	8.11	-1	49.9	8	15		

COMMENTS

Reaction. **(.1)** Selected values ([1]) gives proof of homogeneity. Rate is first order over course of reaction but first order constants dependent upon initial concentration of reactant at lower pressures. Data of all investigators essentially in agreement. ([3]) determines relative efficiency of foreign gases to increase low pressure rate to same high pressure value. These have been converted to calculated pressures required to increase lowest pressure rate by factor of 10 bringing it to rate at 84 mm initial pressure of A. For comparison of effect of foreign gases upon cyclo-C_4H_8 reaction see 571.413. Mechanism postulated by ([2]) involved di-radical formation as intermediate, shown to be invalid by ([3]). Chemical evidence for lack of di-radicals is behavior of such additives as toluene and mesitylene which normally interact strongly with free radicals. ([4]) on theoretical grounds, using molecular spectra of A but no adjustible parameters, concludes that the detailed process is the direct attack of a hydrogen atom on an adjacent carbon atom. **(.2) (.3)** Occur simultaneously with less than 5 % of other products formed.

LITERATURE

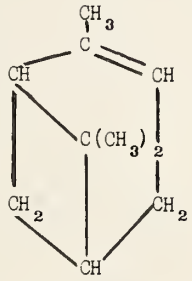
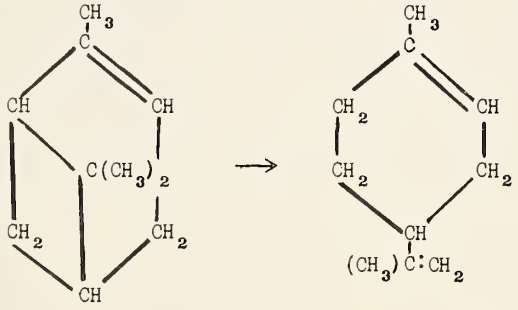
([1]) T.S. Chambers, G.B. Kistiakowsky, *ACS* 1934, **56**, 399. ([2]) E.S. Corner, R.N. Pease, *ACS* 1945, **67**, 2067. ([2a]) J.E. Hawkins, J.W. Vogh, *JPC* 1953, **57**, 902. ([3]) H.O. Pritchard, R.G. Sowden, A.F. Trotman-Dickenson, *PRS*^{A} 1953, **217**, 563. ([4]) N.B. Slater, *PRS*^{A} 1953, **218**, 224.

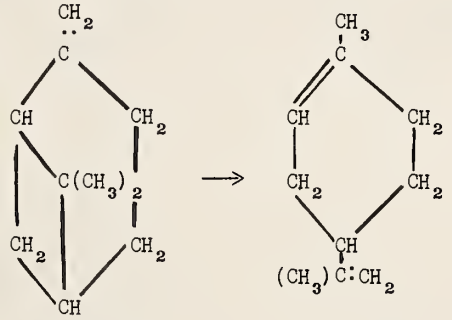
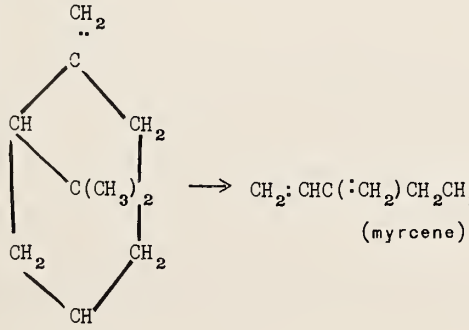
Supplement 1953

ISOMERIZATION
Ring opening to Double bond

Liquid phase

Amounts are in wt %.
Rate constants are per sec.

No.	Reaction	Medium (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	 $\longrightarrow (CH_3)_2C{:}CHCH{:}CHC(CH_3){:}CHCH_3$ (dipentene) (α-pinene)	A	pure A			kA	185	7.2	-7				*	(7)
							189	1.00	-6					(2) (3)
							198	2.8	-6					(1) (4) (6)
							204	3.5	-6	37	2	13		(2) (3)
			99	C_6H_5COOH			204	3.8	-6					
				p-$C_6H_4(OH)_2$			204	3.4	-6					
				quinoline			204	3.5	-6					
							218	1.2	-5					(7)
.2	 (α-pinene) (allo-ocimene)	A	(see .1)				189	5.0	-7				*	(2) (3)
							204	2.17	-6	43	4	15		

No.	Reaction	Medium (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	 (β-pinene) (l-limonene)	A	pure A			k A	220	1.1	-6				*	(3)
			99	p-$C_6H_4(OH)_2$	1		220	1.3	-6					
			99	quinoline			220	1.3	-6					
			50	L			220	1.2	-6					
			pure A				235	4.8	-6	50	2	16		
.4	 $\longrightarrow$ $CH_2{:}CHC(:CH_2)CH_2CH_2CH{:}C(CH_3)_2$ (myrcene) (β-pinene)	A	(see .3)			k A	220	2.4	-6				*	(3)
							235	1.02	-5	47	2	15		
.5	$CH_2CH_2CH_2CHOSO_2C_6H_4CH_3 \longrightarrow CH_2{:}CH_2CH_2CH_2OSO_2C_6H_4CH_3$	CH_3COOH	A = 0.50	CH_3COOK	0.50	k A	50	5.6	-6				*	(5)
			0.09		0.10		55	1.1	-5					
			0.09		0.11		60	2.0	-5					

COMMENTS

Reaction. **(.1) (.2)** Simultaneous reactions and rate of disappearance of A is sum of (.1) and (.2). ([6]) measured loss of optical activity and treated it as racemization. ([1]) showed formation of dipentene and considered loss of optical activity to be caused by (.1) alone. ([4]) recalculated data of ([6]) on this basis. Allo-ocimene, produced by (.2), subsequently dimerizes to a large extent and also forms small amounts of α- and β-pyronenes. Racemization of α-pinene also occurs and rate constant calculated by ([2]). **(.3) (.4)** Simultaneous reactions and rate of disappearance of A is sum of (.3) and (.4). Myrcene, produced by (.4), polymerizes rapidly under conditions of experiment, and was determined as polymer. **(.5)** Occurs simultaneously with ester exchange reaction. See 222.461.

LITERATURE

([1]) J.B. Conant, G.H. Carlson, *ACS* 1929, **51**, 3464. ([2]) R.E. Fuguitt, J.E. Hawkins, *ACS* 1947, **69**, 319. ([3]) H.G. Hunt, J.E. Hawkins, *ACS* 1950, **72**, 5618. ([4]) L.S. Kassel, *ACS* 1930, **52**, 1935. ([5]) J.D. Roberts, V.C. Chambers, *ACS* 1951, **73**, 5034. ([6]) D.F. Smith, *ACS* 1927, **49**, 43. ([7]) F.H. Thurber, C.H. Johnson, *ACS* 1930, **52**, 786.

ISOMERIZATION
Oxide ring to Double bond

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Wt % of H_2O in Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Comments
					(X)	$10^4 \times X =$							
.1	$(C_6H_5)_2C\text{-}C(C_6H_5)_2$ (epoxide) $\longrightarrow (C_6H_5)_3CC{:}OC_6H_5$	C_2H_5OH	0.03	0.0048 -	$HClO_4$	2.83	k A	75	1.16	-3			*
			0.03	0.0084		1.88		75	7.55	-4			
			0.07			1.43		75	3.95	-4			
			0.08			3.19		75	8.01	-4			
			0.08			4.05		75	1.03	-3			
			0.15			4.14		75	7.14	-4			
			0.28			3.39		75	3.88	-4			
			0.28			5.02		75	5.76	-4			
			0.52			8.20		75	5.44	-4			
			0.92			11.7		75	4.18	-4			
			1.00			22.9		75	7.16	-4			
			1.03			21.7		75	6.15	-4			
			1.87			55.6		75	7.91	-4			
			1.89			55.1		75	7.57	-4			
									(k')				
		C_2H_5OH	0.03	0.0048 -		2.83	k' AX	75	4.33	0			
			0.03	0.0084		1.88		75	4.25	0			
			0.07			1.43		75	2.93	0			
			0.08			3.19		75	2.68	0			
			0.08			4.05		75	2.68	0			
			0.15			4.14		75	1.82	0			
			0.28			3.39		75	1.21	0			
			0.28			5.02		75	1.21	0			

No.	Reaction	Solvent (Medium)	Wt % of H_2O in Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments
.1	$(C_6H_5)_2\underset{O}{\overset{\diagup\diagdown}{C}}-C(C_6H_5)_2 \longrightarrow (C_6H_5)_3CC{:}OC_6H_5$ *(continued)*	C_2H_5OH	0.52	0.0048 -	(X) $HClO_4$	$10^4 \times X =$	$k'AX$	75	(k')				
			0.92	0.0084		8.20		75	7.01	-1			
			1.00			11.7		75	3.78	-1			
			1.03			22.9		75	3.31	-1			
			1.87			21.7		75	2.99	-1			
			1.89			55.6		75	1.50	-1			
			0.31			55.1		75	1.45	-1			
								55	1.17	-1			
								75	1.22	0			
								85	3.39	0	26.0	14.3	

COMMENTS

(.1) First order rate law holds over course of reaction and second order constant, k', obtained by dividing pseudo first order constant, k, by catalyst concentration, is constant for fixed concentration of water in solvent. Plot of log k' against acidity function, H_o, where $-\log H_o = \alpha_H + f_B/f_{BH^+}$, gives straight line with slope = -0.87. Rate constants were corrected for volume expansion of solvent with temperature. Authors demonstrate that this reaction is partially responsible as an intermediate in the corresponding pinacol rearrangement, see 522.442 and 532.402.

LITERATURE

H.J. Gebhart, K.H. Adams, *ACS* 1954, **76**, 3925.

ESTERIFICATION

Aliphatic carboxylic acid + Alcohol

Liquid phase

Reaction type $RCOOH + R'OH \longrightarrow RCOOR' + H_2O$
(A) (B) (L) (M)

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

Amounts are in M/l. Rate constants are in M/l and sec.

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

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

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	r	E	$A = A^o \times 10^n$ A^o	n
	Paraffinic carboxylic acid												
.75	$(CH_3)_3CCH_2COOH + CH_3OH$	B	A = 0.5	HCl	0.005	G^*	20	8.14	-4	0.20			
							30	1.59	-3	0.25			
							40	3.09	-3	0.32	12.2	1.0	4
.76	$(CH_3)_2CHCH(C_2H_5)COOH + CH_3OH$	B	"	"	"	"	30	3.80	-5	0.25			
							40	7.80	-5	0.32	13.6	2.3	5
.77	$(CH_3)_3CCH_2CH_2COOH + CH_3OH$	B	"	"	"	"	20	2.04	-2	0.20			
							30	3.59	-2	0.25			
							40	6.11	-2	0.32	10.0	5.8	5
.78	$(CH_3)_3CCH(CH_3)COOH + CH_3OH$	B	"	"	"	"	30	3.97	-5	0.25			
							40	8.17	-5	0.32	13.6	2.5	5

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	r	E	$A = A^o \times 10^n$ A^o	n
.79	$(CH_3)_3CCH_2CH(CH_3)COOH + CH_3OH$	B	A = 0.5	HCl	0.005	G*	20	6.29	-4	0.20			
							30	1.13	-3	0.25			
							40	2.03	-3	0.32	11.1	1.1	5
.80	$(CH_3)_3CC(CH_3)_2COOH + CH_3OH$	B	"	"	"	"	40	1.70	-5	0.32			
.81	$(C_2H_5)_3CCOOH + CH_3OH$	B	"	"	"	"	40	2.14	-5	0.32			
.82	$(CH_3)_3CCH_2C(CH_3)_2COOH + CH_3OH$	B	"	"	"	"	20	1.06	-4	0.20			
							30	2.20	-4	0.25			
							40	4.35	-4	0.32	12.7	3.1	5
.83	$(CH_3)_3CCH(C_2H_5)CH_2CH_2COOH + CH_3OH$	B	"	"	"	"	20	4.34	-3	0.20			
							30	7.70	-3	0.25			
							40	1.34	-2	0.32	10.5	2.6	5
.84	$[(CH_3)_3CCH_2]_2CHCOOH + CH_3OH$	B	"	"	"	"	20	2.74	-5	0.20			
							30	5.62	-5	0.25			
							40	1.15	-4	0.32	13.5	3.0	5
.85	*cyclo*-$C_6H_{11}COOH + CH_3OH$	B	"	"	"	$k\,A[H^+]$	20	8.86	-3				
							30	1.60	-2				
							40	2.67	-2				
							50	4.38	-2		10.0	2.7	5

COMMENTS

Validity of the Goldschmidt equation is tantamount to the step $RCOOH + R'OH_2^+ \longrightarrow RCOOR' + H_3O^+$ being rate determining for the esterification. The rate constants k listed apply to this rate determining step.

CORRECTION

Homogeneous Reaction Kinetics, May 1950, table 202.441, page 18 (book page 80),

COMMENTS (General): (G^*) The integrated form of the Goldschmidt equation is

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

LITERATURE

K.L. Loening, A.B. Garrett, M.S. Newman, *ACS* 1952, **74**, 3929.

H.A. Smith, H.S. Levenson, *ACS* 1940, 62, 2733. (Reaction .85)

ESTERIFICATION

Aliphatic carboxylic polyacid and Alcohol

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Rate measured $-dA/dt$

G* = Goldschmidt equation, $k\,A[H^+]\tau/(M+\tau)$ $\quad \tau = [BH^+][M]/[MH^+]$

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	τ	E	$A = A^o \times 10^n$ A^o	n
	Cycloalkyl - substituted aliphatic polyacid												
.1	*cyclo-cis*-1,2-$C_6H_{10}(COOH)_2$ + $2CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + 2H_2O$	B	see reactions (.2) (.3)										
.2	*cyclo-cis*-1,2-$C_6H_{10}(COOH)_2$ + $CH_3OH \longrightarrow C_6H_{10}(COOH)COOCH_3 + H_2O$	B	~0.5	HCl	~0.005	G*	25	1.67	-3	0.22			
							35	3.24	-3	0.28			
							45	6.86	-3	0.36			
							55	1.23	-2	0.48	13.1	6.8	6
.3	*cyclo-cis*-2-$CH_3OOCC_6H_{10}COOH + CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + H_2O$	B	~0.5	HCl	~0.005	G*	25	2.91	-4	0.22			
							35	5.66	-4	0.28			
							45	1.14	-3	0.36			
							55	2.12	-3	0.48	13.1	1.2	6
.4	*cyclo-trans*-1,2-$C_6H_{10}(COOH)_2$ + $2CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + 2H_2O$	B	see reactions (.5) (.6)										
.5	*cyclo-trans*-1,2-$C_6H_{10}(COOH)_2$ + $CH_3OH \longrightarrow CH_3OOCC_6H_{10}COOH + H_2O$	B	~0.5	HCl	~0.005	G*	25	7.78	-4	0.22			
							35	1.71	-3	0.28			
							45	3.33	-3	0.36			
							55	6.28	-3	0.48	13.5	6.8	6

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	r	E	$A = A^o \times 10^n$ A^o	n
.6	*cyclo-trans*-2-$CH_3OOCC_6H_{10}COOH + CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + H_2O$	B	~0.5	HCl	~0.005	G*	25	4.25	-4	0.22			
							35	8.24	-4	0.28			
							45	1.56	-3	0.36			
							55	2.93	-3	0.48	12.5	6.4	5
.7	*cyclo-cis*-1,3-$C_6H_{10}(COOH)_2 + 2CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + 2H_2O$	B	see reactions (.8)(.9)										
.8	*cyclo-cis*-1,3-$C_6H_{10}(COOH)_2 + CH_3OH \longrightarrow CH_3OOCC_6H_{10}COOH + H_2O$	B	~0.5	HCl	~0.005	G*	25	3.11	-2	0.22			
							35	4.65	-2	0.28			
							45	8.67	-2	0.36			
							55	1.45	-1	0.48	10.3	1.0	6
.9	*cyclo-cis*-3-$CH_3OOCC_6H_{10}COOH + CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + H_2O$	B	~0.5	HCl	~0.005	G*	25	1.18	-2	0.22			
							35	1.98	-2	0.28			
							45	3.44	-2	0.36			
							55	5.51	-2	0.48	10.1	3.1	5
.10	*cyclo-trans*-1,3-$C_6H_{10}(COOH)_2 + 2CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + 2H_2O$	B	see reactions (.11)(.12)										
.11	*cyclo-trans*-1,3-$C_6H_{10}(COOH)_2 + CH_3OH \longrightarrow CH_3OOCC_6H_{10}COOH + H_2O$	B	~0.5	HCl	~0.005	G*	25	1.72	-2	0.22			
							35	3.14	-2	0.28			
							45	5.40	-2	0.36			
							55	8.93	-2	0.48	10.7	7.7	5
.12	*cyclo-trans*-3-$CH_3OOCC_6H_{10}COOH + CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + H_2O$	B	~0.5	HCl	~0.005	G*	25	6.94	-3	0.22			
							35	1.20	-2	0.28			
							45	2.00	-2	0.36			
							55	3.09	-2	0.48	9.7	9.3	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	r	E	$A = A^o \times 10^n$ A^o	n
.13	*cyclo-cis*-1,4-$C_6H_{10}(COOH)_2 + 2CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + 2H_2O$	B	see reactions (.14) (.15)										
.14	*cyclo-cis*-1,4-$C_6H_{10}(COOH)_2 + CH_3OH \longrightarrow CH_3OOCC_6H_{10}COOH + H_2O$	B	~0.5	HCl	~0.005	G*	25	1.62	-2	0.22			
							35	3.04	-2	0.28			
							45	5.38	-2	0.36			
							55	8.28	-2	0.48	10.6	1.1	6
.15	*cyclo-cis*-4-$CH_3OOCC_6H_{10}COOH + CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + H_2O$	B	~0.5	HCl	~0.005	G*	25	6.76	-3	0.22			
							35	1.24	-2	0.28			
							45	1.95	-2	0.36			
							55	3.04	-2	0.48	9.7	9.7	4
.16	*cyclo-trans*-1,4-$C_6H_{10}(COOH)_2 + 2CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + 2H_2O$	B	see reactions (.17) (.18)										
.17	*cyclo-trans*-1,4-$C_6H_{10}(COOH)_2 + CH_3OH \longrightarrow CH_3OOCC_6H_{10}COOH + H_2O$	B	~0.5	HCl	~0.005	G*	25	2.84	-2	0.22			
							35	5.06	-2	0.28			
							45	8.78	-2	0.36			
							55	1.42	-1	0.48	10.4	1.3	6
.18	*cyclo-trans*-4-$CH_3OOCC_6H_{10}COOH + CH_3OH \longrightarrow C_6H_{10}(COOCH_3)_2 + H_2O$	B	~0.5	HCl	~0.005	G*	25	1.32	-2	0.22			
							35	2.27	-2	0.28			
							45	3.84	-2	0.36			
							55	5.96	-2	0.48	9.8	2.1	5

COMMENTS

Reaction. **(.1)** composed of consecutive steps (.2) and (.3). **(.4)** composed of consecutive steps (.5) and (.6). **(.7)** composed of consecutive steps (.8) and (.9). **(.10)** composed of consecutive steps (.11) and (.12). **(.13)** composed of consecutive steps (.14) and (.15). **(.16)** composed of consecutive steps (.17) and (.18). **(.2) (.5) (.8) (.11) (.14)** and **(.17)** calculated by extrapolation to zero time k from integrated form of the Goldschmidt equation,

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

where (a) is the original concenteation of dibasic acid and (x) is concentration of monoester present at time t. **(.3) (.6) (.9) (.12) (.15)** and **(.18)** calculated from integrated form of Goldschmidt equation,

$$k = \frac{1}{(t_2 - t_1) r[H^+]} \left[(2a + r) \ln \frac{a - x_1}{a - x_2} - x_2 + x_1\right]$$

where a is the original concentration of dibasic acid but expression has factor $(2a + r)$ since moles of water equal mols of monoester present, as reaction had been previously allowed to proceed until conversion to monoester almost complete. Direct measurements of (.3) (.6) (.9) starting with pure monomethyl esters also made. Slow change in catalyst concentration due to reaction with solvent at higher temperatures corrected for.

LITERATURE

H. A. Smith, F.P. Byrne, *ACS* 1950, **72**, 4406.

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. Rate constants are in M/l and sec.

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

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$ k^0	n	E	$A = A^0 \times 10^n$ A^0	n	Comments	Literature
.83	.1	$HCOOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.42	-3					(15)
.84		$HCOOCH_3 + OH^-$	H_2O	A = 0.01			$k\,AB$	5	1.16	1				*	(7)
								15	2.06	1					
								25	3.67	1					
								35	6.21	1	9.6	3.7	8		
.85	.2	$HCOOC_2H_5 + H_2O$	H_2O	A = 0.2			$k\,AL^{\frac{1}{2}}$	0	3.5	-6				*	(10)
								20	2.5	-5	15				
			H_2O		HCl		$k\,A[H^+]$	25	3.12	-3					(15)
.86		$HCOOC_2H_5 + OH^-$	H_2O	A = 0.1			$k\,AB$	5	8.49	0				*	(7)
								15	1.50	1					
								25	2.57	1					
								35	4.07	1	8.9	9	7		
.87		$HCOOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.80	-3					(15)

No.	Supplementing 1951 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
.88		$HCOOCH_2CH_2CH_3 + OH^-$	H_2O	A = 0.01			k AB	5	8.05	0					(7)
								15	1.40	1					
								25	2.28	1					
								35	3.62	1	8.5	4.0	7		
.89		$HCOOCH(CH_3)_2 + OH^-$	H_2O	A = 0.01			k AB	5	3.98	0					(7)
								15	6.89	0					
								25	1.09	1					
								35	1.73	1	8.3	1.3	7		
.90		$HCOOCH_2CH_2CH_2CH_3 + OH^-$	H_2O	A = 0.01			k AB	5	7.60	0					(7)
								15	1.31	1					
								25	1.72	1					
								35	3.07	1	8.0	1.5	7		
.91		$HCOOCH_2C_6H_5 + OH^-$	WA*	A = B			k AB	25	2.58	1	11.6	9	9		(21)
.92	.7	$CH_3COOCH_3 + H_2O$	WA62*	$A \simeq 0.1$	HCl	0.106	k A[H^+]	30	8.66	-5				*	(13)
						0.083		40	2.00	-4	15.7	1.6	7		
.93	.8	$CH_3COOCH_3 + OH^-$	WA62*	A=0.008-0.015			k AB	0	1.52	-2				*	(13)
				B=0.02-0.045				11	3.47	-2					
								20	6.60	-2	12.2	8	7		
.94	.9	$CH_3COOC_2H_5 + H_2O$	H_2O	A = 0.2	HCl	0.0002	k A[Acid]	25	1.07	-4				*	(3)
						0.0005		25	1.08	-4					
						0.001		25	1.08	-4					
						0.002		25	1.08	-4					
						0.01		25	1.09	-4					

No.	Supplementing 1951 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
.94	.9	$CH_3COOC_2H_5 + H_2O$ *(cont.)*	H_2O	A = 0.2	HCl	0.02	k A[Acid]	25	1.07	-4					
						0.04		25	1.08	-4					
						0.1		25	1.08	-4					(3) (9) (15)
						0.2		25	1.09	-4					(3)
						0.5		25	1.12	-4					
					CF_3COOH	0.1		25	1.00	-4					(9)
					CHF_2COOH	0.1		25	6.09	-5					
.95		$CH_3COOC_2H_5 + OH^-$	H_2O	A=0.01; B=0.02			k AB	0	1.82	-2					(11)
								10	3.90	-2					
								19	7.23	-2	11	1.2	7		
.96	.12	$CH_3COOC_2H_5 + OH^-$	WE* (D=65)	A=0.01; B=0.02	$NaNO_3$	μ = 0.02	k AB	0	8.65	-3				*	(1) (11)
								10	2.35	-2					
								19	5.03	-2	14.6	4.4	9		
						μ = 0.05		0	8.43	-3					
								10	2.25	-2					
								19	4.93	-2	14.7	4.6	9		
						μ = 0.1		0	8.25	-3					
								10	2.15	-2					
								19	4.87	-2	14.8	5.1	9		
						μ = 0.2		0	7.80	-3					
								10	2.08	-2					
								19	4.67	-2	14.9	6.0	9		
			(D=80)	A=0.01; B=0.02		μ = 0.2		0	1.93	-2					
								10	4.02	-2					
								19	7.52	-2	11.3	2.0	7		
			(D=50)	A=0.01; B=0.02		μ = 0.2		0	2.68	-3					
								10	7.10	-3					
								19	1.82	-2	15.9	1.4	10		

No.	Supplementing 1951 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
.97	.13	$CH_3COOC_2H_5 + OH^-$	WA62*	$A \sim 0.01$; $B \sim 0.05$		$\mu \sim 0.05$	k AB	1	6.8	-3				*	(13)
								11	1.51	-2					
								20	2.92	-2	12.0	3	7		
						$\mu = 0.02$		0	1.43	-2				*	(2)
								16	3.98	-2					
								26	7.47	-2	10.3	2.5	6		
			WAD*	$A \sim 0.01$; $B \sim 0.02$	$NaNO_3$	$\mu = 0.02$	k AB	0	2.23	-2					(2)
			(D=75)			0.05		0	2.15	-2					
						0.10		0	2.07	-2					
						0.20		0	1.93	-2					
						0.30		0	1.80	-2					
						0.02		16	7.07	-2					
						0.05		16	6.90	-2					
						0.10		16	6.72	-2					
						0.20		16	6.48	-2					
						0.30		16	6.27	-2					
						0.02		26	1.35	-1	11.2	2.0	7		
						0.05		26	1.34	-1	11.4	2.7	7		
						0.10		26	1.33	-1	11.6	3.6	7		
						0.20		26	1.30	-1	11.9	5.9	7		
						0.30		26	1.28	-1	12.2	1.0	8		
			(D=67)	$A \sim 0.01$; $B \sim 0.02$	$NaNO_3$	$\mu = 0.20$		0	2.00	-2					
								16	6.15	-2					
								26	1.16	-1	10.7	8	6		
			(D=54)	$A \sim 0.01$; $B \sim 0.02$	$NaNO_3$	$\mu = 0.20$		0	1.68	-2					
								16	5.02	-2					
								26	9.20	-2	10.5	4	6		

No.	Supplementing 1951 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
.98		$CH_3COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.17	-5					(15)
.99		$CH_3COOCH_2CH_2CH_3 + OH^-$	H_2O	A = 0.01–0.02; B = 0.01			$k\,AB$	25	9.70	-2					(8a)
.100		$CH_3COOCH(CH_3)_2 + H_2O$	WA62*	A = 0.07–0.08	HCl	0.09–0.10	$k\,A[H^+]$	30	3.33	-5					(13)
								40	7.85	-5	16	2	7	*	
.101		$CH_3COOCH(CH_3)_2 + OH^-$	WA62*	A = 0.013–0.016			$k\,AB$	0	1.05	-3					(13)
				B = 0.04–0.08				10	2.33	-3					
								20	4.82	-3	12.2	8	6		
.102		$CH_3COOCH_2CH(CH_3)_2 + H_2O$	WA62*	A = 0.07–0.10	HCl	0.09–0.1	$k\,A[H^+]$	30	5.15	-5				*	(13)
								40	1.19	-4	16.0	1.6	7		
.103		$CH_3COOCH_2CH(CH_3)_2 + OH^-$	WA62*	A = 0.011–0.015			$k\,AB$	0	2.45	-3					(13)
				B = 0.056–0.060				10	5.23	-3					
								20	1.13	-2	12.4	2.0	7		
.103.1		$CH_3COOCH(CH_3)(C_2H_5) + OH^-$	H_2O	A = 0.01–0.02; B = 0.01			$k\,AB$	25	1.74	-2					(8a)
.104		$CH_3COOC(CH_3)_3 + H_2O$	WA62*	A = 0.07–0.10	HCl	0.09–0.1	$k\,A[H^+]$	30	1.33	-5				*	(13)
								40	4.5	-5	23	6	11		
.105	.15	$CH_3COOC(CH_3)_3 + OH^-$	WA62*	A = 0.01–0.02			$k\,AB$	30	4.66	-4					(13)
				B = 0.05–0.06				40	1.01	-3	14	8	6		

No.	Supplementing 1951 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
.105.1		$CH_3COOC(CH_3)(C_2H_5)_2 + OH^-$	H_2O				k AB	25	4.2	-4					(8a)
.106		$CH_3COOCH_2CH{:}CH_2 + H_2O$	WA62*	A = 0.05-0.07	HCl	0.05-0.06	k A$[H^+]$	42	1.15	-4				*	(8)
								56	3.48	-4					
								69	9.36	-4	17.3	1.2	8		
.107		$CH_3COOCH_2CH{:}CH_2 + OH^-$	H_2O	A = 0.01-0.015; B = 0.01			k AB	25	2.09	-1					(8a)
			WA62*	A = 0.05-0.06;				-11	4.1	-3					(8)
				B = 0.08-0.10				0	9.0	-3	10	1	6		
.107.1		$CH_3COOCH_2C{:}CH + OH^-$	H_2O	A = 0.01-0.012; B = 0.01			k AB	25	7.3	-1					(8a)
.107.2		$CH_3COOCH(CH_3)CH{:}CH_2 + OH^-$	H_2O	A = 0.01-0.02; B = 0.01			k AB	25	7.17	-2					(8a)
.107.3		$CH_3COOCH(CH_3)C{:}CH + OH^-$	H_2O	A = 0.01-0.015; B = 0.01			k AB	25	3.65	-1					(8a)
.107.4		$CH_3COOC(CH_3)(C_2H_5)CH{:}CH_2 + OH^-$	H_2O	A = B = 0.01			k AB	25	4.0	-3					(8a)
.107.5		$CH_3COOC(CH_3)(C_2H_5)C{:}CH + OH^-$	H_2O	A = 0.01-0.015; B = 0.01			k AB	25	2.20	-2					(8a)

No.	Supplementing 1951 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		$CH_3COOCH_2CH_2C_6H_5 + OH^-$	WA*	A = B			k AB	25	4.14	-2	12.0	3.0	7		(21)
.109		$CH_3COOCH_2CH_2CH_2C_6H_5 + OH^-$	WA*	A = B			k AB	25	2.94	-2	12.0	2.1	7		(21)
.110		$CH_3COOCH_2[p\text{-}C_6H_4CH(CH_3)_2] + OH^-$	WA*	A = B			k AB	25	3.58	-2	12.5	5.6	7		(21)
.111		$CH_3COOC(C_6H_5)_3 + H_2O$	WA*	A = 0.001			k A	25	7.2	-4				*	(20)
.112		$CH_3COOCH_2CH_2OCH_3 + H_2O$	H_2O		HCl		k A$[H^+]$	25	8.05	-5					(15)
.113		$CH_3COOCH_2CH_2OC_2H_5 + H_2O$	H_2O		HCl		k A$[H^+]$	25	7.94	-5					(15)
.114		$CH_3COOCH_2CH_2CH_2OCH_3 + H_2O$	H_2O		HCl		k A$[H^+]$	25	9.56	-5					(15)
.115		$CH_3COOCH_2CH_2CH_2OC_2H_5 + H_2O$	H_2O		HCl		k A$[H^+]$	25	9.65	-5					(15)
.116		$CH_3COOCH_2C{:}OCH_3 + H_2O$	H_2O		HCl		k A$[H^+]$	25	3.43	-5					(15)
.117		$CH_3COOCH_2COOH + H_2O$	H_2O		HCl		k A$[H^+]$	25	3.00	-5					(15)
.118		$CH_3COOCH_2(p\text{-}C_6H_4OCH_3) + OH^-$	WA*	A = B			k AB	25	4.99	-2	12.5	7.7	7		(21)
.119		$CH_3COOCH_2C{:}\dot{N} + H_2O$	H_2O		HCl		k A$[H^+]$	25	3.15	-5					(15)
.120		$CH_3COOCH_2CH_2C{:}\dot{N} + H_2O$	H_2O		HCl		k A$[H^+]$	25	8.00	-5					(15)
.121		$CH_3COOCH_2CH_2CH_2C{:}\dot{N} + H_2O$	H_2O		HCl		k A$[H^+]$	25	9.65	-5					(15)
.122		$CH_3COOCH_2(p\text{-}C_6H_4C{:}\dot{N}) + OH^-$	WA*	A = B			k AB	25	1.97	-1	11.8	1.0	8		(21)

No.	Supplementing 1951 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
.123		$CH_3COOCH_2CH_2(p\text{-}C_6H_4NO_2) + OH^-$	WA*	A = B			k AB	25	7.79	-2	11.9	4.5	7		(21)
.124		$CH_3COOCH_2CH_2CH_2(p\text{-}C_6H_4NO_2) + OH^-$	WA*	A = B			k AB	25	4.16	-2	11.9	2.4	7		(21)
.125		$CH_3COOCH_2CHF_2 + H_2O$	AW*		H^+	0.1	k A	25	2.0	-6					(6)
.126		$CH_3COOCH_2CF_3 + H_2O$	AW*		H^+	0.1	k A	25	1.4	-6					(6)
.127		$CH_3COOCH_2CF_3 + OH^-$	AW*	B = 0.01			k AB	25	6	-1					(6)
.128		$CH_3COOCH_2CH_2CF_3 + H_2O$	AW*		H^+	0.1	k A	25	2.6	-6					(6)
.129		$CH_3COOCH(CH_3)CF_3 + H_2O$	AW*		H^+	0.1	k A	25	1.2	-6					(6)
.130		$CH_3COOCHCH_3CF_3 + OH^-$	AW*	B = 0.01			k AB	25	1.5	-1					(6)
.131		$CH_3COOCH_2(p\text{-}C_6H_4F) + OH^-$	WA*	A = B			k AB	25	9.00	-2	12.2	7.1	7		(21)
.132		$CH_3COOCH_2CH_2Cl + H_2O$	H_2O		HCl		k A$[H^+]$	25	7.80	-5					(15)
.133		$CH_3COOCH_2CH_2CH_2Cl + H_2O$	H_2O		HCl		k A$[H^+]$	25	1.02	-4					(15)
.134		$CH_3COOCH_2CCl_3 + H_2O$	DW*		HCl		k A$[H^+]$	25	2.67	-5					(17)
								35	6.40	-5	15.9	1.3	7		
.135		$CH_3COOCH_2(p\text{-}C_6H_4Cl) + OH^-$	WA*	A = B			k AB	25	1.07	-1	12.3	1.0	8		(21)
.136		$CH_3COOCH_2CH_2Br + H_2O$	H_2O		HCl		k A$[H^+]$	25	9.30	-5					(15)

No.	Supplementing 1951 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
.137		$CH_3COOCH_2(p\text{-}C_6H_4Br) + OH^-$	WA*	A = B			$k\,AB$	25	1.03	-1	12.1	8.7	7		(21)
.138		$CH_3COOCH_2(m\text{-}C_6H_4I) + OH^-$	WA*	A = B			$k\,AB$	25	1.00	-1	12.2	9.5	7		(21)
.139		$CH_3COOCH_2(p\text{-}C_6H_4I) + OH^-$	WA*	A = B			$k\,AB$	25	1.04	-1	12.1	8.4	7		(21)
.140		$C_2H_5COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.21	-4					(15)
.141	.31	$C_2H_5COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.18	-4					(15)
.142		$C_2H_5COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.51	-5					(15)
.143		$C_2H_5COOCH_2C_6H_5 + OH^-$	WA*	A = B			$k\,AB$	25	3.43	-2	12.3	4.1	7		(21)
.144		$n\text{-}C_3H_7COOCH_2C_6H_5 + OH^-$	WA*	A = B			$k\,AB$	25	1.77	-2	12.4	2.2	7		(21)
.145		$n\text{-}C_4H_9COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	7.35	-5					(15)
.146		$n\text{-}C_4H_9COOCH_2C_6H_5 + OH^-$	WA*	A = B			$k\,AB$	25	1.37	-2	12.5	2.3	7		(21)
.147		$(CH_3)_2CHCH_2COOCH_2C_6H_5 + OH^-$	WA*	A = B			$k\,AB$	25	4.46	-3	12.8	1.1	7		(21)
.148		$C_2H_5CH(CH_3)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.30	-5					(15)
.149		$n\text{-}C_5H_{11}COOCH_2C_6H_5 + OH^-$	WA*	A = B			$k\,AB$	25	1.14	-2	12.4	1.6	7		(21)
.150		$(CH_3)_2CHCH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.68	-5					(15)
.151		$n\text{-}C_7H_{15}COOCH_2C_6H_5 + OH^-$	WA*	A = B			$k\,AB$	25	1.12	-2	12.4	1.5	7		(21)

No.	Supplementing 1951 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
Ester of Cyclo-Alkyl-substituted aliphatic carboxylic acid															
.152		*cyclo*-$C_6H_{11}COOC_2H_5 + OH^-$	Et85*	A = B = 0.05			k AB	35	8.48	-4				*	(19)
								45	1.91	-3					
								55	4.03	-3					
								65	8.19	-3	15.6	1.0	8		
Ester of Unsaturated aliphatic carboxylic acid															
.153		$CH_2{:}CHCOOCH_3 + H_2O$	H_2O		HCl		$k A[H^+]$	25	4.70	-6					(15)
.154		$CH_2{:}CHCH_2COOCH_3 + H_2O$	H_2O		HCl		$k A[H^+]$	25	7.05	-5					(15)
.155		$CH_2{:}CHCH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$k A[H^+]$	25	5.75	-5					(15)
.156		$CH_2{:}CHCH_2CH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$k A[H^+]$	25	5.76	-5					(15)
.157		$C_6H_5CH{:}CHCOOC_2H_5 + OH^-$	WA*	A = B $\simeq$ 0.03			k AB	25	4.79	-3	15.1	7.1	8		(23)
Ester of Hydroxy or Alkoxy-substituted aliphatic carboxylic acid with aliphatic alcohol															
.158		$HOCH_2COOCH_3 + H_2O$	H_2O		HCl		$k A[H^+]$	25	1.21	-4					(15)
.159		$HOCH_2COOCH_3 + OH^-$	H_2O	B $\simeq$ 0.01			k AB	15	1.00	0					(16)
								25	1.92	0	11.1	3	8		
.160		$HOCH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k A[H^+]$	25	1.20	-4					(15)
.161		$HOCH_2COOC_2H_5 + OH^-$	H_2O	B $\simeq$ 0.01			k AB	15	5.59	-1					(16)
								25	1.01	0	10.1	3	7		

No.	Supplementing 1951 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
.162		$HOCH_2COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.43	-5					(15)
.163		$HOCH_2COOCH_2CH_2CH_3 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	5.93	-1					(16)
								25	9.20	-1	8	1	6		
.164		$HOCH_2COO(CH_2)_3CH_3 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	4.60	-1					(16)
								25	8.46	-1	10.5	4	7		
.165		$HOCH_2COOCH_2CH(CH_3)_2 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	1.24	-1					(16)
								25	2.18	-1	9.6	2	6		
.166		$HOCH_2COOCH_2CH{:}CH_2 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	1.07	0					(16)
								25	1.88	0	9.6	2	7		
.167		$HOCH_2COOCH_2CH_2OCH_3 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	1.24	0					(16)
								25	2.38	0	11.1	3	8		
.168		$HOCH_2COOCH_2CH_2OC_2H_5 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	1.28	0					(16)
								25	2.42	0	10.8	2	8		
.169		$HOCH_2COOCH_2CH_2OCH_2CH_2CH_3 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	1.11	0					(16)
								25	2.12	0	11.0	3	8		
.170		$HOCH_2COOCH_2CH_2CH_2OCH_3 + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	6.83	-1					(16)
								25	1.28	0	10.7	9	7		
.171		$HOCH_2COOCH_2CH_2Cl + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	1.76	0					(16)
								25	3.10	0	9.6	4	7		

No.	Supplementing 1951 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
.172		$HOCH_2COOCH_2CH_2CH_2Cl + OH^-$	H_2O	$B \tilde{=} 0.01$			$k\,AB$	15	9.30	-1					(16)
								25	1.67	0	10.0	4	7		
.173		$CH_3OCH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.21	-5					(15)
.174		$CH_3OCH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.55	-5					(15)
.175		$CH_3OCH_2COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	3.73	-5					(15)
.176		$CH_3OCH_2COOCH_2CH_2OC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.57	-5					(15)
								25	4.51	-5					
								35	1.11	-4	17	1	8		
.177		$CH_3OCH_2COOCH_2CH_2OC_3H_7 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.56	-5					(15)
								25	4.18	-5					
								35	1.08	-4	17.1	1.2	8		
.178		$C_2H_5OCH_2COOCH_2CH_2OCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.55	-5					(15)
								25	4.14	-5					
								35	1.09	-4	17.1	1.2	8		
.179		$C_2H_5OCH_2COOCH_2CH_2OC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.56	-5					(15)
								25	4.13	-5					
								35	1.06	-4	16.8	9	7		
.180		$C_2H_5OCH_2COOCH_2CH_2OC_3H_7 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.52	-5					(15)
								25	4.14	-5					
								35	1.03	-4	16.8	9	7		

No.	Supplementing 1951 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		
.181		n-$C_3H_7OCH_2COOCH_2CH_2OCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.51	-5					(15)
								25	4.33	-5					
								35	1.05	-4	17	1	8		
.182		n-$C_3H_7OCH_2COOCH_2CH_2OC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.50	-5					(15)
								25	3.95	-5					
								35	1.06	-4	17	1	8		
.183		n-$C_3H_7OCH_2COOCH_2CH_2OC_3H_7 + H_2O$	H_2O		HCl		$k\,A[H^+]$	15	1.59	-5					(15)
								25	4.16	-5	16	5	7		
.184		$(CH_3)_2CHOCH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.31	-5					(15)
.185		$CH_3OCH_2CH_2OCH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	7.06	-5					(15)
.186		$CH_3CH(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.30	-4					(15)
.187		$CH_3CH(OH)COOCH_3 + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	1.00	0					(16)
								25	1.82	0	10.2	6	7		
.188		$CH_3CH(OH)COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.28	-4					(15)
.189		$CH_3CH(OH)COOC_2H_5 + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	4.94	-1					(16)
								25	9.09	-1	10.4	6	7		
.190		$CH_3CH(OH)COOC_3H_7 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	7.31	-5					(15)
.191		$CH_3CH(OH)COOC_3H_7 + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	4.43	-1					(16)
								25	7.69	-1	9.4	6	6		

No.	Supplementing 1951 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
.192		$CH_3CH(OH)COO(n\text{-}C_4H_9) + OH^-$	H_2O	B ≃ 0.01			kAB	15	3.83	-1					(16)
								25	6.85	-1	9.9	1	7		
.193		$CH_3CH(OH)COOCH_2CH(CH_3)_2 + OH^-$	H_2O	B ≃ 0.01			kAB	15	1.18	-1					(16)
								25	2.05	-1	9.4	2	6		
.194		$CH_3CH(OH)COOCH_2CH{:}CH_2 + OH^-$	H_2O	B ≃ 0.01			kAB	15	9.35	-1					(16)
								25	1.75	0	10.7	1	8		
.195		$CH_3CH(OH)COOCH_2CH_2OCH_3 + OH^-$	H_2O	B ≃ 0.01			kAB	15	1.14	0					(16)
								25	2.08	0	10.2	6	7		
.196		$CH_3CH(OH)COOCH_2CH_2OC_2H_5 + OH^-$	H_2O	B ≃ 0.01			kAB	15	1.18	0					(16)
								25	2.06	0	9.4	2	7		
.197		$CH_3CH(OH)COO(CH_2)_3OCH_3 + OH^-$	H_2O	B ≃ 0.01			kAB	15	6.75	-1					(16)
								25	1.14	0	9.0	4	6		
.198		$CH_3CH(OH)COO(CH_2)_4OCH_3 + OH^-$	H_2O	B ≃ 0.01			kAB	15	5.56	-1					(16)
								25	1.03	0	10.5	5	7		
.199		$CH_3CH(OH)COOCH_2CH_2Cl + OH^-$	H_2O	B ≃ 0.01			kAB	15	1.73	0					(16)
								25	2.96	0	9.2	1.5	7		
.200		$CH_3CH(OH)COO(CH_2)_3Cl + OH^-$	H_2O	B ≃ 0.01			kAB	15	9.15	-1					(16)
								25	1.65	0	10.0	4	7		
.201		$CH_3CH(OCH_3)COOCH_3 + H_2O$	H_2O		HCl		$kA[H^+]$	25	3.98	-5					(15)

No.	Supplementing 1951 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
.202		$C_2H_5CH(OCH_3)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.24	-5					(15)
.203		$C_2H_5OCH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.45	-5					(15)
.204		$C_2H_5OCH_2CH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.22	-5					(15)
.205		$C_2H_5OCH_2CH_2COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.26	-5					(15)
.206		$(CH_3)_2C(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	3.90	-5					(15)
.207		$(CH_3)_2C(OH)COOCH_3 + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	2.20	-1					(16)
								25	4.15	-1	10.8	3	7		
.208		$(CH_3)_2C(OH)COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	3.42	-5					(15)
.209		$(CH_3)_2C(OH)COOC_2H_5 + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	6.59	-2					(16)
								25	1.29	-1	11.5	4	7		
				A = 0.05-0.10				25	1.47	-1				*	(14)
				B = 0.05-0.10				25	1.55	-1				*	(12)
.210		$(CH_3)_2C(OH)COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.73	-5					(15)
.211		$(CH_3)_2C(OH)COOCH_2CH_2CH_3 + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	5.80	-2					(16)
								25	1.02	-1	9.6	1.2	6		
.212		$(CH_3)_2C(OH)COO(n\text{-}C_4H_9) + OH^-$	H_2O	$B \simeq 0.01$			$k\,AB$	15	4.65	-2					(16)
								25	8.65	-2	10.6	5	6		

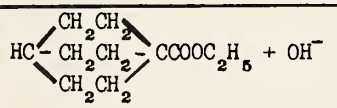
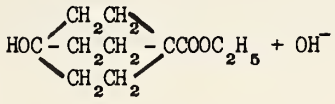
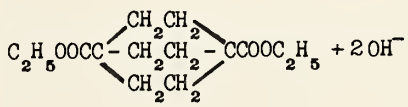
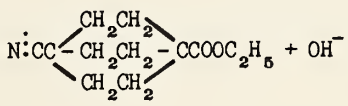
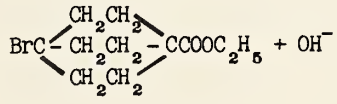
No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.213		$(CH_3)_2C(OH)COOCH_2CH(CH_3)_2 + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	1.17	-2					(16)
								25	2.10	-2	10.0	5	5		
.214		$(CH_3)_2C(OH)COOCH_2CH{:}CH_2 + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	2.08	-1					(16)
								25	3.84	-1	10.4	2	7		
.215		$(CH_3)_2C(OH)COOCH_2CH_2OCH_3 + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	2.45	-1					(16)
								25	4.70	-1	11.1	7	7		
.216		$(CH_3)_2C(OH)COOCH_2CH_2OC_2H_5 + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	2.68	-1					(16)
								25	4.93	-1	10.4	2	7		
.217		$(CH_3)_2C(OH)COOCH_2CH_2CH_2OCH_3 + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	1.30	-1					(16)
								25	2.65	-1	12.2	2	8		
.218		$(CH_3)_2C(OH)COOCH_2CH_2Cl + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	3.55	-1					(16)
								25	7.66	-1	13.1	3	9		
.219		$(CH_3)_2C(OH)COOCH_2CH_2CH_2Cl + OH^-$	H_2O	$B \tilde{<} 0.01$			$k\,AB$	15	1.47	-1					(16)
								25	3.25	-1	13.5	3	9		
.220		$(CH_3)_2C(OCH_3)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.09	-5					(15)
.221		$CH_3OCH_2CH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.65	-5					(15)
.222		$C_2H_5OCH_2CH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.40	-5					(15)
.223		$n\text{-}C_3H_7CH(OCH_3)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.24	-5					(15)

No.	Supplementing 1951 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
.224		$(CH_3)_2CHCH(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.23	-5					(15)
.225		$C_2H_5C(CH_3)(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	1.30	-5					(15)
.226		$(CH_3)_2C(OH)CH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.26	-6					(15)
.227		$CH_3O(CH_2)_4COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.54	-5					(15)
.228		$(CH_3)_2CHCH_2CH(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.26	-5					(15)
.229		$(CH_3)_3CCH(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	3.05	-6					(15)
.230		$C_2H_5(CH_3)C(OH)CH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	4.30	-6					(15)
.231		$(CH_3)_2C(OH)CH(CH_3)COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.7	-7					(15)
.232		$C_2H_5(CH_3)C(OH)CH(CH_3)COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.61	-7					(15)
.233		$(CH_3)_2C(OH)CH(C_2H_5)COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.28	-7					(15)
Ester of Cyclo-alkoxy substituted aliphatic carboxylic acid and aliphatic alcohol															
.234		*cyclo*-$C_5H_9OCH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.66	-5					(15)
.235		*cyclo*-$C_6H_{11}OCH_2COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.14	-5					(15)
Ester of Hydroxy substituted cyclo-aliphatic carboxylic acid and aliphatic alcohol															
.236		$\overline{CH_2CH_2CH_2CH_2C}(OH)COOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.43.	-5					(15)

No.	Supplementing 1951 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
.237		$CH_2CH_2CH_2CH_2C(OH)COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	6.24	-5					(15)
.238		$CH_2CH_2CH_2CH_2C(OH)COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.92	-5					(15)
.239		$CH_2CH_2CH_2CH_2CH_2C(OH)CH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	4.28	-6					(15)
Ester of Carboxy substituted aliphatic carboxylic acid and aliphatic alcohol															
.240		$CH_3C{:}CCH_2CH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.52	-5					(15)
.241		$(CH_3)_3CC{:}OCOOCH_3 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	5.55	-6					(15)
Ester of amino substituted aliphatic carboxylic acid and aliphatic alcohol															
.242		$NH_2CH_2COOC_2H_5 + OH^-$	H_2O				$k\,AB$	25	5.97	-1	10.9	6	7		(5)
.243		$(CH_3)_3N^+CH_2COOC_2H_5 + OH^-$	H_2O				$k\,AB$	25	6.64	+1					(5)
.244		$C_5H_5N^+CH_2COOC_2H_5 + OH^-$	H_2O				$k\,AB$	25	1.81	+2					(5)
Ester of nitrile or aromatic-nitro substituted aliphatic carboxylic acid															
.245		$N{:}CCH_2CH_2COOC_2H_5 + H_2O$	H_2O		HCl		$k\,A[H^+]$	25	2.16	-5					(15)
.246		$m\text{-}NO_2C_6H_4CH{:}CHCOOC_2H_5 + OH^-$	WA*	A = B = 0.03			$k\,AB$	15	1.38	-2					(23)
								25	3.02	-2					
								40	8.90	-2					
								50	1.76	-1	13.4	2.2	8		

No.	Supplementing 1951 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
.247		p-$NO_2C_6H_4CH{:}CHCOOC_2H_5 + OH^-$	WA*	A = B ≃ 0.03			k AB	25	6.11	-2	13.0	2.2	8		(23)
Ester of halogen substituted aliphatic carboxylic acid															
.248		$FCH_2COOC_2H_5 + H_2O$	WA62*	A ≃ 0.1	HCl	0.09-0.11	k A[H^+]	25	2.53	-5					(4)
								35	6.95	-5	18				
								50	2.50	-4					
.249		$F_2CHCOOC_2H_5 + H_2O$	WA62*	A ≃ 0.1	$k = k' + k''[H^+]$		k'A	25	6	-7				*	(4)
					HCl	0.045-0.055	k''A[H^+]	25	9.5	-5					
					HCl	0.05	k A	0	6.0	-7					
								15	2.4	-6					
								25	5.35	-6	14				
.250		$F_3CCOOC_2H_5 + H_2O$	WA62*	A ≃ 0.1	HCl	0	k A	0	4.43	-6				*	(4)
						0		15	1.26	-5					
						0		25	2.40	-5	10.9				
						0.05		0	8.3	-6					
					L	0.01		25	2.45	-5					
.251		$ClCH_2COOCH_3 + H_2O$	H_2O		HCl		k A[H^+]	25	7.60	-5					(15)
.252		$ClCH_2COOC_2H_5 + H_2O$	H_2O		HCl		k A[H^+]	25	7.50	-5					(15)
.253		$ClCH_2COOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		k A[H^+]	25	6.15	-5					(15)
.254		$ClCH_2COOCH_2CCl_3 + H_2O$	DW*		$k = k' + k''[H^+]$		k'A	35	7.2	-7					(17)
					HCl		k''A[H^+]	25	4.51	-5					
								35	1.09	-4	16.1	3	7		

No.	Supplementing 1951 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
.255		$Cl_2CHCOOCH_3 + H_2O$	H_2O				kA	25	1.70	-5					(17)
					HCl		$kA[H^+]$	25	2.12	-4					(15)
.256		$Cl_2CHCOOC_2H_5 + H_2O$	H_2O				kA	25	5.52	-6					(17)
					HCl		$kA[H^+]$	25	1.20	-4					(15)
.257		$Cl_2CHCOOCH_2CH_2CH_3 + H_2O$	H_2O		HCl		$kA[H^+]$	25	3.83	-5					(15)
.258		$Cl_2CHCOOCH_2CH_2OCH_3 + H_2O$	H_2O				kA	25	1.14	-5					(17)
.259		$Cl_2CHCOOCH_2CH_2Cl + H_2O$	H_2O				kA	25	3.67	-5					(17)
.260		$Cl_2CHCOOCH_2CCl_3 + H_2O$	DW*		HCl		$k'A + k''A[H^+]$								(17)
							$k'A$	25	3.12	-5					
								35	5.04	-5	8.7				
							$k''A[H^+]$	25	2.04	-4					
								35	5.24	-4	17.2	8	8		
.261		$ClCH_2CH(OH)COOCH_3 + H_2O$	H_2O		HCl		$kA[H^+]$	25	2.35	-5					(15)
.262		$ClCH_2CH_2CH_2COOCH_3 + H_2O$	H_2O		HCl		$kA[H^+]$	25	5.19	-5					(15)

No.	Supplementing 1951 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
Tricyclic alkyl esters															
.263			Et88*	A = B = 0.024			k AB	30	2.70	-5					(12a)
.264			Et88*	A = B = 0.024			k AB	30	1.26	-4					(12a)
.265			Et88*	A = B = 0.024		-dB/dt =	k AB	30	2.78	-4					(12a)
.266			Et88*	A = B = 0.024			k AB	30	5.30	-4					(12a)
.267			Et88*	A = B = 0.024			k AB	30	2.88	-4					(12a)

SOLVENTS

AW* 50 vol % H_2O + 50 vol % $(CH_3)_2CO$ (7) (18)

DW* 50 vol % H_2O + 50 vol % dioxane (17)

Et85*(88) C_2H_5OH wt % indicated + H_2O (19) (12a)

WA* 60 vol % $(CH_3)_2CO$ + 40 vol % H_2O (~54 wt % $(CH_3)_2CO$) (6) (18) (20) (21) (23)

WA62* 62 wt % $(CH_3)_2CO$ + H_2O 38 wt % (~67 vol % $(CH_3)_2CO$) (2) (8) (9) (13) (16) (23)

WAD* $(CH_3)_2CO$ + H_2O ratio varied to produce solution of dielectric constant = D at each temperature. (2)

WE* C_2H_5OH + H_2O ratio varied to produce solution of dielectric constant = D at each temperature. (1) (11)

COMMENTS

General. Arrangement of the esters is first in order of increasing complexity of aliphatic acid and secondly in order of increasing complexity of esterifying alcohol, i.e. each of the esters of a given acid is listed before any ester of the next higher acid. The order is, unsubstituted saturated, unsaturated, substituted by hydroxy or alkoxy, substituted by nitrogen (in order of increasing nitrogen valence), substituted by halogen.

Reactions. (.84) Values slightly higher than those reported by earlier investigators. (.85) An increasing trend over the course of reaction for rate law $k\,AL^{\frac{1}{2}}$ but gives better fit to data than $k\,AL$ for observed conditions. (.86) Values slightly higher than those reported by earlier investigators. (.92) Rate law $k\,A[H^+]$ presumed used by (13) based upon agreement with results of (2) (18) and others. (.93) Presumed rate law calculated using natural logarithms on basis of reference of (13) to calculations of (18). (.94) Initial rates only, which were obtained by extrapolation to zero time

COMMENTS *(cont.)*

in order to eliminate autocatalysis by L. (.96) Solvent ratio adjusted to produce solutions of same dielectric constant at each temperature. (.97) Unexplained differences between results of (2) (13) and G. Davis, D.P. Evans, *CSL*, **1940**, 339 (see "Tables" 1951 Edition). (.100) (.102) (.104) (.106) Rate law $k\,A[H^+]$ presumed used by (13) based upon agreement with results of other investigators, see (.92). (.111) Variety of nucleophilic reagents produce different products with no change in rate law for reaction of A, see 212.471. (.152) Rate constants calculated between 20 and 80 % reaction show less than 2 % deviations. (.209) Method based upon temperature rise for constant flow mixing used by (12) and titrimetric method for constant flow mixing used by (14). (.249) Catalysis by L appreciable after first 25 % reaction and rate constants calculated for first 25 % reaction only. (.250) Catalysis by L shown to be negligible up to 0.02 M/l.

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ESTER SOLVOLYSIS

Ester of Aromatic carboxylic acid and Aliphatic alcohol

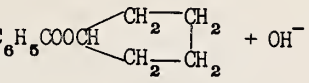
Reaction types

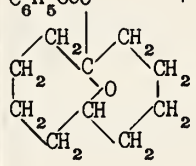
$$ArCOOR + R'OH \longrightarrow ArCOOH + ROR'$$
(A) (B) (L) (M)

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

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.
*Coded solvents, Comments, Literature at end of table.

No.	Supplementing 1951 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
.54	.2	$C_6H_5COOCH_3 + OH^-$	Mt80*	A = B ≃ 0.05			k AB	25	4.21	-4					(11)
								40	1.87	-3	18.4	1.3	10		
.55	.6	$C_6H_5COOC_2H_5 + OH^-$	S*	A = B = 0.05			k AB	See Supplementary Table							(21)
.56	.7	$C_6H_5COOC_2H_5 + OH^-$	Et80*	A = B ≃ 0.05			k AB	25	8.76	-4					(11)
			Et88*					25	6.14	-4					(1)
			Et90*	A=B=(0.02-.04)				30	8.30	-4					(6) (8)
			Et80*	A = B ≃ 0.05				40	3.42	-3	16.9	2	9		(11)
			Et90*	A=B=(0.02-.04)				60	7.24	-3	14.4	2.1	7		(6)
.57	.7	$C_6H_5COOC_2H_5 + OH^-$	DW*	A = B = 0.05			k AB	25	3.43	-3					(14)
								40	1.07	-2	14.0	7	7		
.58		$C_6H_5COOCH_2CH_2CH_3 + OH^-$	M*	A = B ≃ 0.05			k AB	25	8.94	-4					(11)
								40	3.17	-3	15.6	2	8		
.59		$C_6H_5COOCH_2CH_2CH_3 + OH^-$	WA*	A = B			k AB	25	1.93	-3	14.6	1.1	8		(16)

No.	Supplementing 1951 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		
.60		$C_6H_5COOCH(CH_3)_2 + OH^-$	WA*	A = B			k AB	25	4.64	-4	14.9	4.7	7		([16])
.61		$C_6H_5COOCH_2CH{:}CH_2 + OH^-$	WA*	A = B			k AB	25	5.98	-3	14.8	4.4	8		([16])
.62		$C_6H_5COO(CH_2)_3CH_3 + OH^-$	WA*	A = B			k AB	25	1.67	-3	14.6	9.4	7		([16])
.63		$C_6H_5COOCH_2CH(CH_3)_2 + OH^-$	WA*	A = B			k AB	25	1.43	-3	14.6	7.9	7		([16])
.64		$C_6H_5COOCH(CH_3)C_2H_5 + OH^-$	WA*	A = B			k AB	25	2.26	-4	15.1	2.7	7		([16])
.65		$C_6H_5COOC(CH_3)_3 + OH^-$	WA*	A = B			k AB	25	1.33	-5	17.2	6.3	7		([16])
.66		$C_6H_5COOCH_2CH_2CH(CH_3)_2 + OH^-$	WA*	A = B			k AB	25	1.20	-3	14.6	6.6	7		([16])
.67		$C_6H_5COOCH(CH_3)CH_2CH_2CH_3 + OH^-$	WA*	A = B			k AB	25	1.49	-4	15.2	2.4	7		([16])
.68		$C_6H_5COOC(CH_3)_2C_2H_5 + OH^-$	WA*	A = B			k AB	25	5.02	-6	17.9	7.1	7		([16])
.69		 $+ OH^-$	WA*	A = B			k AB	25	2.68	-4	15.3	5.3	7		([16])
.70		$C_6H_5COO(CH_2)_5CH_3 + OH^-$	WA*	A = B			k AB	25	1.27	-3	14.6	7.7	7		([16])
.71		$C_6H_5COO(CH_2)_7CH_3 + OH^-$	WA*	A = B			k AB	25	1.26	-3	14.6	7.1	7		([16])
.72		$C_6H_5COOC_6H_5 + OH^-$	WA*	A = B			k AB	25	3.77	-2	14.3	1.3	9	*	([16])
.73		$C_6H_5COOCH_2C_6H_5 + OH^-$	WA*	A = B			k AB	25	5.19	-3	15.4	1.0	9		([16])

No.	Supplementing 1951 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
.74		$C_6H_5COOCH_2CH_2C_6H_5 + OH^-$	WA*	A = B			kAB	25	2.80	-3	15.0	3.0	8		(16)
.75		$C_6H_5COOC(C_6H_5)_3 + H_2O$	WA*	10^4A = 5-10			kA	25	4.1	-4				*	(15)
			WA50*					25	1.2	-3					
.76		$C_6H_5COOC(C_6H_5)_3 + C_2H_5OH$	EA*	A = 0.028			kA	55	1.8	-4				*	(5)
					C_2H_5ONa	0.044		55	2.7	-4					
					C_2H_5ONa	0.088		55	3.0	-4					
					$NaClO_4$	0.044		55	5.0	-4					
.77		$C_6H_5COOC(C_6H_5)_3 + C_2H_5OH$	EB*	A = 0.028	KOH + $(C_6H_5)_3CCl$	0.007 0.006	kA	55	2.3	-4					(5)
.78		C_6H_5COO + CH_3OH 	B	A = 0.12	% A reacted		kA	100	9-15	-7				*	(4)
					26			100	8.8	-7					
					42			100	1.08	-6					
					57			100	1.27	-6					
					68			100	1.31	-6					
					80			100	1.62	-6					
					84			100	1.52	-6					
.79	.9	$o\text{-}CH_3C_6H_4COOC_2H_5 + OH^-$	WA*	A = B			kAB	25	3.38	-4	14.7	2.1	7		(18)
.80		$o\text{-}CH_3C_6H_4COOCH(CH_3)_2 + OH^-$	WA*	A = B			kAB	25	3.93	-5	15.9	1.9	7		(16)
.81		$m\text{-}CH_3C_6H_4COOCH_3 + OH^-$	WA*				kAB	25	5.06	-3	14.8	4.1	8		(19)
.82		$m\text{-}CH_3C_6H_4COOCH_3 + OH^-$	Mt80*	A = B $\simeq$ 0.05			kAB	25	3.07	-4					(11)
								40	1.42	-3	19	2	10		

No.	Supplementing 1951 No.	Reaction	Addend (Catalyst)	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
.83	.10	m-$CH_3C_6H_4COOC_2H_5 + OH^-$	Et80*	$A = B \simeq 0.05$			k AB	25	5.94	-4					(11)
			Et90*					30	5.8	-4					(8)
			Et80*					40	2.51	-3	17.8	8	9		(11)
.84		m-$CH_3C_6H_4COOCH_2CH_2CH_3 + OH^-$	M*	$A = B \simeq 0.05$			k AB	25	5.86	-4					(11)
								40	2.23	-3	16.5	8	8		
.85		p-$CH_3C_6H_4COOCH_3 + OH^-$	WA*				k AB	25	3.77	-3	14.8	2.7	8		(19)
.86		p-$CH_3C_6H_4COOCH_3 + OH^-$	Mt80*	$A = B \simeq 0.05$			k AB	25	1.91	-4					(11)
								40	8.94	-4	19.1	2	10		
.87		p-$CH_3C_6H_4COOC_2H_5 + OH^-$	Mt75*	$A = B = 0.05$			k AB	25	2.59	-4	18.3	6.5	9		(21)
.88	.15	p-$CH_3C_6H_4COOC_2H_5 + OH^-$	Et80*	$A = B \simeq 0.05$			k AB	25	3.91	-4					(11)
								40	1.66	-3	17.9	5	9		
			Et88*	$A = B = 0.052$				25	2.73	-4					(1)
			Et90*	$A=B=0.02$-0.04				30	3.84	-4					(6) (8)
								60	3.32	-3	14.4	9.5	6		(6)
.89		p-$CH_3C_5H_4COOC_2H_5 + OH^-$	DW*	$A = B = 0.05$			k AB	25	1.50	-3					(14)
.90		p-$CH_3C_6H_4COOCH_2CH_2CH_3 + OH^-$	M*	$A = B \simeq 0.05$			k AB	25	3.98	-4					(11)
								40	1.55	-3	16.8	8	8		
.91		p-$CH_3C_6H_4COOCH_2CH_2CH_3 + OH^-$	WA*				k AB	25	7.81	-4	15.1	1.0	8		(19)
.92		p-$C_2H_5C_6H_4COOC_2H_5 + OH^-$	WA*	$A = B \simeq 0.05$			k AB	25	1.06	-3					(1)

No.	Supplementing 1951 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		
.93		p-$C_2H_5C_6H_4COOC_2H_5 + OH^-$	Et88*	A = B ≃ 0.05			k AB	25	2.93	-4					(1)
			Et90*	A = B = 0.04				30	3.77	-4					(6)
			Et90*					60	3.28	-3	14.6	1.3	7		
.94		p-$CH_3CH_2CH_2C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.03-0.04			k AB	30	3.65	-4					(6)
								60	3.20	-3	14.5	1.1	7		
.95		p-$(CH_3)_2CHC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	1.6	-3	14.7	1.1	8		(20)
				A = B = 0.06				25	9.6	-4					(1)
.96		p-$(CH_3)_2CHC_6H_4COOC_2H_5 + OH^-$	Et88*	A = B = 0.06			k AB	25	3.14	-4					(1)
			Et90*	A = B = 0.04				30	3.60	-4					(6)
								60	3.15	-3	14.5	1.1	7		
.97		p-$CH_3(CH_2)_3C_6H_4COOC_2H_5 + OH^-$	Et90*	A = B = 0.04			k AB	30	2.90	-4					(6)
								60	2.57	-3	14.6	9.8	6		
.98		p-$C_2H_5CH(CH_3)C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.03-0.04			k AB	30	2.82	-4					(6)
								60	2.54	-3	14.6	9.5	6		
.99		m-$(CH_3)_3CC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	25	1.00	-3					(13)
								40	3.40	-3	15.1	8	8		
.100		p-$(CH_3)_3CC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.058			k AB	25	9.1	-4					(1)
				A = B = 0.05				25	1.02	-3					(13)
								40	3.30	-3	14.5	4	7		
.101		p-$(CH_3)_3CC_6H_4COOC_2H_5 + OH^-$	Et88*	A = B = 0.058			k AB	25	3.42	-4					(1)
			Et90*	A = B = 0.04				30	2.70	-4					(6)
								60	2.44	-3	14.7	1.1	7		

No.	Supplementing 1951 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
.102		p-$CH_3CH_2CH_2CH(CH_3)C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.034-0.039			k AB	30	2.45	-4					(6)
								60	2.25	-3	14.8	1.2	7		
.103		p-$C_2H_5(CH_3)_2CC_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.038-0.040			k AB	30	2.52	-4					(6)
								60	2.30	-3	14.8	1.2	7		
.104		o-$C_6H_5C_6H_4COOC_2H_5 + OH^-$	WA*				k AB	25	4.53	-5	16.4	5.0	7		(19)
.105		p-$C_6H_5C_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	2.68	-3	14.4	1.0	8		(20)
.106		p-$C_6H_5C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.025-0.03			k AB	25	5.5	-4					(2)
								40	2.32	-3	17.8	6	9		
.107		4,4'-$CH_3C_6H_4C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.025-0.03			k AB	25	4.37	-4					(2)
								40	1.90	-3	18.2	1.0	10		
.108		*trans*-3-$C_6H_5CH{:}CHC_6H_4COOC_2H_5 + OH^-$	WA*	A=0.01; B=0.016			k AB	25	3.5	-3					(9)
.109		*trans*-4-$C_6H_5CH{:}CHC_6H_4COOC_2H_5 + OH^-$	WA*	A=0.01; B=0.016			k AB	25	2.71	-3					(9)
.110		m-$C_6H_5C{:}CC_6H_4COOC_2H_5 + OH^-$	WA*	A=0.01; B=0.016			k AB	25	8.04	-3					(9)
.111		p-$C_6H_5C{:}CC_6H_4COOC_2H_5 + OH^-$	WA*	A=0.01; B=0.016			k AB	25	1.07	-2					(9)
.112		4,4'-$CH_3OC_6H_4C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.025-0.03			k AB	25	3.55	-4					(2)
								40	1.56	-3	18.3	9	9		

No.	Supplementing 1951 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
.113		$3,5\text{-}(CH_3)_2C_6H_3COOC_2H_5 + H_2O$	WA*	A = 0.05	$C_6H_5SO_3H$	0.05	$k\,A[H^+]$	60	3.01	-6				*	(17)
								80	1.93	-5					
								100	9.2	-5					
								111	2.16	-4	21.2	2.5	8		
.114		$3,5\text{-}(CH_3)_2C_6H_3COOC_2H_5 + OH^-$	WA*	A = B = 0.05			$k\,AB$	15	3.96	-4					(17)
								25	9.78	-4					
								40	3.34	-3					
								50	6.97	-3	15.1	1.4	8		
.115	.21	$2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3COOCH_3 + OH^-$	Et85*	A = B			$k\,AB$	25	5.75	-5					(10)
								35	1.47	-4					
								50	7.10	-4	19.2	7	9		
.116	.22	$2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3COOC_2H_5 + OH^-$	Et85*	A = B			$k\,AB$	25	5.05	-5					(10)
								35	1.32	-4					
								50	5.53	-4	18.3	2	9		
.117		$m\text{-}CH_3OC_6H_4COOCH_3 + OH^-$	WA*	A = B			$k\,AB$	25	1.10	-2	14.0	2.3	8		(20)
.118		$m\text{-}CH_3OC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			$k\,AB$	25	3.92	-3	14.4	1.4	8		(18)
.119		$o\text{-}C_2H_5OC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			$k\,AB$	25	1.16	-3	15.0	1.2	8		(18)
.120		$m\text{-}C_2H_5OC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			$k\,AB$	25	3.18	-3	14.6	1.6	8		(20)
.121		$p\text{-}C_2H_5OC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			$k\,AB$	25	5.98	-4	15.4	1.4	8		(20)
.122		$m\text{-}HC{:}OC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			$k\,AB$	25	8.07	-3	14.6	4.3	8		(20)

No.	Supplementing 1951 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
.123		p-HC:O$C_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	8.72	-3	14.5	3.8	8		(20)
.124		o-$C_6H_5OC_6H_4COOC_2H_5$ + OH^-	WA*				k AB	25	1.67	-3	13.9	2.7	7		(19)
.125		p-$C_6H_5OC_6H_4COOC_2H_5$ + OH^-	WA*				k AB	25	1.62	-3	15.4	3.2	8		(19)
.126		o-C_6H_5C:O$C_6H_4COOC_2H_5$ + OH^-	WA*				k AB	25	2.64	-2	12.8	7.1	7		(19)
.127		p-C_6H_5C:O$C_6H_4COOC_2H_5$ + OH^-	WA*				k AB	25	3.20	-2	13.0	1.2	8		(19)
.128		o-N:$CC_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	1.22	-1	12.8	3.4	8		(18)
.129		m-N:$CC_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	1.03	-1	13.0	3.8	8		(18)
.130		p-N:$CC_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	1.57	-1	12.6	2.7	8		(18)
.131		o-$NH_2C_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	2.80	-4	15.6	8.1	7		(18)
.132		m-$NH_2C_6H_4COOCH_3$ + OH^-	WA*	A = B			k AB	25	5.40	-3	14.8	4.4	8		(20)
.133	.27	m-$NH_2C_6H_4COOC_2H_5$ + OH^-	Et90*	A = B = 0.024			k AB	30	3.4	-4					(8)
.134		m-$NH_2C_6H_4COOCH_2CH_2CH_3$ + OH^-	WA*	A = B			k AB	25	1.17	-3	14.6	6.6	7		(20)
.135		p-$NH_2C_6H_4COOCH_3$ + OH^-	WA*	A = B			k AB	25	2.92	-4	16.5	4.3	8		(18)
.136		m-$(CH_3)_2NC_6H_4COOCH_3$ + OH^-	WA*	A = B $\simeq$ 0.05			k AB	25	4.25	-3					(11)

No.	Supplementing 1951 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	$k = k^o \times 10^n$ n	E	$A = A^o \times 10^n$ A^o	$A = A^o \times 10^n$ n	Comments	Literature
.137		m-$(CH_3)_2NC_6H_4COOCH_3 + OH^-$	M*	A = B ≃ 0.05			k AB	25	2.20	-4					(11)
								40	1.03	-3	19.1	2.0	10		
.138		m-$(CH_3)_2NC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	25	1.28	-3				(11)	(11) (13)
								40	3.97	-3	14.1	2.9	7		(13)
.139		m-$(CH_3)_2NC_6H_4COOC_2H_5 + OH^-$	Et80*	A = B ≃ 0.05			k AB	25	4.31	-4					
								40	1.70	-3	17.0	1.3	9		(11)
.140		m-$(CH_3)_2NC_6H_4COOCH_2CH_2CH_3 + OH^-$	M*	A = B ≃ 0.05			k AB	25	4.36	-4					(11)
								40	1.66	-3	16.5	5	8		
.141		p-$(CH_3)_2NC_6H_4COOCH_3 + OH^-$	WA*	A = B ≃ 0.05			k AB	25	2.10	-4					(11)
.142		p-$(CH_3)_2NC_6H_4COOCH_3 + OH^-$	Mt80*	A = B ≃ 0.05			k AB	25	1.16	-5					(11)
								40	6.34	-5	21.0	2.5	10		
.143		p-$(CH_3)_2NC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	25	6.32	-5				(11) (13)	(18)
								40	2.36	-4	16.8	1.6	8	(13)	(18)
.144		p-$(CH_3)_2NC_6H_4COOC_2H_5 + OH^-$	Et80*	A = B ≃ 0.05			k AB	25	2.26	-5					(11)
								40	1.09	-4	19.5	4	9		
.145		p-$(CH_3)_2NC_6H_4COOCH_2CH_2CH_3 + OH^-$	M*	A = B ≃ 0.05			k AB	40	1.17	-4					(11)
.146		m-$(C_2H_5)_2NC_6H_4COOCH_3 + OH^-$	WA*	A = B ≃ 0.05			k AB	25	2.13	-3					(11)
.147		m-$(C_2H_5)_2NC_6H_4COOCH_3 + OH^-$	Mt80*	A = B ≃ 0.05			k AB	25	1.45	-4					(11)
								40	7.06	-4	19.6	3	10		

No.	Supplementing 1951 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
.148		m-$(C_2H_5)_2NC_6H_4COOC_2H_5 + OH^-$	WA*	$A = B \simeq 0.05$			k AB	25	6.51	-4					(11)
.149		m-$(C_2H_5)_2NC_6H_4COOC_2H_5 + OH^-$	Et80*	$A = B \simeq 0.05$			k AB	25	2.79	-4					(11)
								40	1.13	-3	17.3	1.3	9		
.150		m-$(C_2H_5)_2NC_6H_4COOCH_2CH_2CH_3 + OH^-$	WA*	$A = B \simeq 0.05$			k AB	25	4.16	-4					(11)
.151		m-$(C_2H_5)_2NC_6H_4COOCH_2CH_2CH_3 + OH^-$	M*	$A = B \simeq 0.05$			k AB	25	2.78	-4					
								40	1.05	-3	16.4	3	8		(11)
.152		p-$(C_2H_5)_2NC_6H_4COOCH_3 + OH^-$	Mt80*	$A = B \simeq 0.05$			k AB	25	6.4	-6					(11)
								40	3.63	-5	21.4	3	10		
.153		p-$(C_2H_5)_2NC_6H_4COOC_2H_5 + OH^-$	Et80*	$A = B \simeq 0.05$			k AB	25	1.31	-5					(11)
								40	6.85	-5	20.4	1.3	10		
.154		m-$(n\text{-}C_3H_7)_2NC_6H_4COOCH_3 + OH^-$	Mt80*	$A = B \simeq 0.05$			k AB	25	1.25	-4					(11)
								40	6.05	-4	19.5	2.5	10		
.155		m-$(n\text{-}C_3H_7)_2NC_6H_4COOC_2H_5 + OH^-$	Et80*	$A = B \simeq 0.05$			k AB	25	2.20	-4					(11)
								40	9.56	-4	18.2	5	9		
.156		m-$(n\text{-}C_3H_7)_2NC_6H_4COOCH_2CH_2CH_3 + OH^-$	M*	$A = B \simeq 0.05$			k AB	25	2.19	-4					(11)
								40	8.47	-4	16.7	4	8		
.157		p-$(n\text{-}C_3H_7)_2NC_6H_4COOCH_3 + OH^-$	Mt80*	$A = B \simeq 0.05$			k AB	25	5.72	-6					(11)
								40	3.53	-5	22.5	1.6	11		
.158		p-$(n\text{-}C_3H_7)_2NC_6H_4COOC_2H_5 + OH^-$	Et80*	$A = B \simeq 0.05$			k AB	25	1.27	-5					(11)
								40	6.47	-5	20.2	8	9		

No.	Supplementing 1951 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	$k = k^o \times 10^n$ n	E	$A = A^o \times 10^n$ A^o	$A = A^o \times 10^n$ n	Comments	Literature
.159		p-(n-C_3H_7)$_2$NC_6H_4COOCH$_2$CH$_2$CH$_3$ + OH$^-$	M*	A = B $\simeq$ 0.05			k AB	25	1.27	-5					(11)
								40	6.2	-5	19.5	2.5	9		
.160		3-NH$_2$-4-CH$_3$C$_6$H$_3$COOC$_2$H$_5$ + OH$^-$	WA*	A = B = 0.05			k AB	25	9.1	-4					(13)
								40	2.90	-3	14.3	3	7		
.161		3-(CH$_3$)$_2$N-4-CH$_3$C$_6$H$_3$COOC$_2$H$_5$ + OH$^-$	WA*	A = B = 0.05			k AB	25	1.10	-3					(13)
								40	3.42	-3	14.1	3	7		
.162		4-(CH$_3$)$_2$N-3-CH$_3$C$_6$H$_3$COOC$_2$H$_5$ + OH$^-$	WA*	A = B = 0.05			k AB	25	4.28	-4					(13)
								40	1.37	-3	14.4	1.6	7		
.163	.32	o-NO$_2$C$_6$H$_4$COOC$_2$H$_5$ + OH$^-$	WA*	A = B			k AB	25	1.69	-2	12.8	4.3	7		(18)
.164	.32	o-NO$_2$C$_6$H$_4$COOC$_2$H$_5$ + OH$^-$	Mt75*	A = B = 0.05			k AB	25	2.76	-3	16.4	2.9	9		(21)
.165		m-NO$_2$C$_6$H$_4$COOCH$_3$ + OH$^-$	WA*	A = B			k AB	25	3.47	-1	12.8	8.9	8		(20)
.166	.35	m-NO$_2$C$_6$H$_4$COOC$_2$H$_5$ + OH$^-$	Mt75*	A = B = 0.05			k AB	25	2.20	-2	17.0	6.0	10		(21)
.167	.36	m-NO$_2$C$_6$H$_4$COOC$_2$H$_5$ + OH$^-$	Et90*	A = B = 0.017			k AB	30	5.2	-2					(8)
.168		m-NO$_2$C$_6$H$_4$COOCH$_2$CH$_2$CH$_3$ + OH$^-$	WA*	A = B			k AB	25	8.31	-2	12.8	2.2	8		(20)
.169	.41	p-NO$_2$C$_6$H$_4$COOC$_2$H$_5$ + OH$^-$	Mt75*	A = B = 0.05			k AB	25	3.16	-2	16.7	5.2	10		(21)
.170	.42*	p-NO$_2$C$_6$H$_4$COOC$_2$H$_5$ + OH$^-$	Et85*	A= 0.1; B= 0.005			k AB	25	6.45	-2					(3) (7)
		(Correction of .42 as in 1951 Tables)						35	1.62	-1	14.8				(3)
								40	1.83	-1	14.5	2.3	9		(7)

No.	Supplementing 1951 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
.171		p-$NO_2C_6H_4COOCH(CH_3)_2 + OH^-$	WA*				k AB	25	3.84	-2	12.6	6.9	7		(19)
.172		p-$NO_2C_6H_4COOCH_2CH_2CH_2CH_3 + OH^-$	WA*				k AB	25	1.45	-1	12.1	1.2	8		(19)
.173		4-(3'-$NO_2C_6H_4$)$C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.01-0.015			k AB	40	5.95	-3					(2)
.174		4,4'-$NO_2C_6H_4C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.01-0.015			k AB	25	1.58	-3					(2)
								40	6.58	-3	17.6	1.3	10		
.175		3,5-$(NO_2)_2C_6H_3COOC_2H_5 + H_2O$	WA*	A = 0.05	$C_6H_5SO_3H$	0.05	k A[H^+]	60	3.46	-6				*	(17)
								80	1.90	-5					
								100	8.80	-5					
								111	1.96	-4	20.0	5.3	7		
.176		m-$CH_3SC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	25	5.36	-3					(12)
								40	1.78	-2	14.8	4	8		
.177		m-$CH_3SC_6H_4COOC_2H_5 + OH^-$	BC*	A = B = 0.05			k AB	0	8.1	-5					(12)
								25	1.41	-3					
								40	9.4	-3	20.2	9	11		
.178		p-$CH_3SC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	25	2.05	-3					(12)
								40	7.09	-3	15.3	4	8		
.179		p-$CH_3SC_6H_4COOC_2H_5 + OH^-$	BC*	A = B = 0.05			k AB	25	5.3	-4					(12)
								45	4.25	-3	19	4	10		
.180		m-$CH_3SOC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	0	7.01	-3					(12)

No.	Supplementing 1951 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
.181		m-$CH_3SOC_6H_4COOC_2H_5 + OH^-$	BC*	A = B = 0.05			k AB	0	7.5	-4					(12)
								25	9.5	-3	16.5	1.2	10		
.182		p-$CH_3SOC_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	0	7.69	-3					(12)
.183		p-$CH_3SOC_6H_4COOC_2H_5 + OH^-$	BC*	A = B = 0.05			k AB	0	5.0	-4					(12)
								25	7.6	-3	17.6	6.3	10		
.184		m-$CH_3SO_2C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	0	1.52	-2					(12)
.185		m-$CH_3SO_2C_6H_4COOC_2H_5 + OH^-$	BC*	A = B = 0.05			k AB	0	1.75	-3					(12)
								25	2.60	-2	17.6	2.3	11		
.186		p-$CH_3SO_2C_6H_4COOC_2H_5 + OH^-$	WA*	A = B = 0.05			k AB	0	2.86	-2					(12)
.187		p-$CH_3SO_2C_6H_4COOC_2H_5 + OH^-$	BC*	A = B = 0.05			k AB	0	2.27	-3					(12)
								25	3.12	-2	16.9	8.6	10		
.188	.43	o-$FC_6H_4COOC_2H_5 + OH^-$	WA*				k AB	25	1.21	-2	13.4	7.7	7		(19)
.189		m-$FC_6H_4COOC_2H_5 + OH^-$	WA*				k AB	25	1.53	-2	13.6	1.5	8		(19)
.190	.44	p-$FC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	5.86	-3	14.2	1.5	8		(18)
.191	.44*	p-$FC_6H_4COOC_2H_5 + OH^-$	Et85*	A=0.1; B=0.005			k AB	25	1.26	-3					(3)
		(Correction to .44 in 1951 Tables)						35	3.20	-3					
								50	1.20	-2	17.2	5.3	9		
.192	.45	o-$ClC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	4.40	-3	13.1	2.0	7		(18)

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$		E	$A = A^0 \times 10^n$		Comments	Literature
									k^0	n		A^0	n		
.193	.45	$o\text{-}ClC_6H_4COOC_2H_5 + OH^-$	Mt75*	A = B = 0.05			k AB	25	8.67	-4	16.6	1.2	9		(21)
.194	.46	$m\text{-}ClC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	1.82	-2	13.6	1.7	8		(18)
.195	.46	$m\text{-}ClC_6H_4COOC_2H_5 + OH^-$	Mt75*	A = B = 0.05			k AB	25	3.50	-3	17.3	1.8	10		(21)
.196	.49	$p\text{-}ClC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	1.17	-2	13.8	1.8	8		(18)
.197	.49	$p\text{-}ClC_6H_4COOC_2H_5 + OH^-$	Mt75*	A = B = 0.05			k AB	25	2.02	-3	17.0	6.3	9		(21)
.198	.49	$p\text{-}ClC_6H_4COOC_2H_5 + OH^-$	DW*	A = B = 0.05			k AB	25	1.23	-2					(14)
.199		$4,4'\text{-}ClC_6H_4C_6H_4COOC_2H_5 + OH^-$	Et90*	A=B=0.025-0.03			k AB	25	7.5	-4					(2)
								40	3.13	-3	17.6	6	9		
.200		$3,4'\text{-}Cl_2C_6H_3COOC_2H_5 + OH^-$	WA*				k AB	25	5.04	-2	13.0	1.9	8		(19)
.201		$o\text{-}BrC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	2.99	-3	13.3	1.9	7		(18)
.202		$m\text{-}BrC_6H_4COOCH_3 + OH^-$	WA*	A = B			k AB	25	4.70	-2	13.7	5.4	8		(20)
.203		$m\text{-}BrC_6H_4COOC_2H_5 + OH^-$	WA*	A=0.01; B=0.016			k AB	25	1.79	-2	13.6	1.8	8		(9) (18)
.204		$m\text{-}BrC_6H_4COOC_2H_5 + OH^-$	Mt75*	A = B = 0.05			k AB	25	3.30	-3	17.5	2.2	10		(21)
.205		$m\text{-}BrC_6H_4COOCH_2CH_2CH_3 + OH^-$	WA*	A = B			k AB	25	1.02	-2	13.6	9.8	7		(20)
.206	.52	$p\text{-}BrC_6H_4COOC_2H_5 + OH^-$	WA*	A = B			k AB	25	1.39	-2	13.7	1.8	8		(18)

No.	Supplementing 1951 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
.207		4-(3'-BrC_6H_4)$C_6H_4COOC_2H_5$ + OH^-	Et90*	A=B=0.025-0.03			k AB	25	9.3	-4					(2)
								40	3.88	-3	17.6	7.4	9		
.208		4,4'-$BrC_6H_4C_6H_4COOC_2H_5$ + OH^-	Et90*	A=B=0.025-0.03			k AB	25	7.6	-4					(2)
								40	3.18	-3	17.7	7.1	9		
.209		3;5-$Br_2C_6H_3COOC_2H_5$ + OH^-	WA*				k AB	25	9.0	-2	12.9	3.0	8		(19)
.210		o-$IC_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	1.66	-3	13.8	2.4	7		(18)
.211		m-$IC_6H_4COOCH_3$ + OH^-	WA*	A = B			k AB	25	3.98	-2	13.7	5.2	8		(20)
.212		m-$IC_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	1.50	-2	13.7	1.7	8		(18)
.213	.53	p-$IC_6H_4COOC_2H_5$ + OH^-	WA*	A = B			k AB	25	1.22	-2	13.8	1.7	8		(18)
		Substituted - napthoic acid esters													
.214		$C_{10}H_7$-2-$COOC_2H_5$ + OH^-	DW*	A = B = 0.05			k AB	25	3.46	-3					(14)
								40	1.13	-2	14.7	2.4	8		
.215		6-CH_3O-$C_{10}H_6$-2-$COOC_2H_5$ + OH^-	DW*	A = B = 0.05			k AB	25	1.50	-3					(14)
								40	4.79	-3	14.3	4.9	7		
.216		7-CH_3O-$C_{10}H_6$-2-$COOC_2H_5$ + OH^-	DW*	A = B = 0.05			k AB	25	2.85	-3					(14)
								40	9.33	-3	14.7	1.6	8		
.217		5-NH_2-$C_{10}H_6$-2-$COOC_2H_5$ + OH^-	DW*	A = B = 0.05			k AB	25	2.50	-3					(14)

No.	Supplementing 1951 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
.218		$8\text{-}NH_2C_{10}H_6\text{-}2\text{-}COOC_2H_5 + OH^-$	DW*	A = B = 0.05			k AB	25	1.20	-3					(14)
.219		$8\text{-}(CH_3)_2NC_{10}H_6\text{-}2\text{-}COOC_2H_5 + OH^-$	DW*	A = B = 0.05			k AB	25	2.46	-3					(14)
								40	9.14	-3	14.8	1.7	8		
.220		$5\text{-}NO_2C_{10}H_6\text{-}2\text{-}COOC_2H_5 + OH^-$	DW*	A = B = 0.05			k AB	15	1.41	-2					(14)
								25	3.14	-2	13.7	3	8		
.221		$8\text{-}NO_2C_{10}H_6\text{-}2\text{-}COOC_2H_5 + OH^-$	DW*	A = B = 0.05			k AB	15	9.12	-3					(14)
								25	2.0	-2	13.5	2	8		

SUPPLEMENTARY TABLE

(.55) $C_6H_5COOC_2H_5 + OH^-$ (21); S* = Solvent

$H_2O + CH_3OH$ x wt %

x	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n
36.2	25	5.02	-3	14.6	2.4	8
45.7	25	2.71	-3	15.7	8.4	8
55.3	25	1.53	-3	17.0	4.4	9
71.2	25	5.84	-4	17.8	6.1	9
87.7	25	1.23	-4	19.3	1.6	10

SOLVENTS

BC*	95 % *n*-butyl cellosolve [12]
DW*	70 vol % dioxane + H_2O 30 vol % [14]
EA*	50 vol % C_2H_5OH + 50 vol % $CH_3COC_6H_5$ [5]
EB*	50 vol % C_2H_5OH + 50 vol % C_6H_6 [5]
Et80*	C_2H_5OH 80 vol % + H_2O 20 vol % [11]
Et85*	C_2H_5OH 85 vol % + H_2O 15 vol % [3] [7] [10]
Et88*	C_2H_5OH 87.8 vol % + H_2O; (85 wt % C_2H_5OH) [1]
Et90*	C_2H_5OH 90.1 vol % + H_2O; (87.8 wt % C_2H_5OH) [2] [6] [8]
M*	80 vol % in product of reaction M + 20 vol % H_2O [11]
Mt75*	75 vol % CH_3OH + 25 vol % H_2O [21]
Mt80*	80 vol % CH_3OH + 20 vol % H_2O [11]
S*	See Supplementary Table [21]
WA*	$(CH_3)_2CO$ + 40 ml H_2O/100 ml of solution (~56 wt % $(CH_3)_2CO$) [1] [9] [11] [12] [13] [15] [16] [17] [18] [19] [20]
WA50*	50 vol % $(CH_3)_2CO$ + 50 vol % H_2O [15]

COMMENTS

Reactions: (.72) Belongs in 212.444 but included in this section for comparative purposes. (.75) Order with respect to A confirmed but B in excess and rate law dependence upon B not determined. Authors postulate a carbonium ion, $(C_6H_5)_3C^+$, intermediate as a wide variety of nucleophilic reagents have no effect upon rate of reaction but cause change in final product. See 212.471. (.76) No catalysis observed by weak acid L as first order rate law followed over 93 % of course of reaction. Catalysis by sodium ethylate assumed to be predominantly salt effect. See effect of $NaClO_4$. Authors conclude that ionization of neutral acid is rate determining step. (.78) Increase of first order rate constant over course of reaction probably due to catalysis by product acid L. (.113) Reaction followed defined rate law up to about 50 % of the course of the reaction. (.175) Reaction followed defined rate law up to about 50 % of the course of the reaction.

LITERATURE

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ESTER SOLVOLYSIS

Aliphatic carboxylic acid and Polyalcohol

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

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	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
.9	$CH_3COOCH_2CH_2OH + H_2O \longrightarrow HOCH_2CH_2OH + CH_3COOH$	H_2O	HCl	$k\,A[H^+]$	25	8.09	-5			
.10	$CH_3COOCH_2CH_2CH_2OH + H_2O \longrightarrow HOCH_2CH_2CH_2OH + CH_3COOH$	H_2O	HCl	$k\,A[H^+]$	25	1.00	-4			
	Ester of alkoxy substituted carboxylic acid and polyalcohol									
.11	$CH_3OCH_2COOCH_2CH_2OOCCH_2OCH_3 + 2\,H_2O \longrightarrow HOCH_2CH_2OH + 2\,CH_3OCH_2COOH$	H_2O	HCl	$k\,A[H^+]$	15	1.63	-5			
					25	4.35	-5			
					35	1.10	-4	16.8	9	7
.12	$CH_3OCH_2COOCH_2CH_2OH + H_2O \longrightarrow HOCH_2CH_2OH + CH_3OCH_2COOH$	H_2O	HCl	$k\,A[H^+]$	15	1.75	-5			
					25	4.66	-5			
					35	1.20	-4	17.0	1.4	8
.13	$C_2H_5OCH_2COOCH_2CH_2OOCCH_2OC_2H_5 + 2\,H_2O \longrightarrow HOCH_2CH_2OH + 2\,C_2H_5OCH_2COOH$	H_2O	HCl	$k\,A[H^+]$	15	1.61	-5			
					25	4.20	-5			
					35	1.09	-4	16.8	8	7
.14	$C_2H_5OCH_2COOCH_2CH_2OH + H_2O \longrightarrow HOCH_2CH_2OH + C_2H_5OCH_2COOH$	H_2O	HCl	$k\,A[H^+]$	15	1.67	-5			
					25	4.43	-5			
					35	1.19	-4	17	1	8

No.	Reaction	Medium (Solvent)	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
.15	$n\text{-}C_3H_7OCH_2COOCH_2CH_2OH + H_2O \longrightarrow HOCH_2CH_2OH + n\text{-}C_3H_7OCH_2COOH$	H_2O	HCl	$k\,A[H^+]$	15 25 35	1.65 4.40 1.13	-5 -5 -4	17.0	1.3	8

LITERATURE

E.J. Salmi, *BDC* 1939, 72, 1767.

ESTER SOLVOLYSIS

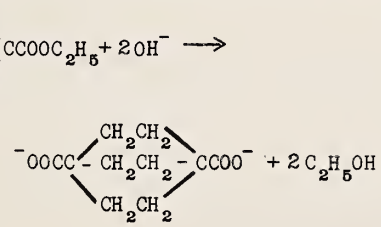
Ester of aliphatic carboxylic polyacid and alcohol

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.
* Coded solvents at end of table.

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

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
.13	$(COOCH_3)_2 + 2H_2O \longrightarrow (COOH)_2 + 2CH_3OH$	B		HCl		$k\,A[H^+]$	25	1.60	-4					(2)
.14	$(COOC_2H_5)_2 + 2H_2O \longrightarrow (COOH)_2 + 2C_2H_5OH$	B	A = 0.01			$k\,A$	15	2	-6				*	(4)
							25	5	-6					
							30	1.0	-5					
				HCl		$k\,A[H^+]$	25	8.85	-5					(2)
.15	$(COOC_2H_5)_2 + OH^- \longrightarrow C_2H_5OOCCOO^- + C_2H_5OH$	H_2O	A= B= 0.01			$k\,AB$	2	1.49	-3				*	(4)
							15	2.56	-3					
							25	3.96	-3					
							35	5.97	-3	7.1	6.2	8		
.16	$^-OOCCOOC_2H_5 + OH^- \longrightarrow (COO^-)_2 + C_2H_5OH$	H_2O	B = 0.01	(slower than .15)										(4)
.17	$^-OOCCH_2COOC_2H_5 + OH^- \longrightarrow CH_2(COO^-)_2 + C_2H_5OH$	H_2O	A= B≃0.015	NaCl	0.1-0.5	$k\,AB$	25	1.32	-2				*	(3)
	Dielectric Constant = 75	Et*					25	1.09	-2					
	70						25	8.44	-3					
	60						25	4.52	-3					
	50						25	2.44	-3					
	75	Ip*					25	1.21	-2					
	70						25	1.06	-2					
	50						25	5.34	-3					

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
.17	$^-OOCCH_2COOC_2H_5 + OH^- \longrightarrow$ *(continued)*	H_2O	$A = B \simeq 0.015$	NaCl	0.1-0.5	$k\,AB$							*	(3)
	Dielectric Constant = 75	An*					25	1.14	-2					
	60						25	7.17	-3					
	50						25	5.94	-3					
	75	D1*					25	1.21	-2					
	60						25	8.55	-3					
	50						25	6.24	-3					
.18	$(CH_2COOCH_3)_2 + H_2O \longrightarrow CH_3OOCCH_2CH_2COOH + CH_3OH$	B		HCl		$k\,A[H^+]$	25	2.32	-5					(2)
.19	$HOOCCH_2CH_2COOCH_3 + H_2O \longrightarrow (CH_2COOH)_2 + CH_3OH$	B		HCl		$k\,A[H^+]$	25	2.32	-5					(2)
.20	$CH_2(CH_2COOCH_3)_2 + H_2O \longrightarrow CH_3OOCCH_2CH_2CH_2COOH + CH_3OH$	B		HCl		$k\,A[H^+]$	25	5.79	-5					(2)
.21	$HOOCCH_2CH_2CH_2COOCH_3 + H_2O \longrightarrow CH_2(CH_2COOH)_2 + CH_3OH$	B		HCl		$k\,A[H^+]$	25	5.79	-5					(2)
.22	$(CH_2CH_2COOCH_3)_2 + H_2O \longrightarrow CH_3OOC(CH_2)_4COOH + CH_3OH$	B		HCl		$k\,A[H^+]$	25	6.70	-5					(2)
.23	$HOOC(CH_2)_4COOCH_3 + H_2O \longrightarrow (CH_2CH_2COOH)_2 + CH_3OH$	B		HCl		$k\,A[H^+]$	25	6.70	-5					(2)
.24	$C_2H_5OOCC(CH_2CH_2)_2CCOOC_2H_5 + 2OH^- \longrightarrow$  $^-OOCC(CH_2CH_2)_2CCOO^- + 2C_2H_5OH$	Et88*	$A = B = 0.024$			$k\,AB$	30	2.78	-4					(1)

COMMENTS

Reaction. **(.14)** Observed in conjunction with (.15). First order rate law arbitrarily selected to express data, given in % hydrolysis after 300 min. **(.15)** Rate constant calculated on basis of reaction of first ester group only as reaction sufficiently more rapid than (.16).

LITERATURE

([1]) J.D. Roberts, W.T. Moreland, *ACS* 1953, **75**, 2167. ([2]) E.J. Salmi, *BDC* 1939, **72**, 1767.

([3]) W.J. Svirbely, B.W. Lewis, *JPC* 1952, **56**, 1006. ([4]) E. Tommila, H. Sternberg, *Suomen Kemistilehti* 1946, **19B**, 19.

ESTER SOLVOLYSIS

Ester of Aromatic carboxylic polyacid and Alcohol

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

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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	$o\text{-}C_6H_4(COOC_2H_5)_2 + 2OH^- \rightarrow o\text{-}C_6H_4(COO^-)_2 + 2C_2H_5OH$	H_2O	See (.2) (.3)								*	
.2	$o\text{-}C_6H_4(COOC_2H_5)_2 + OH^- \rightarrow o\text{-}C_2H_5OOCC_6H_4COO^- + C_2H_5OH$	H_2O	B=0.25	k AB	0	4.81	-4				*	(1)
					15	1.77	-3					
					25	3.58	-3					
					40	1.02	-2	12.9	1.1	7		
.3	$o\text{-}(^-OOC)C_6H_4COOC_2H_5 + OH^- \rightarrow o\text{-}C_6H_4(COO^-)_2 + C_2H_5OH$	H_2O	B=0.25	k AB	25	8.07	-4	14.4	3.1	7		(2)
.4	$m\text{-}C_6H_4(COOC_2H_5)_2 + 2OH^- \rightarrow m\text{-}C_6H_4(COO^-)_2 + 2C_2H_5OH$	H_2O	See (.5) (.6)								*	
.5	$m\text{-}C_6H_4(COOC_2H_5)_2 + OH^- \rightarrow m\text{-}C_2H_5OOCC_6H_4COO^- + C_2H_5OH$	H_2O	B=0.25	k AB	0	3.03	-3				*	(1)
					15	1.05	-2					
					25	2.32	-2					
					40	7.02	-2	13.3	1.5	8		
.6	$m\text{-}(^-OOC)C_6H_4COOC_2H_5 + OH^- \rightarrow m\text{-}C_6H_4(COO^-)_2 + C_2H_5OH$	H_2O	B=0.25	k AB	15	3.31	-3	13.6	6.7	7		(2)
.7	$p\text{-}C_6H_4(COOC_2H_5)_2 + 2OH^- \rightarrow p\text{-}C_6H_4(COO^-)_2 + 2C_2H_5OH$	H_2O	See (.8) (.9)								*	

No.	Reaction	Medium (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
.8	$p\text{-}C_6H_4(COOC_2H_5)_2 + OH^- \longrightarrow p\text{-}C_2H_5OOCC_6H_4COO^- + C_2H_5OH$	H_2O	B=0.25	k AB	0	6.75	-3				*	(1)
					15	2.52	-2					
					25	5.37	-2					
					40	1.43	-1	13.0	2.0	8		
.9	$p\text{-}(^-OOC)C_6H_4COOC_2H_5 + OH^- \longrightarrow p\text{-}C_6H_4(COO^-)_2 + C_2H_5OH$	H_2O	B=0.25	k AB	40	2.22	-2	13.5	6.6	7		(2)

COMMENTS

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

LITERATURE

(1) E. Kivinen, E. Tommila, *Suomen Kemistilehti* 1941, **14B**, 7. (2) S. Tommila, E. Tommila, *Ann. Acad. Sci. Fennicae* 1942, **A59**, No. 5, 3.

SOLVOLYSIS
Ester of aliphatic alcohol and nitric acid

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

*Coded solvents at end of table.

No.	Reaction	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
						$k = k_S + k_E$							
.1	$(CH_3)_3CONO_2 + H_2O \longrightarrow (CH_3)_3COH + HNO_3$ (S) $\longrightarrow (CH_3)_2C{:}CH_2 + HNO_3 + H_2O$ (E)	DW40*	A = 0.06–0.14			kA	0	5.22	-5				*
							10	2.18	-4				
						k_SA	0	5.0	-5				
						k_SA	10	2.08	-4	23	1	14	
						k_EA	0	2.2	-6				
						k_EA	10	1.0	-5	25	2	14	
	(See supplementary table)			$NaClO_4$	0.1	kA	0	6.2	-5				
				"	0.1	k_SA	0	5.9	-5				
				"	0.1	k_EA	0	2.5	-6				
				"	0.1	kA	10	2.58	-4				
				"	0.1	k_SA	10	2.46	-4				
				"	0.1	k_EA	10	1.2	-5				
				NaOH	0.1	kA	10	2.14	-4				
					0.1	k_SA	10	2.03	-4				
					0.1	k_EA	10	1.1	-5				
		DW25*	A = 0.1			kA	25	1.93	-4				
						k_SA	25	1.76	-4				
						k_EA	25	1.7	-5				

No.	Reaction	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
.1	$(CH_3)_3CONO_2 + H_2O \longrightarrow (CH_3)_3COH + HNO_3$ (S) $\longrightarrow (CH_3)_2C{:}CH_2 + HNO_3 + H_2O$ (E) *(continued)*	DW15*	A = 0.1			$k = k_S + k_E$							
						k A	25	3.33	-5				
						k_SA	25	2.82	-5				
						k_EA	25	5.1	-6				
		DW5*	A = 0.1			k A	25	1.4	-6				
						k_SA	25	8	-7				
						k_EA	25	6	-7				
.2	$C_6H_5CH_2ONO_2 + H_2O \longrightarrow C_6H_5CH_2OH + HNO_3$ (S) $\longrightarrow C_6H_5CHO + HNO_2 + H_2O$ (E)	DW40*	A = 0.13 A = 0.11			$k = k_S + k_E$							*
						k A	25	6.5	-8				
							50	1.57	-6				
						k_SA	25	5.9	-8				
							50	1.47	-6	24.2	4	10	
						k_EA	25	5.6	-9				
							50	9.8	-8				
	(See supplementary table)		A = 0.15 A = 0.08	$NaClO_4$	0.11 0.11	k A	25	7.3	-8				
							50	1.86	-6				
						k_SA	25	6.8	-8				
							50	1.72	-6				
						k_EA	25	5.2	-9				
							50	1.37	-7				
			A = 0.08	p-$C_6H_4(OH)_2$	0.05	k A	50	1.66	-6				
						k_SA	50	1.66	-6				
.3	$C_6H_5CH_2ONO_2 + OH^- \longrightarrow C_6H_5CH_2OH + NO_3^-$ (S) $\longrightarrow C_6H_5CHO + NO_2^- + H_2O$ (E)	DW40*	A = 0.15; B = 0.11			$k = k_S + k_E$							*
						k AB	25	3.08	-5				
			A = 0.08; B = 0.11				25	3.26	-5				
			A = 0.16; B = 0.11				50	3.62	-4				
			A = 0.08; B = 0.11				50	4.54	-4				
			A = 0.15; B = 0.11			k_SAB	25	9.7	-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	$A = A^0 \times 10^n$ A^0	n	Comments
						$k = k_S + k_E$							
.3	$C_6H_5CH_2ONO_2 + OH^- \longrightarrow C_6H_5CH_2OH + NO_3^-$ (S) $\longrightarrow C_6H_5CHO + NO_2^- + H_2O$ (E) *(continued)*	DW40*	A = 0.08; B = 0.11			k_SAB	25	1.3	-5				*
			A = 0.16; B = 0.11				50	2.36	-4				
			A = 0.08; B = 0.11				50	2.95	-4	24.0	5	12	
			A = 0.15; B = 0.11			k_EAB	25	2.11	-5				
			A = 0.08; B = 0.11				25	1.96	-5				
			A = 0.16; B = 0.11				50	1.26	-4				
			A = 0.08; B = 0.11				50	1.59	-4	14.9	2	6	
			A = 0.15; B = 0.055	$NaClO_4$	0.055	k AB	25	2.87	-5				
			A = 0.08; B = 0.055		0.055		25	2.94	-5				
			A = 0.16; B = 0.055		0.055		50	3.41	-4				
			A = 0.08; B = 0.055		0.055		50	4.79	-4				
			A = 0.08; B = 0.11	p-$C_6H_4(OH)_2$	0.055		25	5.7	-5				
			A = 0.15; B = 0.055	$NaClO_4$	0.055	k_SAB	25	8.6	-6				
			A = 0.08; B = 0.055		0.055		25	9.6	-6				
			A = 0.16; B = 0.055		0.055		50	1.86	-4				
			A = 0.08; B = 0.055		0.055		50	2.83	-4				
			A = 0.15; B = 0.055		0.055	k_EAB	25	2.01	-5				
			A = 0.08; B = 0.055		0.055		25	1.98	-5				
			A = 0.16; B = 0.055		0.055		50	1.55	-4				
			A = 0.08; B = 0.055		0.055		50	1.96	-4				
			A = 0.08; B = 0.11	p-$C_6H_4(OH)_2$	0.055	k_SAB	25	5.7	-5				

SUPPLEMENTARY TABLES

Effect of salts (0.1 M/l) on overall rate, $k_S + k_E = k$

(.1) $(CH_3)_3CONO_2 + H_2O$

°C	wt % B	Added solute	% change in initial rate
10	40	$NaClO_4$	+16
10	40	NaOH	-4.3
25	25	$NaClO_4$	+37
25	25	$HClO_4$	+37
25	25	KNO_3	+16
25	25	NaCl	+10
25	25	$CH_3C_6H_4SO_3Na$	+10

Effect of salts (0.1 M/l) on overall rate, $k_S + k_E = k$

(.2) $C_6H_5CH_2ONO_2 + H_2O$

°C	Added solute	% change in initial rate
25	$NaClO_4$	+16.4
50	$NaClO_4$	+15.6
50	$HClO_4$	+15.5
50	KNO_3	+ 2.7

SOLVENTS

DWX* Dioxane (100-X) wt. % + X wt. % H_2O

COMMENTS

Reactions general. Empirical first order rate constants increased during course of reaction and all rates tabulated are initial rates only. Solvolysis and elimination reactions occurred simultaneously and separation of rate constants into k_S and k_E factor was by quantitative product analysis. For similar behavior in solvolysis and elimination see 212.471 and 422.471.

Reactions. (.1) Selected data. Extensive variation of salt and solvent indicated rate effect paralleled effect of same salts upon activity coefficient of water. (.2) Selected data. Solvolysis reaction accompanied by elimination reaction leading to nitrous ion and aldehyde rather than customary nitrate and olefin. (.3) Selected data. Rate constants were corrected for simultaneous solvent reaction (.2) and represent only second order reaction with hydroxyl ion. Values tabulated are initial rates.

LITERATURE

G.R. Lucas, L.P. Hammett, *ACS* 1942, **64**, 1928.

ESTER SOLVOLYSIS

Aryl phosphates

Liquid phase

Amounts are in M/l.
Rate constants are in sec^{-1}

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.1	$C_6H_5OPO_3H_2 + H_2O \longrightarrow C_6H_5OH + H_3PO_4$	H_2O	$\simeq 0.03$	HCl	1.0	$\simeq 0$	$\simeq 1$	$k\,A$	85	2	-6			*	(3)
				NaOH	1.0	$\simeq 14$	$\simeq 1$	$k\,A$	40	5	-6				
									85	1.4	-5				
.2	$(C_6H_5O)_2PO_2H + 2H_2O \longrightarrow 2C_6H_5OH + H_3PO_4$	H_2O	$\simeq 0.02$	HCl	1.0	$\simeq 0$	$\simeq 1$	$-dA/dt =$	85	1	-6			*	(3)
				NaOH	1.0	$\simeq 14$	$\simeq 1$	$k\,A$	40	1.3	-5				
.3	$(C_6H_5O)_3PO + 3H_2O \longrightarrow 3C_6H_5OH + H_3PO_4$	H_2O	$\simeq 0.015$	HCl	1.0	$\simeq 0$	$\simeq 1$	$-dA/dt =$	85	2	-6			*	(3)
				NaOH	1.0	$\simeq 14$	$\simeq 1$	$k\,A$	85	4	-6				
.4	$o\text{-}HOOCC_6H_4OPO_3H_2 + H_2O \longrightarrow o\text{-}HOOCC_6H_4OH + H_3PO$	H_2O + 0-4% CH_3OH	0.0013	KCl+ buffers		2.3	0.16	$k\,A$	37	1.04	-5			*	(2)
						2.3	0.16		42	1.83	-5				
						2.3	0.16		47	4.03	-5				
						3.0	0.16		37	1.90	-5				
						3.0	0.16		42	3.42	-5				
						3.0	0.16		47	6.75	-5				
						3.8	0.16		37	4.70	-5				
						3.8	0.16		42	9.28	-5				
						3.8	0.16		47	1.72	-4				
						4.9	0.22		37	9.11	-5				
						4.9	0.22		42	1.62	-4				
						4.9	0.22		47	3.61	-4				
						5.7	0.1		31	5.0	-5				(1)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.4	$o\text{-HOOCC}_6\text{H}_4\text{OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $o\text{-HOOCC}_6\text{H}_4\text{OH} + \text{H}_3\text{PO}_4$ *(continued)*	H_2O	0.0013	KCl + buffers		5.7	0.1	$k\,\text{A}$	37	1.03	-4	23.5	-1.2		
						5.7	0.27		37	9.11	-5				(2)
						5.7	0.27		42	1.62	-4				
						5.7	0.27		47	3.80	-4				
						6.9	0.20		37	3.97	-5				
						6.9	0.20		42	9.50	-5				
						6.9	0.20		47	1.86	-4				
						7.7	0.19		37	1.04	-5				
						7.7	0.19		42	2.06	-5				
						7.7	0.19		47	5.68	-5				
.5	$o\text{-HOOCC}_6\text{H}_4\text{OPO}_2\text{H}^- + \text{H}_2\text{O} \longrightarrow$ $o\text{-HOOCC}_6\text{H}_4\text{OH} + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .4)					$k_1\text{A}^-$	32	4.39	-6			*	(2)
									37	8.90	-6				
									42	1.56	-5				
									47	3.35	-5	22.4			
.6	$o\text{-OOCC}_6\text{H}_4\text{OPO}_2\text{H}^= + \text{H}_2\text{O} \longrightarrow$ $o\text{-OOCC}_6\text{H}_4\text{OH}^- + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .4)					$k_2\text{A}^=$	27	2.46	-5			*	(2)
									37	1.02	-4				
									47	4.29	-4	23.5	-1		
Napthyl phosphates															
.7	$\alpha\text{-C}_{10}\text{H}_7\text{OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $\alpha\text{-C}_{10}\text{H}_7\text{OH} + \text{H}_3\text{PO}_4$	H_2O				2-6		$k\,\text{A}$	37	4.5	-8			*	(2)
						>6			37	<4.5	-8				
.8	$\beta\text{-C}_{10}\text{H}_7\text{OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $\beta\text{-C}_{10}\text{H}_7\text{OH} + \text{H}_3\text{PO}_4$	H_2O				2-6		$k\,\text{A}$	37	1.6	-7			*	(1)
						>6			37	<1.6	-7				

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.9	$2\text{-HOOCC}_{10}\text{H}_6\text{-1-OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $1\text{-OH-2-HOOCC}_{10}\text{H}_6 + \text{H}_3\text{PO}_4$	H_2O	0.0013	KCl + buffer		2.3	0.1	$k\,\text{A}$	37	4.62	-5			*	(1)
						3.0	0.1		37	7.14	-5				
						3.7	0.1		37	2.10	-4				
					4.8-6.7		0.1		37	3.61	-4				
						7.2	0.1		37	3.56	-4				
						7.9	0.1		37	2.26	-4				
						8.5	0.1		37	8.25	-5				
.10	$2\text{-HOOCC}_{10}\text{H}_6\text{-1-OPO}_3\text{H}^- + \text{H}_2\text{O} \longrightarrow$ $1\text{-OH-2-HOOCC}_{10}\text{H}_6 + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .9)					$k_1\text{A}^-$	37	3.9	-5			*	(1)
.11	$2\text{-OOCC}_{10}\text{H}_6\text{-1-OPO}_3\text{H}^= + \text{H}_2\text{O} \longrightarrow$ $2\text{-OOCC}_{10}\text{H}_6\text{-1-OH}^- + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .9)					$k_2\text{A}^=$	37	3.65	-4			*	(1)
.12	$2\text{-HOOCC}_{10}\text{H}_6\text{-1-OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $2\text{-HOOCC}_{10}\text{H}_6\text{-1-OH} + \text{H}_3\text{PO}_4$	H_2O + 4 % CH_3OH	0.0013	KCl + buffer		5.7	0.1	$k\,\text{A}$	31	1.68	-4			*	(1)
						5.7	0.1		37	3.72	-4	24	3		
.13	$2\text{-HOOCC}_{10}\text{H}_6\text{-1-OPO}_3\text{H}^- + \text{H}_2\text{O} \longrightarrow$ $2\text{-HOOCC}_{10}\text{H}_6\text{-1-OH} + \text{H}_2\text{PO}_4^-$	H_2O + 4 % CH_3OH	(calculated from data of .12)					$k_1\text{A}^-$	37	3.73	-5			*	(1)
.14	$2\text{-OOCC}_{10}\text{H}_6\text{-1-OPO}_3\text{H}^= + \text{H}_2\text{O} \longrightarrow$ $2\text{-OOCC}_{10}\text{H}_6\text{-1-OH}^- + \text{H}_2\text{PO}_4^-$	H_2O + 4 % CH_3OH	(calculated from data of .12)					$k_2\text{A}^=$	31	1.68	-4			*	(1)
									37	3.76	-4	24	3		
.15	$1\text{-HOOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $1\text{-HOOCC}_{10}\text{H}_6\text{-2-OH} + \text{H}_3\text{PO}_4$	H_2O	0.0013	KCl + buffers		2.3	0.1	$k\,\text{A}$	37	9.9	-7			*	(1)
						2.9	0.1		37	1.56	-6				
						3.7	0.1		37	2.41	-6				
						4.8	0.1		37	2.80	-6				

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.15	$1\text{-HOOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $1\text{-HOOCC}_{10}\text{H}_6\text{-2-OH} + \text{H}_3\text{PO}_4$ *(continued)*	H_2O	0.0013	KCl + buffers		5.7	0.1	$k\,A$	37	2.31	-6			*	(1)
						6.2	0.1		37	1.50	-6				
						7.2	0.1		37	2.0	-7				
						5.6	0.1		60	7.33	-5	28	6		
.16	$1\text{-HOOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}^- + \text{H}_2\text{O} \longrightarrow$ $1\text{-HOOCC}_{10}\text{H}_6\text{-2-OH} + \text{H}_2\text{PO}^-$	H_2O	(calculated from data of .15)					k_1A^-	37	7.33	-5			*	(1)
.17	$1\text{-OOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}^= + \text{H}_2\text{O} \longrightarrow$ $1\text{-OOCC}_{10}\text{H}_6\text{-2-OH}^- + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .15)					$k_2A^=$	37	3.03	-6			*	(1)
									60	7.33	-5				
.18	$3\text{-HOOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}_2 + \text{H}_2\text{O} \longrightarrow$ $3\text{-HOOCC}_{10}\text{H}_6\text{-2-OH} + \text{H}_3\text{PO}_4$	H_2O + 0-4 % CH_3OH	0.0013	KCl + buffers		5.6	0.1	$k\,A$	31	2.36	-5			*	(1)
						2.3	0.1		37	6.2	-6				
						2.9	0.1		37	1.17	-5				
						3.7	0.1		37	3.11	-5				
						4.8	0.1		37	5.22	-5				
						5.7	0.1		37	4.69	-5				
						6.6	0.1		37	2.5	-5				
						7.2	0.1		37	8.5	-6				
						7.9	0.1		37	2.4	-6				
						8.5	0.1		37	5.3	-7				
.19	$3\text{-HOOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}^- + \text{H}_2\text{O} \longrightarrow$ $3\text{-HOOCC}_{10}\text{H}_6\text{-2-OH} + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .18)					k_1A^-	37	4.8	-6			*	(1)
.20	$3\text{-OOCC}_{10}\text{H}_6\text{-2-OPO}_3\text{H}^= + \text{H}_2\text{O} \longrightarrow$ $3\text{-OOCC}_{10}\text{H}_6\text{-2-OH}^- + \text{H}_2\text{PO}_4^-$	H_2O	(calculated from data of .18)					$k_2A^=$	31	2.36	-5			*	(1)
									37	5.64	-5	25	4		

COMMENTS

Reaction. **(.1) (.2) (.3)** First order rate law assumed by reviewer on basis of similar reactions. Scattered data for (.1) at 85°C upon calculation showed good agreement with assumed rate law. Values should be considered as showing only order of magnitude. **(.4)** Is overall reaction supposed to be made up of (.5) and (.6). In empirical rate law k A, A represents the sum of the concentrations of A in all stages of ionization. The data, represented in terms of two reacting forms (.5) an d (.6), and their respective rate constants such that $k\,A = k_1A^- + k_2A^=$ where A^- is $o\text{-}HOOCC_6H_4OPO_3H^-$ and $A^=$ is $o\text{-}OOCC_6H_4OPO_3H^=$. **(.5) (.6)** Simultaneous reactions purportedly responsible for total reaction represented by (.4). Calculated from data of (.4) using dissociation constants of each acid species to determine concentration of each ion present. Reaction of the species $o\text{-}HOOC_6H_4OPO_3H_2$ and $o\text{-}OOCC_6H_4OPO_3^{\equiv}$ considered negligible since reaction very slow at pH = 0 and pH = 8.5. Temperature dependence of ionization constants not included in calculations. **(.7) (.8)** Rate law not verified but assumed on basis of similar reactions. k calculated from $t^{\frac{1}{2}}$ in hours. **(.9)** represents the sum of simultaneous reactions (.10) and (.11). In the empirical rate expression k A, A represents the sum of the concentrations of A, in all stages of ionization. **(.10) (.11)** Represent simultaneous reactions purportedly responsible for (.9). Rate constants calculated from data of (.9) and ionization constants for all acids, $k\,A = k_1A^- + k_2A^=$ where A^- is the concentration of $1\text{-}HPO_4\text{-}2\text{-}HOOCC_{10}H_6^-$ and $A^=$ represents the concentration of $1\text{-}HPO_4\text{-}2\text{-}OOCC_{10}H_6^=$. **(.12) (.13) (.14)** See (.9) and (.10) (.11). **(.15)** Represents the overall reaction of two simultaneous reactions (.16) and (.17). In the empirical rate expression k A, A represents the total concentration of A in all stages of ionization **(.16) (.17)** The two simultaneous reactions comprising (.15) such that $k\,A = k_1A^- + k_2A^=$ where A^- is the concentration of $1\text{-}HOOCC_{10}H_6\text{-}2\text{-}OPO_2H^-$ and $A^=$ is the concentration of $1\text{-}OOCC_{10}H_6\text{-}2\text{-}OPO_3H^=$. Rate constants k_1 and k_2 calculated using data of (.15) and ionization constants for each of the acid forms of A. **(.18)** Is supposedly the total reaction of the two simultaneous reactions (.19) and (.20). In the empirical rate expression k A, A represents the total. concentration of A in all stages of ionization. **(.19) (.20)** are simultaneous reactions purportedly responsible for (.18). Rate constants calculated from data of (.18) and ionization constants for each acid form. $k\,A = k_1A^- + k_2A^=$ where A^- represents the concentration of $3\text{-}HOOCC_{10}H_6\text{-}2\text{-}OPO_3H^-$ and $A^=$ the concentration of $3\text{-}OOCC_{10}H_6\text{-}2\text{-}OPO_3H^=$.

LITERATURE

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(2) J.D. Chanley, E.M. Gindler, H. Sobotka, *ACS* 1952, 74, 4347.

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SOLVOLYSIS
Alkyl Sulfates

Liquid phase

Reaction types: $ROSO_3^- + R'OH \longrightarrow ROR' + HSO_4^-$

$ROSO_3^- + R'O^- \longrightarrow ROR' + SO_4^=$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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	$CH_3OSO_3^- + OH^-$	H_2O	A = B = 0.50 1.00 1.50			k AB	100	8.3 1.13 1.32	-5 -4 -4	*	(2)
.2	$CH_3OSO_3^- + C_6H_5O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	7.4	-5	*	(2)
.3	$CH_3OSO_3^- + o\text{-}CH_3C_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	6.7	-5	*	(2)
.4	$CH_3OSO_3^- + m\text{-}CH_3C_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	8.3	-5	*	(2)
.5	$CH_3OSO_3^- + p\text{-}CH_3C_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	9.3	-5	*	(2)
.6	$CH_3OSO_3^- + p\text{-}C_2H_5(CH_3)_2CC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	1.05	-4	*	(2)
.7	$CH_3OSO_3^- + o\text{-}CH_3OC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	6.7	-5	*	(2)
.8	$CH_3OSO_3^- + m\text{-}CH_3OC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	6.0	-5	*	(2)
.9	$CH_3OSO_3^- + p\text{-}CH_3OC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	1.01	-4	*	(2)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.10	$CH_3OSO_3^- + m\text{-}C_2H_5OC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	6.0	-5	*	(2)
.11	$CH_3OSO_3^- + p\text{-}C_2H_5OC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	1.10	-4	*	(2)
.12	$CH_3OSO_3^- + 3,5\text{-}(CH_3O)_2C_6H_3O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	5.2	-5	*	(2)
.13	$CH_3OSO_3^- + o\text{-}NO_2C_6H_4O^-$	H_2O	A = 1.0 B = 0.05	NaOH	1.0	k AB	100	2.5	-6	*	(2)
.14	$CH_3OSO_3^- + m\text{-}NO_2C_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	2.6	-5	*	(2)
.15	$CH_3OSO_3^- + p\text{-}NO_2C_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	5	-6	*	(2)
.16	$CH_3OSO_3^- + m\text{-}FC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	4.3	-5	*	(2)
.17	$CH_3OSO_3^- + p\text{-}FC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	7.2	-5	*	(2)
.18	$CH_3OSO_3^- + o\text{-}ClC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	3.0	-5	*	(2)
.19	$CH_3OSO_3^- + m\text{-}ClC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	4.2	-5	*	(2)
.20	$CH_3OSO_3^- + p\text{-}ClC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	5.45	-5	*	(2)
.21	$CH_3OSO_3^- + p\text{-}BrC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	5.3	-5	*	(2)
.22	$CH_3OSO_3^- + p\text{-}IC_6H_4O^-$	H_2O	A = 1.0; B = 0.05	NaOH	1.0	k AB	100	5.1	-5	*	(2)
.23	$C_2H_5OSO_3^- + OH^-$	H_2O	A = B = 1.00			k AB	100	1.05	-5	*	(2)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.24	$(CH_3)(C_2H_5)CHOSO_3^- + H_2O$	H_2O	A = 0.91	NaOH	5.0	k A	99	1.0	-5	*	[1]
			0.92	K_2CO_3	5.4		99	6	-6		
			0.92	$KHCO_3$	5.0		99	7	-6		
			0.91	H_2SO_4	0.5		92	2	-4		
			0.30		1.05		101	4.4	-4		
			0.68		2.3		103	1.2	-3		
			1.66		5.7		111	4.6	-4		
			2.3		2.3		99	6	-4		
			0.68	$C_2H_5SO_3H$	2.3		103	7.2	-4		
			1.67		5.7		108	2.9	-3		
			1.67	$C_7H_7SO_3H$	5.7		108	3.3	-3		

COMMENTS

References: [3] [4] [5] Determined rate of solvolysis of dialkyl sulfates which react faster than mono-alklyl sulfates but are less soluble. [3] used aqueous alcohol. [4] used two-phase system with rapid stirring. [5] used aqueous alcohol and assumed first order constants. These decreased with progress of reaction.

Reactions: **(.1)** Rate law with respect to A and B individually not established as A = B at all times. Corrected for volume expansion of solvent with temperature. **(.2) through (.22)** Reaction in presence of excess NaOH competes with (.1) and correspondingly corrected. **(.23)** Rate law with respect to A and B individually not established as A = B at all times. Corrected for volume expansion of solvent with temperature. **(.24)** Rate law not established but first order constants

COMMENTS *(continued)*

calculated from time of half life for comparison and tabulating. Reaction also accompanied by olefin formation. In basic solution ratio of alcohol to olefin ~7.7; in dilute acid ~5.9 increasing to ~1 in 6 M/l H_2SO_4 at 111°C. In basic solution the alcohol produced has inverted configuration with practically no loss of activity. In acid solution the alcohol produced has same optical configuration and is partly racemized.

LITERATURE

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([3]) A. Klemenc, E. Edhofer, *MHC* 1917, **38**, 353. ([4]) R. Kremann, *MHC* 1907, **28**, 13.

([5]) J. Pollak, A. Baar, *MHC* 1917, **38**, 501.

SOLVOLYSIS
Alkyl arylsulfonates

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction types

$$\underset{(A)}{ArSO_3R} + \underset{(B)}{R'OH} \longrightarrow \underset{(L)}{ROR'} + \underset{(M)}{ArSO_3H}$$

$$ArSO_3R + R'O^- \longrightarrow ROR' + ArSO_3^-$$

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.6	p-$CH_3C_6H_4SO_3CH_3 + C_2H_5OH$	B	10^2A= 4-6			kA	75	6.9	-5				(15)
.7	p-$CH_3C_6H_4SO_3CH_3 + HCOOH$	B	10^2A= 7.4-8.5			kA	75	1.06	-5				(15)
.8	p-$CH_3C_6H_4SO_3CH_3 + CH_3COOH$	B	10^2A= 2.7-4.1			kA	75	8.5	-7				(15)
							100	7.9	-6	22	-23		
.9	p-$CH_3C_6H_4SO_3C_2H_5 + C_2H_5OH$	B	10^2A= 3.6-4.6			kA	75	2.95	-5	21.6	-17.5	(10)	(14)
.10	p-$CH_3C_6H_4SO_3C_2H_5 + HCOOH$	B	A= 0.10-0.13			kA	60	4.3	-6			(14)	(15)
							75	1.85	-5	22.1	-16.5		
				HCOONa	0.1		75	1.90	-5				
.11	p-$CH_3C_6H_4SO_3C_2H_5 + CH_3COOH$	B	10^2A= 3-4.6	$(CH_3CO)_2O$	0.0066	kA	75	7.7	-7			(14)	(15)
							100	8.5	-6	24.4	-16.7		
.12	p-$CH_3C_6H_4SO_3CH_2CH(CH_3)_2 + C_2H_5OH$	B	10^2A= 3-4			kA	75	1.33	-6				(15)
.13	p-$CH_3C_6H_4SO_3CH_2CH(CH_3)_2 + HCOOH$	B	10^2A= 4.5-5.6			kA	75	2.3	-5				(15)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.14	p-$CH_3C_6H_4SO_3CH_2CH(CH_3)_2 + CH_3COOH$	B	10^2A= 2-2.8			kA	75	2.34	-7				
							100	3.79	-6	28.1	-8.4		(15)
.15	p-$CH_3C_6H_4SO_3CH_2C(CH_3)_3 + C_2H_5OH$	B	10^2A= 6			kA	100	4	-7			*	(18)
.16	p-$CH_3C_6H_4SO_3CH_2C(CH_3)_3 + HCOOH$	B	10^2A= 6-10			kA	60	3.1	-6				
							75	1.82	-5	27	-3		
.17	p-$CH_3C_6H_4SO_3CH_2C(CH_3)_3 + CH_3COOH$	B	10^2A= 4-40	$(CH_3CO)_2O$	0.019	kA	75	8.1	-8			*	(18)
							100	1.70	-6	31.5	-1.0		
.18	p-$CH_3C_6H_4SO_3CH(CH_3)CH(CH_3)_2 + HCOOH$	B	A= 0.15			kA	24	2.5	-4				(15)
Mono-aryl-substituted alkyl Tolylsulfonates													
.19	p-$CH_3C_6H_4SO_3CH_2C_6H_5 + H_2O$	$(CH_3)_2CO$	A = 0.5-1	$LiClO_4$	0	kA	25	1.02	-4			*	(3)
			Mol % B =		1.83		25	1.07	-4				
			76.5		2.21		25	1.10	-4				
			29.0		1.83		25	1.03	-6				
			44.8		1.83		25	4.15	-6				
			55.0		1.83		25	1.02	-5				
			62.0		1.83		25	1.93	-5				
			67.0		1.83		25	3.05	-5				
			71.1		1.83		25	4.81	-5				
			74.1		1.83		25	7.50	-5				
			76.6		1.83		31	1.93	-4				
			76.6		1.83		40	4.61	-4	17.9	-16.6		
.20	p-$CH_3C_6H_4SO_3$-m-$CH_2C_6H_4CH_3 + H_2O$	$(CH_3)_2CO$	A ≃ 0.01; Mol % B = 76.6	$LiClO_4$	0.16	kA	25	1.92	-4			*	(3)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.21	p-$CH_3C_6H_4SO_3$-p-$CH_2C_6H_4CH_3 + H_2O$	$(CH_3)_2CO$	Mol % B= 13.5	$LiClO_4$	0.16-1.83	kA	25	5.41	-6			*	(3)
			29.0				25	1.98	-5				
			44.8				25	9.40	-5				
			55.0				25	2.51	-4				
			62.0				25	5.41	-4				
			67.0				25	9.82	-4				
			71.1				25	1.54	-3				
			74.4				25	2.30	-3				
			76.6				25	3.19	-3				
			10^2A = 1.0-1.4										
.22	p-$CH_3C_6H_4SO_3CH_2CH_2C_6H_5 + C_2H_5OH$	B	A= 0.023			kA	75	7.08	-6				(14)
.23	p-$CH_3C_6H_4SO_3CH_2CH_2C_6H_5 + HCOOH$	B	A=0.07			kA	75	3.94	-5				(14)
.24	p-$CH_3C_6H_4SO_3CH_2CH_2C_6H_5 + CH_3COOH$	B	10^2A= 3.7-4.1			kA	75	2.88	-7				(14)
			= 2.4-2.7				100	3.31	-6	24.9	-17.3		
			= 2.6	CH_3COOK	0.0370		75	4.90	-7				
			= 1.7		0.0375		75	5.12	-7				
.25	p-$CH_3C_6H_4SO_3CH_2CH(CH_3)C_6H_5 + HCOOH$	B				kA	25	1.51	-6				(14)
.26	p-$CH_3C_6H_4SO_3CH_2CH(CH_3)C_6H_5 + CH_3COOH$	B				kA	50	7.2	-8				(14)
.27	p-$CH_3C_6H_4SO_3CH(CH_3)CH_2C_6H_5 + C_2H_5OH$	B	10^2A= 1.8-1.9			kA	50	1.41	-6				(6)
.28	p-$CH_3C_6H_4SO_3CH(CH_3)CH_2C_6H_5 + HCOOH$	B	10^2A= 7.6-8.4			kA	25	1.37	-5			(6)	(14)
.29	p-$CH_3C_6H_4SO_3CH(CH_3)CH_2C_6H_5 + CH_3COOH$	B	10^2A= 2.1-3.2			kA	50	5.8	-7			(6)	(14)
							75	1.31	-5	27.3	-2.7		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.30	p-$CH_3C_6H_4SO_3CH_2C(CH_3)_2C_6H_5 + C_2H_5OH$	B	$10^2A = 4$			kA	75	5.2	-6			*	(18)
.31	p-$CH_3C_6H_4SO_3CH_2C(CH_3)_2C_6H_5 + CH_3COOH$	B				kA	50	3.54	-7				(14)
			$10^2A = 4$-5	$(CH_3CO)_2O$	0.02	kA	75	1.93	-5				(18)
					0.02		100	2.47	-4	25.7	-6.4		
.32	p-$CH_3C_6H_4SO_3CH(CH_3)CH(CH_3)C_6H_5 + C_2H_5OH$	B	$10^2A = 2.1$			kA	75	3.0	-5			*	(19)
.33	p-$CH_3C_6H_4SO_3CH(CH_3)CH(CH_3)C_6H_5 + HCOOH$	B	$10^2A = 7$			kA	25	2.22	-4			*(14)	(19)
.34	p-$CH_3C_6H_4SO_3CH(CH_3)CH(CH_3)C_6H_5 + CH_3COOH$	B	$10^2A = 3$-11			kA	50	2.42	-6			*	(19)
							75	5.15	-5	26.3	-2.9		
				H_2O	0.3		50	4.01	-6				
				CH_3COONa	0.11		75	6.7	-5				
				$CH_3C_6H_4SO_3Na$	0.086		75	5.2	-5				
	(racemate with m.p. = 130-131)			$(CH_3CO)_2O$	0.02		50	2.38	-6				(18)
					0.02		75	5.0	-5	26.3	-2.9		
	(racemate with m.p. = 156-157)				0.02		50	2.72	-6				
					0.02		75	5.8	-5	26.5	-2.1		
.35	p-$CH_3C_6H_4SO_3CH(CH_3)C(CH_3)_2C_6H_5 + CH_3COOH$	B				kA	50	7.4	-5				(14)
.36	p-$CH_3C_6H_4SO_3CH(C_6H_5)C(CH_3)_3 + CH_3COOH$	B		H_2O	0.36	kA	24	2.4	-5				(16)
.37	p-$CH_3C_6H_4SO_3CH_2$-m-$C_6H_4OCH_3 + H_2O$	$(CH_3)_2CO$	$10^3A = 7.5$-10 Mol % B = 76.6	$LiClO_4$	0.16	kA	25	6.53	-5			*	(3)
.38	p-$CH_3C_6H_4SO_3CH_2$-p-$C_6H_4OCH_3 + H_2O$	$(CH_3)_2CO$	$10^2A \simeq 1$; $B \sim 7.5$	$LiClO_4$	0.16	kA	25	5	-3			*	(3)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.39	p-$CH_3C_6H_4SO_3CH_2CH_2$-o-$C_6H_4OCH_3$ + C_2H_5OH	B	10^2A= 2.9			kA	75	8.25	-6				(14)
.40	p-$CH_3C_6H_4SO_3CH_2CH_2$-o-$C_6H_4OCH_3$ + HCOOH	B	10^2A= 6.3-7			kA	75	1.75	-3				(14)
.41	p-$CH_3C_6H_4SO_3CH_2CH_2$-o-$C_6H_4OCH_3$ + CH_3COOH	B	10^2A= 2.8			kA	75	6.9	-6			*	(14)
			= 3.6-4				100	9.0	-5	26.7	-5.7		
.42	p-$CH_3C_6H_4SO_3CH_2CH_2$-p-$C_6H_4OCH_3$ + C_2H_5OH	B	10^2A= 2.2			kA	75	1.35	-5				(14)
.43	p-$CH_3C_6H_4SO_3CH_2CH_2$-p-$C_6H_4OCH_3$ + HCOOH	B	10^2A = 4.3-5.2			kA	50	1.46	-4			*	(14)
			= 7.3-7.5				75	1.77	-3	21.7	-9.2		
.44	p-$CH_3C_6H_4SO_3CH_2CH_2$-p-$C_6H_4OCH_3$ + CH_3COOH	B	10^2A= 1.8-2.9			kA	75	8.4	-6			*	(14)
							100	1.01	-4	25.5	-8.8		
			10^2A = 2.8	CH_3COOK	0.070		75	2.6	-5				
			= 3.4		0.046		75	2.5	-5				
.45	p-$CH_3C_6H_4SO_3CH_2CH(CH_3)$-$p$-$C_6H_4OCH_3$ + CH_3COOH	B	$10^2A\sim3$			kA	50	6.6	-6				(14)
.46	p-$CH_3C_6H_4SO_3CH(CH_3)CH_2$-$p$-$C_6H_4OCH_3$ + C_2H_5OH	B	10^2A= 3			kA	50	8.3	-6				(6)
.47	p-$CH_3C_6H_4SO_3CH(CH_3)CH_2$-$p$-$C_6H_4OCH_3$ + HCOOH	B	10^2A= 5-7			kA	25	5.1	-4				(6)
.48	p-$CH_3C_6H_4SO_3CH(CH_3)CH_2$-$p$-$C_6H_4OCH_3$ + CH_3COOH	B	10^2A= 5			kA	50	1.20	-5				(6) (14)
							75	1.94	-4	24.1	-6.4		
.49	p-$CH_3C_6H_4SO_3CH(CH_3)CH(CH_3)$-$p$-$C_6H_4OCH_3$ + CH_3COOH	B	10^2A= 4			kA	50	1.87	-4				(6) (14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.50	$p\text{-}CH_3C_6H_4SO_3CH_2\text{-}p\text{-}C_6H_4NO_2 + H_2O$	$(CH_3)_2CO$	10^3A= 5.3-57 Mol % B= 76.6	$LiClO_4$	0.16	kA	25	2.34	-6			*	(3)
.51	$p\text{-}CH_3C_6H_4SO_3CH_2\text{-}m\text{-}C_6H_4Br + H_2O$	$(CH_3)_2CO$	10^3A = 5-6.5 Mol % B= 76.6	$LiClO_4$	0.16	kA	25	8.81	-6			*	(3)
							40	3.95	-5	17	-23		
.52	$p\text{-}CH_3C_6H_4SO_3CH_2\text{-}p\text{-}C_6H_4Br + H_2O$	$(CH_3)_2CO$	10^3A= 6-9 Mol % B= 76.6	$LiClO_4$	0.16	kA	25	4.35	-5			*	(3)
							40	2.05	-4	19.0	-14.6		
Di-aryl-substituted alkyl Tolylsulfonates													
.53	$p\text{-}CH_3C_6H_4SO_3CH_2CH(C_6H_5)_2 + OCH_3^-$	MC*	A= B= 0.046			kAB	78	1.9	-2			*	(1)
.54	$p\text{-}CH_3C_6H_4SO_3CH_2CH(C_6H_5)_2 + C_2H_5OH$	B	10^3A= 8			kA	100	2	-5			*	(18)
.55	$p\text{-}CH_3C_6H_4SO_3CH_2CH(C_6H_5)_2 + CH_3COOH$	B	10^2A= 5.1	CH_3COOK	0.053	kA	99	3.51	-5			*	(1)
			= 1.5	$(CH_3CO)_2O$	0.019		75	2.61	-6			*	(18)
					0.019		100	3.81	-5	27.1	-6.4		
.56	$p\text{-}CH_3C_6H_4SO_3CH_2CH(C_6H_5)\text{-}p\text{-}C_6H_4CH_3 + CH_3O^-$	MC*	A= B= 0.046			kAB	78	1.17	-2			*	(1)
.57	$p\text{-}CH_3C_6H_4SO_3CH_2CH(C_6H_5)\text{-}p\text{-}C_6H_4CH_3 + CH_3COOH$	B	10^2A= 4.8	CH_3COOK	0.053	kA	100	5.68	-5			*	(1)
.58	$p\text{-}CH_3C_6H_4SO_3CH_2CH(\text{-}p\text{-}C_6H_4CH_3)_2 + CH_3O^-$	MC*	A= B= 0.046			kAB	78	7.2	-3			*	(1)
.59	$p\text{-}CH_3C_6H_4SO_3CH_2CH(\text{-}p\text{-}C_6H_4CH_3)_2 + CH_3COOH$	B	10^2A = 5.3	CH_3COOK	0.053	kA	99	2.92	-4			*	(1)
.60	$p\text{-}CH_3C_6H_4SO_3CH_2\text{-}m\text{-}C_6H_4CH{:}CHC_6H_5 + H_2O$	WA*	$10^3A \sim 3$	$LiClO_4$	1.83	kA	25	5.36	-5			*	(4)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.61	p-$CH_3C_6H_4SO_3CH_2$-p-$C_6H_4CH{:}CHC_6H_5$ + H_2O	AW*	10^3A = 1-3 B* = 44.8	$LiClO_4$	1.83	kA	25	7.47	-4			*	(4)
			55.0				25	1.89	-3				
			62.0				25	3.56	-3				
.62	p-$CH_3C_6H_4SO_3CH_2$-m-$C_6H_4C{:}CC_6H_5$ + H_2O	WA*	10^2A= 3	$LiClO_4$	1.83	kA	25	1.56	-5			*	(4)
.63	p-$CH_3C_6H_4SO_3CH_2$-p-$C_6H_4C{:}CC_6H_5$ + H_2O	AW*	10^3A = 2-3 B* = 62.0	$LiClO_4$	1.83	kA	25	2.38	-5			*	(4)
			71.1				25	6.66	-5				
			74.1				25	1.01	-4				
			76.6				25	1.47	-4				
Tri-aryl-substituted alkyl Tolysulfonates													
.64	p-$CH_3C_6H_4SO_3CH_2C(C_6H_5)_3$ + C_2H_5OH	B	10^2A= 1			kA	50	7.5	-6				(18)
.65	p-$CH_3C_6H_4SO_3CH_2C(C_6H_5)_3$ + CH_3COOH	B	10^2A= 9	$(CH_3CO)_2O$	0.019	kA	50	1.7	-5			*	(18)
							75	3.1	-4	25.2	-2.5		
Cyclo-alkyl Tolylsulfonates													
.66	p-$CH_3C_6H_4SO_3$-*cyclo*-C_5H_9 + C_2H_5OH	B	10^2A= 2.4-4			kA	50	5.0	-5				(17)
.67	p-$CH_3C_6H_4SO_3$-*cyclo*-C_5H_9 + HCOOH	B	10^2A= 9-15			kA	25	7.5	-4				(17)
.68	p-$CH_3C_6H_4SO_3$-*cyclo*-C_5H_9 + CH_3COOH	B	10^2A= 2.8-4.2			kA	50	3.84	-5				(17)
							75	5.46	-4	23.7	-6.4		
.69	p-$CH_3C_6H_4SO_3$-*cyclo*-C_6H_{11} + HCOOH	B	10^2A= 8			kA	25	4.0	-5				(17)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.70	p-$CH_3C_6H_4SO_3$-*cyclo*-C_6H_{11} + CH_3COOH	B	$10^2A = 3$			kA	50	1.85	-6			*	(5)
							75	4.3	-5				(8)
							100	6.4	-4	27.0	-1.1		
				H_2O	0.36		35	2.61	-7				(9)
					0.36		75	4.9	-5				
				DPG*	0.095		75	6.13	-5				(8)
					0.10		100	8.7	-4				(8)
.71	p-$CH_3C_6H_4SO_3$-*cis*-2-$C_6H_{10}OOCCH_3$ + CH_3COOH	B	$A \simeq 0.1$			kA	100	2.9	-7			*	(8)
							131	8.0	-7	25	-22		
				DPG*	0.11		100	5.3	-7				
.72	p-$CH_3C_6H_4SO_3$-*trans*-2-$C_6H_{10}OOCCH_3$ + C_2H_5OH	B	$10^2A = 4$	CH_3COOK	0.085	kA	75	1.00	-5				(11)
.73	p-$CH_3C_6H_4SO_3$-*trans*-2-$C_6H_{10}OOCCH_3$ + CH_3COOH	B	$10^2A = 2.5$-20			kA	100	1.90	-4			*	(11)
				H_2O	0.055		100	1.95	-4				
					0.33		75	1.50	-5				
					0.33		100	2.07	-4	27	-4.6		
					0.55		100	2.25	-4				
				CH_3COOK	0.025-0.14		100	2.0-2.1	-4				
				$(CH_3CO)_2O$	0.046		100	1.9	-4				
.74	p-$CH_3C_6H_4SO_3$-*d-trans*-2-$C_6H_{10}C{:}OCH_3$ + CH_3COOH	B	$10^2A = 6.3$	CH_3COOK	0.074	kA	75	1.35	-5			*	(12)
.75	p-$CH_3C_6H_4SO_3$-*trans*-2-$C_6H_{10}I$ + CH_3COOH	B	$10^2A = 3$-5	H_2O	0.36	kA	24	5.64	-5				(7) (9)
							35	2.26	-4	21.7	-4.9		
.76	p-$CH_3C_6H_4SO_3\overline{CHCH_2CH(CH_3)CH_2CH_2CHCH(CH_3)_2}$ + C_2H_5OH (menthyl-p-tolylsulfonate)	B	$10^2A = 3$-4			kA	75	1.34	-5				(17)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.77	p-$CH_3C_6H_4SO_3\overline{CHCH_2CH(CH_3)CH_2CH_2CHCH(CH_3)_2}$ + CH_3COOH (menthyl-p-tolylsulfonate)	B	10^2A= 3-5			kA	50 75	1.28 4.0	-6 -5	29.9	7.1		(17)
.78	p-$CH_3C_6H_4SO_3\overline{CHCH_2CH(CH_3)CH_2CH_2CHCH(CH_3)_2}$ + C_2H_5OH (neomenthyl-p-tolylsulfonate)	B	10^2A= 3.7			kA	50	7.1	-5				(17)
.79	p-$CH_3C_6H_4SO_3\overline{CHCH_2CH(CH_3)CH_2CH_2CHCH(CH_3)_2}$ + CH_3COOH (neomenthyl-p-tolylsulfonate)	B	10^2A = 3			kA	34 50	1.34 9.9	-5 -4	24.6	-0.7		(17)
.80	p-$CH_3C_6H_4SO_3C_{10}H_{17}$ + C_2H_5OH (bornyl-p-tolylsulfonate)	B	10^2A = 3			kA	75	1.29	-5				(17)
.81	p-$CH_3C_6H_4SO_3C_{10}H_{17}$ + CH_3COOH (bornyl-p-tolylsulfonate)	B	10^2A= 2.8-3.8			kA	50 75	2.55 5.9	-6 -5	27.3	0.2		(17)
	Alkyl-bromobenzene sulfonate												
.82	p-$BrC_6H_4SO_3CH(CH_3)_2$ + H_2O	Et*	10^2A= 1.1			kA	70	1.7	-3				(2)
.83	p-$BrC_6H_4SO_3CH(CH_3)_2$ + CH_3OH	B	10^2A= 1.8-2.3			kA	70	7.3	-4				(2)
.84	p-$BrC_6H_4SO_2CH(CH_3)_2$ + C_2H_5OH	B	10^2A= 2.3			kA	70	2.6	-4				(2)
.85	p-$BrC_6H_4SO_3CH(CH_3)_2$ + HCOOH	B	10^2A= 4.4			kA	25 40	6.1 3.5	-5 -4	15	-28		(15)
.86	p-$BrC_6H_4SO_3CH(CH_3)_2$ + CH_3COOH	BA*	10^2A= 2.7-4.3			kA	35 70	1.02 6.9	-6 -5	24.8	-5.5	*	(18)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Comments	Literature
.86	p-$BrC_6H_4SO_3CH(CH_3)_2 + CH_3COOH$ *(continued)*	B	10^2A= 2.4-4.3	$(CH_3CO)_2O$ + CH_3COOK	0.01 0 0.025	kA	70	6.9	-5				(2)
					0.025		70	7.4	-5				
		AA*	10^2A= 2-4 B=	CH_3COOK	0-0.02	$k_1A + k_2A[CH_3COOK]$							
								k_1					
			0.45				70	1.4	-6				
			3.5				70	8.5	-6				
								k_2					
			0.45				70	3.61	-4				
.87	p-$BrC_6H_4SO_3CH(CH_3)C_2H_5$ + HCOOH	B	10^2A= 8-9			kA	25	1.5	-4				(15)
.88	p-$BrC_6H_4SO_3CH(CH_3)C_2H_5 + CH_3COOH$	BA*				kA	40	4.05	-6			*	(18)
							70	1.23	-4	23.7	-7.7		
				CH_3COOK	0.025		70	1.27	-4				
.89	p-$BrC_6H_4SO_3CH(CH_3)CH(CH_3)_2$ + HCOOH	B	10^2A= 4			$k'A$	25	8.5	-4				(15)
.90	p-$BrC_6H_4SO_3CH(CH_3)CH(CH_3)_2 + CH_3COOH$	BA*	10^2A= 1.6			kA	35	5.85	-6			*	(18)
							70	4.02	-4	24.7	-2.3		
				CH_3COOK	0.025		70	4.14	-4				
.91	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_3 + H_2O$	Et*	10^2A= 1			kA	70	1.37	-3				(2)
.92	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_3 + CH_3OH$	B	10^3A= 6-20			kA	70	3.2	-4				(2)
.93	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_3 + C_2H_5OH$	B	10^3A= 7-16			kA	70	7.0	-5				(2)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.94	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_3 + HCOOH$	B	$10^2A = 9$			kA	25	8.6	-4				(15)
.95	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_3 + CH_3COOH$	BA*	$10^2A = 2$-3			kA	50	2.37	-5				(18)
							70	2.73	-4	26.3	1.5		
				CH_3COOK	0.025		70	2.81	-4				(2)
.96	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_3 + CH_3COOH$	AA*	$10^2A = 2$-3										
			$B = 0.45$	CH_3COOK	0.02	kA	70	1.15	-5				(2)
			0.45		0.009		70	1.17	-5				
			3.5		0		70	7.9	-5				
.97	p-$BrC_6H_4SO_3CH_2C(CH_3)_2OCH_3 + H_2O \longrightarrow$ $(CH_3)_2CHCHO + CH_3OH + p$-$BrC_6H_4SO_3H$	DW*	$10^2A = 5$	CH_3COOK	0.059	kA	100	3.89	-5			*	(13)
.98	p-$BrC_6H_4SO_3CH_2C(CH_3)_2OCH_3 + CH_3COOH \longrightarrow$ $(CH_3)_2CHCHO + CH_3COOCH_3 + p$-$BrC_6H_4SO_3H$	B	$10^2A = 5$			kA	75	3.55	-6			*	(13)
Mono-aryl-substituted alkyl bromobenzene sulfonate													
.99	p-$BrC_6H_4SO_3CH_2CH(CH_3)C_6H_5 + C_2H_5OH$	B	$10^2A \simeq 3$			kA	17	4.4	-6				(20)
.100	p-$BrC_6H_4SO_3CH_2CH(CH_3)C_6H_5 + HCOOH$	B	$10^2A = 3$-5			kA	25	3.3	-6				(20)
.101	p-$BrC_6H_4SO_3CH_2CH(CH_3)C_6H_5 + CH_3COOH$	B	$10^2A = 2$-4			kA	75	1.6	-6			*	(20)
							100	4.2	-5	33	+10		
				CH_3COONa	0.04		75	3.3	-6				
					0.04		100	4.4	-5				

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.101	p-$BrC_6H_4SO_3CH_2CH(CH_3)C_6H_5 + CH_3COOH$ *(continued)*	B	10^2A= 2-4	H_2O	0.3	kA	75	3.6	-6			*	(20)
				$LiClO_4$	0.03		75	3.1	-6				
				DPGB*[4]	0.04		75	2.4	-6				
.102	p-$BrC_6H_4SO_3CH(CH_3)CH_2C_6H_5 + HCOOH$	B	10^2A= 8-9			kA	25	3.01	-5				(6)
.103	p-$BrC_6H_4SO_3CH(CH_3)CH_2C_6H_5 + CH_3COOH$	B	10^2A= 2.6-3			kA	75	3.9	-5			*	(6)
							100	4.7	-4	25.2	-6.6		
				CH_3COONa	.03-.04		75	4.18	-5				(20)
					0.04		100	5.7	-4	26	-3		
				$LiClO_4$	0.03		75	6.0	-5				
				H_2O	0.3		75	5.3	-5				
				DPGB*	.02-.03		75	4.1	-5				
.104	p-$BrC_6H_4SO_3CH(CH_3)C(CH_3)_2C_6H_5 + CH_3COOH$	B	10^2A= 1-3	$(CH_3CO)_2O$	0.019	kA	25	2.04	-5			*	(18)
							50	4.65	-4	23.6	-1.0		
.105	p-$BrC_6H_4SO_3CH_2CH(OCH_3)C_6H_5 + HCOOH$	B	10^2A= 3	HCOONa	0.032	kA	75	4.8	-5				(14)
.106	p-$BrC_6H_4SO_3CH_2CH(OCH_3)C_6H_5 + CH_3COOH$	B	10^2A= 5.5			kA	75	7.15	-7				(14)
Di-aryl-substituted alkyl bromobenzene sulfonates													
.107	p-$BrC_6H_4SO_3CH(CH_3)CH(C_6H_5)_2 + C_2H_5OH$	B	10^2A= 2.4			kA	75	1.12	-4			*	(18)
.108	p-$BrC_6H_4SO_3CH(CH_3)CH(C_6H_5)_2 + CH_3COOH$	B	10^2A= 1.4	$(CH_3CO)_2O$	0.019	kA	49	1.13	-5			*	(18)
							75	2.31	-4	25.7	-1.7		
.109	p-$BrC_6H_4SO_3CH_2C(OCH_3)(C_6H_5)_2 + H_2O$	DW*	10^2A= 4-5	CH_3COOK	0.039	kA	48	4.0	-7			*	(14)
					0.055		75	1.03	-5	26	-7		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.110	p-$BrC_6H_4SO_3CH_2C(OCH_3)(C_6H_5)_2$ + CH COOH	B	$10^2A = 5.1$	CH_3COOK	0.053	kA	75	3.35	-5			*	(14)
	Cyclo-alkyl bromobenzene sulfonate												
.111	p-$BrC_6H_4SO_3$-*cyclo*-C_6H_{11} + HCOOH	B	10^2A = 8-9			kA	25	1.07	-4				(17)
.112	p-$BrC_6H_4SO_3$-*cyclo*-C_6H_{11} + CH_3COOH	B				kA	25	1.71	-7			*	(9)
			10^2A= 3-5	$(CH_3CO)_2O$	0.046		35	7.52	-7				
					0.046		75	1.24	-4	26.6	-0.3		
				H_2O	0.36		35	9.68	-7				
					0.36		75	1.73	-4	27.0	1.5		
		BA*		CH_3COOK	0.025		75	1.50	-4				
.113	p-$BrC_6H_4SO_3$-*trans*-2-$C_6H_{10}OCH_3$ + CH_3COOH	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046	kA	75	7.04	-6				(9)
				H_2O	0.36		75	9.04	+6				
					0.36		100	1.31	-4	27.3	-3.4		
		BA*		CH_3COOK	0.025		75	7.86	-6				
.114	p-$BrC_6H_4SO_3$-*cis*-2-$C_6H_{10}OCCH_3$ + CH_3COOH	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046	kA	75	4.7	-8			*	(9)
							100	9.7	-7	30.9	-3.5		
				H_2O	0.36		75	1	-7				
		BA*		CH_3COOK	0.025		75	5.9	-8				
.115	p-$BrC_6H_4SO_3$-*trans*-2-$C_6H_{10}OCCH_3$ + CH_3COOH	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046	kA	75	2.97	-5			*	(9)
				+ $NaClO_4$	0.025		75	3.99	-5				
				H_2O	0.36		75	4.07	-5				
					0.36		100	5.23	-4	26.0	-4.2		
		BA*		CH_3COOK	0.025		75	3.75	-5				
.116	p-$BrC_6H_4SO_3$-*trans*-2-$C_6H_{10}Cl$ + CH_3COOH	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046		75	5.64	-8				(9)
							100	1.43	-6	33.0	2.7		

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.117	p-$BrC_6H_4SO_3$-*trans*-2-$C_6H_{10}Br$ + CH_3COOH	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046	kA	75	1.25	-5			*	(9)
				H_2O	0.36		75	1.57	-5				
					0.36		100	2.53	-4	28.4	0.8		
		BA*		CH_3COOK	0.025		75	1.36	-5				
.118	*cis*-1,2-(p-$BrC_6H_4SO_3$)$_2$$C_6H_{10}$ + $2CH_3COOH$	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046	$-dA/dt = kA$	75	9.5	-8			*	(9)
.119	*trans*-1,2-(p-$BrC_6H_4SO_3$)$_2$$C_6H_{10}$ + $2CH_3COOH$	B	10^2A= 3-5	$(CH_3CO)_2O$	0.046	$-dA/dt = kA$	75	8.5	-9			*	(9)
.120	p-$BrC_6H_4SO_3C_{10}H_{17}$ + H_2O (endo-norbornyl-p-bromobenzene sulfonate)	AW*	10 A= 3 B* ≃ 50			kA	75	2.4	-4			*	(21)
.121	p-$BrC_6H_4SO_3C_{10}H_{17}$ + C_2H_5OH (endo-norbornyl-p-bromobenzene sulfonate)	B	10 A= 3			kA	75	6.2	-5			*	(21)
.122	p-$BrC_6H_4SO_3C_{10}H_{17}$ + HCOOH (endo-norbornyl-p-bromobenzenesulfonate)	B				kA	25	8.5	-5			*	(17)
.123	p-$BrC_6H_4SO_3C_{10}H_{17}$ + CH_3COOH (endo-norbornyl-p-bromobenzenesulfonate)	B	10^2A= 2			kA	50	8.2	-6				(17)
							75	1.54	-4	26.0	-1.5		
			= 2-3	CH_3COOK	0.4		75	1.9	-4				(21)
.124	p-$BrC_6H_4SO_3C_{10}H_{17}$ + H_2O (exo-norbornyl-p-bromobenzenesulfonate)	AW*	10 A= 2; B*= 50			kA	25	5.4	-4			*	(22)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.125	p-$BrC_6H_4SO_3C_{10}H_{17}$ + C_2H_5OH (exo-norbornyl-p-bromobenzenesulfonate)	B	$10A = 3$			kA	25	2.66	-5			*	(22)
.126	p-$BrC_6H_4SO_3C_{10}H_{17}$ + CH_3COOH	B	$10^2A = 2$			kA	25	8.8	-5				(17)
							34	3.04	-4	24	+5		
			$= 2\text{-}20$	CH_3COOK	0.25		25	1.22	-4			*	(22)

SOLVENTS

AA* $(CH_3CO)_2O$

AW* $(CH_3)_2CO + H_2O$ where B* under amount of reactant = mol % H_2O in $(CH_3)_2CO$

BA* CH_3COOH +~0.2 % $(CH_3CO)_2O$

DW* Dioxane 80 % + H_2O 20 %

Et* C_2H_5OH 80 % + H_2O 20 %

MC* $CH_3OCH_2CH_2OCH_3$, (methyl cellosolve)

WA* H_2O 76.6 mol % + $(CH_2)_2CO$ 23.4 mol %

ADDENDS

DPG* diphenylguanidinium acetate

DPGB* diphenylguanidinium bromobenzenesulfonate

COMMENTS

Classification. The Alkyl arylsulfonates undergoing solvolysis are grouped under the headings: Saturated alkyl tolylsulfonates; Mono-aryl-substituted alkyl tolylsulfonates; Di-aryl substituted alkyl tolylsulfonates; Tri-aryl-substituted alkyl tolylsulfonates; Cyclo-alkyl tolylsulfonates; Saturated alkyl bromobenzene sulfonates; Mono-aryl-substituted alkyl bromobenzenesulfonates; Di-aryl-substituted alkyl bromobenzenesulfonates; Cyclo-alkyl bromobenzenesulfonates. In each group the sulfonates are arranged as usual in the order of increasing numbers of C atoms in the alkyl, straight chain and primary preceding the branched chain, and secondary preceding tertiary isomers.

Comments by Reaction. **(.15)** Reaction followed to less than 44 % completion and solvolysis is probably accompanied by partial rearrangement. **(.17)** Reaction followed to only 17 % completion at 75°C and 44 % at 100°C and is probably accompanied by partial rearrangement. **(.19)** Rate law followed up to 99 % completion. Authors attribute rate dependence upon concentration of B as primarily a dielectric constant effect, since plot of log k vs. $(D-1)/(2D+1)$ is almost linear. Log k vs. mol % B also gives linear plot from 29 to 67 mol % B. At higher mol % B log k values fall on line with steeper slope. Plot of log k vs. log B gives curve with slope of 2.5 at 29 % mol B and 10 at 76.6 mol % B. **(.20)** Rate law followed up to 91 % reaction. **(.21)** Rate law followed up to 98 % reaction. **(.30) (.31)** Rate law followed up to 70 % reaction. **(.32)** Solvolysis accompanied by racemization. Rate constant for racemization about double the rate constant for solvolysis. Authors attribute this to simultaneous group migration giving inverted form. **(.33)** Solvolysis accompanied by racemization which occurs at faster rate than solvolysis. See (.32) and 112.440. **(.34)** Rate law followed up to 70 % reaction. Solvolysis accompanied by racemization when optically active isomer used. See 112.440. Higher melting racemate gave slightly greater rate of solvolysis. **(.37)** Rate law followed up to 81 % reaction. Authors attribute rate dependence upon mol % B to changes in dielectric constant of solvent. See (.19). **(.38)** Reaction followed to 100 % completion but only magnitude of rate constant considered certain. **(.41)** Rate constant decreases by about 10 % over course of reaction. Cause of drift

COMMENTS *(continued)*

not investigated. (.43) Addition of HCOOK showed negligible effect upon rate constant. Product gave negative phenolic and olefinic tests before and after reduction with lithium aluminum hydrate. Infrared spectrum showed no measurable migration of $CH_3OC_6H_4$ from β to α-carbon. (.44) Rate constant decreased about 10 % over course of reaction in absence of CH_3COOK. (.50) (.51) Rate law followed up to 75 % reaction. Authors attribute effect of concentration of B upon rate constant to be due to dielectric constant of solvent effect and state that plot of log k vs. $(D-1)/(2D+1)$ is linear in agreement with equation developed by Glasstone, Laidler and Eyring. See (.19). (.52) Rate law followed up to 97 % reaction. For dependence upon B see (.19) (.50). (.53) Rate law followed up to 75 % reaction. Products not determined and may be stilbene or a methyl ether. Acetolysis in glacial acetic acid gave almost entirely stilbene and tolylsulfonic acid. (.54) Rate law followed up to 70 % reaction. Solvolysis probably accompanied by rearrangement, (migration of phenyl group). (.55) Rate law followed up to 60 % of reaction. (.56) Second order rate constant followed up to 75 % reaction. Products of reaction not determined but acetolysis leads to stilbene formation. Reaction of

$$p\text{-}CH_3C_6H_4SO_3C^{14}H_2CH(C_6H_5)(p\text{-}CH_3C_6H_4) + CH_3O^- \longrightarrow$$

to determine extent of p-tolyl rearrangement showed on oxidative degradation of oily products less than 2 % group migration. Products were difficult to oxidize. In the acetolysis in acetic acid p-tolyl migration represented 72 % of products. (.57) First order rate law followed up to 60 % reaction. Reaction using labeled C^{14}, see (.56), gave good yield of p-methyl stilbene which on degradative oxidation showed p-tolyl responsible for 72 % of migration. (.58) Second order rate law followed up to 75 % reaction. Products not determined and reaction may be either solvolysis or elimination. (.59) (.60) First order rate law followed up to 80 % reaction. (.61) Rate law followed up to 98 % reaction. This reaction too rapid to follow in the standard reagent 76.6 mol % water. For effect of concentration of B upon rate of reaction see (.19) and (.50). (.62) Rate law followed up to 85 % reaction. For influence of B upon rate see (.19) and (.50). (.63) Rate law followed up to 93 % reaction. For influence of B upon rate see (.19) and (.50). (.65) Rate law followed up to 70 % reaction. (.70) Rate law followed up to 80 % reaction. (.71) Rate law followed to only 6 % reaction at 100°C. (.73) Rate law holds over course of reaction except in experiments with no added water. Under these conditions rate first decreases to a minimum at a concentration of L = 0.01 for initial A from 0.10 to 0.028. $10^5 k_{min.}$ = 6.1 and 9.8 at initial A = 0.10 and 0.028 respectively. The rate constant increases over the remainder of the reaction. Values tabulated were obtained by extrapolating to rate at zero time. In anhydrous B with added

COMMENTS *(continued)*

CH_3COOK product L retains original configuration of A, while in excess acid, inversion of configuration is observed with no appreciable effect upon reaction kinetics. **(.74)** Rate law followed over course of reaction by titration and polarimetrically. Racemization and solvolysis rates identical within experimental accuracy in contrast with (.33) and (.34). **(.86) (.88) (.90) (.95)** Rate law followed up to 70 % reaction. Solvolysis possibly accompanied by rearrangement. **(.97) (.98)** L isolated in 72 % yield as the dinitro phenylhydrazone indicating it to be a major product of the solvolysis. **(.101)** First order rate constants increase over course of reaction due to accompanying rearrangement to $p\text{-}BrC_6H_4SO_3CH(CH_3)CH_2C_6H_5$ which undergoes solvolysis at greater rate, (see 152.446). Values tabulated are from kinetic analysis of mixtures of $p\text{-}BrC_6H_4SO_3CH_2CH(CH_3)C_6H_5$ and $p\text{-}BrC_6H_4SO_3CH(CH_3)CH_2C_6H_5$. Rate of, solvolysis of the latter, which does not rearrange, also determined independently. Values with added H_2O and $LiClO_4$ obtained by extrapolation of rate constant to zero time. **(.103)** Good first order rate constants over course of reaction interpreted to indicate no rearrangement accompanying solvolysis, see (.101). **(.104) (.107) (.108)** Rate law followed up to 70 % reaction. Solvolysis possibly accompanied by partial rearrangement. **(.109) (.110)** Rate law valid over course in presence of CH_3COOK. In absence of added salt, rate constants fall off rapidly with course of reaction. **(.112)** Rate constants tabulated obtained by extrapolation of rate constant to zero time as values showed gradual increase with extent of reaction. **(.114)** In presence of added CH_3COOK rate law valid over course but in presence of added H_2O rate constants climb rapidly. The instantaneous rate constant $k' = dM/Adt = 10^{-3}(27.76\ M^{0.5} - 0.23)$ at 75°C. Reaction followed to only 15 % completion. **(.115)** Rate constant tabulated obtained by extrapolation to zero time as constants decreased slightly with extent of reaction. **(.117)** Slight upward drift in rate constants with course of reaction considered to be within experimental error and results were averaged. **(.118)** Rate constant calculated on basis of solvolysis of both ester groups but reaction followed to only 15 % completion. Solvolysis of second ester group actually slower, see (.114). **(.119)** Rate constant calculated on basis of both ester groups reacting which is valid, see (.115). Reaction followed to only 15 % completion. **(.120) (.121)** Rate followed both by titration and polarimetrically with identical rate constants within experimental limits. **(.122)** Rate constant based upon only one preliminary run. **(.124)** Rate of racemization 1.4 times faster than rate of solvolysis. See (.33) and 112.440. **(.125)** Rate of solvolysis approximately one third rate of racemization. See (.33) and 112.440. **(.126)** Rate of solvolysis between one third and one fourth rate of racemization but both show good first order behavior over course of reaction, see (.33) and 112.440

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SOLVOLYSIS

Ester of aliphatic alcohol and thiocyanic acid

Liquid phase

Amounts are in M/l. Rate constants are per sec.

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Temperature	$k = k^o \times 10^n$	
.1	$(C_6H_5)_3CSCN + H_2O \longrightarrow (C_6H_5)_3COH + HSCN$	$(CH_3)_2CO$	$10^4A = 7.5\text{–}10$ $B = 3.3$ $B = 28$	kA	25	 2.4 2.2	 -4 -3

COMMENTS

Pseudo first order with respect to A over course. Addition of various nucleophilic reagents has no effect upon rate of loss of A but does yield a variety of products as the nucleophilic reagents compete with B. For similar behavior see supplementary table 212.471.

LITERATURE

C. G. Swain, C. B. Scott, K. H. Lohmann, *ACS* 1953, 75, 136.

ESTER SOLVOLYSIS

Ester of Aliphatic alcohol and hydrohalic acid

Reaction types: $RX + R'OH \longrightarrow HX + ROR'$ (A) (B) (L) (M)

$RX + R'O^- \longrightarrow X^- + ROR'$

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

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents, Comments, literature, at the end of the table.

No.	Supplementing 1951 No.	Reaction	Medium (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
.179	.2	$CH_3Br + H_2O$	HCOOH	A = 0.17-0.21;	B = 0.3		kA	100	2.36	-6				*	(10)
					0.8			100	2.80	-6					
					1.4			100	3.50	-6					
					3.0			100	4.64	-6					
					5.8			100	7.66	-6					
.180	.5	$C_2H_5Br + H_2O$	HCOOH	A = 0.17-0.21;	B = 0.3		kA	100	4.03	-6				*	(10)
					5.8			100	8.75	-6					
.181	.12	$C_2H_5I + C_2H_5O^-$	C_2H_5OH	A = 0.1;	Pressure	Kg/cm^2 = 1	kAB	25	1.29	-4	21	2	11	(33a)	(60a)
				B = (0.05-0.5)		3,000		25	2.06	-4	21	4	11	*	
						5,000		25	2.66	-4	20	2	11		
						8,500		25	2.84	-4					
						12,000		25	3.11	-4					
.182	.13	n-$C_3H_7Br + H_2O$	D1W70*	A = 0.025	Hg^{++}	0.025	$kA[Hg^{++}]$	25	1.35	-3					(59)
					HNO_3	0.025		41	5.03	-3	15.8	5	8		
								25	1.75	-3					(12a)

No.	Supplementing 1951 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
.183		$n\text{-}C_3H_7Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = B = 0.1		$k = (k_S + k_E)$; k A		55	6.0	-4					(32)
		$Br^- + n\text{-}C_3H_7OC_2H_5$ (S)					k_SA	55	5.5	-4					
		$Br^- + C_3H_6 + C_2H_5OH$ (E)					k_EA	55	5.3	-5					
.184	.16	$(CH_3)_2CHBr + H_2O \longrightarrow$	Et6O*	A = 0.1-0.15		$k = (k_S + k_E)$; k A		80	7.06	-5	21.3	1.1	9		(31)
		$HBr + (CH_3)_2CHOH$ (S)					k_SA	80	6.74	-5					
		$HBr + C_3H_6 + H_2O$ (E)					k_EA	80	3.2	-6					
			HCOOH	A = 0.17-0.21;		$k = (k_S + k_E)$; k A		100	1.05	-4					(10)
				B = 0.3			k_SA	100	9.9	-5					
							k_EA	100	6	-6					
				B = 5.8			k A	100	1.72	-4					
							k_SA	100	1.60	-4					
							k_EA	100	1.2	-5					
.184.1		$(CH_3)_2CHBr + H_2O + Hg(NO_3)_2$	D1W70*	A = 0.022; C = 0.025	HNO_3	0.28 k A$[Hg^{++}]$		25	5.1	-1					(12a)
.185	.17	$(CH_3)_2CHBr + OH^- \longrightarrow$	C_2H_5OH	A = 0.1-0.2;		$k = (k_S + k_E)$; k AB		80	1.62	-3					(31)
	.18			B = 4.0			k_SAB	80	2.1	-4					
		$Br^- + (CH_3)_2CHOH$ (S)					k_EAB	80	1.41	-3					
		$Br^- + C_3H_6 + H_2O$ (E)													
.186		$(CH_3)_2CHBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.2; B = 1.0		$k = (k_S + k_E)$; k AB		25	2.95	-6					(31)
		$Br^- + (CH_3)_2CHOC_2H_5$ (S)					k_SAB	25	5.8	-7					
		$Br^- + C_3H_6 + C_2H_5OH$ (E)					k_EAB	25	2.37	-6					
				A = 0.05; B = 1.0			k_SAB	25	1.06	-6				*	(61)
.187		$(CH_3)_2CDBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.05; B = 1.0			k_SAB	25	1.06	-6				*	(61)
		$Br^- + (CH_3)_2CDOC_2H_5$ (S)													

No.	Supplementing 1951 No.	Reaction	Medium (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
.188		$(CD_3)_2CHBr + C_2H_5O^- \longrightarrow Br^- + (CD_3)_2CHOC_2H_5$ (s)	C_2H_5OH	A= 0.05; B= 1.0			$k_s AB$	25	9.4	-7				*	(61)
.189		$n\text{-}C_4H_9F + C_2H_5O^-$	C_2H_5OH	A= 0.85; B= 1.1			$k AB$	90	1.42	-6				*	(23)
								105	4.5	-6					
								121	1.53	-5	21.8	2	7		
.190	.21	$n\text{-}C_4H_9Br + H_2O$	HCOOH	A= 0.09; B= 0.3			$k A$	100	2.37	-6				*	(10)
				" 3.0				100	3.39	-6					
				" 5.8				100	4.49	-6					
				" 0.3	$(HCOO)_2Ca$	0.05		100	2.99	-6					
			Et50*	A= 0.09				100	9.36	-5					
			D1W70*	A = 0.025	Hg^{++} +	0.025	$k A[Hg^{++}]$	25	1.12	-3					(59)
					HNO_3	0.025		41	4.22	-3	15.9	5	8		
.191		$n\text{-}C_4H_9Br + \begin{cases} H_2O \\ CH_3OH \end{cases} \longrightarrow$	CH_3OH / H_2O(N)	A = 0.09;	H_2O(N)	$k = (k_a + k_b)$; $k A$									(14a)
					0			59	3.8	-7					
					0.141			59	7.3	-7					
					0.263			59	1.16	-6					
					0.31			59	1.39	-6					
					0.48			59	2.46	-6					
					0.60			59	3.64	-6					
		$\longrightarrow \begin{cases} HBr + n\text{-}C_4H_9OH & (a) \\ HBr + n\text{-}C_4H_9OCH_3 & (b) \end{cases}$			0.141		$k_a A$	59	9	-8					
					0.263			59	3.1	-7					
					0.31			59	4.0	-7					
					0.48			59	9.8	-7					
					0.60			59	1.78	-6					

N = mol fraction

No.	Supplementing 1951 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
.191		$n\text{-}C_4H_9Br + \begin{cases} H_2O \\ CH_3OH \end{cases} \longrightarrow$	CH_3OH $H_2O(N)$	A = 0.09;	$H_2O(N)$	$k = (k_a + k_b)$; kA									(14a)
					0.141		k_bA	59	6.4	-7					
					0.263			59	8.5	-7					
		$\longrightarrow \begin{cases} HBr + n\text{-}C_4H_9OH & (a) \\ HBr + n\text{-}C_4H_9OCH_3 & (b) \end{cases}$			0.31			59	9.9	-7					
					0.48			59	1.48	-6					
			(continued)		0.60			59	1.86	-6					
.192		$n\text{-}C_4H_9Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow$	C_2H_5OH $H_2O(N)$	A = 0.09;	$H_2O(N)$	$k = (k_a + k_b)$; kA									(14a)
					0			75	7.8	-7					
					0.26			75	2.48	-6					
		$\longrightarrow \begin{cases} HBr + n\text{-}C_4H_9OH & (a) \\ HBr + n\text{-}C_4H_9OC_2H_5 & (b) \end{cases}$			0.56			75	5.67	-6					
					0.74			75	1.11	-5					
					0.26		k_aA	75	9.7	-7					
					0.56			75	2.9	-6					
					0.74			75	7.2	-6					
					0.26		k_bA	75	1.5	-6					
					0.56			75	2.8	-6					
					0.74			75	3.9	-6					
.193		$n\text{-}C_4H_9Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = B = 0.1		$k = (k_S + k_E)$; kAB		55	4.4	-4					(32)
		$\begin{cases} Br^- + n\text{-}C_4H_9OC_2H_5 & (S) \\ Br^- + C_4H_8 + C_2H_5OH & (E) \end{cases}$					k_SAB	55	4.0	-4					
							k_EAB	55	4	-5					
.194	.22.1	$(CH_3)_2CHCH_2Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = B = 0.1		$k = (k_S + k_E)$; kAB		55	1.43	-4					(32)
		$\begin{cases} Br^- + (CH_3)_2CHCH_2OC_2H_5 & (S) \\ Br^- + (CH_3)_2C{:}CH_2 + C_2H_5OH & (E) \end{cases}$					k_SAB	55	5.8	-5					
							k_EAB	55	8.5	-5					
.194.1		$(CH_3)_2CHCH_2Br + H_2O + Hg(NO_3)_2$	D1W70*	A = 0.022; C = 0.025	HNO_3	0.28	$kA[Hg^{++}]$	25	4.8	-4					(12a)

No.	Supplementing 1951 No.	Reaction	Medium (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
.195		$C_2H_5(CH_3)CHF + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.8; B = 1			$k = (k_S + k_E)$; k AB	120	9.4	-7				*	(23)
		$F^- + C_2H_5(CH_3)CHOC_2H_5$ (S)					k_SAB	120	2.7	-7					
		$F^- + C_4H_8 + C_2H_5OH$ (E)					k_EAB	120	6.7	-7					
.196	.23	$C_2H_5(CH_3)CHBr + H_2O \longrightarrow$	Et6O*	A = (0.1-0.15)			$k = (k_S + k_E)$; k A	80	7.41	-5					(31)
		$HBr + C_2H_5(CH_3)CHOH$ (S)					k_SA	80	6.78	-5					
		$HBr + C_4H_8 + H_2O$ (E)					k_EA	80	6.3	-6					
.197		$C_2H_5(CH_3)CHBr + OH^- \longrightarrow$	C_2H_5OH	A = (0.1-0.2);			$k = (k_S + k_E)$; k AB	80	2.09	-3					(31)
		$Br^- + C_2H_5(CH_3)CHOH$ (S)		B = 4.0			k_SAB	80	1.8	-4					
		$Br^- + C_4H_8 + H_2O$ (E)					k_EAB	80	1.91	-3					
.198		$C_2H_5(CH_3)CHBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.2; B = 1			$k = (k_S + k_E)$; k AB	25	4.22	-6					(31)
		$Br^- + C_2H_5(CH_3)CHOC_2H_5$ (S)					k_SAB	25	7.5	-7					
		$Br^- + C_4H_8 + C_2H_5OH$ (E)					k_EAB	25	3.47	-6					
.199		$(CH_3)_3CF + H_2O$	Et8O*				k A	25	1	-10					(26) (70)
				A = (0.2-0.8)	HCl	.0074		80	1.1	-5					(23)
						.0148		80	1.9	-5					
						.0742		80	1.2	-4					
					HCl	0.007-0.07	k' A[H^+]	80	1.4	-3					

No.	Supplementing 1951 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
.200		$(CH_3)_3CF + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.8; B = 1		$k = (k_S + k_E)$; k AB		118	1.46	-6				*	(23)
		$\begin{cases} F^- + (CH_3)_3COC_2H_5 & (S) \\ F^- + (CH_3)_2C{:}CH_2 + C_2H_5OH & (E) \end{cases}$						138	6.9	-6	24.8	1.0	8		
							k_SAB	118	7	-8					
								138	3	-7					
							k_EAB	118	1.39	-6					
								138	6.6	-6					
.201	.24	$(CH_3)_3CCl + \begin{cases} H_2O \\ CH_3OH \end{cases} \longrightarrow$	CH_3OH / H_2O(N)	A =	H_2O(N)	(S + E) = k A								(30)	(66)
		$\longrightarrow \begin{cases} HCl + (CH_3)_3COH \\ HCl + (CH_3)_3COCH_3 \end{cases}$ (S)		0.26	0			25	6.70	-7				*	
				0.05	0			25	7.34	-7					
				0.02	0			25	7.50	-7					
				0.1-0.15	0.065			25	1.28	-6					
				0.15	0.124			25	2.18	-6					
				0.024	0.40			25	3.31	-5					
		$\longrightarrow HCl + (CH_3)_2C{:}CH_2$ (E)		0.022-0.027	0.60			25	2.82	-4	22.1			*	
				0.26	0			30	1.42	-6					
		(see supplementary table)		0.05	0			30	1.55	-6					
				0.02	0			30	1.69	-6	27				
				0.14	0.057			30	2.49	-6					
				0.05-0.11	0.124			30	4.50	-6					
				0.02-0.17	0.25			30	1.49	-5					
				0.02	0.50			30	1.79	-4	23				
.202	.25	$(CH_3)_3CCl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow$	Et8O*	A = 0.05		(S + E) = k A		25	8.92	-6					(63)
								35	3.07	-5					
								45	9.75	-5					
		$\longrightarrow \begin{cases} HCl + (CH_3)_3COH \\ HCl + (CH_3)_3COC_2H_5 \end{cases}$ (S)						55	2.84	-4	22.4	2.5	11		
		$\longrightarrow HCl + (CH_3)_2C{:}CH_2$ (E)													

No.	Supplementing 1951 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
.202	.25	$(CH_3)_3CCl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow$	Et8O*	A = 0.05	Pressure	atm.	k A								
						1		15	2.3	-6				*	(21)
						1500		15	6.3	-6					
						3000		15	1.02	-5					
		$\longrightarrow \begin{cases} HCl + (CH_3)_3COH \\ HCl + (CH_3)_3COC_2H_5 \end{cases}$ (S)				1		35	1.70	-5	18				
						1500		35	3.8	-5	16				
		$\longrightarrow HCl + (CH_3)_2C{:}CH_2$ (E)				3000		35	9.0	-5	19				
		(continued)													
.203	.26	$(CH_3)_3CCl + H_2O \longrightarrow$	$(CH_3)_2C{:}O$ H_2O(N)	A =	H_2O(N)	(S + E) = k A									
		$\begin{cases} HCl + (CH_3)_3COH \\ HCl + (CH_3)_2C{:}CH_2 + H_2O \end{cases}$ (S) (E)		0.07	0.51			25	1.92	-6				*	(30)
				0.014	0.61			25	7.78	-6					
				0.015	0.70			25	3.53	-5					
				0.012	0.80			25	2.00	-4					
				A = 0.014	0.51			30	3.39	-6					
					0.61			30	1.49	-5					
					0.70			30	6.81	-5					
					0.80			30	4.05	-4	23				
				A = 0.1	0.97			26	2.20	-2				*	(52)
					0.99			26	2.59	-2				(52)	(69)
			dioxane + H_2O;	A = 0.14–0.19			k A							*	(30)
				N_{H_2O} = 0.75				5	2.98	-6					
				0.80				5	9.34	-6					
				0.70				25	1.46	-5					
				0.75				25	4.15	-5					
				0.80				25	1.09	-4					
				0.56				30	3.26	-6					
				0.66				30	1.24	-5					
				N = 0.70				30	2.90	-5					

N = mol fraction

No.	Supplementing 1951 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
.203	.26	$(CH_3)_3CCl + H_2O \longrightarrow$	dioxane + H_2O	A = 0.14-0.19			kA							*	(30)
		$\begin{cases} HCl + (CH_3)_3COH & (S) \\ HCl + (CH_3)_2C{:}CH_2 + H_2O & (E) \end{cases}$		N_{H_2O} = 0.75				30	8.06	-5	22.4				
				0.80				30	2.13	-4					
				0.88				30	1.75	-3					
		(continued)													
.204		$(CH_3)_3CCl + \begin{cases} H_2O \\ HCOOH \end{cases} \longrightarrow$	HCOOH + ~0.5 % H_2O	A = 0.17	$(HCOO)_2Ca$	0.05	kA	15	3.8	-4					(10)
					$(HCOO)_2Ca$	(sat.)		15	2.7	-4					
		$\longrightarrow \begin{cases} HCl + (CH_3)_3COH \\ (CH_3)_3COOCH \end{cases}$			$(CH_2ClCOO)_2Ca$	1.3		15	1.95	-4				*	
.205	.27	$(CH_3)_3CBr + H_2O$	Et80*	A = 0.1			kA	25	3.58	-4					(12)
					NaOH	0.1		25	3.61	-4					
			An70*	A = 0.1			kA	25	5.37	-4				(8)	(11)
			An90*					25	1.40	-5				*	
								50	2.08	-4					
					LiBr	0.1		50	2.86	-4					
					NaN_3	0.1		50	2.65	-4					
			$(CH_3)_2CO$ + H_2O(N)	A = 0.013	H_2O(N)									*	(30)
					0.41		kA	5	3.06	-6					
					0.51			5	1.08	-5					
					0.61			5	4.75	-5					
					0.70			5	1.48	-4					
					0.80			5	8.40	-4					
					0.17			25	1.53	-6					
					0.22			25	2.98	-6					
					0.32			25	1.04	-5					
					0.41			25	3.48	-5					

N = mol fraction

No.	Supplementing 1951 No.	Reaction	Medium (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
.205	.27	$(CH_3)_3CBr + H_2O$ *(continued)*	$(CH_3)_2CO$ / H_2O(N)	A = 0.013	H_2O(N)		k A							*	(30)
					N = mol fraction 0.51			25	1.22	-4					
					0.61			25	4.15	-4					
					0.17			30	3.05	-6					
					0.22			30	5.40	-6					
					0.32			30	1.89	-5					
					0.51			30	2.21	-4	20.4				
			D1W60*	A = 0.1	NaOH	0.1	k A	10	2.89	-4				*	(12)
								10	2.87	-4					
.206		$(CH_3)_3CBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.10; B = 0		$k = (k_S + k_E)$; k A		25	4.51	-6					(31)
		$Br^- + (CH_3)_3COC_2H_5$ (S)		0.017 0.024				25	5.22	-6					
		$Br^- + (CH_3)_2C{:}CH_2 + C_2H_5OH$ (E)		0.064 0.083				25	6.37	-6					
				0.038 1.02				25	3.29	-5					
				0.038 2.01				25	4.20	-5					
				A = 0.1-0.04; B = 0-1.0			k_SA	25	3.6	-6					
				A = 0.1 B = 0			k_EA	25	8.6	-7					
				0.017 0.024				25	1.35	-6					
				0.064 0.083				25	2.94	-6					
				0.038 1.0				25	3.00	-5					
.207		n-$C_5H_{11}F + H_2O$	Et70*	A = 0.42	HCl	0.037	k	160	2.71	-7				*	(23)
.208		n-$C_5H_{11}F + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = (0.4-0.9); B = (0.5-1)		$k = (k_S + k_E)$; k AB		80	5.7	-7				*	(23)
		$F^- + C_5H_{11}OC_2H_5$ (S)						90	1.40	-6					
		$F^- + C_5H_{10} + C_2H_5OH$ (E)						120	1.45	-5					
								139	6.0	-5	22.1	2.5	7		
							k_SAB	80	5.6	-7					
							k_EAB	80	1	-8					

No.	Supplementing 1951 No.	Reaction	Medium (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
.209	.29	$n\text{-}C_5H_{11}Br + H_2O$	D1W70*	A = 0.025	Hg^{++}	0.025	$k\,A[Hg^{++}]$	25	1.11	-3					(59)
					HNO_3	0.025		40	4.17	-3	16	5	8		
.210		$n\text{-}C_5H_{11}Br + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = B = 0.1		$k = (k_S + k_E)$; k AB		55	3.9	-4					(32)
		$Br^- + C_5H_{11}OC_2H_5$ (S)					k_SAB	55	3.5	-4					
		$Br^- + C_5H_{10} + C_2H_5OH$ (E)					k_EAB	55	3.5	-5					
.211		$(CH_3)_2CHCH_2CH_2F + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.8; B = 1		$k = (k_S + k_E)$; k AB		90	5.2	-7				*	(23)
		$F^- + (CH_3)_2CHCH_2CH_2OC_2H_5$ (S)						119	4.9	-6	22	8	7		
		$F^- + (CH_3)_2CHCH{:}CH_2 + C_2H_5OH$ (E)					k_SAB	119	4.4	-6					
							k_EAB	119	5	-7					
.212		$C_2H_5CH(CH_3)CH_2F + H_2O$	Et80*	A = 0.172	HCl	0.0074	k	138	1.79	-8				*	(23)
.213		$C_2H_5CH(CH_3)CH_2F + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.8; B = 1		$k = (k_S + k_E)$; k AB		90	3.3	-7				*	(23)
		$F^- + C_2H_5CH(CH_3)CH_2OC_2H_5$ (S)						100	8.9	-7					
		$F^- + C_2H_5(CH_3)C{:}CH_2 + C_2H_5OH$ (E)						121	3.5	-6	21	1	6		
							k_SAB	121	3.1	-6					
							k_EAB	121	4	-7					
.214		$C_3H_7(CH_3)CHF + H_2O$	Et80*	A = 0.17	HCl	0.0074	k	138	1.29	-7				*	(23)
.215		$C_3H_7(CH_3)CHF + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.8; B = 1		$k = (k_S + k_E)$; k AB		139	3.6	-6				*	(23)
		$F^- + C_3H_7(CH_3)CHOC_2H_5$ (S)						162	1.9	-5	27	5	8		
		$F^- + C_5H_{10} + C_2H_5OH$ (E)					k_SAB	139	6	-7					
								162	8	-6					
							k_EAB	139	3.0	-6					
								162	1.1	-5					

No.	Supplementing 1951 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
.216		$C_3H_7(CH_3)CHBr + H_2O \longrightarrow$	Et6O*	A = (0.1-0.15)			$k = (k_S + k_E)$; k A	80	5.61	-5					(31)
		$\left\{ \begin{array}{ll} Br^- + C_3H_7(CH_3)CHOC_2H_5 & (S) \\ Br^- + C_5H_{10} + C_2H_5OH & (E) \end{array} \right.$					k_SA	80	5.23	-5					
							k_EA	80	3.8	-6					
.217		$C_3H_7(CH_3)CHBr + OH^- \longrightarrow$	C_2H_5OH	A = (0.1-0.2); B = 4.0			$k = (k_S + k_E)$; k AB	80	1.65	-3				*	(31)
		$\left\{ \begin{array}{ll} Br^- + C_3H_7(CH_3)CHOH & (S) \\ Br^- + C_5H_{10} + H_2O & (E) \end{array} \right.$					k_SAB	80	1.6	-4					
							k_EAB	80	1.49	-3					
.218		$C_3H_7(CH_3)CHBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.2; B = 1			$k = (k_S + k_E)$; k AB	25	3.43	-6				*	(31)
		$\left\{ \begin{array}{ll} Br^- + C_3H_7(CH_3)CHOC_2H_5 & (S) \\ Br^- + C_5H_{10} + C_2H_5OH & (E) \end{array} \right.$					k_SAB	25	6.6	-7					
							k_EAB	25	2.77	-6					
.219		$(C_2H_5)_2CHBr + H_2O \longrightarrow$	Et6O*	A = (0.1-0.15)			$k = (k_S + k_E)$; k A	80	5.97	-5					(31)
		$\left\{ \begin{array}{ll} HBr + (C_2H_5)_2CHOH & (S) \\ HBr + C_5H_{10} + H_2O & (E) \end{array} \right.$					k_SA	80	5.07	-5					
							k_EA	80	9.0	-6					
.220		$(C_2H_5)_2CHBr + OH^- \longrightarrow$	C_2H_5OH	A = (0.1-0.2); B = 4			$k = (k_S + k_E)$; k AB	80	2.11	-3					(31)
		$\left\{ \begin{array}{ll} Br^- + (C_2H_5)_2CHOH & (S) \\ Br^- + C_5H_{10} + H_2O & (E) \end{array} \right.$					k_SAB	80	7	-5					
							k_EAB	80	2.04	-3					
.221		$(C_2H_5)_2CHBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.2; B = 1			$k = (k_S + k_E)$; k AB	25	4.54	-6					(31)
		$\left\{ \begin{array}{ll} Br^- + (C_2H_5)_2CHOC_2H_5 & (S) \\ Br^- + C_5H_{10} + C_2H_5OH & (E) \end{array} \right.$					k_SAB	25	5.4	-7					
							k_EAB	25	4.00	-6					

No.	Supplementing 1951 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
.222		$C_2H_5(CH_3)_2CF + H_2O$	Et80*	A = (0.1-0.9)	HCl	0	(see supplementary table)							*	(23)
						(0.007-0.015)	$k\,A[H^+]$	80	1.9	-3					
						0.074		80	2.4	-3					
.223		$C_2H_5(CH_3)_2CF + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 1.15; B = 1.0		$k = (k_S + k_E)$; $k\,AB$		120	1.27	-6				*	(23)
		$F^- + C_2H_5(CH_3)_2COC_2H_5$ (S)						140	5.8	-6	24.4	5	7		
		$F^- + C_5H_{10} + C_2H_5OH$ (E)					$k_S AB$	120	6	-8					
								140	6	-7					
							$k_E AB$	120	1.21	-6					
								140	5.2	-6					
.224	.31.1	$C_2H_5(CH_3)_2CCl + H_2O \longrightarrow$	Et80*	A = 0.05		$k = (k_S + k_E)$; $k\,A$		25	1.51	-5				(16) (50)	(63)
		$HCl + C_2H_5(CH_3)_2COH$ (S)						35	5.23	-5				*	(63)
		$HCl + C_5H_{10} + H_2O$ (E)						45	1.62	-4					
								55	4.54	-4	22.0	2.8	11		
							$k_S A$	25	9.7	-6				(50)	(63)
							$k_E A$	25	5.4	-6					
.225		$CH_3CD_2(CH_3)_2CCl + H_2O \longrightarrow$	Et80*	A = 0.04		$k = (k_S + k_E)$; $k\,A$		25	1.12	-5					(62)
		$HCl + CH_3CD_2(CH_3)_2COH$ (S)					$k_S A$	25	8.5	-6					
		$DCl, HCl, C_5H_9D, C_5H_8D_2$ (E)					$k_E A$	25	2.7	-6					
.226		$C_2H_5(CD_3)_2CCl + H_2O \longrightarrow$	Et80*	A = 0.04		$k = (k_S + k_E)$; $k\,A$		25	8.83	-6					(62)
		$HCl + C_2H_5(CD_3)_2COH$ (S)					$k_S A$	25	5.6	-6					
		$DCl, HCl, C_5H_4D_6, C_5H_5D_5$ (E)					$k_E A$	25	3.3	-6					

No.	Supplementing 1951 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
.227		$CH_3CD_2(CD_3)_2CCl + H_2O \longrightarrow$	Et8O*	A = 0.04		$k = (k_S + k_E)$; k A		25	6.69	-6					(62)
		$\left\{ HCl + CH_3CD_2(CD_3)_2COH \quad (S) \right.$					k_SA	25	5.2	-6					
		$\left\{ DCl + C_5H_3D_7 + H_2O \quad (E) \right.$					k_EA	25	1.5	-6					
					NaOH	0.05	k A	25	6.30	-6					
.228		$C_2H_5(CH_3)_2CCl + (CH_3)_3CO^-$	$(CH_3)_3COH$	A = B			k AB	25	5.83	-8					(20)
.229		$C_2H_5(CH_3)_2CBr + CH_3OH$	CH_3OH	A = 1			k A	25	7.3	-5					(20)
.230		$C_2H_5(CH_3)_3CBr + CH_3O^-$	CH_3OH	A = B			k AB	25	3.29	-5				*	(20)
.231		$C_2H_5(CH_3)_3CBr + C_2H_5OH$	C_2H_5OH	A = 1			k A	25	9.6	-6					(20)
					KI	1.0		25	1.3	-5					
.232		$C_2H_5(CH_3)_2CBr + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.073; B = 0		$k = (k_S + k_E)$; k A		25	1.09	-5				*	(31)
		$\left\{ Br^- + C_2H_5(CH_3)_2COC_2H_5 \quad (S) \right.$		0.073 0			k_SA	25	6.6	-6					
		$\left\{ Br^- + C_5H_{10} + C_2H_5OH \quad (E) \right.$		0.073 0			k_EA	25	4.3	-6					
				0.016 0.023			k A	25	1.16	-5					
				0.016 0.023			k_SA	25	6.2	-6					
				0.016 0.023			k_EA	25	5.4	-6					
				0.064 0.084			k A	25	1.57	-5					
				0.064 0.084			k_SA	25	6.9	-6					
				0.064 0.084			k_EA	25	8.8	-6					
				0.039 1.015			k A	25	6.24	-5					
				0.039 1.015			k_SA	25	1.2	-6					
				0.039 1.015			k_EA	25	6.12	-5					
				A = B			k AB	25	1.51	-5				*	(20)
.233		$C_2H_5(CH_3)_2CBr + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 1			k A	25	2.6	-6					(20)

No.	Supplementing 1951 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
.234		$C_2H_5(CH_3)_2CBr + (CH_3)_2CHO^-$	$(CH_3)_2CHOH$	A = B			k AB	25	7.69	-6				*	(20)
.235		$C_2H_5(CH_3)_2CBr + (CH_3)_3COH$	$(CH_3)_3COH$	A = 1			k A	25	9.0	-7					(20)
.236		$C_2H_5(CH_3)_2CBr + (CH_3)_3CO^-$	$(CH_3)_3COH$	A = B			k AB	25	3.38	-6				*	(20)
.237		$C_2H_5(CH_3)_2CI + (CH_3)_3CO^-$	$(CH_3)_3COH$	A = B			k AB	25	2.34	-5					(20)
.238		$C_3H_7(CH_3)_2CCl + H_2O$	Et8O*	A = 0.06			k A	25	1.44	-5					(16)
.239		$(CH_3)_2CH(CH_3)_2CCl + H_2O \longrightarrow$	Et8O*	A = 0.05		$k = (k_S + k_E)$; k A		25	8.68	-6				(16) (63) (75)	
		$\left\{ \begin{array}{l} HCl + (CH_3)_2CH(CH_3)_2COH \quad (S) \\ HCl + C_6H_{12} + H_2O \quad (E) \end{array} \right.$						36	3.50	-5					(63)
								45	9.87	-5					
								55	2.94	-4	22.8	5	11		
							k_SA	25	2.67	-6					
								36	1.05	-5					
							k_SA	45	2.88	-5					
								55	8.5	-5					
							k_EA	25	6.01	-6					
								36	2.45	-5					
								45	6.99	-5					
								55	2.09	-4					
.240		$(CH_3)_2CD(CH_3)_2CCl + H_2O \longrightarrow$	Et8O*	A = 0.05		$k = (k_S + k_E)$; k A		25	6.76	-6					(63)
		$\left\{ \begin{array}{l} HCl + (CH_3)_2CD(CH_3)_2COH \quad (S) \\ DCl, HCl, C_6H_{12}, C_6H_{11}D \quad (E) \end{array} \right.$						36	2.85	-5					
								45	8.26	-5					
								55	2.50	-4	23.4	9	11		
							k_SA	25	2.50	-6					

No.	Supplementing 1951 No.	Reaction	Medium (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
.240		$(CH_3)_2CD(CH_3)_2CCl + H_2O \longrightarrow$	Et80*	A = 0.05		$k = (k_S + k_E)$; $k_S A$		36	1.03	-5					(63)
		(S) $HCl + (CH_3)_2CD(CH_3)_2COH$						45	2.81	-5					
								55	8.4	-5					
		(E) $DCl, HCl, C_6H_{12}, C_6H_{11}D$					$k_E A$	25	4.26	-6					
		(continued)						36	1.82	-5					
								45	5.45	-5					
								55	1.66	-4					
.241		$CH_3(C_2H_5)_2CCl + H_2O \longrightarrow$	Et80*	A = 0.05		$k = (k_S + k_E)$; $k A$		25	2.39	-5				(15) (16) (17) (50)	
		(S) $HCl + CH_3(C_2H_5)_2COH$					$k_S A$	25	1.4	-5				*	
		(E) $HCl + C_6H_{12} + H_2O$					$k_E A$	25	1.0	-5					
.242		$(n\text{-}C_4H_9)(CH_3)_2CCl + H_2O$	Et80*	A = 0.06			$k A$	25	1.31	-5				(15) (16)	
.243		$(CH_3)_3C(CH_3)_2CCl + H_2O$	Et80*	A = 0.06			$k A$	25	1.11	-5				(16) (75)	
.244		$(C_2H_5)_3CCl + H_2O$	Et80*	A = 0.06			$k A$	25	2.75	-5					(16)
.245		$(CH_3)_3CCH_2(CH_3)_2CCl + H_2O \longrightarrow$	Mt80*			$k = (k_S + k_E)$; $k A$		25	8.00	-4					(15)
		(S) $HCl + (CH_3)_3CCH_2(CH_3)_2COH$	Et70*				$k A$	0	1.94	-5					
		(E) $HCl + C_8H_{16} + H_2O$						15	1.71	-4					
								25	6.48	-4	22.8	3	13		
			Et79.6*				$k A$	0	6.1	-6					
								15	5.37	-5					
								25	2.09	-4					
								35	7.40	-4	22.9	1.2	13		
			Et80*				$k A$	25	1.90	-4				*	(50)
							$k_S A$	25	6.1	-5					

No.	Supplementing 1951 No.	Reaction	Medium (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
.245		$(CH_3)_3CCH_2(CH_3)_2CCl + H_2O \longrightarrow$	Et80*			$k = (k_S + k_E)$; $k_E A$		25	1.29	-4				*	(50)
		$\begin{cases} HCl + (CH_3)_3CCH_2(CH_3)_2COH & (S) \\ HCl + C_8H_{16} + H_2O & (E) \end{cases}$	Et90*				$k\,A$	15	1.14	-5					(15)
								25	4.56	-5					
								35	1.54	-4	23.0	3	12		
		(continued)	*i*-Pr80*				$k\,A$	25	7.92	-5					
			t-Bu80*				$k\,A$	25	4.39	-5					
.246		$(CH_3)_2CH(CH_3)CH(CH_3)_2CCl + H_2O$	Et80*				$k\,A$	25	8.76	-6				*	(18)
.247		$(C_2H_5)_2CH(CH_3)_2CCl + H_2O$	Et82*				$k\,A$	30	7.19	-5					(64)
.248		$C_2H_5(CH_3)_2C(CH_3)_2CCl + H_2O$	Et80*				$k\,A$	25	5.0	-5					(19)
.249		$(CH_3)_3C(C_2H_5)(CH_3)CCl + H_2O$	Et80*				$k\,A$	25	6.2	-5					(19)
.250		$(CH_3)_2CH(C_2H_5)_2CCl + H_2O$	Et80*	A = 0.06			$k\,A$	25	1.7	-5					(16)
			Et82*					30	2.55	-5					(64)
.251		$CH_3[(CH_3)_2CH]_2CCl + H_2O$	Et80*				$k\,A$	25	1.34	-4				*	(18)
.252		$CH_3CH_2CH_2(C_2H_5)CH(CH_3)_2CCl + H_2O$	Et82*				$k\,A$	30	5.29	-5					(64)
.253	.52.1	$(CH_3)_3C(C_2H_5)_2CCl + H_2O$ (α-component)	Et80*	0.06			$k\,A$	25	4.44	-4					(16)
		(β-component)						25	1.11	-4					
.254		$(CH_3)_2CH(CH_3CH_2CH_2)(C_2H_5)CCl + H_2O$	Et82*				$k\,A$	30	2.50	-5				*	(64)
.255		$[(CH_3)_3CCH_2]_2(CH_3)CCl + H_2O$	Et80*		(see 422.471)									*	(15)

No.	Supplementing 1951 No.	Reaction	Medium (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
Cyclo-alkyl halides															
.256		*cyclo*-$C_6H_{11}F + H_2O$	Et80*	A = 0.90	HCl	0.074	none	119	% reaction		$10^{-4} \times t$ secs			*	(23)
									8		2				
									17		4				
									41		8				
									62		12				
				A = 0.98	HCl	0.074	none	138	16		1				
									50		2				
									67		3				
									72		4				
				A = 0.15	HCl	0.0074	none	138	12		6				
									20		12				
									29		18				
									40		27				
.257		*cyclo*-$C_6H_{11}F + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.9; B = 1.1		$k = (k_S + k_E)$; k AB		139	1.95	-6				*	(23)
								148	4.0	-6					
		$F^- + C_6H_{11}OC_2H_5$ (S)						161	1.02	-5	26.4	1.6	8		
		$F^- + C_6H_{10} + C_2H_5OH$ (E)					k_SAB	139	1.9	-7					
								161	2.2	-6					
							k_EAB	139	1.76	-6					
								161	8.0	-6					
.258		*cyclo*-$C_6H_{11}Cl + H_2O$	Et80*				k A	125	8.87	-6					(48)
.258.1		*cyclo*-$C_6H_{11}Br + H_2O$	Et70*	$A \simeq 0.05$			k A	95	3.58	-5					(58a)
.258.2		*cyclo*-$C_6H_{11}Br + H_2O + Hg(NO_3)_2$	D1W70*	A = 0.022; B = 0.025	HNO_3	0.28	k A$[Hg^{++}]$	25	1.4	-1					(12a)
.259		*cyclo*-$C_5H_9(CH_3)_2CCl + H_2O$	Et82*				k A	30	5.0	-5				*	(64)

No.	Supplementing 1951 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
.260		$\overline{CH_2CH_2CH_2CH_2[(CH_3)_2CH]}Cl + H_2O$	Et82*				kA	30	3.8	-4				*	(64)
.261		*cyclo*-$C_6H_{11}(CH_3)_2CCl + H_2O$	Et82*				kA	30	2.62	-5					(64)
.262		$\overline{CH_2CH_2CH_2CH_2CH_2[(CH_3)_2CH]}Cl + H_2O$	Et82*				kA	30	1.15	-5					(64)
.263		$\overline{CH_2CH_2CH(CH_3)CH_2CH_2[(CH_3)_2CH]}Cl + H_2O$	Et80*	A= 0.04; B= 0.05			kA	64	2.6	-4					(48)
.264		$C_{10}H_{19}Cl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow$	Et80*	A = 0.12		$k = (k_S + k_E)$; kA		125	3	-6					(48)
		(menthyl chloride)					k_SA	125	1	-6					
							k_EA	125	2	-6					
		$\longrightarrow \begin{cases} HCl + C_{10}H_{19}OH \\ HCl + C_{10}H_{19}OC_2H_5 \end{cases}$ (S)	C_2H_5OH	A = 0.12			kA	160	7.4	-6					
							k_SA	160	6	-7					
							k_EA	160	6.8	-6					
		$\longrightarrow HCl + C_{10}H_{18}$ (E)													
.265		$C_{10}H_{19}Cl + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.018-0.2		(S+E) = $k_1A + k_2AB$; k_1A		160	9.1	-6				*	(48)
				B = 0.018-2.4			k_2AB	160	1.02	-4					
		$\begin{cases} Cl^- + C_{10}H_{19}OC_2H_5 & \text{(S)} \\ Cl^- + C_{10}H_{18} + C_2H_5OH & \text{(E)} \end{cases}$													
		(menthyl chloride)													
.266		(+)$C_{10}H_{19}Cl + \begin{cases} H_2O \\ C_2H_5OH \end{cases} \longrightarrow$	Et80*	A = 0.09		$k = (k_S + k_E)$; kA		125	1.63	-4					(48)
		(neomenthyl chloride)					k_SA	125	6	-6					
							k_EA	125	1.57	-4					
		$\longrightarrow \begin{cases} HCl + C_{10}H_{19}OH \\ HCl + C_{10}H_{19}OC_2H_5 \end{cases}$ (S)													
		$\longrightarrow HCl + C_{10}H_{18}$ (E)													

No.	Supplementing 1951 No.	Reaction	Medium (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
.267		(+)$C_{10}H_{19}Cl + C_2H_5O^- \longrightarrow$	C_2H_5OH	A = 0.0105; B = 1.7		$k = (k_S + k_E)$; k AB		100	1.84	-4					(48)
		$\begin{cases} Cl^- + C_{10}H_{19}OC_2H_5 & (S) \\ Cl^- + C_{10}H_{18} + C_2H_5OH & (E) \end{cases}$		0.061	1.5			125	1.41	-3					
				0.067	1.0			125	1.46	-3					
				0.099	0.36			125	1.61	-3					
				0.094	0.16			125	1.93	-3					
		(neomenthyl chloride)		0.061	1.5		k_SAB	125	1.4	-4					
				0.099	0.36			125	1.6	-4					
				0.094	0.16			125	1.9	-4					
							k_EAB	125	1.27	-3					
								125	1.45	-3					
								125	1.74	-3					
.268		$C_{10}H_{17}Cl + H_2O$	Et80*				k A	25	7	-11	30				(33)
				A = 0.02				75	1.50	-7					(77)
		(bornyl chloride)						100	2.45	-6	28.3	1.0	11		
.269		$C_{10}H_{17}Cl + H_2O$	Et80*	A = 0.008			k A	25	3.41	-5					(77)
								49	6.0	-4	21.8	3	11		
		(isobornyl chloride)													
Hydroxy-substituted alkyl halide															
.270		$CH_2(OH)CH_2F + H_2O$	H_2O				k A	70	3.0	-9					(27)
.271		$CH_2(OH)CH_2Cl + H_2O$	H_2O				k A	56	6.1	-8					(27)
								65	1.36	-7					
								79	7.0	-7					
								99	5.0	-6	26.2	1.4	10		

No.	Supplementing 1951 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
.272		$CH_2(OH)CH_2Br + H_2O$	H_2O				$k\,A$	40	7.9	-8					(27)
								60	1.05	-6					
								70	3.45	-6	27.0	6	11		
.273		$CH_2(OH)CH_2Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et85*				$k\,A$	70	4.62	-7					(27)
			Et67*					70	1.02	-6					
			Et24*					70	2.54	-6					
.274		$CH_2(OH)CH_2I + H_2O$	H_2O				$k\,A$	60	3.75	-7					(27)
								70	1.36	-6					
								80	4.30	-6	28.9	3	12		
.275		$CH_2(OH)CH_2I + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et68*				$k\,A$	70	4.83	-7					(27)
			Et24*					70	1.04	-6					
.276		$CH_2(OH)CH_2CH_2Cl + H_2O$	H_2O	A = (0.05-0.1)			$k\,A$	72	1.72	-6					(44)
								86	6.72	-6					
								97	1.75	-5	23.9	2	9		
.277		$CH_2(OH)CH_2CH_2CH_2Cl. \longrightarrow HCl + \overbrace{OCH_2CH_2CH_2CH_2}$	H_2O				(see 432.471)								(44)
.278		$(CH_3)_2C(OH)CH_2Br + H_2O$	D160*				$k\,A$	45	5	-7					(67)
.279		$(CH_3)_2C(OH)(CH_3)CHBr + H_2O$	D160*				$k\,A$	45	2.7	-5				*	(67)

No.	Supplementing 1951 No.	Reaction	Medium (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
Carboxyl-substituted alkyl halide															
.280		$CH_2(COO^-)Cl + OH^-$	H_2O	A= 1.0; B= 0.9			k AB	40	1.58	-5					(57)
				1.0 2.0				40	2.31	-5					
				1.0 4.1				40	4.06	-5					
				2.0 1.0				40	1.94	-5					
				2.0 1.9				40	3.06	-5					
				2.0 4.0				40	6.4	-5					
				2.0 5.0				40	9.0	-5					
				1.0 1.0				50	4.58	-5					
				1.0 3.9				50	1.19	-4					
				2.0 1.9				50	9.3	-5					
			H_2O	A= B= 0.1-0.25	pressure =	1 atm.		60	6.9	-5	22.7	6	10	(74)	(60a)
						2,880		60	1.30	-4	22.4	7	10		
				A = B = 0.125		7,350		60	2.90	-4	21.3	3	10		
						11,600		60	4.38	-4	20.7	1.7	10		
						pH									
.281		$CH_3(COOH)CHBr + H_2O$	H_2O	A = (0.006-0.02)	H_2SO_4, buffers, NaOH	0.03	k A	50	5	-7	40.8			*	(54)
						3		50	1.9	-6	42.6				
						5.7-13		50	1.8	-5					
				A = (0.05-0.1)	$NaHCO_3$	0.25		60	7.08	-5					
								69	2.60	-4	30	2	15	(43)	(53)
.282		$CH_3(COO^-)CHBr + OH^-$	H_2O	A = B = 0.03			k A	64	1.25	-4				*	(75)
					NaBr	0.476		64	9.54	-5					
						0.976		64	7.48	-5					
					$NaClO_4$	0.4-1		64	1.31	-4					
					$NaNO_3$	0.4-1		64	1.31	-4					

No.	Supplementing 1951 No.	Reaction	Medium (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
.282		$CH_3(COO^-)CHBr + OH^-$ *(continued)*	H_2O	A = (0.04-0.2)			$dM/dt = k_1A + k_2AB$								
				B = 0.4			k_1A	49	1.4	-5				(22)	(28)
				0.4			k_1A	60	7.0	-5	31	1	16		
				0.4			k_2A	49	9.0	-5					
				0.4			k_2A	60	2.60	-4	21	1.6	10		
				1.0			k_2A	49	1.23	-4					
				1.0			k_2A	60	3.38	-4					
				A = 0.03	μ=		$dM/dt = k_1A + k_2AB$								(75)
				B = (0.03-1.0)	0.06-0.08		k_1A	64	1.25	-4					
					0.50		k_1A	64	1.29	-4					
					0.50		k_2A	64	3.65	-4					
					1.0		k_1A	64	1.32	-4					
					1.0		k_2A	64	4.63	-4					
.283		$CH_3(COO^-)CHBr + CH_3O^-$	CH_3OH	A = B = 0.03			kA	64	5.1	-5				*	(75)
					NaBr	0.24		64	3.43	-5					
						0.42		64	2.66	-5					
						0.855		64	1.72	-5					
						0.883		64	1.48	-5					
				A = (0.02-0.03)	$NaClO_4$	0.2-0.9		64	5.7	-5					
				B = (0.03-1.0)		0.04-0.07	k_1A	64	5.1	-5					
						0.3	k_1A	64	5.76	-5					
						0.37	k_2A	64	1.69	-4					
						0.54	k_1A	64	5.71	-5					
						0.74	k_2A	64	3.51	-4					
						1.0	k_1A	64	5.84	-5					
						1.0	k_2A	64	5.57	-4					

No.	Supplementing 1951 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
.284		$CH_3(COOH)CHBr + H_2O + Ag^+ \longrightarrow CH_3CH(COOH)OH + AgBr + H^+$	H_2O	A = (0.1-0.25) C = (0.15-0.37)	HNO_3	0.1	kAC	50	5.8	-3				*	(28)
						2.0		50	4.92	-4					
					HNO_3 + $NaNO_3$	1.0 1.0		50	8.25	-4					
.285		$HOOCCH_2CH_2Br + H_2O$	H_2O	A = (0.05-0.1)	$NaHCO_3$	0.25	kA	50	1.72	-4					(43) (53)
								63	9.78	-4	28.7	4	15		
.286		$CH_3(COOCH_3)CHBr + CH_3OH + Ag^+ \longrightarrow CH_3(COOCH_3)OCH_3 + AgBr + H^+$	CH_3OH	A = B = 0.12			kAC	64	5.0	-4				*	(28)
.287		$CH_3(CH_2COO^-)CHBr + H_2O$	H_2O				kA	25	1.82	-5				*	(60)
								38	1.55	-4	30	1	17		
.288		$CH_3(CH_2COO^-)CHBr + OH^-$	H_2O				kAB	25	1.32	-3					(60)
.289		$HOOCCH_2CH_2(CH_3)CHBr + H_2O$	H_2O	A = (0.05-0.1)	$NaHCO_3$	0.25	kA	0	1.72	-4					(43) (53)
								5	3.83	-4	22	2	15		
.290		$CH_3(CH_2)_3(COOH)CHBr + H_2O$	H_2O	A = (0.05-0.1)	$NaHCO_3$	0.25	kA	49	2.43	-5					(43) (53)
								60	1.04	-4	29	4	14	*	
.291		$CH_3(CH_2)_2(CH_2COOH)CHBr + H_2O$	H_2O	A = (0.05-0.1)	$NaHCO_3$	0.25	kA	31	9.40	-5					(43) (53)
								40	3.72	-4	27	3	15		
.292		$HOOCCH_2CH_2(C_2H_5)CHBr + H_2O$	H_2O	A = (0.05-0.1)	$NaHCO_3$	0.25	kA	0	2.47	-4					(43) (53)

No.	Supplementing 1951 No.	Reaction	Medium (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
.293		$HOOC(CH_2)_5Br + H_2O$	H_2O	A = (0.04-0.1)	$NaHCO_3$	0.25	kA	50	2.33	-5					(43)
								63	1.07	-4					
								70	2.20	-4	25	2	12		
.294		$HOOC(CH_2)_6Br + H_2O$	H_2O	A = (0.04-0.1)	$NaHCO_3$	0.25	kA	60	2.97	-5					(43)
								70	8.08	-5					
								80	2.02	-4	22	1.1	10		
.295		$(COO^-)_2CHBr + H_2O$	H_2O	A = 0.05			kA	25	3.63	-8					(56)
					NaOH	0.055		65	2.22	-5					(51)
						0.116		100	2.02	-3					
						0.243		100	1.99	-3	32.5	2	16		
						1.02		100	3.70	-3					
					NaOH + NaBr	0.055									
						0.20		100	1.32	-3					
						0.50		100	8.14	-4					
.296		$(COO^-)_2(CH_3)CBr + H_2O$	H_2O	A = 0.05	NaOH	0.051	kA	35	5.17	-5					(51)
						0.051		65	4.35	-3					
						0.15		65	4.18	-3					
						1.0		65	4.50	-3	30.3	1.6	17		
.297		$(COO^-)CH_2NHCO(CH_3)CHBr + H_2O$	H_2O	A = (0.04-0.2)	$NaNO_3$	0-1	kA	49	1.8	-5					(22) (28)
								60	7.0	-5	26	1	13	*	
.298		$(COO^-)CH_2NHCO(CH_3)CHBr + OH^-$	H_2O	A = (0.04-0.2)	$NaNO_3$	0-1									(22) (28)
				B = 0.4			kAB	49	1.78	-4				*	
				1.0				49	2.05	-4					
				0.4				60	4.8	-4					
				1.0				60	5.8	-4	20	4	9		

No.	Supplementing 1951 No.	Reaction	Medium (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
.299		$(COO^-)CH_2NHCOCH_2NHCO(CH_3)CHBr + H_2O$	H_2O	A = (0.04-0.2)			k A	49	1.2	-6					(22) (28)
								60	3.7	-6	23	8	9	*	
.300		$(COO^-)CH_2NHCOCH_2NHCO(CH_3)CHBr + OH^-$	H_2O	A = (0.04-0.2)											
				B = 0.4			k AB	49	1.08	-3					(22) (28)
				1				49	1.3	-3				*	
				0.4				60	2.95	-3	20	6	10		
Halogen-substituted alkyl halide															
.301		$CHCl_3 + \begin{cases} 3OH^- \\ 4OH^- \end{cases} \longrightarrow$	H_2O	A = 0.03; B = (0.02-0.04)			$-dA/dt = (a+b) = k$ AB							*	(46)
		$\longrightarrow \begin{cases} 3CL^- + CO + 2H_2O & (a) \\ 3Cl^- + HCOO^- + 2H_2O & (b) \end{cases}$			$NaClO_4$	0.08		35	2.32	-4					
						0.16		35	2.37	-4					
						1.7		35	1.98	-4					
					$NaNO_3$ or NaF	0.08		35	2.38	-4					
						0.16		35	2.32	-4					
					NaCl	0.08		35	2.16	-4					
						0.16		35	2.02	-4					
					NaBr	0.08		35	1.95	-4					
					NaI	0.08		35	1.39	-4					
						0.16		35	1.00	-4					
.302		$ICH_2(CH_3)_2CCl + H_2O$	D1W48*	A = 0.033			k A	35	1.45	-4				*	(75)
.303		$ICH_2(CH_3)_2CCl + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et80*	A = 0.085			k A	25	4.44	-6				*	(75)
								35	1.50	-5	22	9	10		
.304		$BrCH_2(CH_3)_2CBr + H_2O$	D1W60*				k A	45	2	-6				*	(67)

No.	Supplementing 1951 No.	Reaction	Medium (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
.305		$BrCH_2(CH_3)_2CBr + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et80*	A = 0.065			kA	25	5.8	-8				*	(75)
.306		$CH_3CHBr(CH_3)_2CBr + H_2O$	D1W60*				kA	45	3.5	-5				*	(67)
								80	1.5	-3	24	1	12		
.307		$(CH_3)_2CCl(CH_3)_2CCl + 2\begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et80*				$-dA/dt = kA$	100	1.3	-5				(67)	(73)
Unsaturated alkenyl halide															
.308		$CH_2{:}CHCH_2Cl + H_2O$	H_2O	A = L = 0.4	CuCl	0.035	none	40	78 % reaction at 1 hour						(37)
.309		$CH_2{:}CHCH_2Cl + OH^-$	Et50*	A = 0.12; B = 0.05			kAB	25	4.55	-5					(2)
.310		$CH_2{:}CHCH_2Cl + C_2H_5O^-$	C_2H_5OH	A = 0.15; B = 0.19			kAB	25	1.72	-5					(2)
				A = 0.15; B = 0.09				25	1.86	-5				(2)	(65)
				A = B = 0.055				35	6.54	-5				(65)	(72)
								50	3.30	-4	20.9	4	10	(35)	(72)
.311		$CH_3CH{:}CHCl + C_2H_5O^-$	C_2H_5OH	A = B = 0.05			kAB	50	< 5	-6				*	(35)
.311.1		$CH_2{:}C(CH_3)Cl + C_2H_5O^-$	C_2H_5OH	A = B = 0.2				45	no observed reaction at 200 hours.						(65)
.312		$CH_3CH{:}CHCH_2Cl + C_2H_5O^-$	C_2H_5OH	A = B = 0.055			kAB	35	2.53	-4					(72)
.313		$CH_2{:}C(CH_3)CH_2Cl + H_2O$	H_2O	A = L = 0.4	CuCl	0.035	none	84 % reaction at 1 hour							(37)

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ 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	Literature
.314		$CH_2{:}C(CH_3)CH_2Cl + C_2H_5O^-$	C_2H_5OH	A = B = 0.05			k AB	35	6.90	-5					(72)
								50	3.2	-4	19	4	9	(35)	(72)
.315		$CH_2{:}CH(CH_3)CHCl + H_2O$	H_2O	10^4A = 6-35			k A	27	1.1	-3					(75)
.316		$(CH_3)_2C{:}CHCH_2Cl + H_2O$	H_2O	A = L = 0.4	CuCl	0.035	none		time	% reaction					(38)
								0	1800	39					
								0	3600	82					
								0	7200	87					
.317		$(CH_3)_2C{:}CHCH_2Cl + C_2H_5O^-$	C_2H_5OH	A = B = 0.055			k AB	-50	8	-2				*	(38)
.318		$CH_3CH{:}C(CH_3)CH_2Cl + C_2H_5O^-$	C_2H_5OH	A = B = 0.055			k AB	35	3.72	-4					(72)
.319		$(CH_3)_2C{:}C{:}CHCl + OH^- + C_2H_5OH \longrightarrow Cl^- + (CH_3)_2C(OC_2H_5)C{:}CH + H_2O$	Et80*	A = 0.1; B = 0.5-2.0			k AB	25	2.3	-6				*	(45)
Unsaturated alkynyl halides															
.320		$CH{:}C(CH_3)_2CCl + H_2O$	Et80*	A = 0.3			k A	25	2.1	-7					(45)
			Et60*					25	1.2	-6					
			An60*					25	5.4	-7					
.321		$CH{:}C(CH_3)_2CCl + OH^- + C_2H_5OH \longrightarrow Cl^- + (CH_3)_2C(OC_2H_5)C{:}CH + H_2O$	Et80*	A = 0.05-0.2; B = 0.1			k AB	25	3.9	-4					(45)

No.	Supplementing 1951 No.	Reaction	Medium (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
Unsaturated alkenyl Di-halide															
.322		$CH_2{:}CClCH_2Cl + H_2O \longrightarrow$ $HCl + CH_2{:}CClCH_2OH$	H_2O	A = L = 0.4	CuCl	0.035	none	70	12 % reaction at 1 hour						(37)
.323		$CH_2{:}CClCH_2Cl + C_2H_5O^- \longrightarrow$ $Cl^- + CH_2{:}CClCH_2OC_2H_5$	C_2H_5OH	A = B = 0.2			k AB	35	1.89	-5					(65)
								45	6.36	-5					
				A = B = 0.05				50	1.56	-4					(35)
				A = B = 0.2				55	1.71	-4					(65)
								65	4.83	-4	21.6	4	10		
.324	.69.1	*cis*-$CHCl{:}CHCH_2Cl + H_2O \longrightarrow$ $HCl + CHCl{:}CHCH_2OH$ (low boiling isomer)	H_2O	A = L = 0.4	CuCl	0.035	none	40	11 % reaction at 1 hour						(37)
								70	73 % reaction at 1 hour						
.325		*cis*-$CHCl{:}CHCH_2Cl + OH^- \longrightarrow$ $Cl^- + CHCl{:}CHCH_2OH$ (low boiling isomer)	Et50*	A = 0.07-0.05; B = 0.05-0.08			k AB	25	1.02	-4					(2)
.326		*cis*-$CHCl{:}CHCH_2Cl + C_2H_5O^- \longrightarrow$ $Cl^- + CHCl{:}CHCH_2OC_2H_5$ (low boiling isomer)	C_2H_5OH	A = 0.097; B = 0.24			k AB	25	4.67	-5					(2)
				0.194 0.24				25	4.98	-5					
				0.194 0.12				25	5.61	-5					
				0.25 0.25				35	1.63	-4					(65)
								45	4.75	-4					
				0.05 0.05				50	9.13	-4					(35)
								55	1.24	-3	20.6	7	10		(65)

No.	Supplementing 1951 No.	Reaction	Medium (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
.327	.69.1	*trans*-$CHCl:CHCH_2Cl + H_2O \longrightarrow HCl + CHCl:CHCH_2OH$	H_2O	A = L = 0.4	CuCl	0.035	none	70	96 % reaction at 30 minutes						(37)
.328		*trans*-$CHCl:CHCH_2Cl + OH^- \longrightarrow Cl^- + CHCl:CHCH_2OH$	Et50*	A = 0.071; B = 0.077			k AB	25	6.40	-5					(2)
				0.086 0.047				25	7.25	-5					
.329		*trans*-$CHCl:CHCH_2Cl + C_2H_5O^- \longrightarrow Cl^- + CHCl:CHCH_2OC_2H_5$	C_2H_5OH	A = 0.097; B = 0.244			k AB	25	5.36	-5					(2)
				0.194 0.244				25	5.61	-5					
				0.194 0.122				25	6.41	-5					
				A = B = 0.25				25	5.83	-5					(65)
								35	1.94	-4					
								45	5.80	-4					
				A = B = 0.05				50	1.14	-3					(35)
				A = B = 0.25				55	1.64	-3	21.0	1.6	11		(65)
.330		*cis*-$CH_3CCl:CHCl + C_2H_5O^-$ (higher boiling isomer)	C_2H_5OH	A = B = 0.25			k AB	45	3.83	-6				*	(65)
								55	2.07	-5					
								65	8.44	-5	31.9	4	16		
.331		*trans*-$CH_3CCl:CHCl + C_2H_5O^-$ (low boiling isomer)	C_2H_5OH	A = B = 0.25			k AB	55	8.6	-7				*	(65)
								65	3.53	-6	32	2	15		
.332		$CH_2:CHCHCl_2 + C_2H_5O^- \longrightarrow Cl^- + CH_2:CHCHClOC_2H_5$	C_2H_5OH	A = 0.41; B = 0.94			k AB	25	1.03	-7					(2)
				0.41 0.58				25	1.11	-7					
				A = B = 0.25				45	1.81	-6					(65)
								55	6.1	-6					
								65	2.08	-5	26.9	6	12		

No.	Supplementing 1951 No.	Reaction	Medium (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
.333		$CH_3CH{:}CCl_2 + C_2H_5O^- \longrightarrow Cl^- + CH_3CH{:}CClOC_2H_5$	C_2H_5OH	A = B = 0.25			k AB	55 65	1.53 9.4	-7 -7	41	3	20		(65)
.334		$CH_2{:}CBrCH_2Cl + H_2O \longrightarrow HCl + CH_2{:}CBrCH_2OH$	H_2O	A = L = 0.4	CuCl	0.035	none	70	15 % reaction at 1 hour						(37)
.335		$CH_2{:}CBrCH_2Cl + C_2H_5O^- \longrightarrow Cl^- + CH_2{:}CBrCH_2OC_2H_5$	C_2H_5OH	A = B = 0.05			k AB	50	2.7	-4					(35)
.336		*cis*-$ClCH{:}C(CH_3)CH_2Cl + H_2O \longrightarrow HCl + ClCH{:}C(CH_3)CH_2OH$	H_2O	A = L = 0.4	CuCl	0.035	none	70	13 % reaction at 1 hour						(37)
.337		*cis*-$ClCH{:}C(CH_3)CH_2Cl + C_2H_5O^- \longrightarrow Cl^- + ClCH{:}C(CH_3)CH_2OC_2H_5$	C_2H_5OH	A = B = 0.05			k AB	50	8.7	-4					(35)
.338		*trans*-$ClCH{:}C(CH_3)CH_2Cl + H_2O \longrightarrow HCl + ClCH{:}C(CH_3)CH_2OH$	H_2O	A = L = 0.4	CuCl	0.035	none	70	54 % reaction at 1 hour						(37)
.339		*trans*-$ClCH{:}C(CH_3)CH_2Cl + C_2H_5O^- \longrightarrow Cl^- + ClCH{:}C(CH_3)CH_2OC_2H_5$	C_2H_5OH	A = B = 0.05			k AB	50	9.0	-4					(35)
.340		α-$ClC(CH_3){:}CHCH_2Cl + H_2O \longrightarrow \begin{cases} HCl + ClC(CH_3){:}CHCH_2OH \\ 2HCl + CH_2{:}CH(C{:}O)CH_3 \end{cases}$	H_2O	A = L = 0.4	CuCl	0.035	none	40	32.8 % reaction at 1 hour 57.3 % reaction at 2 hours					*	(36) (37)

No.	Supplementing 1951 No.	Reaction	Medium (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
.341		α-ClC(CH$_3$):CHCH$_2$Cl + C$_2$H$_5$O$^-$ ⟶ Cl$^-$ + ClC(CH$_3$):CHCH$_2$OC$_2$H$_5$	C$_2$H$_5$OH	A = B = 0.05			k AB	50	1.35	-3					(36) (40)
.342		β-ClC(CH$_3$):CHCH$_2$Cl + H$_2$O ⟶ {HCl + ClC(CH$_3$):CHCH$_2$OH; 2HCl + CH$_2$:CH(C:O)CH$_3$	H$_2$O	A = L = 0.4	CuCl	0.035	none	40 40	43 % reaction at 1 hour 69 % reaction at 2 hours						(36) (37)
.343		β-ClC(CH$_3$):CHCH$_2$Cl + C$_2$H$_5$O$^-$ ⟶ Cl$^-$ + ClC(CH$_3$):CHCH$_2$OC$_2$H$_5$	C$_2$H$_5$OH	A = 0.025; B = 0.021			k AB	50	4.31	-3					(36) (40)
.344		Cl$_2$C:C(CH$_3$)CH$_2$Cl + H$_2$O ⟶ HCl + Cl$_2$C:C(CH$_3$)CH$_2$OH	H$_2$O	A = L = 0.4	CuCl	0.035	none	70	5 % reaction at 2 hours						(37)
.345		Cl$_2$C:C(CH$_3$)CH$_2$Cl + C$_2$H$_5$O$^-$ ⟶ Cl$^-$ + Cl$_2$C:C(CH$_3$)CH$_2$OC$_2$H$_5$	C$_2$H$_5$OH	A = B = 0.05			k AB	50	2.43	-3					(35)
Mono-aryl-substituted alkyl halide															
.346	.73	C$_6$H$_5$CH$_2$Cl + H$_2$O	D1W61*	A = 0.02			k A	50	1.31	-6					(14)
				0.04				50	1.25	-6					
				0.08				50	1.19	-6					
				0.22				50	1.02	-6					
				0.08	HCl	0.05		50	1.16	-6					
				0.08	NaCl	0.05		50	1.14	-6					
				0.08	NaClO$_4$	0.05		50	1.28	-6					

No.	Supplementing 1951 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
.347		$C_6H_5CH_2Cl + OH^-$	D1W61*	A = 0.08; B = 0.13			kAB	50	1.55	-4				*	(14)
				0.08 0.04				50	2.07	-4					
				0.17 0.04				50	1.78	-4					
				A = 2B = 0.08	NaCl	0.08		50	1.64	-4					
					$NaClO_4$	0.09		50	1.64	-4					
.348		$C_6H_5CH_2Cl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	6.2	-8					(1)
.349		$C_6H_5CH_2Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et90*	A = 0.01-0.05			kA	20	8.17	-7				*	(3)
								30	3.17	-6	24	6	11		
.350	.74	$C_6H_5CH(CH_3)Cl + H_2O$	An60*	A = 0.14			kA	67	1.35	-3					(49)
			An80*					70	9.04	-5					
.351		$C_6H_5CH(CH_3)Cl + CH_3OH$	CH_3OH	A = 0.15			kA	70	4.35	-4					(49)
.352		$C_6H_5CH(CH_3)Cl + CH_3O^-$	CH_3OH	A = 0.1; B = 3			kAB	70	2.46	-4				*	(49)
.353		$C_6H_5CH(CH_3)Cl + C_2H_5OH$	C_2H_5OH	A = 0.15			kA	70	3.75	-5				*	(49)
.354		$C_6H_5CH(CH_3)Cl + C_2H_5O^-$	C_2H_5OH	A = 0.1; B = 3			kAB	70	1.67	-4				*	(49)
.355		$C_6H_5CH_2CH_2Br + H_2O$	D1W70*	A = 0.025	HNO_3	0.025	$kA[Hg^{++}]$	25	5.02	-4					(52)
					Hg^{++}	0.025		41	2.07	-3	17.0	2	9		
.356		$p\text{-}CH_3C_6H_4CH_2Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et90*	A = 0.01-0.05			kA	20	3.53	-6				*	(3)
								30	1.20	-5	24	2	12		

No.	Supplementing 1951 No.	Reaction	Medium (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
.357		$C_6H_5CH_2CH_2CH_2Br + H_2O$	D1W70*	A = 0.025	HNO_3	0.025	$k A[Hg^{++}]$	25	4.48	-4					(59)
					Hg^{++}	0.025		41	1.75	-3	16.7	8	8		
.358		$C_6H_5(CH_2)_4Br + H_2O$	D1W70*	A = 0.025	HNO_3	0.025	$k A[Hg^{++}]$	25	7.53	-4					(59)
					Hg^{++}	0.025		41	2.90	-3	16.2	6	8		
.359		d-$(CH_3)_3C(C_6H_5)CHCl + H_2O$	Et80*	A = 0.03-0.06			$k A$	50	3.36	-7				*	(76)
								75	7.8	-6	27.5	1.3	12		
.360		$C_6H_5(CH_3)CH(CH_3)_2CCl + H_2O$	Et80*	A = 0.016			$k A$	50	3.35	-5					(76)
.361		$C_6H_5(CH_2)_5Br + H_2O$	D1W70*	A = 0.025	HNO_3	0.025	$k A[Hg^{++}]$	25	7.87	-4					(59)
					Hg^{++}	0.025		41	3.03	-3	16.2	6	8		
.362		$C_6H_5(CH_2)_6Br + H_2O$	D1W70*	A = 0.025	HNO_3	0.025	$k A[Hg^{++}]$	25	7.80	-4					(59)
					Hg^{++}	0.025									
.363		p-$CH_3OC_6H_4CH_2Cl + CH_3OH$	CH_3OH	A = 0.05-0.15			$k A$	25	2.8	-4					(1)
.364		p-$NO_2C_6H_4CH_2Br + H_2O$	D1W90*				$k AB$	5	1.0	-9					(34)
								30	1.3	-8					
								60	1.1	-7	15.4	1.6	3		
			D1W70*					5	1.8	-9					
								30	1.8	-8					
								60	3.5	-7	17.2	4	4		
			D1W50*					5	2.8	-9					
								30	4.0	-8					
								60	8.7	-7	18.8	1.0	6		

No.	Supplementing 1951 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
.365		$p\text{-}NO_2C_6H_4CH_2Br + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	Et90*	A = 0.01-0.05			kA	20	1.25	-7				*	(3)
								30	3.50	-7	23	2	10		
.366		$o\text{-}FC_6H_4CH_2Cl + H_2O$	An50*				kA	70	7.66	-6					(13)
								85	2.76	-5	21.2	2	8		
.367		$m\text{-}FC_6H_4CH_2Cl + H_2O$	An50*				kA	70	4.42	-6					(13)
								85	1.53	-5	20.6	6	7		
.368		$p\text{-}FC_6H_4CH_2Cl + H_2O$	An50*				kA	70	3.17	-5					(13)
								85	1.06	-4	20.0	2	8		
.369		$C_6H_5CCl_3 + 2H_2O \longrightarrow 3HCl + C_6H_5COOH$	Et80*	A = 0.02	Pressure	1.0 atm.	kA	15	1.38	-6					(21)
								35	7.9	-6	15.4	7	5		
						1500		15	2.55	-6					
								35	2.30	-5	19.4	1.4	9		
						3000		15	3.6	-6					
								35	3.75	-5	20.6	1.5	10		
.370		$ICH_2(C_6H_5)CHCl + C_2H_5OH \longrightarrow HCl + ICH_2(C_6H_5)CHOC_2H_5$	C_2H_5OH	A = 0.1			kA	70	4.9	-5				*	(75)
.371		$BrCH_2(C_6H_5)CHBr + C_2H_5OH \longrightarrow HBr + BrCH_2(C_6H_5)CHOC_2H_5$	C_2H_5OH	A = 0.1			kA	55	1.90	-7				*	(75)
					$NaClO_3$	0.14		55	2.85	-7					

No.	Supplementing 1951 No.	Reaction	Medium (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
Di-aryl-substituted alkyl halide															
.372	.153	$(C_6H_5)_2CHCl + H_2O$	An90*	A = 0.02–0.1			kA	25	4.60	-6					(8) (24a)
								50	5.80	-5	19.4	7	8	*	
					LiBr	0.1		50	1.00	-4					
					NaN_3	0.1		50	1.24	-4					
			An80*	A = 0.01–0.1				0	2.82	-6					(24a) (50a)
								25	7.32	-5	21.1	2	11		(8) (12)
					HCl	0.096		25	6.90	-5					(8) (24a)
					LiCl	0.1		25	6.09	-5					(12)
					LiBr	0.1		25	8.16	-5					
			An70*					25	3.20	-4					(24a)
					NaN_3	0.1		25	4.18	-4					
			An50*					25	1.6	-2					(71)
			SO_2	A = 0.12; B = 0.14			kA	-17	4.4	-3					(11)
				B = 0.42				-17	8.3	-3					
.373		$(C_6H_5)_2CHCl + CH_3OH$	CH_3OH	A = 0.1			kA	15	2.52	-4					(12)
					$NaOCH_3$			15	2.51	-4					
					NaBr			15	3.06	-4					
					NaI			15	3.10	-4					
				A = 0.05–0.15				25	8.2	-4	20	5	11		(1)
.374		$(C_6H_5)_2CHCl + (CH_3)_2CHOH$	B	A = 0.05–0.15			kA	25	5.7	-6					(1)
.375		$(C_6H_5)_2CHBr + H_2O$	An90*	A = 0.1			kA	25	1.8	-4					(71)
								50	2.01	-3				*	(24a)
					LiBr	0.1		50	1.61	-3					
					NaN_3	0.1		50	4.16	-3					(8)

No.	Supplementing 1951 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
.375		$(C_6H_5)_2CHBr + H_2O$ *(continued)*	An80*	A = 0.1			kA	25	1.53	-3					(12)
					LiCl	0.1		25	1.94	-3					
					LiBr	0.1		25	1.33	-3					
			An70*	A = 0.015-0.1				25	1.2	-2					(71)
					$HClO_4$	0.1		25	1.3	-2					
					$LiClO_4$	0.1		25	1.3	-2					
					NaOH	0.02		25	1.3	-2					
			D1W60*	A = 0.09				8	1.90	-3					(12)
					LiCl	0.09		8	1.52	-3					
					NaOH	0.09		8	1.52	-3					
					LiCl + NaOH	0.09 0.11		8	1.24	-3					
.376		$p\text{-}CH_3C_6H_4(C_6H_5)CHCl + H_2O$	An90*	A = 0.01-0.1			kA	25	9.46	-5					(25)
			An80*					0	8.35	-5					(25) (50a)
								25	1.58	-3	18.9	1.2	11		
					HCl	0.04		25	1.28	-3					(8) (25)
						0.1		25	1.17	-3					
					NaCl	0.04		25	1.20	-3					
.377		$p\text{-}CH_3C_6H_4(C_6H_5)CHCl + C_2H_5OH$	C_2H_5OH	A = 0.01			kA	25	1.24	-3					(50a)
.378		$(p\text{-}CH_3C_6H_4)_2CHCl + H_2O$	An90*	A = 0.04-0.05			kA	0	9.10	-5				*	(8) (11)
					NaN_3	0.05		0	1.55	-4					
			An85*					0	4.70	-4					
					NaN_3	0.05		0	7.05	-4					
					LiCl	0.056		0	2.30	-4					
					LiBr	0.05		0	6.85	-4					

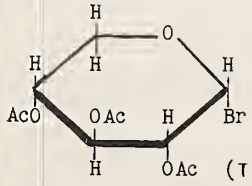
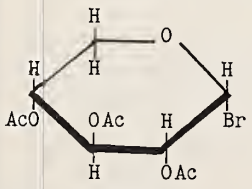
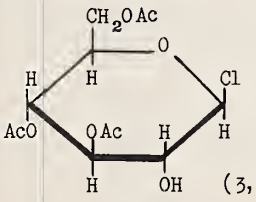
No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	$k = k^o \times 10^n$ n	E	$A = A^o \times 10^n$ A^o	$A = A^o \times 10^n$ n	Comments	Literature
.378		$(p\text{-}CH_3C_6H_4)_2CHCl + H_2O$ *(continued)*	An85*	A = 0.04–0.05	$N(CH_3)_4NO_3$	0.05	kA	0	7.20	-4				*	(8) (11)
			An80*					0	1.60	-3					
					NaN_3	0.05		0	2.24	-3					
.379		$p\text{-}C_2H_5C_6H_4(C_6H_5)CHCl + H_2O$	An80*	A = 0.015			kA	0	6.26	-5				*	(50a)
								25	1.26	-3	19.4	2	11		
.380		$p\text{-}C_2H_5C_6H_4(C_6H_5)CHCl + C_2H_5OH$	C_2H_5OH	A = 0.013			kA	25	1.20	-3					(50a)
.381		$p\text{-}(CH_3)_2CHC_6H_4(C_6H_5)CHCl + H_2O$	An80*	A = 0.015			kA	0	4.70	-5				*	(50a)
								25	1.01	-3	19.8	3	11		
.382		$p\text{-}(CH_3)_2CHC_6H_4(C_6H_5)CHCl + C_2H_5OH$	C_2H_5OH	A = 0.013			kA	25	1.06	-3					(50a)
.383		$p\text{-}C_2H_5CH(CH_3)C_6H_4(C_6H_5)CHCl + H_2O$	An80*	A = 0.015			kA	0	3.59	-5					(50a)
								25	7.96	-4	20.0	4	11		
.384		$p\text{-}C_2H_5CH(CH_3)C_6H_4(C_6H_5)CHCl + C_2H_5OH$	C_2H_5OH	A = 0.013			kA	25	9.9	-4					(50a)
.384.1		$p\text{-}(CH_3)_3CC_6H_4(C_6H_5)CHCl + H_2O$	An90*	A = 0.05			kA	50	5.50	-4				*	(8) (50a)
					LiBr	0.10		50	1.07	-3					
					NaN_3	0.05		50	9.3	-4					
						0.10		50	1.58	-3					
			An80*	A = 0.10				0	3.59	-5					
								25	7.60	-4					
				0.08	NaCl	0.10		25	4.80	-4					
.385		$p\text{-}CH_3OC_6H_4(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05–0.15			kA	25	3	-2					(1)

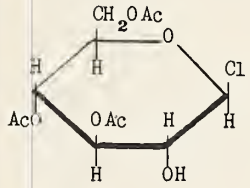
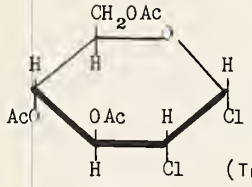
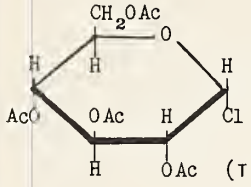
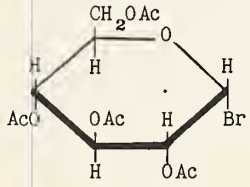
No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.386		m-$C_2H_5OC_6H_4(C_6H_5)CHCl + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 0.05-0.15			kA	25	6.6	-6					(1)
.387		p-$NO_2C_6H_4(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	5.5	-7					(1)
.388		o-$ClC_6H_4(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	1.02	-5					(1)
.389		m-$ClC_6H_4(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	2.12	-5					(1)
.390		p-$ClC_6H_4(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	3.8	-4					(1)
.391		p-$ClC_6H_4(C_6H_5)CHCl + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 0.05-0.15			kA	25	2.92	-6					(1)
.392		$2,4$-$Cl_2C_6H_3(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	5.8	-6					(1)
.393		$3,4$-$Cl_2C_6H_3(C_6H_5)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	1.50	-5					(1)
.394		p-$ClC_6H_4(p$-$CH_3C_6H_4)CHCl + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 0.05-0.15			kA	25	4.6	-5					(1)
.395		m-$ClC_6H_4(p$-$CH_3OC_6H_4)CHCl + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 0.05-0.15			kA	25	8.1	-4					(1)
.396		$3,4$-$Cl_2C_6H_3(4$-$CH_3OC_6H_4)CHCl + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 0.05-0.15			kA	25	4.0	-4					(1)
.397		$(p$-$ClC_6H_4)_2CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	1.04	-4					(1)
.398		$(p$-$ClC_6H_4)_2CHCl + (CH_3)_2CHOH$	$(CH_3)_2CHOH$	A = 0.05-0.15			kA	25	9.5	-7					(1)
.399		$(2,4$-$Cl_2C_6H_3)(4$-$ClC_6H_4)CHCl + CH_3OH$	CH_3OH	A = 0.05-0.15			kA	25	1.88	-6					(1)

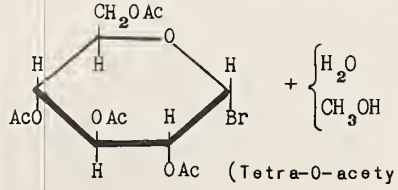
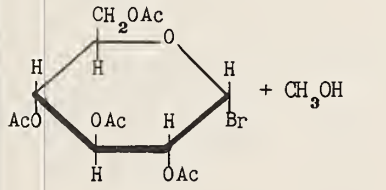
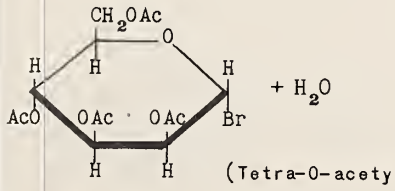
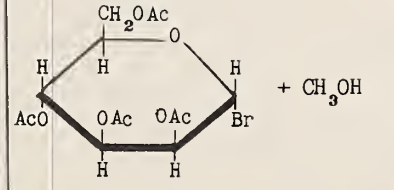
No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
Tri-aryl-substituted alkyl halide															
.400		$(C_6H_5)_3CF + H_2O$	An85*				$k\,A$	25	2.7	-6	22.6	1.0	11	*	(70)
			An60*	A = 0.001			$k\,A$	25	2.08	-4					(68)
			An50*	A = 0.001			$k\,A$	25	8.75	-4					
				A = 0.001-0.008	HNO_3	(2-5) × 10^{-3}		25	7.6	-4					(71)
					NaF	(2-5) × 10^{-3}		25	7.6	-4					
		(see supplementary table)			NaN_3	(2-5) × 10^{-3}		25	7.6	-4				*	
					NaOH	(2-5) × 10^{-3}		25	7.6	-4					
								45	3.8	-3	13.0	7	5		(68)
			An40*	A = 0.001			$k\,A$	25	1.32	-2					
.401		$(C_6H_5)_3CF + CH_3OH$	CH_3OH + 5 % $(CH_3)_2CO$	A = 0.001			$k\,A$	25	1.37	-4					(68)
								45	7.3	-4	14.9	1.1	7		
.402	.156	$(C_6H_5)_3CCl + H_2O$	An85*	A ~ 0.001			$k\,A$	-34	1.3	-2					(70) (71)
					KNO_3	0.003-0.01		-34	1.7	-2					
		(see supplementary table)			KBr	0.003-0.01		-34	1.7	-2				*	
					NaF	0.003-0.01		-34	1.7	-2					
					NaN_3	0.003-0.01		-34	1.7	-2					
					LiBr	0.003-0.01		-34	1.7	-2					
					KCl	0.01		-34	3.8	-3					
								-14	1.1	-1	13	1.0	10		
.403		$(C_6H_5)_3CCl + C_6H_5CH_2OH$	C_6H_6	A = 0.06-0.09; B = 0.07-0.2	$(C_2H_5)_3N$	≃ A	$k\,AB^2$	30	1.68	-3					(42)
.404		$(C_6H_5)_3CCl + p\text{-}CH_3C_6H_4CH_2OH$	C_6H_6	A = 0.06; B = 0.07-0.2	$(C_2H_5)_3N$	≃ A	$k\,AB^2$	30	1.42	-3					(42)

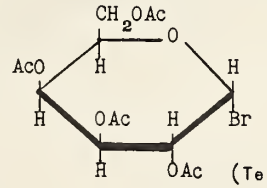
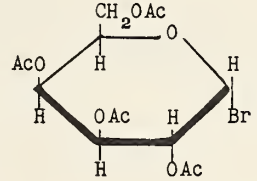
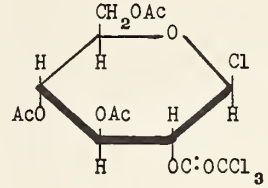
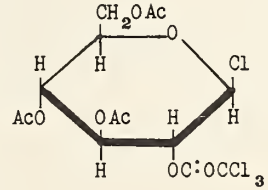
No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.405		$(C_6H_5)_3CCl + p\text{-}CH_3OC_6H_4CH_2OH$	C_6H_6	A = 0.05; B = 0.05-0.2	$(C_2H_5)_3N$	$\simeq$ A	$k\,AB^2$	30	1.92	-3					(42)
.406		$(C_6H_5)_3CCl + p\text{-}NO_2C_6H_4CH_2OH$	C_6H_6	A = 0.05; B = 0.08-0.13	$(C_2H_5)_3N$	$\simeq$ A	$k\,AB^2$	30	4.8	-3				*	(42)
.407		$(C_6H_5)_3CCl + p\text{-}ClC_6H_4CH_2OH$	C_6H_6	A = 0.06; B = 0.14-0.2	$(C_2H_5)_3N$	$\simeq$ A	$k\,AB^2$	30	3.4	-3				*	(42)
.408	.162	$(C_6H_5)_3CBr + H_2O$	An85*	A $\sim$ 0.001	LiBr	0.01	$k\,A$	-34	3	-2					(71)
Aryl-substituted-unsaturated alkenyl halide															
.409		$CH_2{:}C(C_6H_5)CH_2Cl + C_2H_5O^-$	C_2H_5OH	A = B = 0.05			$-dB/dt = k\,AB$	50	3.11	-4					(39)
							$dL/dt = k\,AB$	50	3.66	-4					
.410		*cis*-$p\text{-}NO_2C_6H_4CH{:}CHBr + OH^-$	Et95*	(see 422.471)											(29)
.411		*trans*-$p\text{-}NO_2C_6H_4CH{:}CHBr + C_2H_5O^- + C_2H_5OH \longrightarrow Br^- + p\text{-}NO_2C_6H_4CH_2CH(OC_2H_5)_2$	Et95*	A= 0.008; B= 0.09			$k\,AB$	30	1.70	-5					(29)
								35	3.09	-5					
								40	5.77	-5	24	3	12		
Amino-substituted alkyl halides															
.412		$(C_2H_5)_2NC_2H_4Cl + H_2O \longrightarrow$ (see comments)	An67*	A = 0.044-0.14	Cl^-	0-0.08	$k\,A$	25	3.3	-3				*	(6)
.413		$CH_3N(C_2H_4Cl)_2 + H_2O \longrightarrow$ (see comments)	An67*	A = 0.04-0.08	Cl^-	0-1	$k\,A$	25	3	-4				*	(5) (6)

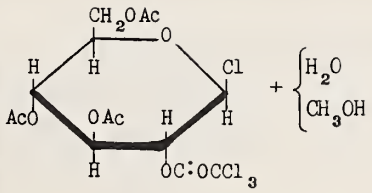
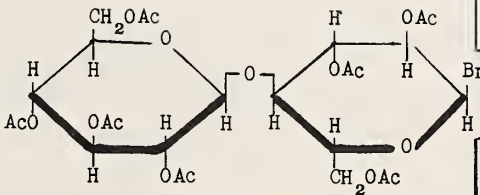
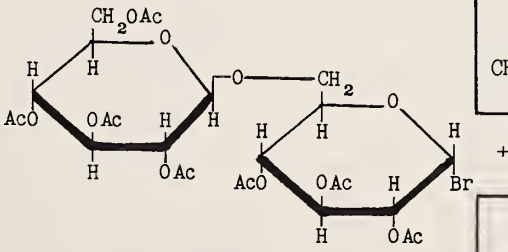
No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.414		$CH_3N(C_2H_4Cl)_2 + 2OH^- \longrightarrow 2Cl^- + CH_3N(C_2H_4OH)_2$	An67*	A = 0.014-0.046;	B = 0.048-0.014		$-dA/dt = kA$	25	3.0	-4					(5)
.415		$C_2H_5(C_2H_4OH)NC_2H_4Cl + OH^-$	An67* An25*				kA	25 25	~3 ~1	-3 -2					(4)
.416		$C_2H_5N(C_2H_4Cl)_2 + H_2O \longrightarrow$ (see comments)	An67* An25*	A= 0.025-0.15 A= 0.024-0.14	Cl^-	0-0.14 0-0.16	kA	25 25	1.42 4.0	-3 -3				*	(4) (6)
.417		$C_2H_5NH(C_2H_4Cl)_2^+ + H_2O \longrightarrow HCl + C_2H_5NH(C_2H_4Cl)(C_2H_4OH)^+$	An67*	A = 0.052			kA	25	3.5	-8					(4)
.418		$N(C_2H_4Cl)_3 + H_2O \longrightarrow HCl + (C_2H_4Cl)_2NC_2H_4OH$	H_2O An67*	A = 0.04	Cl^-	0.1	kA	25 25	5.2 4.8	-3 -6				*	(6)
.419		$N(C_2H_4Cl)_3 + OH^- \longrightarrow Cl^- + (C_2H_4Cl)_2NC_2H_4OH$	An67*	A = 0.04; B = 0.21			kA	25	9.2	-5					(6)
Sulfide-substituted alkyl halide															
.420		$S(C_2H_4Cl)_2 + 2H_2O \longrightarrow 2HCl + S(C_2H_4OH)_2$ (Mustard gas)	An5*	$A \simeq 0.001$	(Consecutive steps see .421 and .422)										(7)
.421		$S(C_2H_4Cl)_2 + H_2O \longrightarrow HCl + S(C_2H_4Cl)C_2H_4OH$	An5*	A = 0.00089	salts	μ = 0.144	kA	25	2.6	-3				*	(7)

No.	Supplementing 1951 No.	Reaction	Medium (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
.422		$S(C_2H_4OH)C_2H_4Cl + H_2O \longrightarrow HCl + S(C_2H_4OH)_2$	An5*	A = 0.00089	salts	μ = 0.144	kA	25	4.3	-3				*	(7)
		Heterocyclic alkyl halide													
.423		$\overline{OCH_2CH_2CH_2CHCl}CHCl + H_2O$	An80*	A = 0.05			kA	21	1.77	-3				*	(58a)
.424		$\overline{OCH_2CH_2CH_2CHCl}CHCl + CH_3OH$	CH_3OH	A = 0.05			kA	21	6.44	-3				*	(58a)
.425		 + H_2O (Tri-O-acetyl-α-D-xylosyl-1-bromide)	An60*	A = 0.025	NaOH	0.025	kA	16 16	7.63 8.20	-4 -4					(58a)
.426		 + CH_3OH (Tri-O-acetyl-α-D-xylosyl-1-bromide)	CH_3OH	A = 0.025			kA	16 21	9.4 1.39	-4 -3					(58a)
.427		 + H_2O (3,4,6-Tri-O-acetyl-β-D-glucosyl-1-chloride)	An80* An60*	A ~ 0.05	NaOH	0.025	kA	21 21 ~24 ~24	2.46 1.20 1.95 1.96	-4 -3 -3 -3					(58a)

No.	Supplementing 1951 No.	Reaction	Medium (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
.428		 + CH_3OH	CH_3OH	A ~ 0.05			kA	21 35	6.66 2.29	-4 -3	16.3	3	8		(58a)
.429		 + CH_3OH	CH_3OH	A ~ 0.05			kA	35	9.6	-6					(58a)
		(Tri-O-acetyl-2-chloro-2-deoxy-α-D-glucosyl-1-chloride)													
.430		 + CH_3OH	CH_3OH	A ~ 0.05			kA	35	4.2	-6					(58a)
		(Tetra-O-acetyl-α-D-glucosyl-1-chloride)													
.431		 + H_2O	An90* An80* An70* An60*	A = 0.05			kA	21 21 21 21	1.4 5.0 1.78 4.89	-6 -6 -5 -5					(58a)
		(Tetra-O-acetyl-α-D-glucosyl-1-bromide)													

No.	Supplementing 1951 No.	Reaction	Medium (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
.432		 + $\begin{cases} H_2O \\ CH_3OH \end{cases}$ (Tetra-O-acetyl-α-D-glucosyl-1-bromide)	Mt90* Mt80* Mt70* Mt60*	A = 0.05			kA	21 21 21 21	5.80 1.11 2.27 3.61	-5 -4 -4 -4					(58a)
.433		 + CH_3OH	CH_3OH MAn90* MAn70* MAn50*	A = 0.05			kA	21 35 21 21 21	2.81 1.21 1.19 8.2 3.5	-5 -4 -5 -6 -6	19	3	9		(58a)
.434		 + H_2O (Tetra-O-acetyl-α-D-mannosyl-1-bromide)	An60*	A = 0.025	NaOH	0.025	kA	16 16	1.31 1.69	-4 -4					(58a)
.435		 + CH_3OH	CH_3OH	A = 0.025	NaOH	0.015	kA	21 21	3.0 3.0	-4 -4					(58a)

No.	Supplementing 1951 No.	Reaction	Medium (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
.436		 + H_2O (Tetra-O-acetyl-α-D-galactosyl-1-bromide)	An80* An60*	A ~ 0.05	NaOH	0.025	k A	21 21 21	1.69 1.36 1.37	-5 -4 -4					(58a)
.437		 + CH_3OH	CH_3OH	A ~ 0.05			k A	16 21 35	8.5 1.24 4.53	-5 -4 -4	15.6	5	7		(58a)
.438		 + H_2O (3,4,6-Tri-O-acetyl-2-O-trichloroacetyl-β-D-glucosyl-1-chloride)	An80* An60*	A = 0.022	NaOH	0.025	k A	35 18 18 35	6.1 1.41 1.44 5.64	-6 -5 -5 -5	14.5	1.1	6		(58a)
.439		 + CH_3OH	CH_3OH MAn90* MAn80* MAn60*	A = 0.022			k A	21 27 35 27 27 27	1.18 2.48 3.48 1.34 1.02 4.8	-5 -5 -5 -5 -5 -6	20.8	3	10		(58a)

No.	Supplementing 1951 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
.440			Mt90* Mt80*	A = 0.022			k A	27 27	6.74 1.18	-5 -4					(58a)
.441		 (Hepta-O-acetyl-α-cellobiosyl-1-bromide)	CH_3OH				k A	35	1.12	-4					(58a)
.442		 (Hepta-O-acetyl-α-gentiobiosyl-1-bromide)	CH_3OH				k A	35	2.98	-4					(58a)

SUPPLEMENTARY TABLES

Composition of products (mol fraction, N) at 20-30°C (30)(66)

(.201) $(CH_3)_3CCl + \begin{cases} H_2O \\ CH_3OH \end{cases}$

Solvent		Temp.	Product	
CH_3OH(N)	H_2O(N)		$(CH_3)_3COH$	$(CH_3)_3COCH_3$
0.844	0.156	20-30	0.19	0.81
0.646	0.354	20-30	0.42	0.58
0.557	0.443	30	0.50	0.50
0.514	0.486	25	0.56	0.44
CH_3OH(N)	H_2O(N)		$(CH_3)_3COH + (CH_3)_3COCH_3$	C_4H_8
0.934	0.066	25	0.818	0.182
0.934	0.066	30	0.803	0.197
0.876	0.124	25	0.820	0.180
0.876	0.124	30	0.806	0.194
0.750	0.250	25	0.833	0.167
0.750	0.250	30	0.820	0.180
0.500	0.500	25	0.865	0.135
0.500	0.500	30	0.856	0.144

SUPPLEMENTARY TABLES *(continued)*

(.222) $C_2H_5(CH_3)_2CF + H_2O$

$10^4 t$	1	2	3	4	6	8	10	Solvent	
% reaction	5	10	30	50	67	75		A = 0.8	Et80*
% reaction		1		2	3	7	15	A = 0.16	Et70*

(.400) (.402)

Relative Rate of Reaction of Nucleophilic Reagents with $(C_6H_5)_3C^+$ Intermediate

Nucleophilic reagent	H_2O	Cl^-	$C_6H_5NH_2$	N_3^-	OH^-	$S_2O_3^=$
solvent		An85*	An50*	An50*	An50*	An50*
relative rate	1	3.1×10^3	3.7×10^3	2.8×10^5	5.3×10^4	1.9×10^4

SOLVENTS

D1W70* (48, 50, 60, 61)

Et60* (24, 50, 67, 70, 79.6, 80, 82, 85, 90, 95)

1,4-dioxane (vol % as indicated) + H_2O

C_2H_5OH (vol % as indicated) + H_2O

(Solvents continued on next page)

SOLVENTS *(continued)*

An70* (5, 25, 40, 50, 60, 67, 80, 85, 90)	$(CH_3)_2CO$ (vol % as indicated) + H_2O
Mt80* (60, 70, 90)	CH_3OH (vol % as indicated) + H_2O
i-Pr80*	$(CH_3)_2CHOH$ 80 vol % + H_2O
t-Bu80*	$(CH_3)_3COH$ 80 vol % + H_2O
MAn90* (70, 50)	CH_3OH (vol % as indicated) + $(CH_3)_2CO$

COMMENTS

Classification. The aliphatic halides undergoing solvolysis are grouped under the headings: Saturated alkyl halide; Cyclo alkyl halide; Hydroxy-substituted alkyl halide; Carboxyl-substituted alkyl halide; Halogen-substituted alkyl halide; Unsaturated alkenyl halide; Unsaturated alkynyl halide; Unsaturated alkenyl dihalide; Mono-aryl-substituted alkyl halide; Di-aryl-substituted alkyl halide; Tri-aryl-substituted alkyl halide; Aryl-substituted-unsaturated alkenyl halide; Amino-substituted alkyl halide; Sulfide substituted alkyl halide; Heterocyclic 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; primary preceding, secondary then tertiary; the order of halides is F, Cl, Br, I.

Comments by reactions. **(.179) (.180)** Reactions also accompanied by small amount of ester exchange and small amount of elimination reaction in (.180). Vapor space above liquid phase kept to a minimum in reaction tubes as rate constants appeared to decrease with increase in free space. Units converted from original hours. **(.181)** Rate constants corrected for volume change of solvent with pressure and temperature. Units converted from original minutes.

COMMENTS *(continued)*

(.186)(.187) **(.188)** Elimination reaction parallels solvolysis and is principal reaction, see 422.471. Rate constants for solvolysis obtained by difference. **(.189)** Rate constants corrected for solvent expansion with temperature. Slight decrease in value with progress of reaction observed, and value extrapolated to zero time. **(.190)** Solvolysis in mixed solvents produced alcohol and ester in wet formic acid and alcohol and ether in water ethanol but no appreciable elimination reaction. **(.195)** Rate constants observed to fall with course of reaction. **(.200)** Rate constants observed to fall with course of reaction. Correction made for change of volume with temperature. **(.201)** Selected data. Dependence of rate law upon mol fraction of H_2O, N', and mol fraction of methanol, N", in solvent given by empirical equation:

$$10^6 k = 1.38(e^{0.80N"}-1) + 1.25(e^{9.88N'}-1)$$

at 30° with an average deviation of 1.2 %; and by:

$$10^7 k = 6.14(e^{0.80N"}-1) + 6.48(e^{9.88N'}-1)$$

with an average deviation of 0.8 % at 25°. Relative amounts of products formed are listed in supplementary table. $N"/(N" + 1.34N') = k"/(k" + k')$ where $k"$ is the portion of the specific rate constant for the reaction with methanol and k' is the portion of the specific rate constant for the reaction with water. **(.202)** Rate constant at one at mosphere pressure of ([21]) lower than values reported by other authors. Included for comparison with results of ([21]) at higher pressures. **(.203)** Rate law given by empirical equation over narrow range of solvent concentration in acetone mol fraction of water, N_{H_2O} = 0.51-0.70 is:

$$\log k = 6.694N_{H_2O}-b.$$

Values of b at 25°C and 30°C are 9.167 and 8.881 respectively. At mole fractions of H_2O greater than 0.70 rate constant increases more rapidly than predicted by equation. ([52]) used automatic recorder with glass electrode to follow pH, and suggest method adaptable to rapid reaction. In dioxane no linear relation between log k and mol fraction of water was observed. **(.204)** In presence of added $(CH_2ClCOO)_2Ca$ formation of $CH_2ClCOOC(CH_3)_3$ also observed to take place. **(.205)** In acetone rate constants observed to fall appreciably after 70 % conversion. Values tabulated extrapolated to zero time by ([8]). Empirical equation suggested by ([30]) for range of mol fraction H_2O, N_{H_2O} = 0.17-0.60 is:

$$\log k = 5.525\, N_{H_2O} + b.$$

Values of b for 5, 25 and 30°C are -7.783, -6.729 and -6.467

COMMENTS *(continued)*

respectively. Above $N_{H_2O} = 0.6$ rate constant increases more rapidly than predicted by equation. In dioxane rate constants increased with course of reaction and values tabulated are initial rates. (.207) Apparent zero order up to 20 % reaction attributed to balance between decrease in A and autocatalysis by L. (.208) Corrected for solvent expansion with temperature increase. Slight downward trend in second order constants with course of reaction more pronounced at higher temperatures. (.211) Slight downward trend in second order rate constants more pronounced at higher temperatures. (.212) Apparent zero order observed up to 5 % reaction which was extent followed. See (.207). (.213) Corrected for volume change with temperature. Decrease of rate constants with course of reaction greater at higher temperatures. (.214) Apparent zero order up to 35 % reaction attributed to balance between decrease in A and autocatalysis by L. (.215) Corrected for change of volume with temperature. Second order rate constants decrease with course of reaction. (.217) (.218) Analysis for isomeric olefins gave

$CH_3CH_2CH{:}CHCH_3$, 71 % and $CH_3CH_2CH_2CH{:}CH_2$, 29 %.

(.222) Reaction first order with respect to A and added acid but in absence of added acid reaction is autocatalytic. Slight catalysis by NaCl with very definite induction period. In anhydrous ethanol at 120°C no reaction observed up to 4 hours but reaction 85 % complete after 22 hours. (.223) Slight decrease in rate constants with course of reaction. Values corrected for volume change with temperature. (.224) Analysis for isomeric olefins gave 27.3 % $(CH_3)_2C{:}CHCH_3$ and 6 % $C_2H_5(CH_3)C{:}CH_2$ in total products. (.230) Second order rate law showed no drift although no correction for concurrent first order solvolysis. (.232) Analysis of products for isomeric olefins by ([31]) yielded

18 % $CH_3CH{:}C(CH_3)_2$ and 82 % $C_2H_5(CH_3)C{:}CH_2$

except in presence of 2 M/l of B where

28 % $CH_3CH{:}C(CH_3)_2$ and 72 % $C_2H_5(CH_3)C{:}CH_2$

was observed. ([20]) claim second order rate law valid over course although they made no correction for parallel first order solvolysis. See (.230). (.234) (.236) Second order rate law claimed to be valid over course although no correction for parallel first order solvolysis. See (.230) and (.232). (.241) Product analysis for isomeric olefins by ([50]) gave

14.7 % $(C_2H_5)_2C{:}CH_2$ and 29.4 % $C_2H_5(CH_3)C{:}CHCH_3$.

(.245) Product analysis for isomeric olefins by ([50]) gave

COMMENTS *(continued)*

5.5 % $(CH_3)_2C:CHC(CH_3)_3$ and 62.6 % $(CH_3)_3CCH_2(CH_3)C:CH_2$. (.246) Rate constants calculated by graphical analysis of data for simultaneous solvolysis of A and $CH_3[(CH_3)_2CH]_2CCl$ in mixture. See (.251). (.251) Rate constants calculated by graphical analysis of data for simultaneous solvolysis of A and $(CH_3)_2CH(CH_3)CH(CH_3)_2CCl$ in mixture. See (.246). (.254) Drift of rate law over course attributed by ([64]) to presence of two isomers. (.255) No measurable amount of tertiary alcohol formed and reaction is 100 % elimination in aqueous ethanol and even in neutral H_2O. (.256) Autocatalysis by product L so pronounced that no rate constants were calculated. In anhydrous ethanol at 140°C, A = 0.87 and [HCl] = 0.12 there is 5 % reaction at 3×10^4 secs. 40 % at 6×10^4 secs and 80 % at 7×10^4 seconds. (.257) Corrected for volume change with temperature. Second order rate constants decrease with course of reaction. (.259) (.260) Drift of first order rate constants with course attributed by ([64]) to presence of two isomers. (.265) Reaction predominantly elimination with only 7 % solvolysis at 125° and 3 % solvolysis at 160°C. (.279) First order rate constants decrease with course of reaction. Reaction followed by slower elimination to give methyl-isopropyl ketone. Elimination reaction is acid catalyzed but solvolysis reaction is uneffected by acid but is base catalyzed. (.281) First order rate law valid up to pH = 13. At pH > 13 rate law ambiguous. First order constant calculate for pH = 13.9 is over five times the value for pH = 13. Borate and citrate buffers give lower value of rate constant at pH = 5.75 and glycine buffers increase rate by a factor of about ten at pH = 10.1. (.282) First order rate law valid at $[OH^-] \leq 0.03$. At $[OH^-] = 0.3$–1.0 second order rate law valid. Combination of parallel first and second order rate laws used at intermediate concentrations. Depression of rate of solvolysis by bromide ion taken as indications of formation of zwitterion intermediate with bromide ion competing with solvent for reaction with intermediate. (.284) Rate law valid over course in solutions of $\mu = 2.0$ but increase in rate constant with reaction observed in presence of 0.1 M/l HNO_3. Reaction accompanied by partial racemization. (.286) Second order rate law valid over 80 % of course of reaction, but authors question significance and consider that reaction may be heterogeneous and proceed at surface of AgBr. (.287) Some lactone formation may occur. Authors report about 15 % of products are in form of

COMMENTS *(continued)*

C_3H_6, CO_2 and Br^-. (.290) Increase of ionic strength to 1.25 by steps with addition of $NaNO_3$ caused no change in observed rate of reaction. (.297) (.298) Proceed simultaneously in aqueous alkali. (.299) (.300) Proceed simultaneously in aqueous alkali. (.301) Second order rate law followed over course of reaction except in presence of NaBr or NaI where second order constants increase with progress of reaction and values tabulated were obtained by extrapolation to zero time. Authors postulate formation of CCl_2 as an intermediate rate determining step and nucleophilic attack by competing H_2O, OH^-, Cl^-, Br^- or I^-. Relative rates of these competing nucleophilic reagents were calculated from the data. (.302) Rate law followed for 20 % of reaction. (.303) Rate law followed for 13 % of reaction. (.304) Reaction followed by consecutive reaction involving second halogen, see (.278). (.305) Rate law followed for 10 % of reaction. (.306) Reaction followed by consecutive reaction of about the same rate involving the second halogen, see (.279). (.311) No measurable reaction in 24 hours at 50°C. (.317) Value based upon assumed rate law and limited experimental points. Should be considered as giving order of magnitude only. (.319) Second order constant drifted with progress of reaction but remained constant over fourfold variation of concentration of base. (.330) (.331) Products of reaction not identified. (.340) Both products obtained in measurable amounts and formed by separate reactions as no measurable solvolysis of $CH_3CCl{:}CHCH_2OH$ occurred after 30 minutes at 80°C or 4.5 hours at 60°C. (.347) Reaction proceeds simultaneously with (.346) and both show definite salt effect. (.349) Rate constant calculated for first 10-20 % reaction, values increase slightly with progress of reaction or with increase in initial A. (.352) Reaction proceeds simultaneously with (.351). (.353) First order rate law holds up to 80 % reaction when followed by titration but calculated rate constants increase with progress of reaction when followed polarimetrically. (.354) Reaction proceeds simultaneously with (.353). (.356) Rate constant calculated for first 10-20 % reaction, values increase slightly with course of reaction or with increase in initial A. (.359) Identical results obtained with *l*-isomer. (.365) Rate constant calculated for first 10-20 % reaction, values increase slightly with progress of reaction or with increase in initial A. (.370) Values obtained by extrapola-

COMMENTS *(continued)*

tion to zero time as calculated constants increased slightly with progress of reaction. **(.371)** Values obtained by extrapolation to zero time as calculated constants decreased with progress of reaction. Attributed by ([75]) to removal of L by reaction with solvent. **(.372)** Initial rates are tabulated as drift of first order constants observed with progress of reaction. Authors believe drift to be due to changing ionic strength. **(.375)** Initial rates tabulated as calculated constants increased slightly with progress of reaction. **(.378)** Values obtained by extrapolation to zero time as calculated first order rate constants fell with progress of reaction. **(.379) (.381)** Reaction presumed to proceed through carbonium ion intermediate produced by removal of chloride ion. Absence of deuterium exchange taken as evidence excluding splitting off of proton. ([50a]) claim no acid or base catalysis observed. **(.400) (.402)** First order rate law is practically independent of a large number of substances which do effect final product. Reaction considered to proceed through carbonium ion intermediate. Relative reactivity of various nucleophilic reagents with the triphenyl carbonium ion are listed in the supplementary table. **(.406) (.407)** Third order rate law followed up to 50 % reaction. Decrease in calculated rate constants upon increase of initial concentration of A and B attributed by ([42]) to a change in dielectric constant of reaction medium. **(.412)** Solvolysis probably proceeds through ethylene immonium ion formation with $k_1 = 3.4 \times 10^{-3}$ followed by competitive reactions with Cl^-, H_2O and internal cyclization with rate constants calculated to be $k_{Cl^-} < 3 \times 10^{-4}$, $k_{H_2O} < 8 \times 10^{-4}$ and $k_I < 2 \times 10^{-2}$ respectively. **(.413)** Solvolysis probably proceeds through ethylene immonium ion formation at rate k A followed by competitive reactions with Cl^-, H_2O and second molecule of A to form dimer. Calculated rate constants for these reactions are $k_{Cl^-} = 2.3 \times 10^{-2}$, $k_{H_2O} = 2 \times 10^{-5}$, and $k_A = 7 \times 10^{-3}$. **(.416)** Solvolysis probably proceeds through formation of ethylene-immonium ion at rate k A followed by competitive reactions with Cl^-, H_2O, and second molecule of A to form dimer. Calculated rate constants for these alternate reactions in An67* are: $k_{Cl^-} = 2 \times 10^{-2}$ to 1×10^{-1}; $k_{H_2O} = 1.0 \times 10^{-4}$; $k_A = 1.4 \times 10^{-3}$; and in An25* $k_{H_2O} = 2.5 \times 10^{-5}$; $k_A = 4 \times 10^{-5}$. **(.418) (.419)** Solvolysis probably proceeds through ethylene immonium ion formation followed by competitive reactions with the nucleophilic reagents, H_2O, OH^-, Cl^- or a second molecule of A.

COMMENTS *(continued)*

Calculated rates of competitive reactions are: $k_{H_2O} \sim 1$; $k_{Cl^-} \simeq 200$; $k_A \leq 20$. **(.421) (.422)** Consecutive reactions calculated from data for overall reaction (.420). In presence of Cl^- reverse reaction is apparent. ([7]) finds no appreciable salt effect upon rate constants of the forward reaction but rate constant of reverse reaction observed to decrease with increase of ionic strength. **(.423) (.424)** Chlorine atoms are probably in trans-position to each other.

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SOLVOLYSIS
Aryl halides

Liquid phase

Reaction type: $ArX + OR^- \longrightarrow ArOR + X^-$

Amounts are in M/l. Rate constants are in M/l and sec.

Group in 1-position reacts unless indicated otherwise

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	k^o	n	E	$A = A^o \times 10^n$ A^o	A^o	n	Comments	Literature
	Mono-substituted Fluorobenzenes													
.3	$o\text{-}NO_2C_6H_4F + CH_3O^-$	CH_3OH		k AB	25	1.16	-4							(24)
.4	$o\text{-}NO_2C_6H_4F + C_2H_5O^-$	C_2H_5OH	A ≃ 0.025 B ≃ 0.033	k AB	32	1.55	-3							(5)
					40	3.86	-3							
					50	9.88	-3							
					61	2.86	-2		20.1	5		11		
.5	$m\text{-}NO_2C_6H_4F + CH_3O^-$	CH_3OH	A ≠ B	k AB	100	6.42	-5							(24)
					113	2.31	-4							
					121	4.64	-4							
					129	1.22	-3		28.7	4		12		(6)
.6	$p\text{-}NO_2C_6H_4F + CH_3O^-$	CH_3OH	10^2A = (1.7-3); 10^2B = (1.7-6.8)	k AB	50	2.42	-3							(6)
					101	1.10	-1		17.9	3		9		(15)
.7	$p\text{-}NO_2C_6H_4F + C_2H_5O^-$	C_2H_5OH	A = 0.02 B = 0.04	k AB	40	2.42	-3							(11)
					51	8.6	-3							(4)
					70	4.7	-2							
					91	1.9	-1		19	5		10		

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
.8	m-$F_3CC_6H_4F + C_2H_5O^-$	C_2H_5OH		k AB	150	1.08	-4					(11)
.9	p-$F_3CC_6H_4F + C_2H_5O^-$	C_2H_5OH		k AB	150	4.5	-3					(11)
.10	o-$ClC_6H_4F + C_2H_5O^-$	C_2H_5OH		k AB	150	8.0	-5					(11)
.11	m-$ClC_6H_4F + C_2H_5O^-$	C_2H_5OH		k AB	150	5.5	-5					(11)
.12	p-$ClC_6H_4F + C_2H_5O^-$	C_2H_5OH		k AB	150	1.2	-5					(11)
.13	p-$BF_4^-N_2^+C_6H_4F + OH^-$	H_2O		k AB	0	1.50	-3					(7)
	Mono-substituted Chlorobenzenes											
.14	o-$NO_2C_6H_4Cl + CH_3O^-$	CH_3OH	A ≃ 0.05	k AB	25	1.5	-7					(3) (9)
			B ≃ 0.1		75	3.62	-5					(12) (20) (21)
					82	6.82	-5					
					101	3.74	-4	23.6	2.5	10	*	(14)
.15	o-$NO_2C_6H_4Cl + C_2H_5O^-$	C_2H_5OH		k AB	90	3.97	-4	22	1	10		(23)
.16	p-$NO_2C_6H_4Cl + CH_3O^-$	CH_3OH			71	8.42	-5					(19) (21)
					82	2.35	-4					
					101	1.37	-3	23.7	9	10		
			A = B = 0.04		110	8.6	-4				*	(14)
.17	p-$NO_2C_6H_4Cl + C_2H_5O^-$	C_2H_5OH	A = 0.02	k AB	91	9.6	-4					(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		
.18	m-$F_3CC_6H_4Cl + C_2H_5O^-$	C_2H_5OH		k AB	150	5.8	-7					(11)
.19	p-$F_3CC_6H_4Cl + C_2H_5O^-$	C_2H_5OH		k AB	150	5.8	-6					(11)
.20	o-$C_6H_4Cl_2 + CH_3O^- \longrightarrow o$-$ClC_6H_4OCH_3 + Cl^-$	CH_3OH	A = 0.3; B = 1.6	k AB	175	1.1	-5				*	(14)
.21	o-$C_6H_4Cl_2 + C_2H_5O^-$	C_2H_5OH		k AB	150	1.8	-7					(11)
.22	m-$C_6H_4Cl_2 + CH_3O^- \longrightarrow m$-$ClC_6H_4OC_2H_5 + Cl^-$	CH_3OH	A = 0.3; B = 1.6	k AB	175	1.4	-5				*	(14)
.23	m-$C_6H_4Cl_2 + C_2H_5O^-$	C_2H_5OH		k AB	150	4.7	-7					(11)
.24	p-$C_6H_4Cl_2 + CH_3O^- \longrightarrow p$-$ClC_6H_4OCH_3 + Cl^-$	CH_3OH	A = 0.3; B = 1.6	k AB	175	3.2	-6				*	(14)
.25	p-$C_6H_4Cl_2 + C_2H_5O^-$	C_2H_5OH		k AB	150	1.3	-7					(11)
	Mono-substituted Bromobenzenes											
.26	o-$NO_2C_6H_4Br + CH_3O^-$	CH_3OH		k AB	0	1.14	-9					(7)
.27	p-$NO_2C_6H_4Br + OH^-$	46 vol % H_2O		k AB	reflux	3.0	-6				*	(27)
.28	p-$NO_2C_6H_4Br + C_2H_5O^-$	C_2H_5OH	A = 0.02; B = 0.04	k AB	91	8.4	-4					(4)
					111	3.7	-3					
					130	1.31	-2	20.3	1.6	9		
	Mono-substituted Iodobenzenes											
.29	p-$NO_2C_6H_4I + C_2H_5O^-$	C_2H_5OH	A = 0.02; B = 0.04	k AB	91	7.1	-5				*	(4)

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
	Di-substituted Fluorobenzenes											
.30	$2\text{-}NO_2\text{-}4\text{-}(COO^-)C_6H_3F + CH_3O^-$	CH_3OH		k AB	25	1.8	-3					(24)
.31	$2\text{-}NO_2\text{-}4\text{-}NH_2C_6H_3F + C_2H_5O^-$	C_2H_5OH	A = 0.025; B = 0.033	k AB	50	9.02	-5					(5)
					69	8.53	-4					
					90	6.70	-3	25.0	5	10		
.32	$2,4\text{-}(NO_2)_2C_6H_3F + C_2H_5O^-$	C_2H_5OH	A = 0.0025; B = 0.0033	k AB	-20	1.66	+1					(5)
.33	$2,4\text{-}(NO_2)_2C_6H_3F + m\text{-}NO_2C_6H_4O^-$	CH_3OH		k AB	0	1.0	-2					(2)
.34	$2,4\text{-}(NO_2)_2C_6H_3F + p\text{-}NO_2C_6H_4O^-$	CH_3OH		k AB	15	3.42	-3					(2)
					25	9.62	-3					
					35	2.53	-2	18	8	10		
.35	$3,5\text{-}(NO_2)_2C_6H_3F + CH_3O^-$	CH_3OH	10^2A = (1.7-3); 10^2B = (1.7-6.8)	k AB	50	4.19	-3	22	2	12		(6)
.36	$2\text{-}NO_2\text{-}4\text{-}FC_6H_3F + C_2H_5O^- \longrightarrow$ $\longrightarrow 2\text{-}NO_2\text{-}4\text{-}FC_6H_3OC_2H_5 + F^-$ $\longrightarrow 3\text{-}NO_2\text{-}4\text{-}FC_6H_3OC_2H_5 + F^-$	C_2H_5OH	A = 0.025; B = 0.033	k AB = $-dB/dt$	22	8.71	-4				*	(5)
					41	7.00	-3					
					51	1.90	-2					
					61	4.80	-2	20.1	8	11		

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
.37	$2\text{-}NO_2\text{-}4\text{-}ClC_6H_3F + C_2H_5O^-$	C_2H_5OH	A = 0.025; B = 0.033	k AB	0	7.49	-4				*	(5)
					37	3.68	-2					
					51	1.39	-1	18.2	2.5	11		
.38	$3\text{-}NO_2\text{-}4\text{-}ClC_6H_3F + CH_3O^-$	CH_3OH	A = B	k_a AB	60	1.29	-5				*	(12)
	$\longrightarrow 3\text{-}NO_2\text{-}4\text{-}ClC_6H_3OCH_3 + F^-$ (a)				82	1.36	-4					
	$\longrightarrow 3\text{-}NO_2\text{-}4\text{-}CH_3OC_6H_3F + Cl^-$ (b)				100	9.34	-4	26.7	4.0	12		
				k_b AB	(See reaction (.70))							
.39	$2\text{-}NO_2\text{-}4\text{-}BrC_6H_3F + C_2H_5O^-$	C_2H_5OH	A = 0.025; B = 0.033	k AB	22	1.35	-2				*	(5)
					31	3.24	-2					
					41	7.99	-2					
					51	1.90	-1	17.4	1.0	11		
.40	$2\text{-}NO_2\text{-}4\text{-}IC_6H_3F + C_2H_5O^-$	C_2H_5OH	A = 0.025; B = 0.033	k AB	21	1.15	-2				*	(5)
					30	2.91	-2					
					41	8.02	-2					
					50	1.66	-1	17.4	1.0	11		
Di-substituted Chlorobenzenes												
.41	$2\text{-}NO_2\text{-}4\text{-}(HC{:}O)C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.05; B = 0.1	k AB	25	2.10	-4					(20)
					35	8.50	-4					
					45	3.16	-3	25.2	6	14		
.42	$2\text{-}CH_3C{:}O\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.005; B = 0.007	k AB	45	1.30	-3					
					60	5.42	-3					
					82	3.70	-2	20.7	2	11		(22)

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
.43	$2\text{-}NO_2\text{-}4\text{-}(CH_3C{:}O)C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.015	k AB	25	3.11	-4				*	(9)
					35	9.1	-4					
					45	2.37	-3	19.1	3	10		
			A = 0.05; B = 0.1		26	4.82	-4				*	(20)
					35	1.17	-3					
					45	3.25	-3	18.7	2	10		
.44	$2\text{-}(COO^-)\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH		k AB	82	1.70	-4					(21) (22)
					88	3.49	-4					
					101	1.39	-3	28.6	7	13		
.45	$2\text{-}NO_2\text{-}4\text{-}(COO^-)C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.05; B = 0.1	k AB	60	4.85	-5					
					75	2.04	-4					
					82	3.64	-4					
					101	1.65	-3	21.5	6	9		(20) (21)
.46	$2\text{-}COOCH_3\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH		k AB	43	9.97	-4					(21) (22)
					60	3.22	-3					
					75	1.01	-2					
					82	1.56	-2	17.0	5	8		
.47	$2\text{-}NO_2\text{-}4\text{-}(COOCH_3)C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.05; B = 0.1	k AB	30	5.57	-4					(20) (21)
					45	2.58	-3					
					60	9.37	-3	18.3	9	9		
.48	$2\text{-}C_6H_5C{:}O\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.005; B = 0.007	k AB	60	4.92	-4					(22)
					75	2.38	-3					
					82	4.35	-3	23.6	1.6	12		

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
.49	$2\text{-}NO_2\text{-}4\text{-}(C_6H_5C{:}O)C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.05; B = 0.1	k AB	35	1.70	-3					(20)
					45	4.42	-3					
					60	1.60	-2	18.1	1.3	10		
.50	$2\text{-}NH_2C{:}O\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.005; B = 0.007	k AB	45	2.44	-3					(22)
					60	1.02	-2					
					75	4.05	-2					
					82	6.91	-2	20.7	4	11		
.51	$2\text{-}NO_2\text{-}4\text{-}(NH_2C{:}O)C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.05; B = 0.1	k AB	35	1.29	-4					(20)
					45	4.03	-4					
					60	1.78	-3	21.3	1.6	11		
.52	$2\text{-}C_6H_5NHC{:}O\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = 0.005; B = 0.007	k AB	35	3.19	-3					(22)
					45	9.07	-3					
					60	3.64	-2	19.8	4	11		
.53	$2\text{-}CN\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = (0.02-0.04)	k AB	25	4.3	-3					(1)
					35	1.37	-2	21	1	13		
.54	$2\text{-}CN\text{-}4\text{-}NO_2C_6H_3Cl + C_2H_5O^-$	CH_3OH	A = B = (0.02-0.04)	k AB	25	1.36	-2					(1)
.55	$2\text{-}NO_2\text{-}4\text{-}(CN)C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.04	k AB	25	2.3	-4					(18)
			A = 0.05; B = 0.1		30	5.22	-4					(20)
					35	1.02	-3					
					45	3.91	-3	25.6	1.5	15		
.56	$2\text{-}NO_2\text{-}4\text{-}(CN)C_6H_3Cl + C_2H_5O^-$	CH_3OH	A = B = 0.04	k AB	25	7.0	-4					(18)

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
.57	$2,3\text{-}(NO_2)_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.04	k AB	0	1.24	-4					(14)
					25	1.67	-3	19	3	11		
.58	$2,4\text{-}(NO_2)_2C_6H_3Cl + 2OH^- \longrightarrow$ $2,4\text{-}(NO_2)_2C_6H_3O^- + Cl^- + H_2O$	40 vol % H_2O 60 % Dioxane	A = 0.015-0.03; B = 0.03-0.06	k AB = dM/dt	25	1.10	-3					(8)
					45	6.98	-3	17.5	7	9		
.59	$2,4\text{-}(NO_2)_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.015-0.04	k AB	0	1.92	-3					(1) (2) (9) (10) (14) (16) (17) (18)
					15	1.01	-2					(19) (21) (28) (29)
					25	2.73	-2	17.1	1.8	11		
					45	1.45	-1					(11)
.60	$2,4\text{-}(NO_2)_2C_6H_3Cl + C_2H_5O^-$	CH_3OH	A = B = 0.0004-0.04	k AB	0	6.3	-3					(16) (17) (28)
					15	3.0	-2					(17) (28)
					25	8.2	-2	16	4	10		
.61	$2,4\text{-}(NO_2)_2C_6H_3Cl + C_6H_5O^-$	40 vol % H_2O 60 % Dioxane	A = B = 0.015	k AB	0	1.22	-3				*	(8)
					25	1.20	-2	14.7	7	8		
.62	$2,4\text{-}(NO_2)_2C_6H_3Cl + p\text{-}NO_2C_6H_4O^-$	CH_3OH		k AB	70	5.18	-4					(2)
					82	1.41	-3					
					101	6.42	-3	20.7	8	9		
.63	$2,5\text{-}(NO_2)_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.04	k AB	0	5.3	-4					(14)
					25	9.3	-3	18	3	11		
.64	$2,6\text{-}(NO_2)_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.04	k AB	0	4.8	-5					(14)
					25	7.2	-4	18.0	1.1	10		(10) (14) (19) (21)
					35	2.26	-3					(19) (21)
					45	4.87	-3					(10)

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
.65	2,6-$(NO_2)_2C_6H_3Cl + C_2H_5O^-$	C_2H_5OH		k AB	50	1.47	-2					(6a) (11)
.66	3,4-$(NO_2)_2C_6H_3Cl + CH_3O^- \longrightarrow$ 3-CH_3O-4-$NO_2C_6H_3Cl + NO_2^-$	CH_3OH	A = B = 0.04	k AB	0 25	5.5 7.3	-4 -3	 16.7	 3	 10		(14)
.67	2-NO_2-4-$(CH_3)_3N^+C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.015	k AB	25 35 45	8.2 2.57 7.13	-4 -3 -3	 20.3	 6	 11		(9)
.68	2-NO_2-4-$C_6H_5N_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B	k AB	45 55	6.79 1.73	-4 -3	 19	 5	 10		(10)
.69	2-NO_2-4-$CH_3SO_2C_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.015	k AB	25 35 45	2.65 7.62 1.92	-3 -3 -2	 18.6	 1.2	 11		(9)
.70	2-NO_2-4-$FC_6H_3Cl + CH_3O^- \longrightarrow$ $\longrightarrow$ 2-NO_2-4-$FC_6H_3OCH_3 + Cl^-$ (b) $\longrightarrow$ 2-NO_2-4-$CH_3OC_6H_3Cl + F^-$ (a)	CH_3OH	A = B	k_b AB k_a AB	60 82 190 (See reaction (.38))	7.20 7.36 3.71	-6 -5 -4	 24.4	 7	 10	*	(12)
.71	2-NO_2-4-$F_3CC_6H_3Cl + CH_3O^-$	CH_3OH	A = B	k AB	25 45	1.56 1.34	-4 -3	 20.4	 1.4	 11		(10)
.72	2-NO_2-3-$ClC_6H_3Cl + CH_3O^- \longrightarrow$ 2-NO_2-3-$ClC_6H_3OCH_3 + Cl^-$	CH_3OH	A = B = 0.04	k AB	85 110	3.8 3.7	-5 -4	 25	 7	 10		(14)

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
.73	$2\text{-}NO_2\text{-}4\text{-}ClC_6H_3Cl + CH_3O^-$	CH_3OH	A = B = 0.04	k AB =	25	1.8	-6				*	[9] [14]
				$-dB/dt$	50	3.4	-5					[14]
				$+dM/dt$	68	2.38	-4					[12] [21]
					82	8.60	-4					
					101	4.18	-3					
					110	9.2	-3	22.8	8.8	10		
.74	$2\text{-}Cl\text{-}3\text{-}NO_2C_6H_3Cl + CH_3O^- \longrightarrow Cl(NO_2)C_6H_3OCH_3 + Cl^-$	CH_3OH	A = B = 0.04	k AB	85	4.8	-4					[14]
					110	4.0	-3	23.6	2	12		
.75	$2\text{-}Cl\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^- \longrightarrow Cl(NO_2)C_6H_3OCH_3 + Cl^-$	CH_3OH	A = B = 0.04	k' AB =	25	9.2	-6				*	[14]
				$-dB/dt$	50	1.67	-4					
					85	4.8	-3	22.1	1.5	11		
				k''AB =	70	7.42	-4				*	[21]
				$+dM/dt$	76	1.25	-3					
					87	3.47	-3	21.9	6	10		
.76	$3\text{-}Cl\text{-}4\text{-}NO_2C_6H_3Cl + CH_3O^- \longrightarrow Cl(NO_2)C_6H_3OCH_3 + Cl^-$	CH_3OH	A = B = 0.04	k AB	25	8.3	-6					[14]
					50	1.75	-4					
					85	5.4	-3	23.0	6	11		
.77	$2\text{-}NO_2\text{-}4\text{-}BrC_6H_3Cl + CH_3O^- \longrightarrow 2\text{-}NO_2\text{-}4\text{-}BrC_6H_3OCH_3 + Cl^-$	CH_3OH	A ≠ B	k AB	61	1.31	-4					[12]
					82	1.12	-3					
					100	6.65	-3	24.6	1.5	12		
.78	$2\text{-}NO_2\text{-}4\text{-}IC_6H_3Cl + CH_3O^- \longrightarrow 2\text{-}NO_2\text{-}4\text{-}IC_6H_3OCH_3 + Cl^-$	CH_3OH	A ≠ B	k AB	61	1.46	-4					[12]
					82	1.16	-3					
					100	6.83	-3	24.0	7	11		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 20$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.79	$1,3,5\text{-}C_6H_3Cl_3 + C_2H_5O^- \longrightarrow 3,5\text{-}Cl_2C_6H_3OC_2H_5 + Cl^-$	C_2H_5OH	A = 0.1; B = 0.05	k AB	149	8.95	-5				*	([25])
					162	2.48	-4					
					174	6.02	-4					
					187	1.42	-3	28.6	6	10		
	Di-substituted Bromobenzenes											
.80	$2\text{-}CN\text{-}4\text{-}NO_2C_6H_3Br + CH_3O^-$	CH_3OH	A = B = 0.02-0.04	k AB	25	3.4	-3					([1]) ([18])
					35	1.06	-2	21	8	12		([1])
.81	$2\text{-}CN\text{-}4\text{-}NO_2C_6H_3Br + C_2H_5O^-$	CH_3OH	A = B = 0.02-0.04	k AB	25	9.2	-3					([1])
.82	$2\text{-}NO_2\text{-}4\text{-}CNC_6H_3Br + CH_3O^-$	CH_3OH	A = B = 0.04	k AB	25	1.7	-4					([18])
.83	$2\text{-}NO_2\text{-}4\text{-}CNC_6H_3Br + C_2H_5O^-$	CH_3OH	A = B = 0.04	k AB	25	5.1	-4					([18])
.84	$2\text{-}NO_2\text{-}4\text{-}N(CH_3)_3{}^+C_6H_3Br + CH_3O^-$	CH_3OH		k AB	0	1.34	-5					([7])
.85	$2,4\text{-}(NO_2)_2C_6H_3Br + CH_3O^-$	CH_3OH		k AB	0	1.38	-3					([2])
					15	7.10	-3					
			A = B = 0.04		25	1.91	-2	17.1	6	10		([2]) ([18])
.86	$2,4\text{-}(NO_2)_2C_6H_3Br + C_2H_5O^-$	CH_3OH	A = B = 0.04		0	3.7	-3					([17])
					15	1.57	-2					
					25	4.1	-2	16	2	10		([18])

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
	Di-substituted Iodobenzenes											
.87	$2,4\text{-}(NO_2)_2C_6H_3I + CH_3O^-$	CH_3OH		k AB	15	1.90	-3					(2)
					25	5.76	-3					
					35	1.63	-2	19.0	5	11		
	Tri-substituted Chlorobenzenes											
.88	$2,4\text{-}(NO_2)_2\text{-}5\text{-}CH_3C_6H_2Cl + CH_3O^-$	CH_3OH		k AB	0	3.71	-4					(15)
					101	4.42	0	18.9	5	11		
.89	$2,4\text{-}(NO_2)_2\text{-}6\text{-}CH_3C_6H_2Cl + CH_3O^-$	CH_3OH		k AB	19	1.14	-3					(21)
					26	2.60	-3					
					35	6.50	-3	19.2	3	11		
.90	$2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3C_6H_2Cl + CH_3O^-$	CH_3OH	A = B	k AB	30	1.86	-4					(21)
					45	7.34	-4					(10)
					60	3.43	-3	19.2	1.3	10		(21)
.91	$2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3C_6H_2Cl + C_2H_5O^-$	C_2H_5OH		k AB	50	2.58	-3					(6a) (11)
.92	$2,6\text{-}(NO_2)_2\text{-}4\text{-}(CH_3)_3CC_6H_2Cl + C_2H_5O^-$	C_2H_5OH		k AB	50	4.55	-3					(6a) (11)
.93	$2,6\text{-}(NO_2)_2\text{-}4\text{-}C_6H_5C_6H_2Cl + CH_3O^-$	CH_3OH	A = B	k AB	25	1.09	-3					(10)
					45	7.70	-3	18.4	3	10		
.94	$2,4\text{-}(NO_2)_2\text{-}5\text{-}(O^-)C_6H_2Cl + OH^-$	H_2O		k AB	101	1.90	-4					(15)

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		
.95	$2,4\text{-}(NO_2)_2\text{-}5\text{-}CH_3OC_6H_2Cl + CH_3O^-$	CH_3OH	A = B = 0.007-0.04	k AB	0	6.2	-4	16				(16)
					15	3.3	-3					
					25	7.8	-3					
					101	8.55	0	19	1	12		(15)
.96	$2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3OC_6H_2Cl + CH_3O^-$	CH_3OH	A = B	k AB	55	2.20	-4					(10)
					69	8.80	-4	23	4	11		
.97	$2,4\text{-}(NO_2)_2\text{-}5\text{-}C_2H_5OC_6H_2Cl + C_2H_5O^-$	CH_3OH	A = B = 0.007-0.04	k AB	0	1.83	-3					(16)
					15	7.8	-3					
					25	1.85	-2	15	2	8		
.98	$2,4\text{-}(NO_2)_2\text{-}6\text{-}(COO^-)C_6H_2Cl + CH_3O^-$	CH_3OH		k AB	35	1.44	-3					(21)
					42	3.08	-3					
					48	6.10	-3	22	6	12		
.99	$2,6\text{-}(NO_2)_2\text{-}4\text{-}(COO^-)C_6H_2Cl + CH_3O^-$	CH_3OH		k AB	0	5.70	-4					(19) (21)
					26	6.86	-3					
					30	9.70	-3	15.2	8	8		
.100	$2,4\text{-}(NO_2)_2\text{-}6\text{-}CH_3OOCC_6H_2Cl + CH_3O^-$	CH_3OH		k AB	-5	6.30	-3					(21)
					0	1.12	-2					
					5	1.96	-2	17	8	11		
.101	$2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3OOCC_6H_2Cl + CH_3O^-$	CH_3OH		k AB	0	3.61	-2					(19) (21)
					5	6.40	-2					
					9	9.17	-2	16	3	11		

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
.102	$2,4\text{-}(NO_2)_2\text{-}6\text{-}NH_2C_6H_2Cl + CH_3O^-$	CH_3OH		k AB	41	4.51	-4					(21)
					70	5.99	-3					
					82	1.48	-2	19.6	1.8	10		
.103	$2,6\text{-}(NO_2)_2\text{-}4\text{-}NH_2C_6H_2Cl + CH_3O^-$	CH_3OH		k AB	82	1.58	-4					(21)
					100	6.17	-4					
					113	1.51	-3	20.4	5	8		
.104	$2,4\text{-}(NO_2)_2\text{-}5\text{-}(CH_3)_2NC_6H_2Cl + CH_3O^-$	CH_3OH		k AB	101	2.26	-1					(15)
.105	$2,3,4\text{-}(NO_2)_3C_6H_2Cl + CH_3O^- \longrightarrow$ $\longrightarrow 2,3,4\text{-}(NO_2)_3C_6H_2OCH_3 + Cl^-$ $\longrightarrow 2,4\text{-}(NO_2)_2\text{-}3\text{-}CH_3OC_6H_2Cl + NO_2^-$	CH_3OH	A = B = 0.02	k AB = -dB/dt	0	1.80	-1					(30)
.106	$3,4,5\text{-}(NO_2)_3C_6H_2Cl + CH_3O^- \longrightarrow$ $\longrightarrow 3,4,5\text{-}(NO_2)_3C_6H_2OCH_3 + Cl^-$ $\longrightarrow 3,5\text{-}(NO_2)_2\text{-}4\text{-}CH_3OC_6H_2Cl + NO_2^-$	CH_3OH	A = B = 0.02	k AB = -dB/dt	0	1.25	-1					(30)
.107	$2,3\text{-}(NO_2)_2\text{-}6\text{-}ClC_6H_2Cl + CH_3O^-$	CH_3OH	A = B = 0.08	k AB	0	5.6	-3					(13)
.108	$2,4\text{-}(NO_2)_2\text{-}3\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$ $\longrightarrow 2,4\text{-}(NO_2)_2\text{-}3\text{-}ClC_6H_2OCH_3 + Cl^-$ $\longrightarrow 2,4\text{-}(NO_2)_2\text{-}3\text{-}CH_3OC_6H_2Cl + Cl^-$	CH_3OH	A = B = 0.08	k AB	0	3.5	-4					(13)
.109	$2,4\text{-}(NO_2)_2\text{-}5\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$ $2,4\text{-}(NO_2)_2\text{-}5\text{-}ClC_6H_2OCH_3 + Cl^-$	CH_3OH	A = B = 0.08	k AB	0	2.3	-2					(13) (15)

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
.110	$2,4\text{-}(NO_2)_2\text{-}6\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$	CH_3OH	A = B = 0.08	k AB	0	6.8	-3				*	[13]
	$\longrightarrow 2,4\text{-}(NO_2)_2\text{-}6\text{-}ClC_6H_2OCH_3 + Cl^-$				0	7.43	-3					[21]
	$\longrightarrow 2,4\text{-}(NO_2)_2\text{-}6\text{-}CH_3OC_6H_2Cl + Cl^-$				5	1.42	-2					
					9	2.21	-2	21	1	15		
.111	$2,6\text{-}(NO_2)_2\text{-}4\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$	CH_3OH		k AB	0	5.18	-4				*	[19] [21]
	$\longrightarrow 2,6\text{-}(NO_2)_2\text{-}4\text{-}ClC_6H_2OCH_3 + Cl^-$				22	5.46	-3					
					25	7.62	-3	17.4	4	10		
			A = B = 0.08		0	4.27	-4					[10] [13]
					25	6.22	-3	17.2				[10]
.112	$2,3\text{-}(NO_2)_2\text{-}4\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$	CH_3OH	A = B = 0.08	k AB = $-dB/dt$	0	4.3	-4					[13]
	$\longrightarrow (NO_2)_2ClC_6H_2OCH_3 + Cl^-$											
	$\longrightarrow 1,4\text{-}Cl_2\text{-}2\text{-}CH_3O\text{-}3\text{-}NO_2C_6H_2 + NO_2^-$											
.113	$2,5\text{-}(NO_2)_2\text{-}3\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$	CH_3OH	A = B = 0.08	k AB = $-dB/dt$	0	2.42	-3					[13]
	$\longrightarrow (NO_2)_2ClC_6H_2OCH_3 + Cl^-$											
	$\longrightarrow 1,3\text{-}Cl_2\text{-}2CH_3O\text{-}5\text{-}NO_2C_6H_2 + NO_2^-$											
.114	$2,5\text{-}(NO_2)_2\text{-}4\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$	CH_3OH	A = B = 0.08	k AB = $-dB/dt$	0	1.15	-2					[13]
	$\longrightarrow (NO_2)_2ClC_6H_2OCH_3 + Cl^-$											
	$\longrightarrow 1,4\text{-}Cl_2\text{-}2\text{-}CH_3O\text{-}5\text{-}NO_2C_6H_2 + NO_2^-$											
.115	$3,4\text{-}(NO_2)_2\text{-}5\text{-}ClC_6H_2Cl + CH_3O^- \longrightarrow$	CH_3OH	A = B = 0.08	k AB = $-dB/dt$	0	2.14	-3					[13]
	$\longrightarrow (NO_2)_2ClC_6H_2OCH_3 + Cl^-$											
	$\longrightarrow 1,5\text{-}Cl_2\text{-}3\text{-}NO_2\text{-}4\text{-}CH_3OC_6H_2 + NO_2^-$											

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
.116	$2\text{-Cl-4,5-}(NO_2)_2C_6H_2Cl + CH_3O^- \longrightarrow$ $\longrightarrow (NO_2)_2ClC_6H_2OCH_3 + Cl^-$ $\longrightarrow 1,2\text{-}Cl_2\text{-4-}CH_3O\text{-5-}NO_2C_6H_2 + NO_2^-$	CH_3OH	A = B = 0.08	k AB = $-dB/dt$	0	6.0	-3					(13)
	Tri-substituted Bromobenzene											
.117	$2,6\text{-}(CH_3)_2\text{-4-}NO_2C_6H_2Br + OH^-$	Dioxane + 46 vol % H_2O	A = 0.028; B = 0.29	k AB reflux	1.3	-7					*	(27)
.118	$3,5\text{-}(CH_3)_2\text{-4-}NO_2C_6H_2Br + OH^-$	Dioxane + 46 vol % H_2O	A = 0.028; B = 0.29	k AB reflux	3.6	-7					*	(27)
	Mono-substituted Chloronapthalene											
.119	$2\text{-}NO_2C_{10}H_6\text{-1-}Cl + OH^-$	Dioxane + 38.5 vol % H_2O	A = 0.077; B = 0.154	k AB = $-dA/dt$	65	3.9	-5				*	(26)
					75	8.7	-5					
					85	2.1	-4	20	8	8		
.120	$2\text{-}NO_2C_{10}H_6\text{-1-}Cl + C_2H_5O^-$	C_2H_5OH + 0.6 wt % H_2O	A = 0.077; B = 0.1	k AB	55	5.86	-4					(26)
					65	1.40	-3					
					75	3.18	-3	19	3	9		
.121	$4\text{-}NO_2C_{10}H_6\text{-1-}Cl + OH^-$	Dioxane + 38.5 vol % H_2O	A = 0.077; B = 0.154	k AB	75	1.67	-5				*	(26)
					80	2.79	-5					
					85	3.34	-5					

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
.122	$4\text{-}NO_2C_{10}H_6\text{-}1\text{-}Cl + C_2H_5O^-$	C_2H_5OH + 0.6 wt % H_2O	A = 0.077; B = 0.1	k AB	55	3.47	-4					(26)
					65	8.22	-4					
					75	2.12	-3	20	2	10		
.123	$1\text{-}NO_2C_{10}H_6\text{-}2\text{-}Cl + OH^-$	Dioxane + 38.5 vol % H_2O	A = 0.077; B = 0.154	k AB	75	4.4	-6				*	(26)
					80	6.9	-6					
					85	8.7	-6					
.124	$1\text{-}NO_2C_{10}H_6\text{-}2\text{-}Cl + C_2H_5O^-$	C_2H_5OH + 0.6 wt % H_2O	A = 0.077; B = 0.1	k AB	55	7.8	-5					(26)
					65	1.14	-4					
					75	2.00	-4					
	Di-substituted Chloronapthalene											
.125	$2,4\text{-}(NO_2)_2C_{10}H_5\text{-}1\text{-}Cl + CH_3O^-$	CH_3OH	A = B = 0.0004-0.0009	k AB	0	5.6	-2					(28)
					15	1.41	-1					
					25	3.40	-1	12.5	5	8		
.126	$2,4\text{-}(NO_2)_2C_{10}H_5\text{-}1\text{-}Cl + C_2H_5O^-$	CH_3OH	A = B = 0.0004-0.0009	k AB	0	1.60	-1					(28)
					15	3.10	-1					
					25	7.40	-1	10	2	7		
	Tri-substituted Chloronapthalene											
.127	$2,4,5\text{-}(NO_2)_3C_{10}H_4\text{-}1\text{-}Cl + CH_3O^-$	CH_3OH	A = B = 0.0004-0.0009	k AB	0	1-3	-1				*	(28)
.128	$1,6,8\text{-}(NO_2)_3C_{10}H_4\text{-}2\text{-}Cl + CH_3O^-$	CH_3OH	A = B = 0.003-0.006	k AB	0	3.7	-2					(29)
					15	1.45	-1					
					25	6.20	-1	18	9	12		

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
.129	$1,6,8\text{-}(NO_2)_3C_{10}H_4\text{-}2\text{-}Cl + C_2H_5O^-$	CH_3OH	A = B = 0.003-0.006	k AB	0	5.2	-2					(29)
	Tri-substituted Bromonapthalene											
.130	$1,6,8\text{-}(NO_2)_3C_{10}H_4\text{-}2\text{-}Br + CH_3O^-$	CH_3OH	A = B = 0.003-0.006	k AB	0	2.0	-2					(29)
					15	5.3	-2					
					25	1.67	-1	14	3	9		
.131	$1,6,8\text{-}(NO_2)_3C_{10}H_4\text{-}2\text{-}Br + C_2H_5O^-$	CH_3OH	A = B = 0.003-0.006	k AB	15	9.5	-2					(29)

COMMENTS

Classification. The aryl halides undergoing solvolysis are grouped under the headings: Mono-substituted fluorobenzenes-Mono-substituted chlorobenzenes-Mono-substituted bromobenzenes-Mono-substituted iodobenzene-Di-substituted fluorobenzenes - Di-substituted chlorobenzenes - Di-substituted bromobenzenes-Di-substituted iodobenzenes-Tri-substituted chlorobenzenes-Mono-substituted napthyl chlorides-Di-substituted napthylchlorides-Tri-substituted napthyl chlorides Tri-substituted napthylbromides. In each group the halides are arranged in order of complexity of substituents: alkyl, aryl, hydroxy, alkoxy, carboxy, nitro, amino, sulfonyl and halo with the halogens arranged in order of increasing atomic weight.

Comments by Literature References. (1) Rate law followed by titration for B for only 10 to 50 % reaction. No proof of order with respect to A and B independently. Original data in min. (8) Original data in minutes. (10) Original data in min. Claim data of (21) is high. Neither author states concentrations used and difference in rate constants may be due to salt effects. (13) Rate law followed by

COMMENTS *(continued)*

titration for B for only 10 to 50 % reaction. No proof of order with respect to A and B independently. Original data in minutes. (14) Original data in hours. (15) Original k assumed to be in seconds. (16)(17)(18) Original data in min. No proof of order with respect to A and B independently. (24)(25) Original data in minutes. (26) Original data in hours. (28)(29)(30) Original data in minutes. No proof of order with respect to A and B independently.

Comments by Reactions. **(.14) (.16)** Values of rate constants by several authors included to indicate extent of variation **(.20) (.22) (.24)** Calculations based upon only two points at 7 and 13 hours. **(.27)** Initial rate. Converted from pseudo first order constant in hours. **(.29)** Rate constant based upon first 10 % reaction as rate decreased very rapidly and I_2 from a side reaction appeared after this point. **(.36) (.37)** No drift of rate constants observed from 5 to 95 % reaction even with neglect of reaction of B with second halogen. **(.38)** Simultaneous solvolysis of both halogens separated into respective rate constants by analysis for remaining B giving total halogen reacted and for Cl^- independently. See (.70). **(.39) (.40)** Rate law valid for 5 to 95 % reaction and L separated and identified to demonstrate that only fluorine reacted. **(.43)** Rate constants of both investigators listed. Differences in value may be due to differences in concentration. **(.61)** Rate law valid over course, but authors estimate value to be about 9 % low because no correction made for partial removal of B by reaction with H_2O in solvent. **(.70)** Simultaneous solvolysis of both fluorine and chlorine. The latter determined by analysis for Cl^- and the former by analysis for unreacted B giving total solvolysis and F^- by difference. See (.38). **(.73)** Plot of log k vs. 1/T shows excellent agreement between data of all investigators whether analysis was for B or M. Average values of A and E obtained from plot. **(.75)** Results of both investigators included as (14) followed disappearance of B and (21) followed formation of M. **(.79)** Less than 1 % deviation from rate law up to 90 % reaction. In presence of excess B at 170° only 15 % solvolysis of second chloride after 50 hours. **(.110)** Initial concentrations not specified by (21) and differences in rate constants may be due to salt effects. **(.111)** Initial concentrations not specified by (10)(19) and (21) so differences in rate constants may be due to salt effects. **(.117) (.118)** Initial rate. Converted from original pseudo first order constant in hours. **(.119) (.121) (.123)** Second

COMMENTS *(continued)*

molecule of B reacts with part of napthol formed to produce naptholate ion. Values listed are average of those calculated by authors on basis of either only napthol, or only naptholate ion forming. (.127) Second order rate law not valid as k does not remain constant over course. Value gives only qualitative reaction velocity at conditions specified.

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ESTER AMMONOLYSIS

Alkyl ester of aliphatic carboxylic acid

Reaction: $RCOOR' + NH_3 \longrightarrow RCONH_2 + R'OH$
(A) (B) (L) (M)

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and 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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$HCOOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	4.3	-4				*	(3)
.2	$HCOOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	7.7	-4				*	(4)
.3	$CH_3COOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	1.4	-6				*	(3)
.4	$CH_3COOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.2	-5				*	(4)
.5	$CH_3COOCH_3 + NH_3$	$CH_3C_2H_3(OH)_2$	A = 0.7; B = 2.5			k AB	30	4.9	-6				*	(4)
.6	$CH_3COOCH_3 + NH_3$	$O(C_2H_4OH)_2$	A = 0.7; B = 2.5			k AB	30	8.0	-6				*	(4)
.7	$CH_3COOCH_3 + NH_3$	$HO(CH_2)_3OH$	A = 0.7; B = 2.5			k AB	30	6.0	-6				*	(4)
.8	$CH_3COOCH_3 + NH_3$	dioxane	A = 1; B = 2	H_2O	5	k AB	25	3.7	-7				*	(1)
					10		25	2.84	-7					(6)
							35	4.38	-7					
							45	6.45	-7	7.7	1.2	-1		
					15		30	1.1	-6					(4)
					30		30	5.86	-6				*	(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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.8	$CH_3COOCH_3 + NH_3$ *(continued)*	dioxane	A = 1; B = 2	CH_3OH	10	k AB	25	3.67	-8					(6)
							35	5.47	-8					
							45	7.78	-8	7.1	6	-3		
				$C_2H_4(OH)_2$	5		25	3.32	-7					
							35	4.77	-7					
							45	6.75	-7	6.7	3	-2		
		dioxane + H_2O 10 M/l		CH_3OH	5		30	4.8	-7					(4)
				$(CH_3)_3COH$	5		30	6.9	-7					
				$1,3\text{-}C_4H_8(OH)_2$	5		30	7.3	-7					
				$1,3\text{-}C_3H_6(OH)_2$	5		30	9.2	-7					
				$C_2H_5OC_2H_4OH$	5		30	9.4	-7					
				$(CH_3)_2C(OH)CH_2OH$	5		30	1.0	-6					
				$1,2\text{-}C_3H_6(OH)_2$	5		30	1.7	-6					
				$C_2H_4(OH)_2$	5		30	2.8	-6					
				$O(C_2H_4OH)_2$	5		30	2.8	-6					
				$C_3H_5(OH)_3$	5		30	8.0	-6					
		dioxane + H_2O 30 M/l	A = 1; B = 2	CH_3OH	3		30	6.56	-6				*	(5)
				$C_2H_4(OH)_2$	1.5		30	9.28	-6					
				sorbitol	0.5		30	1.22	-5					
				cyclo-$1,2\text{-}C_6H_{10}(OH)_2$	1.5		30	8.95	-6					
				$(CH_3)_2NC_2H_4OH$	1.5		30	1.08	-5					
.9	$CH_3COOC_2H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.2	-5				*	(4)
.10	$CH_3COOC_2H_5 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	1.5	-7				*	(3)
			B = 2	$C_2H_4(OH)_2$	5		25	1.82	-7				*	(6)
							35	2.21	-7					
							45	3.42	-7	5.9	4	-3		

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.11	$CH_3COOC_3H_7 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.2	-5				*	(4)
.12	$CH_3COOC_3H_7 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	1.4	-7				*	(3)
			B = 2	$C_2H_4(OH)_2$	5		25	1.58	-7				*	(6)
							35	2.29	-7					
							45	3.21	-7	6.7	1.5	-2		
.13	$CH_3COOCH(CH_3)_2 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	7.5	-6				*	(4)
.14	$CH_3COOCH(CH_3)_2 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	6.4	-8				*	(3)
			B = 2	$C_2H_4(OH)_2$	5		25	4.75	-8				*	(6)
							35	7.06	-8					
							45	1.12	-7	8.1	4	-2		
.15	$CH_3COOC_4H_9 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.2	-5				*	(4)
.16	$CH_3COOC_4H_9 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	7.6	-8				*	(3)
.17	$CH_3COOCH_2CH(CH_3)_2 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.0	-5				*	(4)
.18	$CH_3COOCH_2CH(CH_3)_2 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	5.6	-8				*	(3)
.19	$CH_3COOCH(CH_3)C_2H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	2.5	-6				*	(4)
.20	$CH_3COOCH(CH_3)C_2H_5 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	4.0	-8				*	(3)
.21	$CH_3COOC(CH_3)_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	4.2	-7				*	(4)
.22	$CH_3COOC(CH_3)_3 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	3.1	-8				*	(3)

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.23	$CH_3COOCH_2CH_2CH_2CH_2CH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.1	-5				*	(4)
.24	$CH_3COOCH_2CH_2CH_2CH_2CH_3 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	7.2	-8				*	(3)
.25	$CH_3COOCH_2C_6H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.2	-5				*	(4)
.26	$CH_3COOCH_2C_6H_5 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	25	2.7	-7					(3)
.27	$C_2H_5COOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	7.8	-7				*	(3)
.28	$C_2H_5COOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	7.5	-6				*	(4)
.29	$(CH_3)_2CHCOOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	2.4	-7				*	(3)
.30	$(CH_3)_2CHCOOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.5	-6				*	(4)
.31	$(CH_3)_3CCOOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	4	-9				*	(3)
.32	$(CH_3)_3CCOOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	3	-8				*	(4)
	Ester of Unsaturated aliphatic carboxylic acid and alcohol													
.33	$CH_3CH{:}CHCOOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	8.1	-7				*	(3)
.34	$CH_3CH{:}CHCOOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	2.9	-6				*	(4)

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	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
	Ester of Aryl-substituted aliphatic carboxylic acid and alcohol													
.35	$C_6H_5CH_2COOCH_3 + NH_3$	CH_3OH	A = 0.3; B = 0.1			k AB	25	1.34	-7				*	(2)
			" B = 0.2				25	1.52	-7					
			" B = 0.45				25	2.33	-7					
			" B = 0.57				25	2.70	-7					
			A = 0.2; B = 0.3	NH_4Cl	0.10		25	8.2	-8					
					0.04		25	1.00	-7					
				$NaOCH_3$	0.021		25	1.3	-6					
			A = 0.7; B = 3	H_2O	10		25	1.3	-6					(3)
.36	$C_6H_5CH_2COOCH_3 + NH_3$	$C_2H_4(OH)_2$				k AB	30	1.0	-5				*	(4)
	Ester of Hydroxy-substituted aliphatic carboxylic acid and alcohol													
.37	$CH_3CH(OH)COOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 3	H_2O	10	k AB	25	1.0	-5				*	(3)
.38	$CH_3CH(OH)COOCH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.7	-4				*	(4)
.39	$CH_3CH(OH)COOCH_3 + NH_3$	dioxane	A = 3; B = 2			k AB	25	4.38	-7				*	(6)
							35	6.28	-7	6.6	3	-2		
			A = 5; B = 2				25	1.05	-6					
							35	1.52	-6	6.8	1.0	-1		
			A = 2; B = 2	$C_2H_4(OH)_2$	0.5		25	5.22	-7					
					0.5		35	6.96	-7	5.2	4	-2		
			A = 4; B = 2	$C_2H_4(OH)_2$	0.5		25	1.12	-6					
					0.5		35	1.50	-6	5.4	1.0	-2		
			A = 0.7; B = 3	H_2O	10		30	1.1	-6	12			*	(3)

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ 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	Literature
.40	$CH_3CH(OH)COOC_2H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.5	-4				*	(4)
.41	$CH_3CH(OH)COOC_2H_5 + NH_3$	dioxane	A = 0.7; N = 3	H_2O	10	k AB	30	4.3	-6	10			*	(3)
.42	$CH_3CH(OH)COOC_3H_7 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.2	-4				*	(4)
.43	$CH_3CH(OH)COOC_3H_7 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	2.2	-6	11			*	(3)
.44	$CH_3CH(OH)COOCH(CH_3)_2 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	3.7	-5				*	(4)
.45	$CH_3CH(OH)COOCH(CH_3)_2 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	6.7	-7	10			*	(3)
.46	$CH_3CH(OH)COOCH_2CH_2CH_2CH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	9.5	-5				*	(4)
.47	$CH_3CH(OH)COOCH_2CH_2CH_2CH_3 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	2.0	-6	9			*	(3)
.48	$CH_3CH(OH)COOCH_2CH(CH_3)_2 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	7.8	-5				*	(4)
.49	$CH_3CH(OH)COOCH_2CH(CH_3)_2 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	1.3	-6	12			*	(3)
.50	$CH_3CH(OH)COOCH(CH_3)C_2H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	3.5	-5				*	(4)
.51	$CH_3CH(OH)COOCH(CH_3)C_2H_5 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	5.5	-7	12			*	(3)
.52	$CH_3CH(OH)COOC(CH_3)_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	2.7	-6				*	(4)
.53	$CH_3CH(OH)COOC(CH_3)_3 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	1.2	-8				*	(3)
.54	$CH_3CH(OH)COOCH_2CH_2CH_2CH_2CH_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	9.1	-5				*	(4)

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.55	$CH_3CH(OH)COOCH_2CH_2CH_2CH_2CH_3 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	1.4	-6	10			*	(3)
.56	$CH_3CH(OH)COOCH_2CH{:}CH_2 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	1.5	-4				*	(4)
.57	$CH_3CH(OH)COOCH_2CH{:}CH_2 + NH_3$	dioxane	A = 0.7; B = 3	H_2O	10	k AB	30	1.0	-5	11			*	(3)

COMMENTS

Classification. The esters undergoing ammonolysis are grouped in order of the aliphatic acids, saturated, unsaturated, aryl-substituted and hydroxy-substituted. Within each acid group the esters are arranged in order of increasing complexity of the esterifying alcohol.

General. This reaction system is much more complex than indicated by the pseudo second order rate law, the catalytic effect of hydroxyl compounds not being included in this expression. In most cases this second order rate law is not valid over the course of the reaction and generally rate constants are observed to decrease with the progress of the reaction. In a few isolated cases the calculated rate constants increase with the course of the reaction. For the following reactions the rate constants decrease with the progress of the reaction and values tabulated are essentially initial rates: (.1) (.3) (.16) (.18) (.19) (.20) (.21) (.22) (.24) (.27)(.29)(.30)(.31)(.32) (.33) (.37) (.41) (.43) (.45) (.47) (.49) (.51) (.52) (.53) (.55) (.57). In the case of the following reactions the rate constants decrease with the progress of the reaction and the values tabulated are based upon 50 % reaction: (.2)(.4)(.5)(.6) (.7) (.9) (.11) (.13) (.15) (.17) (.23) (.25)(.28)(.34)(.36)(.38)(.40)(.42)(.44)(.46)(.48)(.50)(.54)(.56).

COMMENTS *(continued)*

Reaction. **(.8)** Selected data of ([4]), rate constants decrease with course andd value is based upon 50 % reaction. In presence of water as a catalyst ([5]) separates rate constants into ammonolysis and solvolysis factors. Values tabulated are for only ammonolysis. With ethylene glycol as catalyst ([6]) observes that rate constants increase with course and values tabulated are for 20 % reaction. **(.10)** **(.12)** **(.14)** Rate constants decrease with course and values of ([3]) are initial rates. With ethylene glycol as catalyst ([6]) observes that rate constants increase with course and values are for 20 % reaction. **(.35)** Rate constants decrease with course except in presence of added NH_4Cl under which conditions rate constants increase markedly. Values are essentially initial rates. **(.39)** Rate constants decrease with course and values of ([3]) are initial rates. With ethylene glycol as catalyst ([6]) observes that rate constants increase as reaction proceeds. Values are based upon 20 % reaction.

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([4]) M. Gordon, J.G. Miller, A.R. Day, *ACS* 1949, 71, 1245.

([5]) T.A. Koch, J.G. Miller, A.R. Day, *ACS* 1953, 75, 953.

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AMMONOLYSIS

Ester of Aromatic carboxylic acid and alcohol

Reaction type: $ArCOOR + NH_3 \longrightarrow ArCONH_2 + ROH$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and 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	E	Comments	Literature
.1	$C_6H_5COOCH_3 + NH_3$	CH_3OH	A = 0.7; B = 2.5-2.8	H_2O	10	k AB	25	5.2	-7		*	(2)
		$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	7.8	-7		*	(3)
		dioxane	A = 0.5-0.7; B = 2.5-2.8	H_2O	10	k AB	25	4.1	-8		*	(2)
.2	$C_6H_5COOC_2H_5 + NH_3$	NH_3	A = 1.4			k A	25	3.9	-8		*	(1)
				NH_4Cl	0.37		0	2.2	-7			
					0.37		25	7.6	-7			
					0.74		0	4.4	-7			
					0.74		25	1.60	-6	8		
				NH_4Br	0.37		25	5.8	-7			
				NH_4ClO_4	0.37		25	4.3	-7			
				$C_6H_5COONH_4$	0.37		25	9.3	-7			
.3	$C_6H_5COOC_3H_7 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	5.0	-7		*	(3)
		dioxane	A = 0.5-0.7; B = 2.5-2.8	H_2O	10	k AB	25	1.8	-8		*	(2)
.4	$C_6H_5COOCH(CH_3)_2 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	2.3	-7		*	(3)
		dioxane	A = 0.5-0.7; B = 2.5-2.8	H_2O	10	k AB	25	1.6	-8		*	(2)

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	E	Comments	Literature
.5	$C_6H_5COOC(CH_3)_3 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	4.5	-8		*	(3)
		dioxane	A = 0.5-0.7; B = 2.5-2.8	H_2O	10	k AB	25	5	-9		*	(2)
.6	$C_6H_5COOC_6H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	7.9	-7		*	(3)
		dioxane	A = 0.5-0.7; B = 2.5-2.8	H_2O	10	k AB	25	1.7	-5		*	(2)
.7	$C_6H_5COOCH_2C_6H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	30	6.4	-7		*	(3)
		dioxane	A = 0.5-0.7; B = 2.5-2.8	H_2O	10	k AB	25	2.4	-8		*	(2)

COMMENTS

General. Reactions much more complex than indicated by second order rate law which does not include role of catalyst. In general calculated specific rate constants decrease with progress of reaction.

COMMENTS *(continued)*

Literature. (1) Pseudo first order rate law observed over course as B in excess. Units converted from original hours. (2) Calculated rate constants decrease with progress of reaction in methanol. Data for reactions in dioxane calculated arbitrarily from only one measured point at about 620 hours. Units converted from original hours. (3) Calculated rate constants observed to decrease over course. Values based upon first 50 % reaction. Units converted from original hours.

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AMMONOLYSIS

Ester of Aliphatic carboxylic acid and phenol

Reaction type: $RCOOAr + NH_3 \longrightarrow RCONH_2 + ArOH$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	% reaction	Temperature	$k = k^o \times 10^n$ k^o	n	Literature
.1	$CH_3COOC_6H_5 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	50	30	2.1	-4	(2)
.2	$CH_3COO\text{-}\alpha\text{-}C_{10}H_7 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	50	30	2.1	-6	(2)
		dioxane	A = 0.7; B = 2.5-2.8	H_2O	10	k AB	initial	25	2.0	-8	(1)
.3	$CH_3COO\text{-}\beta\text{-}C_{10}H_7 + NH_3$	$C_2H_4(OH)_2$	A = 0.7; B = 2.5			k AB	50	30	2.1	-6	(2)
		dioxane	A = 0.7; B = 2.5-2.8	H_2O	10	k AB	initial	25	2.3	-8	(1)

COMMENTS

Calculated second order rate constants drift downward with progress of reaction. See 212.541 and 212.542. Units converted from original data in hours.

LITERATURE

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AMINOLYSIS

Ester of Aliphatic carboxylic acid and alcohol

Liquid phase

Reaction type: $RCOOR' + R''R'''NH \longrightarrow RCONR''R''' + R'OH$

Amounts are in M/l.
Rate constants are in M/l and sec.
sec.

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	% reaction	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$CH_3COOCH_3 + CH_3NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		2.4	-5		(1)
.2	$CH_3COOCH_3 + C_2H_5NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		3.1	-6		(1)
.3	$CH_3COOCH_3 + n\text{-}C_3H_7NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		2.4	-6		(1)
.4	$CH_3COOCH_3 + (CH_3)_2CHNH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		1.2	-7		(1)
.5	$CH_3COOCH_3 + n\text{-}C_4H_9NH_2$	CH_3OH	A = B = (1-2)			k AB	25		4.2	-6	*	(3)
				H_2O	0.5		25		3.9	-6		
				$C_4H_9NH_3Cl$	0.1		25		2.2	-6		
		C_2H_5OH	A = B = (1-2)			k AB	25		9.7	-7		
		$i\text{-}C_3H_7OH$	A = B = (1-2)			k AB	25		3.6	-7		
		CH_3COOCH_3	A = B = (1-2)			k AB	25		2.8	-8		
		pet. ether	A = B = (1-2)			k AB	25		8.1	-7		
		dioxane	A = B = (1-2)			k AB	25		3.0	-8		
				H_2O	11		25		1.3	-6		
			A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5		25		2.9	-6		(1)

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	% reaction	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.6	$CH_3COOCH_3 + (CH_3)_2CHCH_2NH_2$	CH_3OH	A = B = (1-2)			k AB	25		1.8	-6	*	(3)
		dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		1.2	-6		(1)
.7	$CH_3COOCH_3 + C_2H_5(CH_3)CHNH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		6	-8		(1)
.8	$CH_3COOCH_3 + n\text{-}C_5H_{11}NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		2.7	-6		(1)
.9	$CH_3COOCH_3 + CH_2{:}CHCH_2NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		5.7	-7		(1)
.10	$CH_3COOCH_3 + C_6H_5CH_2NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		4.6	-7		(1)
.11	$CH_3COOCH_3 + C_6H_5CH_2CH_2NH_2$	$n\text{-}C_6H_{14}$	A = 1.0; B = 2.0	CH_3OH	10	k AB	30	24	8.6	-7	*	(6)
							30	34	8.8	-7		
							30	57	8.5	-7		
			A = 1.0; B = 1.0	CH_3OH	10	k AB	30	8	5.4	-7		
							30	15	5.4	-7		
							30	32	5.1	-7		
			A = 1.0; B = 0.5	CH_3OH	10	k AB	30	9	3.2	-7		
							30	20	3.1	-7		
							30	28	3.0	-7		
		$cyclo\text{-}C_6H_{12}$	A = 1.0; B = 2.0	CH_3OH	10	k AB	30	26	9.0	-7		
			A = 1.0; B = 1.0		10		30	9	5.6	-7		
			A = 1.0; B = 0.5		10		30	11	3.2	-7		
		C_6H_6	A = 1.0; B = 2.0	CH_3OH	10	k AB	30	11	5.42	-7		
			A = 1.0; B = 1.0		10		30	8	2.26	-7		
			A = 1.0; B = 0.5		10		30	4	1.17	-7		

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	% reaction	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.11	$CH_3COOCH_3 + C_6H_5CH_2CH_2NH_2$ *(continued)*	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	20	8.8	-7		
			A = 1.0; B = 2.0	CH_3OH	10		30	12	3.95	-7		
			A = 1.0; B = 1.0		10		30	8	1.58	-7		
			A = 1.0; B = 0.5		10		30	7	7.3	-8		
			A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5		25		8.9	-7		(1)
.12	$CH_3COOCH_3 + C_6H_5CH_2(CH_3)CHNH_2$	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	20	3.9	-8	*	(6)
.13	$CH_3COOCH_3 + HOC_2H_4NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		3.2	-6		(1)
.14	$CH_3COOCH_3 + 3,4\text{-}(CH_3O)_2C_6H_3CH_2CH_2NH_2$	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	20	1.07	-6	*	(6)
.15	$CH_3COOCH_3 + H_2NC_2H_4NH_2$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	k AB	25		6.6	-6		(1)
.16	$CH_3COOCH_3 + n\text{-}C_4H_9(CH_3)NH$	CH_3OH	A = B = (1-2)			k AB	25		3.0	-8	*	(3)
.17	$CH_3COOCH_3 + (CH_3)_2CHCH_2(CH_3)NH$	CH_3OH	A = B = (1-2)			k AB	25		5	-9	*	(3)
.18	$CH_3COOCH_3 + C_6H_5CH_2CH_2(CH_3)NH$	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	20	3.6	-8	*	(6)
.19	$CH_3COOCH_3 + (-)\text{-}C_6H_5CH_2(CH_3)CH(CH_3)NH$	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	5	1.91	-8	*	(6)
.20	$CH_3COOCH_3 + (\pm)\text{-}C_6H_5CH_2(CH_3)CH(CH_3)NH$	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	5	1.66	-8	*	(6)
.21	$CH_3COOCH_3 + C_6H_5CH_2CH_2(C_2H_5)NH$	dioxane	A = 1.0; B = 2.0	H_2O	10	k AB	30	5	1.96	-8	*	(6)
.22	$CH_3COOCH_3 + C_6H_5CH_2CH_2(n\text{-}C_3H_7)NH$	dioxane	A = 1.0; B = 2.9	H_2O	10	k AB	30	5	9.8	-9	*	(6)
.23	$CH_3COOCH_3 + (CH_2)_5NH$	CH_3OH	A = B = (1-2)			k AB	25		1.3	-7	*	(3)
				$NaOCH_3$	0.02		25		1.4	-6		

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	% reaction	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.24	$CH_3COOCH_3 + O(CH_2CH_2)_2NH$	CH_3OH	A = B = (1-2)			k AB	25		3.6	-8	*	(3)
				$NaOCH_3$	0.02		25		1.9	-6		
.25	$CH_3COOC_2H_5 + n\text{-}C_4H_9NH_2$	CH_3OH	A = B = (1-2)			k AB	25		2.2	-6	*	(3)
		C_2H_5OH				k AB	25		7.0	-8		
		$(CH_3)_2CHOH$	A = B = (1-2)			k AB	25		6.1	-8	*	(3)
		dioxane	A = B = (1-2)			k AB	25		6.1	-9		
.26	$CH_3COOCH(CH_3)_2 + n\text{-}C_4H_9NH_2$	CH_3OH	A = B = (1-2)			k AB	25		7.2	-7	*	(3)
		C_2H_5OH	A = B = (1-2)			k AB	25		1.6	-8		
		$(CH_3)_2CHOH$	A = B = (1-2)			k AB	25		3.1	-9		
		dioxane	A = B = (1-2)			k AB	25		6.1	-9		
.27	$CH_3(CH_2)_4COOCH_3 + n\text{-}C_4H_9NH_2$	CH_3OH	A = B = (1-2)			k AB	25		4.5	-7	*	(3)
		$(CH_3)_2CHOH$	A = B = (1-2)			k AB	25		6.1	-8		
.28	$C_6H_5CH_2COOC_2H_5 + n\text{-}C_4H_9NH_2$	B	A = 2.8			k AB	25		2.4	-7	*	(4) (5)
			B = 5.4	$C_4H_9NH_2 \cdot HCl$	0.1		25		1.29	-6		
				$\cdot HBr$	0.1		25		1.07	-6		
				$\cdot HNO_3$	0.1		25		8.1	-7		
				$\cdot HSCN$	0.1		25		7.8	-7		

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	% reaction	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.28	$C_6H_5CH_2COOC_2H_5 + n\text{-}C_4H_9NH_2$ *(continued)*	B	A = 2.8 B = 5.4	$C_4H_9NH_2 \cdot HI$	0.1	k AB	25		7.1	-7		
				$\cdot HClO_4$	0.1		25		5.8	-7		
				$\cdot HC_2H_3O_2$	0.1		25		1.08	-6		
				H_2O	0.2		25		3.7	-7		
					0.5		25		4.2	-7		
					1.0		25		5.7	-7		
					2.0		25		9.0	-7		
					5.6		25		1.97	-6		
					11		25		2.8	-6		
.29	$CH_3CH(OH)COOCH_3 + (CH_3)_2NH$	dioxane	A = 1.0; B = 2.0			k AB	25	50	2.7	-7	*	(2)
				$C_2H_4(OH)_2$	5		25		2.3	-6		
.30	$CH_3CH(OH)COOCH_3 + (CH_2)_5NH$	dioxane	A = 1.0; B = 2.0			k AB	25		8.7	-8		(2)
				$C_2H_4(OH)_2$	5		25		5.0	-7		
.31	$CH_3CH(OH)COOCH_3 + O(CH_2CH_2)_2NH$	dioxane	A = 1.0; B = 2.0			k AB	25		3.0	-8		(2)
				$C_2H_4(OH)_2$	5		25		6.7	-8		

COMMENTS

Classification. The esters undergoing aminolysis are grouped according to order of increasing complexity of the aliphatic acids. Within each acid group the esters are arranged in the order of increasing complexity of the esterifying alcohol. Each ester is then listed with a series of amines in order of increasing complexity of amine with primary amines preceding secondary and diamines preceding cyclic amines.

General. This reaction system is much more complex than indicated by the pseudo second order rate law, the catalytic

COMMENTS *(continued)*

effect of hydroxyl compounds not being included in this expression. Further, in most cases the second order rate law does not hold over the course but generally decreases with the progress of the reaction as well as with a decrease in the initial concentration of amine. In those reactions where a drift in the rate law was observed, the % reaction for which the rate constant was calculated is listed.

Literature. [1] units converted from hours. In presence of ethylene glycol as catalyst rate law observed to be valid over course. [2] units converted from hours. [3] units converted from hours. Noted that in some reactions values of rate constant decreased, in some increased, and in some increased to maximum and then decreased with progress of reaction. [4] [5] units converted from hours. Authors observed rate law valid over course but value of specific-rate constant dependent upon initial ratio of reactants. [6] Units converted from hours.

Reactions. (.5)(.6) Value of specific constant drifted with progress of reaction but extent of reaction for which rate constant calculated not specified. (.11) Selected data to indicate dependence of specific rate constant upon progress of reaction and initial concentration of reactants. (.12) (.14) For dependence of value of specific rate constant upon extent reaction and initial concentrations see (.11). (.16) (.17) Value of specific rate constant drifted with progress of reaction but extent of reaction for which rate constant calculated not specified. (.18) (.19) (.20) (.21) (.22) For dependence of value of specific rate constant upon extent reaction and initial concentrations see (.11). (.23) (.24) (.25) (.26) (.27) Value of specific rate constant drifted with progress of reaction but extent of reaction for which rate constant calculated not specified. (.28) Selected data. Rate law valid over course, but value of specific rate constant dependent upon ratio of initial concentrations of reactants. (.29) Value of specific rate constant drifted with extent reaction in absence of ethylene glycol but remained constant in presence of ethylene glycol as catalyst.

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AMINOLYSIS

Ester of Aliphatic carboxylic acid and phenol

Reaction type: $RCOOAr + R'R''NH \longrightarrow RCONR'R'' + ArOH$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and 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	Comments
.1	$CH_3COOC_6H_5 + (C_2H_5)_2NH$	dioxane	A = 1.0; B = 2.0			*k* AB	25	7.9	-7	*
.2	$CH_3COOC_6H_5 + (n\text{-}C_3H_7)_2NH$	dioxane	A = 1.0; B = 2.0			*k* AB	25	2.6	-7	
.3	$CH_3COOC_6H_5 + (n\text{-}C_4H_9)_2NH$	dioxane	A = 1.0; B = 2.0			*k* AB	25	3.1	-7	
.4	$CH_3COOC_6H_5 + (HOC_2H_4)_2NH$	dioxane	A = 1.0; B = 2.0	$C_2H_4(OH)_2$	5	*k* AB	25	8.6	-6	*
.5	$CH_3COOC_6H_5 + O(CH_2CH_2)_2NH$	dioxane	A = 1.0; B = 2.0			*k* AB	25	9.5	-5	*
				$C_2H_4(OH)_2$	5		25	7.6	-5	

COMMENTS

General. Units converted from original hours. Usual catalysis by ethylene glycol not observed, see 212.541, 212.542, 212.543, and 212.544. Rate with added ethylene glycol observed to be slow in each case but value of specific rate constant not determined.

Reaction. (.1) Calculated rate constant drifted during course and value is for 50 % reaction. (.4) Calculated rate constant drifted during course and value is for 50 % reaction. System is immiscible in absence of ethylene glycol. (.5) In absence of ethylene glycol calculated rate constant drifted with progress of reaction and value is for 50 % conversion.

LITERATURE

E.M. Arnett, J.G. Miller, A.R. Day, *ACS* 1951, 73, 5393.

AMINOLYSIS
Thio ester

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $RCOSR' + R''R'''NH \longrightarrow RCONR''R''' + R'SH$

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$CH_3COSC_2H_5 + n\text{-}C_4H_9NH_2$	H_2O	$10^4A = (1.2\text{-}7.6)$; B = 0.0049	$-dA/dt = kA$	0	7.62	-5
			B = 0.0104		0	2.25	-4
			B = 0.0166		0	4.70	-4
			B = 0.0182		0	5.25	-4
				$k = k'B[OH^-] + k''[OH^-]$	0	k' = 7.53	+2
					0	k = 1.08	-2
.2	$CH_3COSCH_2CH_2NHCOCH_3 + n\text{-}C_4H_9NH_2$	H_2O	$10^4A = (1.7\text{-}7)$; B = 0.0055	$-dA/dt = kA$	0	1.50	-4
			B = 0.0069		0	2.18	-4
			B = 0.0110		0	4.24	-4
			B = 0.0138		0	5.74	-4
				$k = k'B[OH^-] + k''[OH^-]$	0	k' = 1.25	+3
					0	k'' = 1.85	-2

COMMENTS

Reactions accompanied by direct solvolysis of thioester and rate constant k'' determined in absence of B. Aminolysis reaction could also be expressed in terms of $k'''AB^{1.5}$. Pseudo first order constants measured as B in excess. Units converted from original minutes.

LITERATURE

P.J. Hawkins, D.S. Tarbell, *ACS* 1953, 75, 2982.

SOLVOLYSIS

Alkyl Thio ester of aliphatic carboxylic acid

Liquid phase

Reaction types: $RCOSR' + R''OH \longrightarrow RCOOH + R'SR''$

$RCOSR' + R''O^- \longrightarrow RCOO^- + R'SR''$

or $RCOSR' + 2OH^- \longrightarrow RCOO^- + R'S^- + H_2O$

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents at end of table.

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.3	$CH_3COSCH_3 + H_2O$	WA43*	A = 0.1	HCl	0.1-0.2	$k\,A[H^+]$	30	6.8	-6				*	(4)
							40	1.49	-5	17	6	6		
		WA62*	A = 0.1	HCl	0.13-0.19		30	3.23	-6					
							40	8.03	-6	17	6	6		
.4	$CH_3COSCH_3 + 2OH^-$	WA43*	10^2A = (1.8-3.5)			$k\,AB =$	0	1.01	-2					(4)
			10^2B = (6-9)			$-dA/dt$	10	2.20	-2					
							20	4.58	-2	12	5	7		
		WA62*	10^2A = (1.7-2.5)				0	7.77	-3					
			10^2B = 6				10	1.77	-2					
							20	4.02	-2	13	2	8		
.5	$CH_3COSC_2H_5 + 2OH^-$	H_2O	10^4A = (2.4-4.6)			$k\,AB =$	0	1.08	-2					(1)
			10^3B = (5-10)			$-dA/dt$								
.6	$CH_3COSCH(CH_3)_2 + H_2O$	WA43*	10^2A = (7.7-8.8)	HCl	0.11-0.12	$k\,A[H^+]$	30	3.07	-6				*	(4)
							40	9.0	-6	19	2	8		
		WA62*	10^2A = (7-8)	HCl	0.13-0.19		30	1.83	-6					
							40	5.22	-6	20	2	8		

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.7	$CH_3COSCH(CH_3)_2 + 2OH^-$	WA43*	$10^2A = (1.2\text{-}1.7)$ $10^2B = (4\text{-}6)$			$k\,AB$	0	1.82	-3					(4)
							20	1.46	-2					
							30	4.03	-2	16.8	5	10		
		WA62*	$10^2A = (1.5\text{-}10)$ $10^2B = (4\text{-}7)$				0	1.45	-3					
							20	1.36	-2					
							30	3.52	-2	17.6	1.6	11		
.8	$CH_3COSCH_2CH_2CH_2CH_3 + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$k\,A[H^+]$	25	1.04	-5					(3)
							30	1.66	-5					
							37	3.37	-5	18	2	8		
.9	$CH_3COSCH_2CH_2CH_2CH_3 + 2OH^-$	H_2O	$10^4A = 3$ $10^2B = 1$			$k\,AB$	25	7.98	-2				*	(3)
							30	1.19	-1					
							37	1.88	-1	13	5	8		
.10	$CH_3COSCH_2CH(CH_3)_2 + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$k\,A[H^+]$	25	9.45	-6					(3)
							30	1.40	-5					
							37	3.37	-5	18	1.3	8		
.11	$CH_3COSCH_2CH(CH_3)_2 + H_2O$	WA43*	$10^2A = (6\text{-}7)$	HCl	0.11-0.12	$k\,A[H^+]$	30	2.37	-6				*	(4)
							41	7.2	-6	10	4	8		
		WA62*	$10^2A = 7$	HCl	0.11-0.19		30	1.66	-6					
							41	5.32	-6	11	6	8		
.12	$CH_3COSCH_2CH(CH_3)_2 + 2OH^-$	WA43*	$10^2A = (1.0\text{-}1.8)$ $10^2B = (5\text{-}7)$			$k\,AB$	0	1,38	-3					(4)
							10	4.58	-3					
							20	1.32	-2					
							30	3.73	-2	18.1	4	11		

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.12	$CH_3COSCH_2CH(CH_3)_2 + 2OH^-$ *(continued)*	WA62*	10^2A = (1.0–1.8) 10^2B = (6–7)			k AB	10	4.13	-3					(4)
							20	1.19	-2					
							30	3.53	-2	18.5	2	12		
.13	$CH_3COSC(CH_3)_3 + H_2O$	H_2O	10^4A = (1–2)	HCl	0.5–1.0	$k A[H^+]$	25	8.7	-6					(3)
							30	1.34	-5					
							37	2.62	-5	17	1.7	7		
.14	$CH_3COSC(CH_3)_3 + H_2O$	WA43*	10^2A = (6–8)	HCl	0.13–0.17	$k A[H^+]$	30	2.15	-6				*	(4)
							40	6.27	-6	20	3	8		
		WA62*	10^2A = (7–8)	HCl	0.16–0.18		30	1.37	-6					
							41	4.40	-6	21	1	9		
.15	$CH_3COSC(CH_3)_3 + 2OH^-$	WA43*	10^2A = (1–2) 10^2B = (4–8)			k AB	0	6.9	-4					(4)
							10	1.95	-3					
							30	1.43	-2	16.7	1.3	10		
		WA62*	10^2A = (1.7–2.0) 10^2B = (6–8)				0	4.3	-4					
							10	1.26	-3					
							20	3.7	-3	17.0	1.6	10		
.16	$CH_3COS(CH_2)_4CH_3 + H_2O$	H_2O	10^4A = (1–2)	HCl	0.5–1.0	$k A[H^+]$	25	1.04	-5					(3)
							30	1.78	-5					
							37	3.42	-5	18	2	8		
.17	$CH_3COS(CH_2)_5CH + H_2O$	H_2O	10^4A = (1–2)	HCl	0.5–1.0	$k A[H^+]$	25	1.10	-5					(3)
							30	1.68	-5					
							37	3.28	-5	17	2	7		

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.18	$CH_3COSCH_2CH_2CH(CH_3)_2 + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$kA[H^+]$	25	1.12	-5					(3)
							30	1.78	-5					
							37	3.40	-5	17	2	7		
.19	$CH_3COSCH_2CH{:}CH_2 + H_2O$	WA62*	$10^2A = (5\text{-}7)$	HCl	0.05-0.06	$kA[H^+]$	42	1.05	-5				*	(2)
							56	3.1	-5					
							69	7.6	-5	16.3	2	6		
.20	$CH_3COSCH_2CH{:}CH_2 + OH^-$	WA62*	$10^2A = (3.5\text{-}4.2)$			$kAB =$	-11	3.6	-3				*	(2)
			$10^2B = (9\text{-}10)$			$-dB/dt$	0	1.49	-2	18	4	12		
.21	$CH_3COSCH_2C_6H_5 + H_2O$	WA62*	$10^2A = 4.7$	HCl	0.051	$kA[H^+]$	40	4.4	-6				*	(2)
			7.2		0.070		56	2.01	-5					
			7.2		0.070		69	5.6	-5					
			4.7		0.051		69	6.6	-5	19.8	3	8		
.22	$CH_3COSCH_2C_6H_5 + OH^-$	WA62*	$10^2A = (1.6\text{-}2.4)$			$kAB =$	-11	3.1	-3				*	(2)
			$10^2B = (5.6\text{-}7.6)$			$-dB/dt$	0	1.04	-2	16	7	10		
.23	$CH_3COSC(C_6H_5)_3 + H_2O \longrightarrow$ $CH_3COSH + (C_6H_5)_3COH$	WA62*	$10^3A = 3.1$	HCl	0.011	$kA[H^+]$	40	1.27	-4				*	(2)
			3.7		0.012		56	1.12	-3					
			3.7		0.012		69	6.3	-3					
			3.1		0.011		69	6.8	-3	29.7	7	16		
.24	$CH_3COSC(C_6H_5)_3 + OH^- \longrightarrow$ $CH_3COO^- + (C_6H_5)_3CSH$	WA62*	$10^3A = 3$			kAB	-11	5.6	-4				*	(2)
			$10^2B = (2\text{-}3)$				0	2.2	-3	18	6	11		

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.25	$CH_3COSCH_2COOH + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$k\,A[H^+]$	25	6.96	-6					(3)
							30	1.08	-5					
							37	2.27	-5	18	1.3	8		
.26	$CH_3COSCH_2COO^- + OH^-$	H_2O	$10^4A = 3$ $10^2B = 1$			$k\,AB$	25	4.95	-2				*	(3)
							30	6.05	-2					
							40	1.55	-1	14.2	1.3	9		
.27	$CH_3COSCH_2CH_2COOH + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$k\,A[H^+]$	25	7.26	-6					(3)
							30	1.24	-5					
							37	2.34	-5	18	8	7		
.28	$CH_3COSCH(COOH)CH_2COOH + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$k\,A[H^+]$	25	5.51	-6					(3)
							30	8.99	-6					
							37	1.80	-5	18	8	7		
.29	$CH_3COSCH(COO^-)CH_2COO^- + OH^-$	H_2O	$10^4A = 3$ $10^2B = 1$			$k\,AB$	25	1.47	-2				*	(3)
							30	2.22	-2					
							37	3.78	-2	14	5	8		
.30	$CH_3COSCH_2CH_2NHCOCH_3 + OH^-$	H_2O	$10^4A = (1.7\text{-}7)$ $10^3B = (5\text{-}10)$			$k\,AB$	0	1.85	-2					(1)
.31	$CH_3COSCH_2CH(NHCOCH_3)COOH + H_2O$	H_2O	$10^4A = (1\text{-}2)$	HCl	0.5-1.0	$k\,A[H^+]$	25	6.65	-6					(3)
							30	1.22	-5					
							37	2.16	-5	18	1.0	8		

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	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.32	$CH_3COSCH_2CH(NHCOCH_3)COO^- + OH^-$	H_2O	$10^4A = 3$ $10^2B = 1$			k AB	25 30 37	1.22 1.83 3.05	-1 -1 -1	 14	 3	 9	*	(3)

SOLVENTS

WA43* H_2O 57 wt. % + $(CH_3)_2CO$ 43 wt. %

WA62* H_2O 38 wt. % + $(CH_3)_2CO$ 62 wt. %

COMMENTS

Comments by Literature References. (1) (3) (4) Units converted from original minutes.

Reactions. (.3) (.6) Pseudo first order constants listed by (4) have actually already been divided by concentration of catalyst acid. Confirmed by correspondence with authors. (.9) Rate law holds over at least 80 % of course. Second mole of base is consumed in neutralization of mercaptan. This is apparently a rapid reaction with no effect upon order. (.11) (.14) Pseudo first order constants listed by (4) have actually already been divided by concentration of catalyst acid. Confirmed by correspondence with authors, (.19) Pseudo first order constants listed by (2) assumed to have been divided by concentration of catalyst acid, as done by (4). (.20) Rate law not confirmed. (.21) Pseudo first order constants listed by (2) assumed to have been divided by concentration of catalyst acid, as done by (4). (.22) Rate law not confirmed. (.23) Pseudo first order constants listed by (2) assumed to have been divided by concentration of catalyst acid as done by (4). Reaction yields thio acid and alcohol rather than the customary carboxylic acid and mercaptan. This is in contrast with basic solvolysis see (.24). (.24) Rate law not confirmed. Products are carboxylate ion and

COMMENTS *(continued)*

mercaptan as with most thio esters. Mercaptan undergoes further reactions to disulfide, carbinols and unidentified oil. In contrast see acid solvolysis (.23). (.26) (.29) (.32) Linear plot of either $\log[(a-x)/(b-2x)]$ or $\log[(a-x)/(b-x)]$ since B in such large excess. Rate constant calculated from latter.

LITERATURE

(1) P.J. Hawkins, D.S. Tarbell, *ACS* 1953, **75**, 2982.

(2) B.K. Morse, D.S. Tarbell, *ACS* 1952, **74**, 416.

(2) L.H. Noda, S.A. Kuby, H.A. Lardy, *ACS* 1953, **75**, 913.

(4) P.W. Rylander, D.D. Tarbell, *ACS* 1950, **72**, 3021.

AMINOLYSIS

Alkyl Thio ester of aliphatic carboxylic acid

Reaction type: $RCOSR' + NH_2X \longrightarrow RCONX + R'SH$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and 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
.1	$CH_3COSCH_2CH_2CH_2CH_3 + NH_2OH$	H_2O	$10^4A = (1\text{-}2)$; $10^2B \simeq 1$	$NH_2OH \cdot HCl$	.03-0.4 pH = 5.4-5.9	k AB	20	9.01	-3			
							25	1.20	-2			
							30	1.73	-2	12	4	6
.2	$CH_3COSCH_2COOH + NH_2OH$	H_2O	$10^4A = (1\text{-}2)$; $10^2B \simeq 1$	$NH_2OH \cdot HCl$	.03-.04 pH = 5.4-5.9	k AB	20	1.02	-1			
							25	1.33	-1			
							30	1.7	-1	9	4	5
.3	$CH_3COSCH(COOH)CH_2COOH + NH_2OH$	H_2O	$10^4A = (1\text{-}2)$; $10^2B \simeq 1$	$NH_2OH \cdot HCl$	.03-.04 pH = 5.4-5.9	k AB	20	2.22	-1			
							25	3.02	-1			
							30	3.77	-1	10	1.3	7
.4	$CH_3COSCH_2CH(NHCOCH_3)COOH + NH_2OH$	H_2O	$10^4A = (1\text{-}2)$; $10^2B \simeq 1$	$NH_2OH \cdot HCl$	.03-.04 pH = 5.4-5.9	k AB	20	2.95	-2			
							25	3.82	-2			
							30	4.30	-2	7	3	3

COMMENTS

General. Units converted from original minutes. No correction for acid catalyzed solvolysis as reaction with hydroxyl amine about 10,000 times faster. See 212.641. Pseudo first order constants observed for about 60 % conversion since B in excess. First order constants divided by actual concentration of unionized hydroxyl amine gave second order constants which were valid over a twofold change in hydroxyl amine concentration. Reactions followed spectrophotometrically for thio ester and by ferric chloride test for the hydroxamic acid formed gave about 8 % higher values for former method.

LITERATURE

L.H. Noda, S.A. Kuby, H.A. Lardy, *ACS* 1953, 75, 913.

ESTER EXCHANGE

Aliphatic carboxylic acid + Alkyl carboxylate

Liquid phase

Reaction type: $R_1COOH + RCOOR' \longrightarrow RCOOH + R_1COOR'$
(A) (B) (L) (M)

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E
.1	$C_{17}H_{35}COOC_2H_5 + CH_3COOH$ (ethyl stearate)	trioxane	A = B = 0.28–0.49	k A	164 174	6.7 9.2	-6 -6	12

COMMENTS

Reaction approximately follows first order rate law over first two hours but variation of initial concentration indicates approximate second order rate law over 5 hour period. At 164°C the conversion is 28.8 % in 6 hours. Maximum conversion in pure liquid phase of equimolar mixtures determined to be 25.7, 35.8, 41.8 and 47 % at 122, 168, 183 and 250°C respectively.

LITERATURE

V.V. Korshak, S.V. Vinogradova, *Izv. AN SSSR, OKhN* **1951**, 179.

ESTER EXCHANGE

Alkyl carboxylate + Alkyl carboxylate

Liquid phase

Reaction type: $RCOOR' + R_1COOR'' \rightleftharpoons RCOOR'' + R_1COOR'$
(A) (B) (L) (M)

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Amount of addend	Temperature	Time (hours)	% reaction	Defined mass-action law	$k = k^o \times 10^n$ k^o	n
.1	$C_{17}H_{35}COOC_2H_5 + CH_3COOC_{16}H_{33}$ (ethyl stearate + cetyl acetate)	A + B	A = B			183	1	0	k AB	6	-6
							3	10.3			
							5	13.4			
							6	13.5			
						250	1	4.7		1.0	-5
							2	11.5			
							3	13.8			
							4	14.0			
							6	15.5			
				H_2SO_4	0.04	122	1	18.3		3	-5
							2	21.2			
							4	36.4			
							6	36.7			
					0.04	168	1	21.7		4	-5
							2	26.9			
							3	32.4			
							4	40.0			
							6	48.8			
					0.04	183	1	26.8		8	-5
							2	41.0			

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Amount of addend	Temperature	Time (hours)	% reaction	Defined mass-action law	$k = k^o \times 10^n$ k^o	n
.1	$C_{17}H_{35}COOC_2H_5 + CH_3COOC_{16}H_{23}$ (ethyl stearate + cetyl acetate) *(continued)*	A + B	A = B	H_2SO_4	0.04	183	3	51.5	k AB		
							4	52.5			
							5	54.5			
				NaOH	0.08	183	1	7.0		1.2	-5
							2	10.4			
							3	13.0			
							4	18.7			
							5	25.3			
.2	$CH_3COOC_2H_5 + C_{17}H_{35}COOC_{16}H_{33}$	L + M	A = B			183			k AB	4	-6
						250				8	-6
				H_2SO_4	0.04	122				1.7	-5
					0.04	168				3	-5
					0.04	183				6	-5
				NaOH	0.08	183				8	-6

COMMENTS

Authors based their calculated rate constants upon assumed equilibrium values which changed not only with temperature but with added catalyst. All values have been recalculated based upon the maximum conversion in presence of catalyst and negligible temperature dependence of equilibrium constant. No correction for expansion of medium with temperature has been applied and values give only order of magnitude.

LITERATURE

V. V. Korshak, S. V. Vinogradova, *Izv. AN SSSR, OKhN* **1951**, 334.

ESTER EXCHANGE

Alkyl aryl sulfonate + carboxylic acid

Reaction type: $ROSO_2Ar + R'COOH \longrightarrow R'COOR + ArSO_3H$

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.1	$CH_3(C_2H_5)CHOSO_2C_6H_4CH_3 + CH_3COOH$	B	A = 0.62	CH_3COOK	0.61	$kA + k'A[CH_3COO^-]$	60	k 1.7	-5			*	(1)
							60	k'3.9	-5				
			0.46		0.46		65	k 3.1	-5				
							65	k'6.1	-5				
			0.51	CH_3COOK	0.46		65	k 4.4	-5				
				$CH_3C_6H_4SO_3K$	0.45		65	k'5.3	-5				
			0.10	CH_3COOK	0.10		65	k 6.1	-5				
				$CH_3C_6H_4SO_3K$	0.89		65	k'5.3	-5				
.2	$\overline{CH_2CH_2CH}OSO_2C_6H_4CH_3 + CH_3COOH \longrightarrow$ $CH_3COOCH_2CH{:}CH_2 + p\text{-}CH_3C_6H_4SO_3H$	B*	A = 0.097	CH_3COOK	0.115	kA	170	4.64	-5			*	(2)
			0.095		0.102		175	7.05	-5				
			0.469		0.102		175	9.18	-5				
			0.095		0.509		180	1.07	-4	34	-3		
.3	$\overline{CH_2CH_2CH_2CH}OSO_2C_6H_4CH_3 + CH_3COOH$	B*	A = 0.099	CH_3COOK	0.107	kA	50	3.36	-5			*	(2)
			0.496		0.500		50	5.30	-5				
			0.089		0.103		55	7.62	-5				
			0.089		0.107		60	1.38	-4	30	20		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Comments	Literature
.4	$CH_2CH_2CH_2CH_2CHOSO_2C_6H_4CH_3 + CH_3COOH$	B*	A = 0.099	CH_3COOK	0.113	kA	50	4.27	-5			*	(2)
	$\longrightarrow CH_3COOCHCH_2CH_2CH_2CH_2 + p\text{-}CH_3C_6H_4SO_3H$ (S)		0.491		0.515	$k = k_S + k_E$	50	7.19	-5				
	$\longrightarrow CH_3COOH + cyclo\text{-}C_5H_8 + p\text{-}CH_3C_6H_4SO_3H$ (E)		0.098		0.103		55	8.09	-5				
			0.096		0.103		60	1.58	-4	28	7		
.5	$CH_2CH_2CH_2CH_2CH_2CHOSO_2C_6H_4CH_3 + CH_3COOH$	B*	A = 0.098	CH_3COOK	0.102	kA	75	6.03	-5			*	(2)
	$\longrightarrow CH_3COOCHCH_2CH_2CH_2CH_2CH_2 + p\text{-}CH_3C_6H_4SO_3H$ (S)		0.491		0.511	$k = k_S + k_E$	75	1.09	-4				
	$\longrightarrow CH_3COOH + cyclo\text{-}C_6H_{10} + p\text{-}CCH_3C_6H_4SO_3H$ (E)		0.099		0.102		80	1.07	-4				
			0.099		0.104		85	1.86	-4				

SOLVENTS

B* B + 1 % $(CH_3CO)_2O$

COMMENTS

Reaction. **(.1)** Predominantly ester exchange but gives 33 to 38 % olefin in products by elimination. See 422.461. **(.2)** Ester exchange accompanied by complete rearrangement of cyclopropyl to allyl ester. **(.3)** Products are 22 % cyclobutylacetate, 65 % cyclopropycarbinylacetate and 13 % allyl-carbinyl-*p*-tolylsulfonate. **(.4)** Products are 61 % cyclopentylacetate and 39 % cyclopentene by parallel elimination reaction. See 422.461. **(.5)** Products are 15 % cyclohexylacetate and 85 % cyclohexene by elimination reaction. See 422.461.

LITERATURE

(1) J.D. Roberts, W. Bennett, R.E. McMahon, E.W. Holroyd, *ACS* 1952, **74**, 4283. (2) J.D. Roberts, V.C. Chambers, *ACS* 1951, **73**, 5034.

ESTER EXCHANGE

Alkyl halide + carboxylic acid

Liquid phase

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

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

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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
.13	$CH_3CH_2CH_2(CH_3)CHBr + HCOOH$	B	A = 0.1	$HCOONa$	0.11	k A	98	2.24	-4					(3)
.14	$CH_3CH_2CD_2(CD_3)CHBr + HCOOH$	B	A = 0.1	$HCOONa$	0.11	k A	98	1.61	-4					(3)
.15	$(CH_3)_2C{:}CHCH_2Cl + CH_3COOH$	B	A = 0.03	CH_3COOK	0.05	k A	25	2.22	-6					(5)
			0.09		0.09		25	2.5	-6					
			0.05	CH_3COOK	0.047		25	2.83	-6					
				$CH_3C_6H_4SO_3K$	0.047									
			0.03	CH_3COOK	0.025		25	3.01	-6					
				$CH_3C_6H_4SO_3K$	0.07									
			0.03-0.08	CH_3COOLi	0.096		25	2.28	-6					
			0.03-0.05	CH_3COOLi	0.047		25	2.33	-6					
				$LiCl$	0.049									

No.		Medium (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
.16	$CH_2{:}CH(CH_3)_2CCl + CH_3COOH$	B	A = 0.01-0.1	CH_3COOK	0.05	k A	25	1.6	-5				*	(5)
				CH_3COOLi	0.096		25	1.4	-5					
				CH_3COOK	0.036		25	1.6	-5					
				KCl	0.012									
.17	$C_6H_5CH_2Cl + CH_3COOH$	B	A = 0.1-0.7			k A	110	2.35	-6				*	(4)
							120	5.95	-6					
							130	9.43	-6	23	4	7		
.18	$C_6H_5CH_2Cl + CH_3COO^-$	D1W*	A = 0.1; B = 0.15	CH_3COOH	0.01	k AB	50	1.90	-5				*	(1)
			0.2 0.15		0.01		50	1.63	-5					
			0.2 0.10		0.01		50	1.86	-5					
			0.1 0.15	NaCl	0.05		50	1.93	-5					
			0.1 0.15	$NaClO_4$	0.05		50	1.82	-5					
.19	$C_6H_5(CH_3)CHCl + HCOOH$	B	A = 0.15			k A	17	8.56	-4				*	(2)

SOLVENTS

D1W* Dioxane 60.72 wt % + 39.28 % H_2O

COMMENTS

(.16) First order rate constant decreases with course of reaction and levels off after about 30 % reaction at value identical to (.15). Authors attribute this to parallel rearrangement reaction. See 152.471. (.17) Addition of alkali acetate has no effect upon order or rate constant, according to authors but does shift equilibrium toward benzyl acetate. For reverse reaction see 222.741 (.22). (.18) Reaction proceeds simultaneously to solvolysis with H_2O and OH^-. See 212.471 (.346)(.347) (.19) First order rate constants calculated from over-all integrated expression for first order forward reaction and second order reverse reaction. See 222.741 (.21).

LITERATURE

([1]) G.W. Beste, L.P. Hammett, *ACS* 1940, 62, 2481. ([2]) E.D. Hughes, C.K. Ingold, A.D. Scott, *CSL* 1937, 1271.

([3]) E.S. Lewis, C.E. Boozer, *ACS* 1954, 76, 491. ([4]) L. Riccoboni, G.Barbieri, A. Pignedoli, *Ricerca Sci.* 1953, 23, 415.

([5]) W.G. Young, S. Winstein, H.L. Goering, *ACS* 1951, 73, 1958.

ESTER EXCHANGE

Carboxylic acid ester + Hydrogen halide

Liquid phase

Reaction type: $RCOOR' + HX \longrightarrow RCOOH + R'X$
(A) (B) (L) (M)

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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	Literature
.21	$HCOOCH(CH_3)C_6H_5 + HCl$	L	A = B; M = 0.15	k AB	17	3.7	-2				(1)
.22	$CH_3COOCH_2C_6H_5 + HCl$	L	A = B; M = 0.1-0.7	k AB	110	2.1	-4				(2)
					120	3.9	-4				
					130	5.4	-4	15	8	4	

COMMENTS

(.21) Second order rate constants calculated from over-all integrated rate expression for first order forward reaction and second order reverse reaction, see 222.471 (.19). (.22) Rate constants calculated from rate constants of reverse reaction and equilibrium constants, see 222.471 (.17).

LITERATURE

(1) E.D. Hughes, C.K. Ingold, A.D. Scott, *CSL* **1937**, 1271.

(2) L. Riccoboni, G. Barbieri, A. Pignedoli, *Ricerca, Sci.* 1953, 23, 415.

CONDENSATION
B-F bond formation

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$HBF_3(OH) + HF \longrightarrow HBF_4 + H_2O$	H_2O	A = B = 0.013	k AB	25	1.37	-3
			0.056		25	4.06	-3
			0.110		25	6.54	-3

COMMENTS

Reaction is reversible, see 242.370. Equilibrium yields about 86.2 % L.

LITERATURE

C. A. Wamser, *ACS* 1948, **70**, 1209.

CONDENSATION

Alkoxy + Aryl hydrogen

Liquid phase

Reaction type: $ROH + R'H \longrightarrow RR' + H_2O$

or $ROR + 2R'H \longrightarrow 2RR' + H_2O$

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

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments
.1	$C_6H_5CH_2OH + C_6H_6$	B	A = 0.25	TS*	0.128		83	4,900			*
.2	$C_6H_5CH_2OH + CH_3C_6H_5 \longrightarrow p\text{-}C_6H_5CH_2C_6H_4CH_3 + H_2O$	B	A = 0.25	TS*	0.064 0.128		113 113	5,100 650			*
.3	$C_6H_5CH_2OH + p\text{-}(CH_3)_2C_6H_4 \longrightarrow C_6H_5CH_2C_6H_3(CH_3)_2 + H_2O$	B	A = 0.25	TS*	0.064		140	970			*
.4	$C_6H_5CH_2OH + 1,3,5\text{-}(CH_3)_3C_6H_3 \longrightarrow C_6H_5CH_2C_6H_2(CH_3)_3 + H_2O$	B	A = 0.25	TS*	0.064		166	290			*
.5	$C_6H_5CH_2OH + CH_3OC_6H_5 \longrightarrow p\text{-}C_6H_5CH_2C_6H_4OCH_3 + H_2O$	B	A = 0.25	TS*	0.032 0.064	k A	158 158		9.2 3.8	-5 -4	*
.6	$p\text{-}CH_3C_6H_4CH_2OH + CH_3OC_6H_5 \longrightarrow p\text{-}(p\text{-}CH_3C_6H_4CH_2)C_6H_4OCH_3 + H_2O$	B	A = 0.25	TS*	0.016	k A	158		3.8	-4	*
.7	$p\text{-}CH_3OC_6H_4CH_2OH + CH_3CC_6H_5 \longrightarrow p\text{-}(p\text{-}CH_3OC_6H_4CH_2)C_6H_4OCH_3 + H_2O$	B	A = 0.25	TS*	0.00025	k A	158		4.3	-4	*
.8	$p\text{-}ClC_6H_4CH_2OH + CH_3OC_6H_5 \longrightarrow p\text{-}(p\text{-}ClC_6H_4CH_2)C_6H_4OCH_3 + H_2O$	B	A = 0.25	TS*	0.032	k A	158		3.9	-5	*

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments
.9	$(C_6H_5)_2CHOH + C_6H_6$	B	A = 0.25	TS*	0.128 0.51		83 83	650 1,660			*
.10	$(C_6H_5)_2CHOH + CH_3C_6H_5 \longrightarrow p\text{-}(C_6H_5)_2CHC_6H_4CH_3 + H_2O$	B	A = 0.25	TS*	0.064		113	760			*
.11	$(C_6H_5)_2CHOH + CH_3OC_6H_5 \longrightarrow p\text{-}(C_6H_5)_2CHC_6H_4OCH_3 + H_2O$	B	A = 0.25	TS*	0.001		158	8,100			*
.12	$(C_6H_5CH_2)_2O + 2C_6H_6$	B	A = 0.125	TS*	0.128		83	4,300			*
.13	$(C_6H_5CH_2)_2O + 2CH_3C_6H_5 \longrightarrow 2p\text{-}C_6H_5CH_2C_6H_4CH_3 + H_2O$	B	A = 0.125	TS*	0.064		113	5,040			*
.14	$(C_6H_5CH_2)_2O + 2CH_3OC_6H_5 \longrightarrow 2p\text{-}C_6H_5CH_2C_6H_4OCH_3 + H_2O$	B	A = 0.125	TS*	0.128		158	2,050			*
.15	$[(C_6H_5)_2CH]_2O + C_6H_6$	B	A = 0.125	TS*	0.256		83	830			*
.16	$[(C_6H_5)_2CH]_2O + CH_3C_6H_5$	B	A = 0.125	TS*	0.064		113	28,000			*
.17	$[(C_6H_5)_2CH]_2O + 2CH_3OC_6H_5 \longrightarrow 2(C_6H_5)_2CHC_6H_4OCH_3 + H_2O$	B	A = 0.125	TS*	0.004		158	3,700			*

ADDEND

TS* *p*-toluene sulfonic acid

COMMENTS

General. Reaction followed by measuring volume of M removed by continuous distillation.

Reactions. **(.1) (.2) (.3) (.4) (.10) (.11) (.12) (.13) (.14) (.15) (.16) (.17)** Rate curves generally distorted, extremely so in some cases. Yield of M nearly 100 % but yield of L varied from 50 to 97 % from one reaction to another. Varied effect of catalyst. Order of reactions not established. **(.5) (.6) (.7) (.8)** First order rate law followed over 30–80 % reaction.

LITERATURE

E. F. Pratt, R. K. Preston, J. D. Draper, *ACS* 1950, **72**, 1367.

CONDENSATION

Aliphatic alcohols to ether

Liquid phase

Reaction type: $ROH + R'OH \longrightarrow ROR' + H_2O$

Rate measured: dM/dt

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (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	$n\text{-}C_4H_9OH + (C_6H_5)_2CHOH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.0020	kA	82	4.2	-5	*	(1)
.2	$n\text{-}C_4H_9OH + (C_6H_5)_3COH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.00025	kA	82	2.0	-4	*	(1)
					0.00050		82	5.33	-4		
.3	$n\text{-}C_7H_{15}OH + (C_6H_5)_3COH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.00050	kA	82	5.73	-4	*	(1)
.4	$n\text{-}C_{10}H_{21}OH + (C_6H_5)_3COH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.00050	kA	82	5.65	-4	*	(1)
.5	$C_6H_5CH_2OH + (C_6H_5)_2CHOH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.0020	kA	82	1.73	-4	*	(1)
.6	$C_6H_5CH_2OH + (C_6H_5)_3COH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.00025	kA	82	7.2	-4	*	(1)
.7	$(C_6H_5)_2CHOH + (C_6H_5)_2CHOH$	C_6H_6	A = B = 0.25	$p\text{-}CH_3C_6H_4SO_3H$	0.00025	kA	81	1.73	-5	*	(2)
					0.00050		81	5.75	-5		
					0.0010		81	1.83	-4		
					0.0020		82	4.3	-4		(1)
	other addend		amount								
	$p\text{-}C_2H_5OC_6H_4COCH_3$		0.125	$p\text{-}CH_3C_6H_4SO_3H$	0.0010	kA	81	6.89	-5		(2)
	$p\text{-}CH_3OC_6H_4COCH_3$		"	"	"		81	6.92	-5		
	$p\text{-}(CH_3)_3CC_6H_4COCH_3$		"	"	"		81	8.52	-5		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.7	$(C_6H_5)_2CHOH + (C_6H_5)_2CHOH$ *(continued)*	C_6H_6	A = 0.25	p-$CH_3C_6H_4SO_3H$	0.0010	k A	81	1.83	-4	*	[2]
	other addend		amount								
	$CH_3(CH_2)_4COCH_3$		0.125	p-$CH_3C_6H_4SO_3H$	0.0010	k A	81	8.94	-5		
	p-$CH_3C_6H_4COCH_3$		"	"	"		81	9.19	-5		
	$(C_2H_5)_2CO$		0.125	"	"		81	9.76	-5		
	$C_6H_5COCH_3$		0.0625	"	"		81	1.33	-4		
			0.125	"	"		81	1.02	-4		
			0.250	"	"		81	7.74	-5		
	2,4,6-$(CH_3)_3C_6H_2COCH_3$		0.125	"	"		81	1.06	-4		
	p-$ClC_6H_4COCH_3$		"	"	"		81	1.16	-4		
	p-$BrC_6H_4COCH_3$		"	"	"		81	1.20	-4		
	$(C_6H_5)_2CO$		"	"	"		81	1.31	-4		
	m-$NO_2C_6H_4COCH_3$		"	"	"		81	1.55	-4		
	p-$NO_2C_6H_4COCH_3$		"	"	"		81	1.62	-4		
	$CH_3COCH_2CH_2COCH_3$		"	"	"		81	9.78	-5		
	$CH_3COCH_2COCH_3$		"	"	"		81	1.20	-4		
	$CH_3COCOCH_3$		"	"	"		81	1.59	-4		
	$C_6H_5COCOC_6H_5$		"	"	"		81	1.76	-4		
	$C_6H_5CH:CHCOCH:CHC_6H_5$		"	"	"		81	4.50	-5		
	$C_6H_5CH:CHCOCH_3$		"	"	"		81	5.69	-5		
	$(CH_3)_2C:CHCOCH_3$		"	"	"		81	5.92	-5		
	$C_6H_5CH:CHCOC_6H_5$		"	"	"		81	9.30	-5		
	$CH_2(CH_2)_3CO$		"	"	"		81	8.56	-5		
	$CH_2(CH_2)_4CO$		"	"	"		81	8.76	-5		
	p-$CH_3OC_6H_4COOC_2H_5$		"	"	"		81	1.14	-4		
	p-$CH_3C_6H_4COOC_2H_5$		"	"	"		81	1.20	-4		
	2,4,6-$(CH_3)_3C_6H_2COOC_2H_5$		"	"	"		81	1.24	-4		
	$C_6H_5COOC_2H_5$		"	"	0.0005		81	4.60	-5		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.7	$(C_6H_5)_2CHOH + (C_6H_5)_2CHOH$ *(continued)*	C_6H_6	A = 0.25	p-$CH_3C_6H_4SO_3H$	0.0010	k A	81	1.83	-4	*	(2)
	other addend		amount								
	$C_6H_5COOC_2H_5$		0.125	p-$CH_3C_6H_4SO_3H$	0.0010	k A	81	1.31	-4		
	$C_6H_5COOCH_3$		"	"	"		81	1.33	-4		
	p-$ClC_6H_4COOC_2H_5$		"	"	"		81	1.36	-4		
	p-$NO_2C_6H_4COOC_2H_5$		"	"	"		81	1.61	-4		
	$C_2H_5OOC(CH_2)_4COOC_2H_5$		"	"	"		81	6.82	-5		
	$C_2H_5OOC(CH_2)_2COOC_2H_5$		"	"	"		81	8.81	-5		
	$CH_2(COOC_2H_5)_2$		"	"	"		81	1.08	-4		
	$(COOC_2H_5)_2$		"	"	"		81	1.62	-4		
	cis-$C_2H_5OOCCH{:}CHCOOC_2H_5$		"	"	"		81	1.12	-4		
	trans-$C_2H_5OOCCH{:}CHCOOC_2H_5$		"	"	"		81	1.22	-4		
	n-$C_7H_{15}COOC_2H_5$		"	"	"		81	1.00	-4		
	$ClCH_2CH_2CH_2COOC_2H_5$		"	"	"		81	1.27	-4		
	$ClCH_2CH_2COOC_2H_5$		"	"	"		81	1.37	-4		
	$ClCH_2COOC_2H_5$		"	"	"		81	1.59	-4		
	$Cl_2CHCOOC_2H_5$		"	"	"		81	1.73	-4		
	$Cl_3CCOOC_2H_5$		"	"	"		81	1.87	-4		
	n-$C_4H_9OC(CH_3)_3$		"	"	"		81	7.33	-5		
	$(n$-$C_4H_9)_2O$		"	"	"		81	7.60	-5		
	n-$C_4H_9OCH(CH_3)C_2H_5$		"	"	"		81	7.66	-5		
	n-$C_4H_9OCH_2CH_2CH_2C_6H_5$		"	"	"		81	7.86	-5		
	n-$C_4H_9OCH_2CH_2C_6H_5$		"	"	"		81	9.00	-5		
	n-$C_4H_9OCH_2C_6H_5$		"	"	"		81	1.09	-4		
	$(C_6H_5CH_2)_2O$		"	"	"		81	1.36	-4		
	n-$C_4H_9OCH(C_6H_5)_2$		"	"	"		81	1.53	-4		
	$[(C_6H_5)_2CH]_2O$		"	"	"		81	1.63	-4		
	$C_6H_5CH_2OCH(C_6H_5)_2$		"	"	"		81	1.69	-4		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.7	$(C_6H_5)_2CHOH + (C_6H_5)_2CHOH$ *(continued)*	C_6H_6	A = 0.25	p-$CH_3C_6H_4SO_3H$	0.0010	kA	81	1.83	-4	*	(2)
	other addend		amount								
	$CH_3OC_6H_5$		0.125	p-$CH_3C_6H_4SO_3H$	0.0010	kA	81	1.67	-4		
	n-$C_4H_9OC_6H_5$		"	"	"		81	1.76	-4		
	$C_2H_5OC_6H_5$		"	"	"		81	1.79	-4		
	2,6-$(CH_3)_2$-$CH{:}CHCOCH{:}CHO$		0.062	"	0.032		81	7.55	-5		
	C_6H_5CN		0.125	"	0.0010		81	1.67	-4		
	$C_6H_5NO_2$		"	"	"		81	1.77	-4		
	C_6H_5F		"	"	"		81	1.78	-4		
	$C_6H_5CH_3$		"	"	"		81	1.80	-4		
	C_6H_5Cl		"	"	"		81	1.84	-4		

COMMENTS

General. Rate law with respect to each reactant not determined and rate law might be kB instead of kA or $kA^{\frac{1}{2}}B^{\frac{1}{2}}$ or a more complex expression. Pseudo first order rate constant observed over course for each reaction, but initial concentrations of A and B always equal.

Reactions. **(.1)** 93 % yield of n-$C_4H_9OCH(C_6H_5)_2$ inspite of fact that $(C_6H_5)_2CHOH$ alone reacts about ten times faster, see (.7). **(.5)** $(C_6H_5)_2CHOCH_2C_6H_5$ only product of reaction found in measurable amount, inspite of fact that $(C_6H_5)_2CHOH$ alone reacts more rapidly, see (.7).

(.7) Pseudo first order rate law followed up to 80 % reaction and values calculated graphically for 20-80 % reaction. p-$CH_3C_6H_4SO_3H$ is catalyst for this condensation. The influence of the second addend is of decreasing the rate which is considered to give a measure of the basicity of the compound. The second addends are arranged in the following groups: ketones, diketones, alkenyl-ketones, cyclic ketones, aryl esters, diesters, alkyl esters, ethers, and miscellaneous compounds. The compounds in each group are arranged in order of decreasing inhibiting power.

LITERATURE

([1]) E.F. Pratt, J.D. Draper, *ACS* 1949, **71**, 2846. ([2]) E.F. Pratt, K. Matsuda, *ACS* 1953, **75**, 3739.

CONDENSATION

Alkali-metal-(aryl)alkyl + alkyl halide

Liquid phase

Rate measured $-dA/dt$

Amounts are in M/l.
Rate constants are in M/l and 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	$CH_3Li + n\text{-}C_4H_9Cl \longrightarrow n\text{-}C_5H_{12}, CH_4, CH_3CH_2CH{:}CH_2, LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.2; B = 0.14-0.15	k AB	73	1.3	-5				*	(1)
					79	2.0	-5					
					89	4.3	-5	19	1	7		
.2	$CH_3Li + n\text{-}C_4H_9Cl \longrightarrow n\text{-}C_5H_{12} + LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.2; B = 0.14-0.15	k AB	89	1.0	-5				*	(1)
.3	$CH_3Li + n\text{-}C_4H_9Cl \longrightarrow CH_4 + CH_3CH_2CH{:}CH_2 + LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.2; B = 0.14-0.15	k AB	89	3.3	-5				*	(1)
.4	$CH_3Li + (CH_3)_3CCl \longrightarrow CH_4 + (CH_3)_2C{:}CH_2 + LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.06-0.2; B = 0.01-0.1	k AB	73	1.3	-4				*	(1)
					79	2.0	-4					
					89	4.7	-4	21	2	9		
.5	$n\text{-}C_4H_9Li + n\text{-}C_4H_9Cl \longrightarrow$	$(C_2H_5)_2O$	A = B = 0.5	k AB	~25	1	-5				*	(3)
		C_6H_6	A = B = 0.5		~25	(no reaction in 2 days)						
.6	$n\text{-}C_4H_9Li, C_6H_5CH{:}CHCl \longrightarrow C_6H_5CH{:}CHC_4H_9, C_6H_5C{:}CLi, C_4H_{10}, LiCl$	C_6H_6	A = 0.1; B = 0.05	k AB	50	2.3	-3				*	(2)

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
.7	$n\text{-}C_4H_9Li + C_6H_5CH{:}CHCl \longrightarrow C_6H_5CH{:}CHC_4H_9 + LiCl$	C_6H_6	A = 0.1; B = 0.05	k AB	50	1.7	-3				*	[2]
.8	$2n\text{-}C_4H_9Li + C_6H_5CH{:}CHCl \longrightarrow C_6H_5C{:}CLi + 2C_4H_{10} + LiCl$	C_6H_6	A = 0.1; B = 0.05	$dL/dt = k$ AB	50	6	-4				*	[2]
.9	$n\text{-}C_4H_9Li + n\text{-}C_4H_9Br \longrightarrow$	C_6H_6	A = B = 0.5	k AB	~25	6	-6				*	[3]
.10	$n\text{-}C_4H_9Li + n\text{-}C_4H_9I \longrightarrow$	C_6H_6	A = B = 0.5	k AB	~25	2	-4				*	[3]
	Alkali-metal-aryl + alkyl halide											
.11	$C_6H_5Li + n\text{-}C_4H_9Cl \longrightarrow C_6H_5C_4H_9, C_6H_6, CH_3CH_2CH{:}CH_2, LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.6; B = 0.01-0.2	k AB	50 63 80 97	3.2 1.31 5.3 2.5	-6 -5 -5 -4	21.2	8	8		[1]
.12	$C_6H_5Li + n\text{-}C_4H_9Cl \longrightarrow C_6H_5C_4H_9 + LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.6; B = 0.01-0.2	k AB	97	2.4	-4				*	[1]
.13	$C_6H_5Li + n\text{-}C_4H_9Cl \longrightarrow C_6H_6 + CH_3CH_2CH{:}CH_2 + LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.6; B = 0.01-0.2	k AB	97	1.1	-5				*	[1]
.14	$C_6H_5Li + C_2H_5(CH_3)CHCl \longrightarrow$	$(n\text{-}C_4H_9)_2O$	A = 0.3; B = 0.1	k AB	80 80	1.6 1.9	-6 -5	less than 20 % reaction after 20 % reaction *				[1]

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
.15	$C_6H_5Li + (CH_3)_3CCl \longrightarrow C_6H_6 + (CH_3)_2C{:}CH_2 + LiCl$	$(n\text{-}C_4H_9)_2O$	A = 0.1-0.6; B = 0.03-0.2	k AB	49	3.9	-6					(1)
					63	1.69	-5					
					80	8.46	-5					
					97	4.09	-4	22.7	1.0	10		
.16	$2C_6H_5Li + C_6H_5CH{:}CHCl \longrightarrow 2C_6H_6 + C_6H_5C{:}CLi + LiCl$	$(C_2H_5)_2O$	A = 0.1; B = 0.05	$k A^2B$	0	9.2	-2				*	(2)
					20	5.7	-1					

COMMENTS

(.1) Reaction composed of parallel reactions (.2) (.3). Values of rate constants give order of magnitude but actual values observed to vary by factor of six for different batches of reactant A. **(.2) (.3)** Rate constant calculated from value for (.1) and ratio of C_5H_{12} and $CH_3CH_2CH{:}CH_2$ in products. **(.4)** Value of rate constant observed to vary by as much as six times for different batches of reactant A. No C_5H_{12} observed in products. **(.5)** Second order rate law not confirmed but assumed for calculation of rate constant from half life in hours. **(.6) (.7) (.8)** Second order rate law probably not valid but assumed to express data for amount reacted at 22 hours. Ratio of parallel reactions (.7) and (.8) determined from ratio of $C_6H_5CH{:}CHC_4H_9$ and $C_6H_5C{:}CLi$ at 22 hours. **(.9) (.10)** Second order rate law not confirmed but assumed for calculation of rate constant from half life in hours. **(.12) (.13)** Parallel reactions calculated from rate constant for (.11) and ratio of $C_6H_5C_4H_9$ to $CH_3CH_2CH{:}CH_2$ in products. **(.14)** Induction period observed with first 20 % reaction at rate approximately one tenth the rate for latter stages of reaction. **(.16)** Third order rate law questioned by (1) upon grounds that observed decrease in calculated second order rate constants could be due to reactant B consisting of a mixture of cis and trans isomers. These would be expected to react at different rates, see 422.471.

LITERATURE

([1]) S.J. Cristol, J.W. Ragsdale, J.S. Meek, *ACS* 1951, **73**, 810.

([2]) G. Wittig, G. Harborth, W. Merkle, *BDC* 1944, **77B**, 315.

([3]) K. Ziegler, H. Colonius, *Ann.* 1930, **479**, 135.

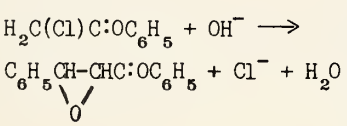
CONDENSATION
C = C bond formation

Liquid phase

Reaction type: $RCHO + H_2CR'R'' \longrightarrow RCH{:}CR'R'' + H_2O$
(A) (B) (L) (M)

Amounts are in M/l. Rate constants are in M/l and sec.

Rate measured: dM/dt

No.	Reaction	Medium (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
	Aliphatic aldehyde + ester													
.1	$CH_3(CH_2)_3CH(C_2H_5)CHO + H_2C(COOC_2H_5)_2$	C_6H_6	A = B = 0.25	PC*	0.125	k B	84	8.6	-5				*	(6)
	Aryl aldehyde + ketone or diketone													
.2	$C_6H_5CHO + H_2C(C_6H_5)COCH_3$	C_6H_6	A = B = 0.25	PC*	0.25	k B	84	1.9	-4				*	(6)
.3	$C_6H_5CHO + H_2C(C_6H_5)COC_6H_5$	C_6H_6	A = B = 0.25	PC*	0.25	k B	84	1.8	-4				*	(6)
.4	$C_6H_5CHO + H_2C(COCH_3)_2$	C_6H_6	A = B = 0.25	PC*	0.008	k AB	84	1.6	-3				*	(6)
.5	$C_6H_5CHO + H_2C(COC_6H_5)_2$	C_6H_6	A = B = 0.25	PC*	0.016	k AB	84	6-7	-4				*	(6)
.6	$C_6H_5CHO + H_2C(Cl)C{:}OC_6H_5 + OH^- \longrightarrow$  $+ Cl^- + H_2O$	D1W*	10^3A = 5-10 10^3B = 0.5-1 10^3C = 1-1.5	$NaClO_4$	0.01	k ABC	0	5.9	-3				*	(1)

SUPPLEMENT 1954

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
	Aryl aldehyde + keto-ester													
.7	$C_6H_5CHO + H_2C(COCH_3)COOC_2H_5$	C_6H_6	A = B = 0.25	PC*	0.016	kB	84	4.4	-4				*	(6)
	Aryl aldehyde + acid or acid anhydrid													
.8	$C_6H_5CHO + H_2C(C_6H_5)COOH$	$(CH_3CO)_2O$	A = 1-2; B = 1-2	R_3N* CH_3COO^-	0.3-0.6	$kAB\frac{[CH_3COO^-]}{[CH_3COOH]}$	26	1.0	-5				*	(2)
							80	6	-5					
							100	6.4	-5					
							120	1.0	-4	6	1	-1		
.9	$C_6H_5CHO + H_2C(COOH)_2 \longrightarrow$	$(CH_2)_5C{:}O$	A = B = 1.4	$(CH_2)_5NH$	0.14			time	% (a)	% (b)			*	(5)
	$C_6H_5CH{:}C(COOH)_2 + H_2O$ (a)						59	3600	21	2				
	$C_6H_5CH{:}CHCOOH + H_2O + CO_2$ (b)							7200	30	2.5				
								10,800	34	3				
		CHP10*	A = B = 1.4	$(CH_2)_5NH$	0.14		59	3600	22	8				
								7200	32	21				
								10,800	36	30				
		CHP40*	A = B = 1.4	$(CH_2)_5NH$	0.14		59	3600	26	14				
								7200	40	34				
								10,800	50	46				
					(a+b)	$= kAB$	59	6.7	-5					
		C_5H_5N	A = B = 1.4		(a+b)	$= kAB$	59	4	-5					
				$(CH_2)_5NH$	0.145		48	8.4	-5					
							59	1.59	-4					
			A = 2.8; B = 1.4				59	1.9	-4					
			A = B = 1.4				76	5.45	-4	15	1.2	6		

No.	Reaction	Medium (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
.9	$C_6H_5CHO + H_2C(COOH)_2 \longrightarrow$ *(continued)*	C_5H_5N	A = B = 1.4			(b) = k'A	48	3.1	-5				*	(5)
							59	8.3	-5					
							76	2.88	-4	19				
				$(CH_2)_5NH$	3	(a) = kAB	59	1.4	-3					
						(b)	59	0						
.10	$C_6H_5CHO + (CH_3CO)_2O \longrightarrow$ $C_6H_5CH{:}C(CH_3)COOCOCH_3 + H_2O$	B	A = 1.2	$(C_2H_5)_3N$	0.69	$-dA/dt =$							*	(2)
				CH_3COOH	1.2	k A[OAc$^-$]	100	1.8	-1					
	Aryl aldehyde + alkyl-di-ester													
.11	$C_6H_5CHO + H_2C(COOC_2H_5)_2$	C_6H_6	A= 0.28; B= 0.25	PC*	0.062	k B	84	1.0	-4					(6)
			0.28 0.25		0.125		84	1.70	-4					
			0.25 0.25		0.125		84	1.66	-4					
			0.25 0.30		0.125		84	1.50	-4					
			0.25 0.50		0.125		84	1.23	-4					
			0.28 0.25		0.25		84	3.6	-4					
			0.25 0.25	$(CH_2)_5NH$	0.125									
				$C_5H_{11}COOH$	0.50		84	1.01	-4					
			0.25 0.25	$(CH_2)_5NH$	0.125									
				$C_5H_{11}COOH$	0.125		84	1.84	-4					
		$C_6H_5CH_3$	A = B = 0.25	PC*	0.062		114	3.8	-4					
.12	p-$CH_3OC_6H_4CHO + H_2C(COOC_2H_5)_2$	C_6H_6	A = B = 0.25	PC*	0.125	k B	84	2.0	-4				*	(6)

No.	Reaction	Medium (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
.13	p-$NO_2C_6H_4CHO + H_2C(COOC_2H_5)_2$	C_6H_6	A = B = 0.25	PC*	0.125	k B	84	1.1	-4				*	(6)
.14	p-$ClC_6H_4CHO + H_2C(COOC_2H_5)_2$	C_6H_6	A = B = 0.25	PC*	0.125	k B	84	1.3	-4				*	(6)
	Aryl aldehyde + alkyl nitrile													
.15	$C_6H_5CHO + H_2C(C{:}N)COOC_2H_5$	C_6H_6	A = B = 0.25	PC*	0.004	k B	84	3.4	-4				*	(6)
.16	$C_6H_5CHO + H_2C(C{:}N)_2$	C_6H_6	A = B = 0.25	PC*	0.002	k AB	84	2.2	-3				*	(6)
	Aryl aldehyde + nitro alkyl													
.17	3-CH_3O-4-$HOC_6H_3CHO + CH_3NO_2$ (vanillin)	CH_3OH	A= 0.008; B= 0.30	CH_3COONH_4	0.5	k AB	25	3.3	-4				*	(4)
			0.027 0.30				25	2.2	-4					
			0.045 0.075				25	2.5	-4					
			0.045 0.037				25	3.3	-4					
			0.027 0.30	CH_3COONa	0.5		25	3	-6					
			0.027 0.30	$CH_3COONH_3C_4H_9$	0.5		25	3	-4					
			0.027 0.30	$CH_3COONH_2(C_2H_5)_2$	0.5		25	5	-6					
			0.027 0.30	$CH_3COONH(C_2H_5)_3$	0.5		25	5	-7					
.18	3,4-$CH_2O_2C_6H_3CHO + CH_3NO_2$ (piperonal)	CH_3OH	A = 0.02-0.04; B = 0.02	$CH_3COONH_3C_4H_9$	0.5	k AB	25	3.68	-4	Induction Period 180 secs.			*	(3)
					0.18-0.2		25	3.22	-4	840				
					0.1		25	2.77	-4	1800				
					0.05		25	2.27	-4	4700				
					0.029		25	1.55	-4	8600				

No.	Reaction	Medium (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
.18.1	$3,4\text{-}CH_2O_2C_6H_3CHO + n\text{-}C_4H_9NH_2 \longrightarrow$ $3,4\text{-}CH_2O_2C_6H_3CH{:}NC_4H_9 + H_2O$	CH_3OH	(from (.18))				25	5.3	-3				*	(3)
				CH_3ONa	0.023		25	3.28	-2					
				CH_3COOH	0.17-0.19		25	5.3	-3					
.18.2	$3,4\text{-}CH_2O_2C_6H_3CH{:}NC_4H_9 + CH_3NO_2 \longrightarrow$ $3,4\text{-}CH_2O_2C_6H_3CH{:}CHNO_2 + n\text{-}C_4H_9NH_2$	CH_3OH	(from (.18))				25	3.2	-4				*	(3)
			A = 0.02; B = 0.2	$CH_3COONH_3C_4H_9$	0.5		25	3.44	-4					
					0.2		25	3.00	-4					
					0.1		25	2.60	-4					
					0.05		25	2.24	-4					
					0.029		25	2.02	-4					
				$CH_3COONH(C_2H_5)_3$	0.2		25	3.24	-4					
.19	$C_6H_5CHO + H_2C(C_6H_5)NO_2$	C_6H_6	A = B = 0.25	PC*	0.13	kB	84	2.0	-4				*	(6)

SOLVENTS

CHP10*(40) Cyclohexane + indicated volume % of pyridine

DIW* Dioxane 50 vol % + H_2O

ADDEND

PC* Piperidine at concentration stated plus caproic acid at double this concentration.

R_3N* $(C_2H_5)_3N$, $(n\text{-}C_3H_7)_3N$, $(n\text{-}C_4H_9)_3N$

COMMENTS

General. See also 232.446 for other reactions.

Comments by reaction. **(.1) (.2) (.3)** Rate law with respect to A or B not established. Total over-all rate is first order, k B selected by comparison with (.11). **(.4) (.5)** Rate law with respect to A or B not established. Total over-all rate is second order. **(.6)** Rate law with respect to A, B and C established by variation of initial concentrations and over course to about 75 % reaction. Values calculated for constants at later stages of reaction decrease. **(.7)** Rate law with respect to A or B not established. Total over-all rate is first order, k B selected by comparison with (.11). **(.8)** Reaction followed by analysis for A which also undergoes competing reactions with solvent and CH_3COOH as well as autoxidation. Esterification of acid by solvent proceeds simultaneously. **(.9)** Reactions (a) and (b) may occur simultaneously or consist of a consecutive process involving (a) followed by elimination of CO_2. Point of inflection in the curve for the rate of production of CO_2 is definitely after the time of maximum concentration of intermediate condensation product. Production of CO_2 appears to follow first order rate law after an induction period. Rate law with respect to either A or B not established. **(.10)** Rate law not confirmed but adopted from rate law for (.8). **(.12) (.13) (.14) (.15)** Rate law with respect to A or B not established. Total over-all rate is first order, k B selected by comparison with (.11). **(.16)** Rate law with respect to A or B not established. Total over-all rate is second order. Value given calculated for first 30 % reaction. At 80 % reaction second order constant falls to 1.3×10^{-3}. **(.17)** Rate constants represent course for about 25 to 65 % reaction after an induction period. Calculated rate constants vary with initial concentrations. Reverse reaction not considered in calculations although reaction proceeds to only 90 % conversion. **(.18) (.18.1) (.18.2)** Reaction (.18) shown to involve consecutive steps (.18.1) and (.18.2) determined from composite reaction (.18) as well as from independent reactions. Second order constants for reaction (.18.1) remain constant in basic solution. In acid solutions second order rate constant was calculated from pseudo first order constant by dividing by butyl ammonium acetate concentration. Mechanism of steps (.18.1) and (.18.2) further substantiated by fact that $CH_3COONH(C_2H_5)_3$ catalyzes (.18.2) about as effectively as $CH_3COONH_3C_4H_9$ but former does not catalyze reaction (.18). **(.19)** Rate law with respect to A or B not established. Total over-all rate is first order, k B selected by comparison with (.11).

LITERATURE

([1]) M. Ballester, P.D. Bartlett, *ACS* 1953, **75**, 2042. ([2]) R.E. Buckles, K.G. Bremmer, *ACS* 1953, **75**, 1487. ([3]) T.I. Crowell, D.W. Peck, *ACS* 1953, **75**, 1075. ([4]) T.I. Crowell, F.A. Ramirez, *ACS* 1951, **73**, 2268. ([5]) S. Patai, J. Edlitz-Pfeffermann, Z. Rozner, *ACS* 1954, **76**, 3446. ([6]) E.F. Pratt, E. Werble, *ACS* 1950, **72**, 4638.

CONDENSATION
(Baeyer Condensation)
Aldehyde + aryl hydrogen

Liquid phase

Reaction type: $RCHO + 2R'H \longrightarrow RCHR'_2 + H_2O$

rate = $-dA/dt = dM/dt$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments
.1	$C_6H_5CHO + 2CH_3C_6H_5$	B	A = 0.50	p-$CH_3C_6H_4SO_3H$	0.512		115	2.2×10^5			
.2	$C_6H_5CHO + 2HOC_6H_5 \longrightarrow (p\text{-}HOC_6H_4)_2CHC_6H_5 + H_2O$	C_6H_6	A = 0.25; B = 1.25	p-$CH_3C_6H_4SO_3H$	0.016		86	1.1×10^4			
.3	$C_6H_5CHO + 2CH_3OC_6H_5 \longrightarrow (p\text{-}CH_3OC_6H_4)_2CHC_6H_5 + H_2O$	C_6H_6	A = 0.25; B = 1.25	p-$CH_3C_6H_4SO_3H$	0.128	k AB	86		1.1	-5	*
.3.1	$C_6H_5CHO + CH_3OC_6H_5 \longrightarrow p\text{-}CH_3OC_6H_4CH(OH)C_6H_5$	C_6H_6	A = 0.25; B = 1.25	p-$CH_3C_6H_4SO_3H$	0.128	k AB	86		1.1	-5	*
.3.2	$p\text{-}CH_3OC_6H_4CH(OH)C_6H_5 + CH_3OC_6H_5 \longrightarrow (p\text{-}CH_3OC_6H_4)_2CHC_6H_5 + H_2O$	C_6H_6	A = 0.25; B = 1.00	p-$CH_3C_6H_4SO_3H$	0.128	k AB	86	300	2.5	-3	*
.4	$C_6H_5CHO + 2C_2H_5OC_6H_5$	C_6H_6	A = 0.25; B = 1.25	p-$CH_3C_6H_4SO_3H$	0.128	k AB	87		1.6	-5	*
.5	$C_6H_5CHO + 2n\text{-}C_4H_9OC_6H_5$	C_6H_6	A = 0.25; B = 1.25	p-$CH_3C_6H_4SO_3H$	0.128	k AB	87		2.3	-5	*
.6	$C_6H_5CHO + 2(CH_3)_2NC_6H_5$	C_6H_6	A = 0.5; B = 2.5 1.0 2.5	p-$CH_3C_6H_4SO_3H$	0.256 0.256	k AB	92 92		9.1 8.4	-6 -6	*

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	Comments
.6	$C_6H_5CHO + 2(CH_3)_2NC_6H_5$ *(continued)*	$C_6H_5CH_3$	A = 0.25; B = 1.25	p-$CH_3C_6H_4SO_3H$	0.064	k AB	118		1.88	-5	*
			0.50 1.25		0.064		118		1.37	-5	
			0.50 1.25		0.128		123		2.7	-5	
			0.50 1.25		0.256		123		3.8	-5	
.7	p-$CH_3C_6H_4CHO + 2(CH_3)_2NC_6H_5$	C_6H_6	A = 0.5; B = 2.5	p-$CH_3C_6H_4SO_3H$	0.256	k AB	92		6.35	-6	*
.8	p-$CH_3OC_6H_4CHO + 2(CH_3)_2NC_6H_5$	C_6H_6	A = 0.5; B = 2.5	p-$CH_3C_6H_4SO_3H$	0.256	k AB	92		3.74	-6	*
.9	p-$(CH_3)_2NC_6H_4CHO + 2(CH_3)_2NC_6H_5$	C_6H_6	A = 0.5; B = 2.5	p-$CH_3C_6H_4SO_3H$	0.256	k AB	92		1.04	-6	*
.10	p-$NO_2C_6H_4CHO + 2(CH_3)_2NC_6H_5$	C_6H_6	A = 0.5; B = 2.5	p-$CH_3C_6H_4SO_3H$	0.256	k AB	92		3.25	-5	*
.11	p-$ClC_6H_4CHO + 2(CH_3)_2NC_6H_5$	C_6H_6	A = 0.5; B = 2.5	p-$CH_3C_6H_4SO_3H$	0.256	k AB	92		1.16	-5	*

COMMENTS

General. Reactions followed by measuring volume of water distilled off and condensed with progress of reaction. Second order rate constants were calculated on basis of $-dA/dt = dM/dt = -\frac{1}{2}dB/dt$.

Reactions. **(.3)** Over-all reaction considered to be result of consecutive reactions (.3.1) and (.3.2). **(.3.1)** Not measured independently but assumed to be rate determining step since (.3.2) approximately 200 times faster than (.3). **(.3.2)** Measured independently of (.3). Calculated second order rate constants increase about 20 % with first 60 % reaction. **(.4) (.5)** Calculated second order rate constants increase as much as 25 % over first 60 % reaction. Tabulated value is for 50 % reaction. **(.6) (.7) (.8) (.9) (.10) (.11)** Second order rate law holds over first 60 % reaction. Beyond 60 % values calculated increase markedly.

LITERATURE

E. F. Pratt, L. Q. Green, *ACS* 1953, **75**, 275.

CONDENSATION

Silanol ⟶ di-siloxane

Liquid phase

Reaction type: $R_3SiOH + R_3SiOR' \longrightarrow R_3SiOSiR_3 + ROH$ (L) (M)

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
				X	$10^4 \times [X]$					
.1	$2(CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + H_2O$	CH_3OH	A = 0.13–0.44	HCl	1–4	$k\{[(CH_3)_3SiOCH_3]^2[H_2O] - K_4L\}[X] = dM/dt$	25	K_4 = 1.3	−1	*
							25	k = 3.1	+2	
				KOH	4–100		25	k = 6.4	−1	
				NaOH	22		25	k = 5.9	−1	
				LiOH	11		25	k = 5.9	−1	
		C_2H_5OH	A = 0.26	HCl	2		25	K_4 = 3.0	−2	
							25	k = 8.0	+1	
.2	$(CH_3)_3SiOH + (CH_3)_3SiOCH_3 \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + CH_3OH$	CH_3OH	A = 0.26; B = 0.07–0.5	HCl	2	$k\{B^2[H_2O] - K_4L\}[X]$	25	K_4 = 1.3	−1	*
							25	k = 3.1	+2	
				KOH	4–100		25	k = 6.4	−1	
				NaOH	22		25	k = 5.9	−1	
				LiOH	11		25	k = 5.9	−1	
.3	$(CH_3)_3SiOH + (CH_3)_3SiOC_2H_5 \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + C_2H_5OH$	C_2H_5OH	A = 0.26	HCl	2	$k\{B^2[H_2O] - K_4L\}[X]$	25	K_4 = 3.0	−2	*
							25	k = 8.0	+1	

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments
				X	$10^4 \times [X]$					
.4	$2(C_2H_5)_3SiOH \longrightarrow (C_2H_5)_3SiOSi(C_2H_5)_3 + H_2O$	CH_3OH	A = 0.26	HCl	2	$dM/dt = k\{[(C_2H_5)_3SiOCH_3][H_2O] - K_4L\}[X]$	25 25	K_4 = 5.5 k = 5	-2 -1	*
.5	$(C_2H_5)_3SiOH + (C_2H_5)_3SiOCH_3 \longrightarrow (C_2H_5)_3SiOSi(C_2H_5)_3 + CH_3OH$	CH_3OH	A = 0.26	HCl	2	$k\{B^2[H_2O] - K_4L\}[X]$	25	K_4 = 5.5 k = 5	-2 -1	*
.6	$2(C_6H_5)_3SiOH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + H_2O$	CH_3OH	A = 0.26	HCl	2	$k[(C_6H_5)_3SiOCH_3]^2[H_2O][X]$	25	< 2	-4	

COMMENTS

General. Rapid equilibrium of tri-alkyl silanol with solvent alcohol appears to precede reaction. Karl Fischer reagent shown to react quantitatively with both silanol and water under these conditions. For solvolysis of di-siloxanes see 242.404. **Reaction.** (.1) Appears to involve rapid equilibrium $(CH_3)_3SiOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3SiOCH_3 + H_2O$ followed by rate determining reaction (.2) which is also reversible $(CH_3)_3SiOH + (CH_3)_3SiOCH_3 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (CH_3)_3SiOSi(CH_3)_3 + CH_3OH$. $k = k_3k_2/k_1$; $K_4 = k_1k_4/k_2k_3$. (.2) Considered to be rate determining step for (.1) in CH_3OH. Rate constant in terms of A, B and catalyst not determined as equilibrium constant not known for reaction $(CH_3)_3SiOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3SiOCH_3 + H_2O$. (.3) Considered to be rate determining step for (.1) in C_2H_5OH. See (.2). (.4) Appears to involve rapid equilibrium $(C_2H_5)_3SiOH + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (C_2H_5)_3SiOCH_3 + H_2O$ followed by rate determining reaction (.5) which is also reversible, $(C_2H_5)_3SiOH + (C_2H_5)_3SiOCH_3 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} (C_2H_5)_3SiOSi(C_2H_5)_3 + CH_3OH$. $k = k_3k_2/k_1$; $K_4 = k_1k_4/k_2k_3$. (.5) Considered to be rate determining step for (.4). See (.2).

LITERATURE

W. T. Grubb, *ACS* 1954, **76**, 3408.

CONDENSATION

C = N bond formation

Liquid phase

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

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	k^o n	E	$A = A^o \times 10^n$ A^o	A^o n	Comments	Literature
.62		3,4-$OCH_2OC_6H_3CHO$ + n-$C_7H_{15}NH_2$	C_2H_5OH	A = B = 0.05				39	1,800							(4)
.63		3,4-$OCH_2OC_6H_3CHO$ + $(CH_3CH_2CH_2)_2CHNH_2$	C_2H_5OH	A = B = 0.05				39	2,300							(4)
.64		3,4-$OCH_2OC_6H_3CHO$ + $[(CH_3)_2CH]_2CHNH_2$	C_2H_5OH	A = B = 0.05				39	17,000							(4)
.65		3,4-$OCH_2OC_6H_3CHO$ + $(C_2H_5)_3CNH_2$	C_2H_5OH	A = B = 0.05				39	very slow							(4)
.66	.23	$(CH_3)(C_6H_5)C{:}O$ + $NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40		2.46 2.69 4.88	-2 -2 -2				*	(3)
.67		$(CH_3)(p\text{-}CH_3C_6H_4)C{:}O$ + $NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30		1.62	-2				*	(1)
.68		$(CH_3)(p\text{-}C_2H_5C_6H_4)C{:}O$ + $NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30		1.65	-2				*	(1)

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	Half-time	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.69		$(CH_3)[p\text{-}(CH_3)_2CHC_6H_4]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30		1.67	-2				*	(1)
.70		$(CH_3)[p\text{-}(CH_3)_3CC_6H_4]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30		1.67	-2				*	(1)
.71		$(CH_3)[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2; B = 0.1	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40		1.84 3.10 4.03	-3 -3 -3				*	(3)
.72		$(CH_3)[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40		1.83 2.47 3.27	-3 -3 -3	11	2	5	*	(2)
.73		$(CH_3)[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1; B = 0.2	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40		1.03 1.24 1.65	-3 -3 -3	9	1	3		(2)
.74		$(C_2H_5)(C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40		1.45 1.84 3.03	-2 -2 -2				*	(3)
.75		$(C_2H_5)(p\text{-}CH_3C_6H_4)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30		9.90	-3				*	(1)
.76		$(C_2H_5)(p\text{-}C_2H_5C_6H_4)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30		9.90	-3				*	(1)

No.	Supplementing 1951 No.	Reaction	Medium (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
.77		$(C_2H_5)[p\text{-}(CH_3)_2CHC_6H_4]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30	1.03	-2				*	(1)
.78		$(C_2H_5)[p\text{-}(CH_3)_3CC_6H_4]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30	1.00	-2				*	(1)
.79		$(C_2H_5)[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2; B = 0.1	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40	8.63 1.10 1.62	-4 -3 -3				*	(3)
.80		$(C_2H_5)[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40	5.75 7.90 1.02	-4 -4 -3	11	5	4		(2)
.81		$(C_2H_5)[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1; B = 0.2	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40	2.32 2.86 3.66	-4 -4 -4	9	2	2		(2)
.82		$(n\text{-}C_3H_7)(C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40	1.06 1.47 2.15	-2 -2 -2				*	(3)
.83		$(n\text{-}C_3H_7)[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2; B = 0.1	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40	5.79 7.92 1.20	-4 -4 -3				*	(3)
.84		$(n\text{-}C_3H_7)[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N $C_5H_5N\cdot HCl$	2.0 0.5	k AB	30 35 40	5.07 6.97 8.91	-4 -4 -4	11	4	4		(2)

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ 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	Literature
.85		$(n\text{-}C_3H_7)[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1; B = 0.2	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.72	-4					(2)
								35	2.03	-4					
								40	3.44	-4	11	2	4		
.86		$[(CH_3)_2CH](C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	2.22	-3				*	(1)
.87		$[(CH_3)_2CH](p\text{-}CH_3C_6H_4)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.79	-3				*	(1)
.88		$[(CH_3)_2CH](p\text{-}C_2H_5C_6H_4)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.73	-3				*	(1)
.89		$[(CH_3)_2CH][p\text{-}(CH_3)_2CHC_6H_4]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.51	-3				*	(1)
.90		$[(CH_3)_2CH][p\text{-}(CH_3)_3CC_6H_4]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.84	-3				*	(1)
.91		$[(CH_3)_2CH][2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2; B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.9	-4					(1)
.92		$(n\text{-}C_4H_9)(C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	1.17	-2				*	(3)
								35	1.67	-2					
								40	2.15	-2					
.93		$(n\text{-}C_4H_9)[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2; B = 0.1	C_5H_5N / $C_5H_5N\cdot HCl$	2.0 / 0.5	k AB	30	5.23	-4					(3)
								35	8.78	-4					
								40	1.19	-3					

No.	Supplementing 1951 No.	Reaction	Medium (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
.94		$(n\text{-}C_4H_9)[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N	2.0	k AB	30	4.83	-4					(2)
					$C_5H_5N\cdot HCl$	0.5		35	6.81	-4					
								40	8.89	-4	11	4	4		
.95		$(n\text{-}C_4H_9)[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1-0.2	C_5H_5N	2.0	k AB	30	2.00	-4					(2)
				B = 0.1-0.2	$C_5H_5N\cdot HCl$	0.5		35	2.18	-4					
								40	3.55	-4	10	2	3		
.96		$(n\text{-}C_5H_{11})(C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N	2.0	k AB	30	1.07	-2					(3)
					$C_5H_5N\cdot HCl$	0.5		35	1.67	-2					
								40	2.15	-2					
.97		$(n\text{-}C_5H_{11})[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2;	C_5H_5N	2.0	k AB	30	5.66	-4					(3)
				B = 0.1	$C_5H_5N\cdot HCl$	0.5		35	8.47	-4					
								40	1.15	-3					
.98		$(n\text{-}C_5H_{11})[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N	2.0	k AB	30	4.93	-4					(2)
					$C_5H_5N\cdot HCl$	0.5		35	6.55	-4					
								40	8.55	-4	10	8	3		
.99		$(n\text{-}C_5H_{11})[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1;	C_5H_5N	2.0	k AB	30	1.59	-4					(2)
				B = 0.2	$C_5H_5N\cdot HCl$	0.5		35	2.40	-4					
								40	2.92	-4	11	1.4	4		
.100		$(n\text{-}C_6H_{13})(C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N	2.0	k AB	30	1.22	-2				*	(3)
					$C_5H_5N\cdot HCl$	0.5		35	1.82	-2					
								40	2.39	-2					

No.	Supplementing 1951 No.	Reaction	Medium (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
.101		$(n\text{-}C_6H_{13})[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N	2.0	k AB	30	5.42	-4					(3)
		A = 0.2; B = 0.1			$C_5H_5N\cdot HCl$	0.5		30	5.58	-4					
								35	8.46	-4					
								40	1.17	-3					
.102		$(n\text{-}C_6H_{13})[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N	2.0	k AB	30	4.69	-4				*	(2)
					$C_5H_5N\cdot HCl$	0.5		40	8.60	-4	11	4	4		
.103		$(n\text{-}C_6H_{13})[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1; B = 0.2	C_5H_5N	2.0	k AB	30	1.47	-4				*	(2)
					$C_5H_5N\cdot HCl$	0.5		35	1.92	-4					
								40	2.29	-4	9	1.3	2		
.104		$(n\text{-}C_7H_{15})(C_6H_5)C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.05	C_5H_5N	2.0	k AB	30	1.15	-2				*	(3)
					$C_5H_5N\cdot HCl$	0.5		35	1.78	-2					
								40	2.22	-2					
.105		$(n\text{-}C_7H_{15})[2,5\text{-}(CH_3)_2C_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.2; B = 0.1	C_5H_5N	2.0	k AB	30	5.52	-4					(3)
					$C_5H_5N\cdot HCl$	0.5		35	8.50	-4					
								40	1.05	-3					
.106		$(n\text{-}C_7H_{15})[2\text{-}CH_3\text{-}5\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = B = 0.1	C_5H_5N	2.0	k AB	30	4.56	-4				*	(2)
					$C_5H_5N\cdot HCl$	0.5		35	5.80	-4					
								40	7.81	-4	10	8	3		
.107		$(n\text{-}C_7H_{15})[5\text{-}CH_3\text{-}2\text{-}(CH_3)_2CHC_6H_3]C{:}O + NH_2OH\cdot HCl$	CH_3OH	A = 0.1; B = 0.2	C_5H_5N	2.0	k AB	30	1.72	-4				*	(2)
					$C_5H_5N\cdot HCl$	0.5		35	2.20	-4					
								40	2.87	-4	9	2	2		

COMMENTS

General. Classification and arrangement based upon carbonyl compound. Aldehydes precede ketones. Order of ketones based upon simplest alkyl group attached to carbonyl-C. Methyl ketones are grouped together in order of the increasing complexity of the other group attached to the carbonyl-C.

References. (1) used equimolar amounts of A and B so rate law with respect to each reactant not confirmed. Rate law justified upon basis of results of (2) and (3). (2) activation energies of (2) rounded off to Kcals and Arrhenius constant recalculated to agree with rounded value of E. More significant figures not justified. (3) show reactions to be quantitative in anhydrous methanol in contrast to aqueous media.

Reactions. **(.102) (.103) (.106) (.107)** Initial rate much faster but consistent rate observed from 25 to 75 % reaction. Authors attribute rapid initial rate to isomeric impurities.

LITERATURE

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CONDENSATION

Amine + nitrous acid (or nitroso compound)

Liquid phase

N = N bond formation

Reaction types: $RNH_3^+ + HNO_2 \longrightarrow RN_2^+ + 2H_2O$

$RNH_2 + R'NO \longrightarrow RN{:}NR' + H_2O$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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
	Alkyl primary amine + HNO_2 (see 332.501)													
.1	$CH_3NH_2 + HNO_2 \longrightarrow CH_3OH + N_2 + H_2O$	(see 332.501)												(6)
.2	$2C_2H_5OOCCH_2NH_3^+ + HNO_2 \longrightarrow (C_2H_5OOCCH_2N)_2$, other products	H_2O	A = 0.05; B = 0.025-0.05		$-dA/dt = k(A)B[NO_2^-]$		25	1.1	-2				*	(6)
	Aryl primary amine + HNO_2													
.3	$C_6H_5NH_3^+ + HNO_2$	H_2O	$10^4(A)$ = 5-50; $10^4(B)$ = 5-1000	HNO_3, $NaNO_3$	$[H^+]$ = 5×10^{-6}-0.2	$k_1AB^2/(k_2[H^+] + A)$	0	k_1 9.2	-1	18			*	(5)
								k_2 6	-2					
			10^3A = 1-5; 10^3B = 1	H_2SO_4, Na_2SO_4	$[H^+] > 0.1$	$kAB^2/[H^+]$	0-5			$(E_1-E_2) = 10$				
							0	1.07	+1					(1) (4)

No.	Reaction	Medium (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	$C_6H_5NH_3^+ + HNO_2$ *(continued)*	H_2O	10^3A = 5-7.5; 10^3B = 2.5-7.5	H_2SO_4, Na_2SO_4	$[H^+]$ = 0.25	$k\,A(B)^2$	0	6.4	+1					(3)
					0.10		0	1.27	+2					
					0.05		0	1.86	+2					
					0.025		0	2.54	+2					
					0.010		0	3.11	+2					
					5×10^{-3}		0	2.95	+2					
					2.5×10^{-3}		0	2.42	+2					
					1.0×10^{-3}		0	1.83	+2					
					5×10^{-4}		0	1.11	+2					
					5×10^{-4}-0.25	$k\,AB^2/(k_2[H^+]+A)$	k_1	1.6	0					
							k_2	6	-2					
			10^4A= 5; (B) = 0.01	$HClO_4$; phthalate	10^{-5}	$k\,B^2$	0	3	0					(2)
			10^3A= 1-5; 10^3B= 1	HCl		$k\,AB[Cl^-]$	0	2.3	0				*	(1) (4)
				HBr		$k\,AB[Br^-]$	0	2.8	2					(1)
.4	$o\text{-}CH_3C_6H_4NH_3^+ + HNO_2$	H_2O	10^4A= 5; (B) = 0.01	$HClO_4$; phthalate	$[H^+] = 1 \times 10^{-5}$	$k\,B^2$	0	3	0				*	(2)
.5	$m\text{-}CH_3C_6H_4NH_3^+ + HNO_2$	H_2O	10^4A= 5; (B) = 0.01	$HClO_4$; phthalate	$[H^+] = 1 \times 10^{-5}$	$k\,B^2$	0	3	0				*	(2)
			A = B = 0.02	H_2SO_4	0.125	$k\,AB^2$	0	8.8	1					(3)
				$NH_2C_6H_4SO_3H$	0.02									
.6	$p\text{-}CH_3C_6H_4NH_3^+ + HNO_2$	H_2O	10^4A= 5; (B) = 0.01	$HClO_4$; phthalate	$[H^+] = 1 \times 10^{-5}$	$k\,B^2$	0	3	0				*	(2)
			A = B = 0.02	H_2SO_4	0.125	$k\,AB^2$	0	1.40	2					(3)
				$NH_2C_6H_4SO_3H$	0.02									
.7	$p\text{-}CH_3OC_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4	0.125	$k\,AB^2$	0	1.98	2				*	(3)
				$NH_2C_6H_4SO_3H$	0.02									

No.	Reaction	Medium (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
.8	$p\text{-}C_2H_5OC_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4 $NH_2C_6H_4SO_3H$	0.125 0.02	$k\,AB^2$	0	2.35	2				*	(3)
.9	$p\text{-}HSO_3C_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4 $C_6H_5NH_2$	0.125 0.02	$k\,AB^2$	0	1.42	2				*	(3)
.10	$m\text{-}NO_2C_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4 $NH_2C_6H_4SO_3H$	0.125 0.02	$k\,AB^2$	0	3.4	0				*	(3)
.11	$p\text{-}NO_2C_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4 $NH_2C_6H_4SO_3H$	0.125 0.02	$k\,AB^2$	0	1.4	-1				*	(3)
.12	$m\text{-}ClC_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4 $NH_2C_6H_4SO_3H$	0.125 0.02	$k\,AB^2$	0	1.42	1				*	(3)
.13	$p\text{-}ClC_6H_4NH_3^+ + HNO_2$	H_2O	A = B = 0.02	H_2SO_4 $NH_2C_6H_4SO_3H$	0.125 0.02	$k\,AB^2$	0	2.60	1				*	(3)
	Secondary amine + HNO_2													
.14	$(CH_3)_2NH_2^+ + HNO_2 \longrightarrow (CH_3)_2NNO + H_2O + H^+$	H_2O	A = 0.05; B = 0.05-0.1			$k\,AB[NO_2^-]$	25	1.1	-2				*	(6)

No.	Reaction	Medium (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
	Aryl amine + nitroso compound													
.15	$C_6H_5NH_2 + C_6H_5NO$	CH_3COOH	$10^2A = 1\text{-}3$; $10^2B = 1\text{-}3$			k AB	21	1.24	-3					(7)
							30	1.83	-3					
							35	2.44	-3	8.9	4	3		
.16	$C_6H_5NH_2 + o\text{-}NO_2C_6H_4NO$	CH_3COOH	$10^2A = 1\text{-}3$; $10^2B = 1\text{-}3$			k AB	19	7.46	-3					(7)
							25	1.11	-2					
							30	1.45	-2					
							35	1.92	-2	10.6	6	5		
.17	$C_6H_5NH_2 + m\text{-}NO_2C_6H_4NO$	CH_3COOH	$10^2A = 1\text{-}3$; $10^2B = 1\text{-}3$			k AB	20	1.42	-2					(7)
							25	1.90	-2					
							30	2.88	-2					
							36	3.97	-2	11.8	1.0	7		
.18	$C_6H_5NH_2 + p\text{-}NO_2C_6H_4NO$	CH_3COOH	$10^2A = 1\text{-}3$; $10^2B = 1\text{-}3$			k AB	21	1.61	-2					(7)
							35	3.87	-2					
							40	5.59	-2	11.8	9	6		
.19	$C_6H_5NH_2 + p\text{-}ClC_6H_4NO$	CH_3COOH	$10^2A = 1\text{-}3$; $10^2B = 1\text{-}3$			k AB	31	3.20	-3					(7)

COMMENTS

Reactions. **(.1)** Most alkyl primary amines with nitrous acid yield alcohol and evolve N_2. For kinetics of these reactions see 332.501. **(.2)** Third order rate law followed for 20 % of reaction course. (A) represents total analytical concentration of all forms of amine. **(.3)** Rate law expressed in variety of forms by different authors. Rate law postulated by ([5]) reduces to expressions proposed by ([1]) ([2]) ([3]) and ([4]) under conditions where $k_2[H^+] >> A$ or $k_2[H^+] << A$. Values of (B) are total analytical concentrations of all molecular and ionic forms of B. Values measured by ([5]) are for initial rates. ([3]) observed third order behavior over course of reaction. Values of ([3]) can be expressed by equation of form used by ([5]) over entire range of acid concentrations with a maximum deviation of about 20 %. Pseudo zero order behavior observed by ([2]) for 80 % of reaction by using a large excess of B in buffered solution. Value of second order rate constant calculated from linear portion of rate plot by dividing observed rate by the square of the calculated concentration of HNO_2. Identical rate of reaction observed by ([2]) for (.4) (.5) (.6) under these conditions. In presence of hydro-halogen acid rate law observed to be first order with respect to halogen ion and rate constant dependent upon halogen used. **(.4) (.5) (.6)** Pseudo zero order rate law observed by ([2]) for up to 80 % reaction in buffered solution with excess B. Value of second order constant calculated from linear portion of plot by dividing observed rate by the square of the calculated concentration of HNO_2. Reaction rate constants of ([3]) were measured relative to sulfanilic acid (.9) and then calculated relative to aniline (.3). Values tabulated were calculated from value for (.3) at same pH and relative rate assuming identical rate laws. Significance of last figure is for comparison of relative rates only. **(.7) (.8)** Rate of reaction relative to sulfanilic acid (.9) measured and rate relative to aniline (.3) calculated. Values tabulated were calculated from value for (.3) at same pH and relative rate assuming identical rate laws. Significance of last figure is for comparison of relative rates only. **(.9)** Rate of reaction relative to aniline (.3) determined and value calculated from relative rate and rate constant for (.3) at same pH assuming identical rate laws. **(.10) (.11) (.12) (.13)** Reaction rate constants were measured relative to sulfanilic acid (.9) and then calculated relative to aniline (.3). Values tabulated were calculated from value for (.3) at same pH and relative rate assuming identical rate laws. Significance of last figure is for comparison of relative rates only. **(.14)** Third order rate law observed up to 20 % reaction without drift.

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([1]) E. Abel, *MHC* 1951, **82**, 189. ([2]) E.D. Hughes, C.K. Ingold, J.H. Ridd, *Nature* 1950, **166**, 642. ([3]) M. Okano, Y. Ogata, *ACS* 1953, **75**, 5175. ([4]) H. Schmid, G. Muhr *BDC* 1937, **70**, 421. ([5]) H. Schmid, A. Wappmann, *MHC* 1952, **83**, 346. ([6]) T.W.J. Taylor, L.S. Price, *CSL* **1929**, 2052. ([7]) K. Ueno, S. Akiyoshi, *ACS* 1954, **76**, 3670.

CONDENSATION
Phenol + Alkyl halide

Liquid phase

Reaction types: $ArOH + RX \longrightarrow ArOR + HX$
$ArOH + RX \longrightarrow RArOH + HX$

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Supplementing 1951 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	Comments	Literature
.6	.3	$C_6H_5OH + (CH_3)_3CCl \longrightarrow$ $p\text{-}(CH_3)_3CC_6H_4OH + HCl$	A	B = 0.3-0.5			kB	45	1.39	-4		*	(3)
				B = 0.5				50	2.02	-4			
								55	3.30	-4	17		
				B = 0.5	$1,4\text{-}Cl_2C_4H_8$	0.58		45	1.19	-4			
						1.28		45	8.47	-5			
						2.18		45	3.62	-5			
						4.11		45	7.55	-6			
				B = 0.6	$1,2\text{-}Cl_2C_4H_8$	2.18		45	6.12	-5			
				B = 0.7	$C_6H_5NO_2$	2.38		35	6.15	-5			
						1.42		45	1.27	-4			
						2.41		45	1.12	-4			
						4.31		45	4.28	-5	13		
				B = 0.5-0.7	$p\text{-}(CH_3)_2C_6H_4$	1.27		45	5.48	-5			
						2.00		45	2.08	-5			
						1.37		50	7.90	-5			(2)
				B = 0.44	dioxane	0.295		50	1.09	-4			
				0.49		0.616		50	6.47	-5			
				0.47		1.07		50	2.52	-5			
				0.48		1.52		50	7.67	-6			

No.	Supplementing 1951 No.	Reaction	Medium (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	.3	$C_6H_5OH + (CH_3)_3CCl \longrightarrow$ $p\text{-}(CH_3)_3CC_6H_4OH + HCl$ *(continued)*	A	B = 0.51	$O(CH_2)_4CH_2$	0.556	kB	50	9.70	-5			(2)
				0.51		1.09		50	4.30	-5			
				0.48		1.46		50	2.72	-5			
.7		$C_6H_5OH + C_2H_5(CH_3)_2CCl \longrightarrow$ $p\text{-}C_2H_5(CH_3)_2CC_6H_4OH + HCl$	A	B = 0.5			kB	45	9.63	-5			(3)
								50	1.62	-4			
								55	1.80	-4	15		
.8		$C_6H_5OH + (CH_3)_2CH(CH_3)_2CCl \longrightarrow$ $p\text{-}(CH_3)_2CH(CH_3)_2CC_6H_4OH + HCl$	A	B = 0.5-0.7			kB	45	2.71	-5			(3)
								50	3.80	-5			
								55	6.60	-5	16		
.9	.3	$C_6H_5OH + (C_6H_5)_3CCl \longrightarrow$ $p\text{-}(C_6H_5)_3CC_6H_4OH + HCl$	$o\text{-}Cl_2C_6H_4$	A = 0.315; B = 0.631		$dM^*/dt = k\,AB + k'ABM^*$		88	k 3.40	-3		*	(1)
									k' 2.90	-5			
				0.610	0.629			88	k 7.25	-3			
									k' 9.00	-5			
				0.913	0.610			88	k 1.31	-2			
									k' 1.36	-4			
				1.184	0.594			88	k 1.81	-2			
									k' 2.18	-4			
.10		$o\text{-}CH_3C_6H_4OH + (CH_3)_3CCl \longrightarrow$ $2\text{-}CH_3\text{-}4\text{-}(CH_3)_3CC_6H_3OH + HCl$	$o\text{-}Cl_2C_6H_4$	A = 1.184; B = 0.592		$dM^*/dt = k\,AB + k'ABM^*$		88	k 5.55	-3		*	(1)
									k' 1.72	-4			
				1.368	0.357			88	k 5.92	-3			
									k' 1.68	-4			
				A = 1.37; B = 0.357; M^* = 117 mm. of Hg			$k'ABM^*$	88	k' 1.63	-4			
.11		$p\text{-}CH_3C_6H_4OH + (CH_3)_3CCl \longrightarrow$ $2\text{-}(CH_3)_3C\text{-}4\text{-}CH_3C_6H_3OH + HCl$	A	B = 0.5			kB	45	3.19	-5			(3)

COMMENTS

General. Reaction between phenol and alkyl halide in the absence of a base leads to nuclear substitution in the para-position of the benzene ring. For other ring alkylation reactions see 312.442. In the presence of a base the nuclear alkylation is superceded by ether formation.

Reactions. **(.6)** Pseudo first order constant with respect to B observed as A always in large excess. Variety of diluents added in an effort to determine order with respect to A. The order with respect to A was estimated to be about six. Diluents such as 1,4-dioxane and tetrahydropyran were considered to inhibit the catalytic activity of the phenol by forming hydrogen bonded complexes. Autocatalysis by HCl not observed as in reactions (.9) and (.10). **(.9)** Induction period typical of autocatalysis observed. Initial rate shown to follow second order law, k AB, and later stages followed third order law, $k'ABM^*$. M^* and dM^* are measured in mm. of Hg rather than usual concentration units of moles per liter. Henry's constant for the reaction system was not evaluated. Units of k are therefore mm. l^2. $mole^{-2}sec^{-1}$. Rate law gave excellent agreement over entire course for each reaction. Variation in rate constants with initial concentrations of reactants attributed to changes in ionizing properties of solution. **(.10)** Induction period typical of autocatalysis observed. Proposed rate law valid over entire course of reaction. When HCl added initially induction period eliminated, and third order rate law, $k'ABM^*$, alone valid over course. M^* and dM^* are measured in mm. of Hg rather than usual concentration units of moles per liter. Henry's constant for the reaction system was not evaluated. Units of k are therefore mm. l^2. $mole^{-2}sec^{-1}$.

LITERATURE

([1]) H. Hart, F.A. Cassis, *ACS* 1954, **76**, 1634. ([2]) H. Hart, F.A. Cassis, J.J. Bordeaux, *ACS* 1954, **76**, 1639.

([3]) H. Hart, J.H. Simons, *ACS* 1949, **71**, 345.

CONDENSATION

Amine + ester

Liquid phase

Reaction type: $R'R''NH + R_1COOR_2 \longrightarrow R_1CONR'R'' + R_2OH$

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Temperature	Half-time
.1	$n\text{-}C_7H_{15}NH_2 + (COOCH_2C_6H_5)_2 \longrightarrow n\text{-}C_7H_{15}NHCOCOOCH_2C_6H_5 + C_6H_5CH_2OH$	$CH_3C_6H_5$	A= B= 0.05	69	800
.2	$(n\text{-}C_3H_7)_2CHNH_2 + (COOCH_2C_6H_5)_2 \longrightarrow (n\text{-}C_3H_7)_2CHNHCOCOOCH_2C_6H_5 + C_6H_5CH_2OH$	$CH_3C_6H_5$	A= B= 0.05	69	17,000
.3	$[(CH_3)_2CH]_2CHNH_2 + (COOCH_2C_6H_5)_2 \longrightarrow [(CH_3)_2CH]_2CHNHCOCOOCH_2C_6H_5 + C_6H_5CH_2OH$	$CH_3C_6H_5$	A= B= 0.05	69	105,000
.4	$(C_2H_5)_3CNH_2 + (COOCH_2C_6H_5)_2 \longrightarrow$	$CH_3C_6H_5$	A= B= 0.05	69	very slow

LITERATURE

G. Vavon, L. Bourgeois, *CRA* 1936, 202, 1593.

CONDENSATION

Amine + acid anhydrid

Liquid phase

Reaction type: $R'R''NH + (R'''CO)O \longrightarrow R'''CONR'R'' + R'''COOH$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Temperature	Half-time
.1	$C_6H_5NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	0	2,200
.2	o-$CH_3C_6H_4NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	0 69	19,000 2,600
.3	p-$CH_3C_6H_4NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	0	540
.4	2,4,6-$(CH_3)_3C_6H_2NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	69	22,000
.5	o-(n-C_4H_9)$C_6H_4NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	69	24,000
.6	p-(n-C_4H_9)$C_6H_4NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	0	780
.7	o-$NO_2C_6H_4NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	69	> 350,000
.8	p-$NO_2C_6H_4NH_2 + (C_6H_5CO)_2O$	$CH_3C_6H_5$	A = 0.05; B = 0.025	69	245,000

LITERATURE

G. Vavon, L. Bourgeois, *CRA* 1936, 202, 1446.

CONDENSATION

Hydroxyl amine and oxygen acid of sulfur

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$H_2SO_3 + NH_2OH \longrightarrow NH_2SO_3H + H_2O$	H_2O	$10^2A = 4.6\text{-}7$; $10^2B = 2\text{-}4$	buffers	0.1	1.0	$k\,AB$	25	3	-3
					0.1	2.0		25	1.0	-2
					0.1	3.0		25	1.9	-2
					0.1	4.0		25	2.0	-2
					0.1	5.0		25	1.4	-2
					0.1	6.0		25	6	-3
					0.1	7.0		25	2	-3

COMMENTS

Parallel reaction forming NH_4^+ and HSO_4^- proceeds at approximately one tenth the rate of the condensation reaction, see 732.651. Second order rate law in terms of total analytical concentrations valid over 85 % of reaction course. Dependence of rate constant upon hydrogen ion concentration given by $10^5k = 3.48[H^+]^2/([H^+] + K_1)([H^+] + K_2)([H^+] + K_3)$ where $K_1 = 1.72 \times 10^{-2} = [H^+][HSO_3^-]/[H_2SO_3]$; $K_2 = 6.2 \times 10^{-8} = [H^+][SO_3^=]/[HSO_3^-]$; and $K_3 = 1.04 \times 10^{-6} = [H^+][NH_2OH]/[NH_2OH \cdot H^+]$.

LITERATURE

D. S. Brackman, W. C. E. Higginson, *CSL* **1953**, 3896.

CONDENSATION
Thio acid and Amine

Liquid phase

Reaction type: $RCOSH + R'R''NH \longrightarrow RCONR'R'' + H_2S$

Amounts are in M/l.
Rate constants are in M/l and 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
.1	$C_6H_5COSH + C_6H_5NH_2$	$C_6H_5NH_2$	A = 0.014-0.08			kA^2	60	8.2	-3				*
.2	$C_6H_5COSH + C_6H_5NH_2$	CH_3COOH	A = 0.14; B = 0.19	H_2O	0.2	kAB	60	5.0	-4				*
			A = 0.13; B = 0.20		2.2		60	4.1	-4				
			A = 0.12; B = 0.29		5.5		60	3.9	-4				
			A = 0.11; B = 0.26		11		60	4.2	-4				
			A = 0.13; B = 0.22		16		60	4.5	-4				
			A = 0.14; B = 0.10		16		60	3.7	-3				
			A = 0.18; B = 0.47		23		60	9.0	-4				
.3	$C_6H_5COSH + C_6H_5NH_2$	C_6H_5Cl	A = (0.20-0.25)			kAB	50	2.48	-5				*
			B ≃ A				60	3.20	-5				
							70	4.50	-5	7.4	2	0	
				H_2S	sat.		60	2.84	-5				
				C_6H_5COOH	0.007		60	9.6	-5				
					0.016		60	1.33	-4				
					0.031		60	1.82	-4				
				$(C_6H_5COS)_2$	0.0052		60	4.96	-5				

COMMENTS

Reaction. (.1) Units converted from original minutes. Rate law valid up to 83 % reaction with about 5 % variation but no trend. Reaction carried out in atmosphere of nitrogen to prevent loss of A by oxidation. (.2) Rate law valid only over early stages of reaction. Extent dependent upon added water. At 5.5 M/l of H_2O rate law valid from 7 to 80 % reaction while at 23 M/l of H_2O and B = 0.14 there is no region over which rate law appears to hold. (.3) Rate law valid over at least 60 % of course of reaction. Variation in specific rate constants observed with different samples of A. Authors considered this due to catalysis by C_6H_5COOH as impurity. Lowest values tabulated. Reaction carried out under atmosphere of nitrogen. Units converted from original minutes.

LITERATURE

P.J. Hawkins, D.S. Tarbell, P. Noble, *ACS* 1953, **75**, 4462.

HYDROLYSIS
B-H bond hydrolysis

Gas phase

Amounts are in M/l except where stated otherwise.

Rate constants are in M/l and sec.

No.	Reaction	Method	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n
.1	$B_2H_6 + m\,H_2O \longrightarrow 6\,H_2 + H_3BO_3,\ HBO_2,\ B_2O_3$	analytical for A and vol. of L	A/B = 5.2-0.086; B < 92 mm of Hg			$k\,A^{\frac{1}{2}}B$	50	4.7	-3
				glass surface	X10		50	6.9	-3
				boric acid surface	X10		50	7.0	-3

COMMENTS

Ratio of products and total pressure dependent upon reactant ratio. Rate law independent of reactant ratio. In excess A amount of HBO_2 and B_2O_3 increases, and total pressure increases as ratio of B consumed per L formed decreases. In all cases L formed = 6 A consumed. In excess B principal product is H_3BO_3 and total pressure decreases.

LITERATURE

H.G. Weiss, I. Shapiro, *ACS* 1953, 75, 1221.

SOLVOLSIS

B-H bond solvolsis

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Ionic strength	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	$NaBH_4 + 3H_2O \longrightarrow NaH_2BO_3 + 4H_2$	H_2O	A = 0.001; $10^{10}B$ = 3-1000	pyrophosphate buffer	0.1	$k\,A[H^+]$	15 25 35	1.45 2.50 4.0	-5 -5 -5	8.9	8	11

COMMENTS

In buffered solution, pseudo first order rate law over 90 % of course. Rate law calculated in terms of concentration of A but in terms of activity of H^+.

LITERATURE

R.L. Pecsok, *ACS* 1953, 75, 2862.

SOLVOLYSIS

B-F bond solvolysis

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium	Amount of reactant	Defined mass-action law	Temperature	$k_1 = k_1^o \times 10^n$ k_1^o	n	$k_2 = k_2^o \times 10^n$ k_2^o	n
.1	$HBF_4 + H_2O \longrightarrow HBF_3OH + HF$	H_2O	A = 0.013	k_1A-k_2LM	25	3.2	-6	1.37	-3
			0.056		25	9.2	-6	4.06	-3
			0.110		25	1.5	-5	6.54	-3

LITERATURE

C. A. Wamser, *ACS* 1948, **70**, 1209.

SOLVOLYSIS
Si-O-C or Si-O-Si bonds

Rate = $-dA/dt$ unless otherwise stated

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

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	Comments	Literature
	Si-O-C bonds											
.1	$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4C_2H_5OH$	CH_3OH or dioxane	A = 0.2; B = 1.2-2.5	HCl	2.2×10^{-5} to 6.3×10^{-2}	$k\,AB[HCl]$	20	5.1	-2		*	(1)
							45	7.1	-1	19		
		CH_3OH	A = 0.16-0.93	NaOH	0.018	$k\,A[OH^-]$	20	3.9	-2			
			B = 0.39-1.3		0.035		20	4.7	-2			
		C_2H_5OH	A= 0.62; B= 2.3	HCl	0.0034	$k\,AB[HCl]$	20	5.9	-2			
			0.21 1.2		0.0016		20	6.5	-2			
			0.62 1.2		0.0037		20	4.2	-2			
.2	$Si(OC_2H_5)_3(OC_6H_{13}) + 4H_2O \longrightarrow Si(OH)_4 + 3C_2H_5OH + n\text{-}C_6H_{13}OH$	dioxane	B ~ 4A	HCl	0.001-0.02	$k\,AB[HCl]$	20	5.0	-2		*	(2)
.3	$Si(OC_2H_5)_2(OC_6H_{13})_2 + 4H_2O \longrightarrow Si(OH)_4 + 2C_2H_5OH + 2n\text{-}C_6H_{13}OH$	dioxane	A= 0.3; B= 1.5	HCl	0.001-0.02	$k\,AB[HCl]$	20	5.0	-2		*	(2)
.4	$Si(OC_2H_5)_2[OCH(CH_3)CH(CH_3)_2]_2 + 4H_2O \longrightarrow Si(OH)_4 + 2C_2H_5OH + 2(CH_3)_2CH(CH_3)CHOH$	dioxane	B ~ 4A	HCl		$k\,AB[HCl]$	20	1.5	-3		*	(2)

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	Comments	Literature
.5	$Si(OC_2H_5)_2[OCH(CH_3)C_5H_{11}]_2 + 4H_2O \longrightarrow Si(OH)_4 + 2C_2H_5OH + 2n\text{-}C_5H_{11}(CH_3)CHOH$	dioxane	B ~ 4A	HCl		$k\,AB[HCl]$	20	9.5	-4		*	(2)
.6	$Si(OC_2H_5)_2\{OCH[CH_2CH(CH_3)_2]_2\}_2 + 4H_2O \longrightarrow Si(OH)_4 + 2C_2H_5OH + 2[(CH_3)_2CHCH_2]_2CHOH$	dioxane	B ~ 4A	HCl		$k\,AB[HCl]$	20	3.8	-4		*	(2)
.7	$Si(OC_2H_5)(OC_6H_{13})_3 + 4H_2O \longrightarrow Si(OH)_4 + C_2H_5OH + 3n\text{-}C_6H_{13}OH$	dioxane	B ~ 4A	HCl		$k\,AB[HCl]$	20	1.1	-2		*	(2)
.8	$Si(OC_4H_9)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4n\text{-}C_4H_9OH$	dioxane	B ~ 4A	HCl		$k\,AB[HCl]$	20	1.9	-2		*	(2)
.9	$Si(OC_6H_{13})_4 + 4H_2O \longrightarrow Si(OH)_4 + 4n\text{-}C_6H_{13}OH$	dioxane	A= 0.24; B~1	HCl	0.001-0.02	$k\,AB[HCl]$	20	8.3	-3		*	(2)
.10	$Si\{OCH[CH_2CH(CH_3)_2]_2\}_4 + 4H_2O \longrightarrow Si(OH)_4 + 4[(CH_3)_2CHCH_2)_2CHOH$	dioxane	B ~ 4A	HCl		$k\,AB[HCl]$	20	3.0	-4		*	(2)
	Si-O-Si bonds											
.11	$(CH_3)_3SiOSi(CH_3)_3 + CH_3OH \longrightarrow (CH_3)_3SiOCH_3 + (CH_3)_3SiOH$	CH_3OH	A = 0-0.13	HCl	$(1\text{-}4) \times 10^{-4}$	$k\,A[HCl]$	25	4	2		*	(3)
				KOH	$(4\text{-}100) \times 10^{-4}$	$k\,A[KOH]$	25	8.3	-2			
				NaOH	2.2×10^{-3}	$k\,A[NaOH]$	25	7.7	-2			
				LiOH	1.1×10^{-3}	$k\,A[LiOH]$	25	7.7	-2			
.12	$(CH_3)_3SiOSi(CH_3)_3 + C_2H_5OH \longrightarrow (CH_3)_3SiOC_2H_5 + (CH_3)_3SiOH$	C_2H_5OH	M = 0.26	HCl	2×10^{-4}	$k\,A[HCl]$	25	2.4	0		*	(3)

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	Comments	Literature
.13	$(C_2H_5)_3SiOSi(C_2H_5)_3 + CH_3OH \longrightarrow (C_2H_5)_3SiOCH_3 + (C_2H_5)_3SiOH$	CH_3OH	M = 0.26	HCl	2×10^{-4}	$kA[HCl]$	25	2.8	-2		*	([3])

COMMENTS

Reactions. (.1) through (.10) Reaction immediately followed by polymerization and dehydration of L,

$$n\ Si(OH)_4 \longrightarrow (SiO_2)_n + 2nH_2O.$$

Therefore net decrease of H_2O is two moles per mole of $Si(OR)_4$ reacted. At low concentrations of alkyl silicate hydrolysis is almost complete. At concentrations higher than those tabulated extent of hydrolysis decreases and rate law is not maintained. For (.1) at A = 0.93 with NaOH as catalyst, pseudo first order rate holds for first 30 % reaction after which calculated constants decrease rapidly and solid is observed to form. Effect of solvent is very slight and no mass action effect observed with CH_3OH or C_2H_5OH as solvents. Reactions of ([2]) used dioxane, or mixtures of alcohols. Solvent used was not specified in each case. Progress of reaction followed using Karl Fischer reagent for B. **(.11) (.12) (.13)** Rate calculated from value of equilibrium constant and rate of condensation reaction. See 232.447. Equilibrium approached from both directions. Evidence of almost complete reaction of M with B, $(CH_3)_3SiOH + CH_3OH \longrightarrow (CH_3)_3SiOCH_3 + H_2O$, is that silanols as well as H_2O may be determined quantitatively in alcohol using Karl Fischer reagent. Solvolysis with H_2O assumed to be negligible as reaction faster in dry methanol than in methanol containing equimolar A and H_2O.

LITERATURE

(1) R. Aelion, A. Loebel, F. Eirich, *ACS* 1950, **72**, 5705.

(2) R. Aelion, A. Loebel, F. Eirich, *RTC* 1950, **69**, 61.

(3) W.T. Grubb, *ACS* 1954, **76**, 3408.

SOLVOLYSIS
Si-H bond

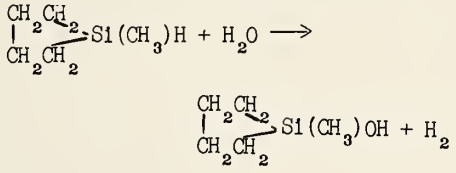
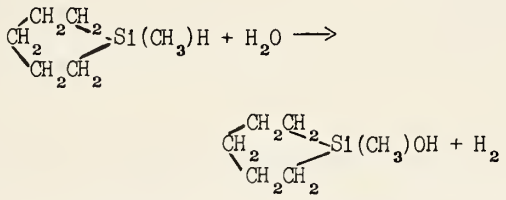
Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction type: $R_1R_2R_3SiH + R'OH \longrightarrow R_1R_2R_3SiOR' + H_2$

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	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger} - \Delta S_o^{\ddagger}$	Comments	Literature
.1	$CH_3(C_2H_5)_2SiH + H_2O \longrightarrow CH_3(C_2H_5)_2SiOH + H_2$	C_2H_5OH	A = 0.1; B = 8.3	NaOH	1.85	$k\,A[OH^-]$	15	2.34	-4				(2)
					1.85		25	5.84	-4				
					0.256		25	1.71	-3				
					1.85		35	1.36	-3				
					0.256		35	4.02	-3				
					0.256		45	8.02	-3	15	0*		
			A = 0.1; B = 3.46	KOH	0.06-0.3	$k\,A[OH^-]$	34	2.74	-3				(1)
			8.61				34	3.90	-3				
			13.86				34	5.30	-3				
			19.07				34	5.87	-3				
			3.46				45	5.82	-3	13	0*		
			8.61				45	7.04	-3				
			13.86				45	8.81	-3				
			19.07				45	1.00	-2				
			A = 0.1; B = 3-19	KOH	$k = k'[C_2H_5OH] + k''[H_2O]$		34	k' 1.05	-4				
							34	k'' 2.80	-4				
							45	k' 2.80	-4	E' 18			
							45	k'' 3.62	-4	E'' 5			
.2	$n\text{-}C_3H_7(CH_3)_2SiH + H_2O \longrightarrow n\text{-}C_3H_7(CH_3)_2SiOH + H_2$	C_2H_5OH	A = 0.1; B = 3.46	KOH	~0.2	$k\,A[OH^-]$	35	5.86	-3				(1)
			8.61				35	8.70	-3				
			13.86				35	1.06	-2				

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	$\Delta H^{\neq}$	$\Delta S^{\neq} - \Delta S_o^{\neq}$	Comments	Literature
.2	$n\text{-}C_3H_7(CH_3)_2SiH + H_2O \longrightarrow$ $n\text{-}C_3H_7(CH_3)_2SiOH + H_2$ *(continued)*	C_2H_5OH	A = 0.1; B = 19.07	KOH	~0.2	$k\,A[OH^-]$	35	1.29	-2				(1)
			3.46				44	1.32	-2	15	7*		
			8.61				44	1.59	-2				
			13.86				44	1.88	-2				
			19.07				44	2.18	-2				
			A = 0.1; B = 3-19	KOH	$k = k'[C_2H_5OH] + k''[H_2O]$		35	k' 2.62	-4			*	(1)
							35	k'' 5.20	-4				
							44	k' 6.45	-4	E' 19			
							44	k'' 7.48	-4	E'' 8			
.3	$(C_2H_5)_3SiH + H_2O \longrightarrow (C_2H_5)_3SiOH + H_2$	C_2H_5OH	A = 0.1; B = 3.46	KOH	0.1-0.3	$k\,A[OH^-]$	34	1.55	-3				(1)
			8.61				34	2.45	-3				
			13.86				34	2.94	-3				
			19.07				34	3.27	-3				
			3.46				45	3.65	-3	16	6*		
			8.61				45	5.25	-3				
			13.86				45	5.94	-3				
			19.07				45	6.51	-3				
.4	$(n\text{-}C_3H_7)_2(CH_3)SiH + H_2O \longrightarrow$ $(n\text{-}C_3H_7)_2(CH_3)SiOH + H_2$	C_2H_5OH	A = 0.1; B = 3.46	KOH	0.1-0.3	$k\,A[OH^-]$	34	1.77	-3				(1)
			8.61				34	2.48	-3				
			13.86				34	2.82	-3				
			19.07				34	3.07	-3				
			3.46				45	4.02	-3	15	4*		
			8.61				45	5.80	-3				
			13.86				45	6.23	-3				
			19.07				45	6.68	-3				

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	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger} - \Delta S_o^{\ddagger}$	Comments	Literature
.5	$(n\text{-}C_3H_7)_3SiH + H_2O \longrightarrow (n\text{-}C_3H_7)_3SiOH + H_2$	C_2H_5OH	A = 0.1; B = 3.46	KOH	0.1-0.3	$k\,A[OH^-]$	35	6.8	-4				(1)
							44	1.60	-3	17	9*		
.6		C_2H_5OH	A = 0.12; B = 8.3	NaOH	0.256	$k\,A[OH^-]$	5	3.39	-3				(2)
							15	8.45	-3				
							25	2.24	-2	16.8	10*		
.7		C_2H_5OH	A = 0.12; B = 8.3	NaOH	1.85	$k\,A[OH^-]$	25	1.06	-4			*	(2)
					1.85		35	2.95	-4	19	6*		
					0.256		35	5.99	-4				
					0.256		45	1.48	-3	18			

*$\Delta S^{\ddagger} - \Delta S_o^{\ddagger}$ Relative entropy of activation with reference to (.1) as 0.

COMMENTS

Method of measurement is rate of evolution of hydrogen. Pseudo first order kinetics over course unless noted otherwise. Second order constants obtained by dividing pseudo first order constant by concentration of catalyst. Probably equilibrium reaction of L with solvent occurs, $R_3SiOH + R'OH = R_3SiOR' + H_2O$, see 232.447.

COMMENTS *(continued)*

Reaction. (.1) At $[OH^-]$ less than 0.3no appreciable salt effect observed by (1) but at $[OH^-]$ = 1.85 definite depression of catalytic rate constant observed by (2). Reaction used as reference for $\Delta S^{\ddagger}$ by (1) and (2). (1) fits data to a sum of two third order rate expressions over range H_2O-C_2H_5OH studied. Data of (1) and (2) agree at 35° but show about 13 % deviation at 45°C. (.2) Sum of two third order rate expressions gives fairly good fit to data over range H_2O-C_2H_5OH studied. (.7) Pseudo first order rate law showed drift, (probably downward) as author attributed it to impure reactant or competing higher order reaction.

LITERATURE

(1) F.P. Price, *ACS* 1947, **69**, 2600. (2) R. West, *ACS* 1954, **76**, 6015.

SOLVOLYSIS
Ethers

Liquid phase

Reaction types: $ROR' + H_2O \longrightarrow ROH + R'OH$

$ArOAr' + ROH \longrightarrow ArOR + Ar'OH$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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
.4	$(CH_2{:}CHOCH_2CH_2C{:}N)_n + H_2O \longrightarrow$ $CH_3OCH_2CH_2OCH_3$ (underlined) $(CH_2{:}CHOH)_n + C{:}NCH_2CH_2OH$		n·A = 0.86; B ≃ 2	NaOH	0.12 0.06-0.14	$k\,A[OH^-]$	25 40 60	1.52 1.82 2.23	-5 -4 -3	31	6	16	*	(2)
	Aryl ether + Alcohol													
.5	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_5 + CH_3OH$	CH_3OH	A = 0.01	KOH	0.004-0.02	$k\,A[OH^-]$	20	4.76	-3					(1)
.6	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_4CH_3\text{-}2' + CH_3OH$	CH_3OH	A = 0.01	KOH	0.016	$k\,A[OH^-]$	20	1.43	-3					(1)
.7	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_4CH_3\text{-}3' + CH_3OH$	CH_3OH	A = 0.01	KOH	0.015-0.016	$k\,A[OH^-]$	20	3.69	-3					(1)
.8	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_4CH_3\text{-}4' + CH_3OH$	CH_3OH	A = 0.01	KOH	0.016	$k\,A[OH^-]$	20	2.84	-3					(1)
.9	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_4NO_2\text{-}4' + CH_3OH$	CH_3OH	A = 0.01	KOH	0.016	$k\,A[OH^-]$	20	6.46	-2					(1)
.10	$2,4\text{-}(NO_2)_2C_6H_3OC_6H_4Cl\text{-}4' + CH_3OH$	CH_3OH	A = 0.01	KOH	0.016	$k\,A[OH^-]$	20	1.07	-2					(1)
.11	$2,4\text{-}(NO_2)_2C_6H_3O\text{-}\alpha\text{-}C_{10}H_7 + CH_3OH$	CH_3OH	A = 0.01	KOH	0.015-0.016	$k\,A[OH^-]$	20	6.26	-3					(1)
.12	$2,4\text{-}(NO_2)_2C_6H_3O\text{-}\beta\text{-}C_{10}H_7 + CH_3OH$	CH_3OH	A = 0.01	KOH	0.015-0.016	$k\,A[OH^-]$	20	8.12	-3					(1)

COMMENTS

Reaction. (.4) Beyond 50 % reaction pseudo first order constants decrease slightly. Solvolysis of ether linkage predominant but slight solvolysis of nitrile noted.

LITERATURE

([1]) Y. Ogata, M. Okano, *ACS* 1949, **71**, 3212. ([2]) J.F. Wright, L.M. Minsk, *ACS* 1953, **75**, 98.

SOLVOLYSIS
Acetals and Ketals

Liquid phase

Reaction type: $RR_1C(OR')(OR'') + H_2O \longrightarrow RR_1C{:}O + R'OH + R''OH$

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

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Supplementing 1951 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
.5		$CH_2(OCH_3)_2 + H_2O$	B	A=0.17-0.23	HCl	0.37	$k A[H^+]$	25	3.40	-5				*	(6)
						0.50		25	3.62	-5					
						1.30		25	6.35	-5					
						2.61		25	1.29	-4					
						3.91		25	5.98	-4					
					$HClO_4$	0.45		25	3.30	-5					
						0.91		25	3.87	-5					
						1.46		25	4.93	-5					
						1.81		25	7.43	-5					
						2.72		25	1.45	-4					
						3.40		25	2.67	-4					
						4.30		25	8.2	-4					
					H_2SO_4	1.23		25	6.08	-5					
						1.72		25	8.38	-5					
						1.96		25	9.90	-5					
					$HClO_4$	0.5 + $NaClO_4$ = 5.5		25	1.19	-3					
						1.0 5		25	1.66	-3					
						2.0 5		25	1.98	-3					
					HCl	0.37 + NaBr = 1.0	$k A$	25	3.75	-5					(5)
						" LiCl "		25	3.25	-5					

No.	Supplementing 1951 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
.5		$CH_2(OCH_3)_2 + H_2O$ *(continued)*	B	A = 0.17-0.23	HCl	0.37 + NaCl = 1.0	kA	25	2.87	-5					(5)
						" KCl "		25	2.62	-5					
						" Me_4NBr "		25	2.62	-5					
						" Et_4NBr "		25	2.25	-5					
						" $C_7H_7SO_3Na$ "		25	1.62	-5					
						" $NaClO_4$ "		25	2.50	-5					
.6	.2	$CH_3CH(OCH_3)_2 + H_2O$	B		HCl	0.002-0.003	$kA[H^+]$	15	7.9	-2					(4)
								25	2.7	-1					
								35	8.8	-1	21	4	14		
.7		$CH_3CH(OCH_3)(OC_2H_5) + H_2O$	B		HCl	0.002	$kA[H^+]$	15	1.9	-1					(4)
								25	6.5	-1					
								35	2.1	0	21	1.0	15		
.8	.3	$CH_3CH(OC_2H_5)_2 + H_2O$	B		HCl	0.0008-0.002	$kA[H^+]$	15	3.8	-1					(4)
				A = 0.05		0-0.001 + salts		20	7.3	-1					(2)
						0.0008-0.002		35	4.0	0	21	2	15		(4)
.9		$CH_3CH(OCH_3)(O\text{-}n\text{-}C_3H_7) + H_2O$	B		HCl	0.00174	$kA[H^+]$	25	6.9	-1					(4)
.10		$CH_3CH(OC_2H_5)(O\text{-}n\text{-}C_3H_7) + H_2O$	B		HCl	0.00174	$kA[H^+]$	25	1.2	0					(4)
.11		$CH_3CH(O\text{-}n\text{-}C_3H_7)_2 + H_2O$	B		HCl	0.00124	$kA[H^+]$	25	1.3	0					(4)
.12		$CH_3CH(OCH_3)(O\text{-}n\text{-}C_4H_9) + H_2O$	B		HCl	0.00174	$kA[H^+]$	25	7.2	-1					(4)

No.	Supplementing 1951 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
.13		$(C_6H_5)_2C(OC_2H_5)_2 + H_2O$	Mol % B	B+M	10^5A =	HCl										
			0.76		5.0		.005	kA	25	2.7	-4					(1)
			0.76		4.5		.0101		25	4.8	-4					
			0.76		5.0		.0202		25	9.8	-4					
			0.76		3.0		.0202		25	1.03	-3					
			6.5		4.9		.0202		25	8.3	-4					
			15.4		5.0		.0101		25	3.3	-4					
			14.8		5.0		0.0202		25	6.9	-4					
			24.8		5.0		0.0202		25	8.2	-4					
			33.0		5.0		0.0202		25	9.0	-4					
			46.1		5.0		0.0202		25	1.12	-3					
			49.6		4.9		0.0050		25	3.5	-4					
			49.6		4.9		0.0101		25	7.2	-4					
			49.6		4.9		0.0202		25	1.25	-3					
			65.6		4.9		0.0202		25	3.24	-3					
			70.8		5.0		0.0202		25	5.3	-3					
.14		$(p\text{-}NO_2C_6H_4)(C_6H_5)C(OC_2H_5)_2 + H_2O$	Mol % B	B+M	10^5A = 3.1	HCl										(3)
			1.0				0.0516	kA	25	1.34	-5					
			1.0				0.103		25	2.42	-5					
			1.0				0.155		25	4.02	-5					
			5.6				0.103		25	2.37	-5					
			14.1				0.103		25	2.08	-5					
			20.6				0.103		25	2.00	-5					
			28.7				0.103		25	2.27	-5					
			35.5				0.103		25	2.68	-5					
			41.6				0.103		25	3.23	-5					
			46.3				0.103		25	3.80	-5					

No.	Supplementing 1951 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
		Di-acetals of pentaerythritol													
.15		$(H_2C)_2(OCH_2)_4C + H_2O \longrightarrow H_2CO + H_2C(OCH_2)_2C(CH_2OH)_2$	B		HCl	1.0	kA	25	3.25	-8				*	(7)
.16		$H_2C(OCH_2)_2C(CH_2OH) + H_2O \longrightarrow H_2CO + C(CH_2OH)_4$	B		HCl	1.0	kA	25	> 2	-8				*	(7)
.17		$(CH_3CH)_2(OCH_2)_4C + H_2O \longrightarrow CH_3CHO + CH_3CH(OCH_2)_2C(CH_2OH)_2$	B		HCl	1.0	kA	25	2.04	-4				*	(7)
.18		$CH_3CHO(OCH_2)_2C(CH_2OH) + H_2O \longrightarrow CH_3CHO + C(CH_2OH)_4$	B		HCl	1.0	kA	25	< 1	-4				*	(7)
.19		$(C_2H_5CH)_2(OCH_2)_4C + H_2O \longrightarrow C_2H_5CHO + C_2H_5CH(OCH_2)_2C(CH_2OH)_2$	B		HCl	1.0	kA	25	3.44	-4				*	(7)
.20		$C_2H_5CH(OCH_2)_2C(CH_2OH)_2 + H_2O \longrightarrow C_2H_5CHO + C(CH_2OH)_4$	B		HCl	1.0	kA	25	< 1.7	-4				*	(7)
.21		$[(CH_3)_2CHCH]_2(OCH_2)_4C + H_2O \longrightarrow$	B		HCl	1.0	kA	25	1.48	-4				*	(7)
.22		$[(CH_3)_2C]_2(OCH_2)_4C + H_2O \longrightarrow (CH_3)_2CO + (CH_3)_2C(OCH_2)_2C(CH_2OH)_2$	B		HCl	1.0	kA	25	3.45	-1				*	(7)

No.	Supplementing 1951 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
.23		$(CH_3)_2C(OCH_2)_2C(CH_2OH)_2 + H_2O \longrightarrow (CH_3)_2CO + C(CH_2OH)_4$	B		HCl	1.0	kA	25	> 1.7	-1				*	(7)

COMMENTS

Reaction. **(.5)** A straight line is obtained upon plotting logarithm of observed pseudo first order constant against the Hammett acidity function. Slope of line is 1.15. **(.13) (.14)** Selected data. **(.15) (.16)** Consecutive reactions with a limiting value of the rate constant for (.16) estimated. **(.17) (.18)** Consecutive reactions with a limiting value of the rate constant for (.18) estimated. **(.19) (.20)** Consecutive reactions with a limiting value of the rate constant for (.20) estimated. **(.22) (.23)** Consecutive reactions with a limiting value of the rate constant for (.23) estimated.

LITERATURE

(1) L.J. Andrews, W.W. Kaeding, *ACS* 1951, **73**, 1007. (2) J.N. Brönsted, W.F.K. Wynne-Jones, *TFS* 1929, **59**, 25. (3) W.W. Kaeding, L.J. Andrews, *ACS* 1952, **74**, 6189. (4) R. Leimu, *Ann. Acad. Sci. Fenn.* 1947, **AII**, No. 19. (5) F.A. Long, D. McIntyre, *ACS* 1954, **76**, 3243. (6) D. McIntyre, F.A. Long, *ACS* 1954, **76**, 3240. (7) A. Skrabal, M. Zlatewa, *ZPC* 1926, **119**, 305.

SOLVOLYSIS
Acid anhydrides

Reaction types: $(RCO)_2O + H_2O \longrightarrow 2RCOOH$

$(RCO)_2O + R'OH \longrightarrow RCOOH + RCOOR'$

$(RCO)(R'CO)O + H_2O \longrightarrow RCOOH + R'COOH$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec^{-1}

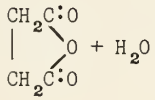
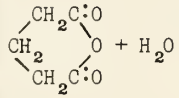
*Coded solvents at end of table.

No.	Supplementing 1951 No.	Reaction	Medium (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
.2		$(HCO)(CH_3CO)O + H_2O$	AnW80*	$A \sim 0.06$			kA	0	1.91	-4				*	(6)
								20	7.52	-4	10.8	8	4		
					C_5H_5N	0.0017		0	5.41	-4					
						0.0033		0	8.60	-4					
						0.0054		0	1.17	-3					
						0.0085		0	1.43	-3					
			AnW50*					0	3.87	-3					
.3	.1	$(CH_3CO)_2O + H_2O$	H_2O	$10^4A = 1\text{-}3.5$			kA	5	6.96	-4	11.3				(4) (12)
								15	1.42	-3	10.5				
								25	2.62	-3					
				$10^2A = 7$	(X)	$kA + k_xAX$		0	k 4.5	-4				*	(7)
					NaCl	0-0.25			k_x -8.7	-5					
					H^+	0-0.25			k_x 5.3	-4					
					$HC_2H_3O_2$	0-0.8			k_x -5.0	-5					
					$C_2H_3O_2^-$	0-0.2			k_x 6.4	-4					
					CHO_2^-	0-0.05			k_x 1.13	-2					

No.	Supplementing 1951 No.	Reaction	Medium (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	.1	$(CH_3CO)_2O + H_2O$ *(continued)*	H_2O	10^2A = 5.0-5.3	C_5H_5N	5.0×10^{-4}	kA	0	5.22	-4				*	(5)
						1.0×10^{-3}		0	5.60	-4					
						2.0×10^{-3}		0	7.10	-4					
						4.0×10^{-3}		0	1.05	-3					
						7.1×10^{-3}		0	1.85	-3					
				10^2A = 5.0	$2\text{-}CH_3C_5H_4N$	5.0×10^{-4}	kA	0	4.69	-4					
						1.0×10^{-3}		0	4.78	-4					
						2.0×10^{-3}		0	4.84	-4					
						4.0×10^{-3}		0	5.01	-4					
						1.0×10^{-2}		0	5.23	-4					
				10^2A = 5.0-5.4	$3\text{-}CH_3C_5H_4N$	5.0×10^{-4}	kA	0	5.11	-4					
						1.0×10^{-3}		0	5.76	-4					
						2.0×10^{-3}		0	7.54	-4					
						4.0×10^{-3}		0	1.12	-3					
				10^2A = 5.1-5.3	$4\text{-}CH_3C_5H_4N$	5.3×10^{-4}	kA	0	5.28	-4					
						1.1×10^{-3}		0	5.89	-4					
						2.1×10^{-3}		0	7.52	-4					
						4.2×10^{-3}		0	1.14	-3					
				10^2A = 5.0	quinoline	5.2×10^{-4}	kA	0	4.63	-4					
						1.0×10^{-3}		0	4.66	-4					
						2.1×10^{-3}		0	4.88	-4					
						4.2×10^{-3}		0	5.18	-4					
				10^2A = 5.1-5.3	isoquinoline	5.2×10^{-4}	kA	0	5.52	-4					
						1.0×10^{-3}		0	6.70	-4					
						2.1×10^{-3}		0	7.87	-4					
						4.2×10^{-3}		0	1.33	-3					
				10^2A = 5.0-5.2	$2,6\text{-}(CH_3)_2C_5H_3N$	5.1×10^{-4}	kA	0	4.57	-4					
						1.0×10^{-3}		0	4.61	-4					

No.	Supplementing 1951 No.	Reaction	Medium (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	.1	$(CH_3CO)_2 + H_2O$ *(continued)*	H_2O	10^2A = 5.0-5.2	2,6-$(CH_3)_2C_5H_3N$	2.0×10^{-3}	kA	0	4.70	-4				*	(5)
						4.0×10^{-3}		0	4.84	-4					
						1.0×10^{-2}		0	5.51	-4					
			AnW50*	10^4A = 1-3.5			kA	5	2.51	-5	11.5				(4)
								15	5.16	-5	10.9				
								25	9.79	-5					(1) (4)
			AnW70*	"			kA	5	1.19	-4	11.2				(4)
								15	2.40	-4	10.5				
								25	4.42	-4					
			AnW80*	"			kA	5	2.37	-4	11.0				
								15	4.75	-4	10.5				
								25	8.66	-4					
			AnW90*	"			kA	5	4.21	-4	11.1				(4)
								15	8.47	-4	10.3				
								25	1.54	-3					
.4		$(CH_3CO)_2O + C_2H_5OH$	C_2H_5OH	A = 0.1	pressure	Kg/cm^2	kAB								(10) (13)
						1		20	5.4	-6	17.6	6	6		
						1000		20	1.02	-5	15.9	8	6		
						2000		20	2.13	-5	15.4	6	6		
						3000		20	3.98	-5	14.0	1	6		
			$CH_3C_6H_5$	A = B = 0.25	"	1		40	4.8	-5	15.2	2	6		
						3000		40	1.83	-4	15.6	1	7		
						5000		40	3.50	-4					
						8500		40	2.16	-4					
			$(C_5H_{11})_2O$	A = B = 0.25	"	1		40	1.04	-4					
						3000		40	3.13	-4					

No.	Supplementing 1951 No.	Reaction	Medium (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
						Kg/cm^2									
.4		$(CH_3CO)_2O + C_2H_5OH$ *(continued)*	C_6H_{14}	A = B = 0.25	pressure	1	k AB	60	5.1	-4					(10) (13)
						3000		60	2.84	-3					
			$(CH_3)_2CO$	A = B = 0.25	"	1		80	6.5	-5					
						3000		80	2.12	-4					
.5		$(C_2H_5CO)_2O + H_2O$	H_2O	A = 0.04			k A	0	2.8	-4				*	(12)
								25	1.45	-3	10.6	9	4		
.6		$(n\text{-}C_3H_7CO)_2O + H_2O$	H_2O	A = 0.02			k A	0	1.62	-4				*	(12)
								25	8.6	-4	8.0	4	2		
.7		$(CH_3OCH_2CO)_2O + H_2O$	H_2O					0	very fast					*	(12)
		Aryl acid anhydrides													
.8		$(C_6H_5CO)_2O + H_2O$	$(CH_3)_2CO$	A = 0.035; B = 28			k A	25	4.7	-6				*	(12)
			AnW50*	A = 0.022			k A	30	4.26	-6					(5)
					C_5H_5N	8.68×10^{-4}		30	8.67	-6					
						1.74×10^{-3}		30	1.11	-5					
						3.48×10^{-3}		30	1.42	-5					
			D1W*	10^2A = 1.5-4.5			k A	58	7.6	-6					(2)
								80	3.3	-5	16.1	3	5		
.9		$(m\text{-}CH_3C_6H_4CO)_2O + H_2O$	D1W*	10^2A = 1.5-4.5			k A	58	4.7	-6					(2)
								80	2.5	-5	17.8	3	6		
.10		$(p\text{-}CH_3C_6H_4CO)_2O + H_2O$	D1W*	10^2A = 1.5-4.5			k A	58	2.7	-6					(2)
								80	1.34	-5	17.6	1.1	6		

No.	Supplementing 1951 No.	Reaction	Medium (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
.11		$[p\text{-}(CH_3)_3CC_6H_4CO]_2O + H_2O$	D1W*	$10^2A = 1.5\text{-}4.5$			kA	58	3.0	-6					(2)
								80	1.45	-5	17.3	8	5		
.12		$(m\text{-}CH_3OC_6H_4CO)_2O + H_2O$	D1W*	$10^2A = 1.5\text{-}4.5$			kA	58	9.8	-6					(2)
								80	4.2	-5	15.8	3	5		
.13		$(p\text{-}CH_3OC_6H_4CO)_2O + H_2O$	D1W*	$10^2A = 1.5\text{-}4.5$			kA	58	9.2	-7					(2)
								80	5.8	-6	20.1	1.7	7		
.14		$(m\text{-}NO_2C_6H_4CO)_2O + H_2O$	D1W*	$10^2A = 1.5\text{-}4.5$			kA	42	5.9	-4					(2)
								58	1.44	-3	11.6	6	4		
.15		$(p\text{-}NO_2C_6H_4CO)_2O + H_2O$	D1W*	$10^2A = 1.5\text{-}4.5$			kA	25	3.8	-4					(2)
								42	1.02	-3					
								58	2.3	-3	10.7	3	4		
.16		$(p\text{-}ClC_6H_4CO)_2O + H_2O$	D1W*	$10^2A = 1.5\text{-}4.5$			kA	58	3.9	-5					(2)
								80	1.64	-4	15.5	7	5		
Dibasic-cyclic acid anhydrides															
.17		 $+ H_2O$	H_2O	$A = 0.04$			kA	0	3.5	-4				*	(12)
								25	2.6	-3	13.1	1.1	7		
			AnW50*					25	2.8	-4					
.18		 $+ H_2O$	H_2O	$A = 0.03$			kA	0	4.3	-4				*	(12)
								25	2.7	-3	9.5	2	4		

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.19		$o\text{-}C_6H_4(CO)_2O + H_2O$	AnW50*					kA	25	1.25	-3	*	([12])
		Organic-inorganic acid anhydride											
.20		$CH_3C{:}OOPO_3H_2 + H_2O \longrightarrow CH_3COOH + H_3PO_4$	H_2O	10^3A = 2-8	buffers		0.63	kA	39	5.5	-4	*	([9])
							1.0		39	3.3	-4		
							2.7		39	1.87	-4		
							4.0		39	1.6	-4		
				10^4A = 1-80			5.5-10		39	6.5	-5	([8]) ([9]) ([11])	
				10^3A = 2-8			11.2		39	2.0	-4	([9])	
							11.5		39	4.0	-4		
					$MgSO_4$	0.05	7.7		39	1.26	-4		
						0.10	7.7		39	1.77	-4		
					$MgCl_2$	0.10	7.7		39	1.80	-4		
						$k = k' + k''[Mg^{++}]$			39	k'6.5	-5		
									39	k''1.2	-3		
					$MgCl_2$	0-0.1	2.7	kA	39	1.87	-4		
					$MgSO_4$	0-0.07	0.63		39	5.5	-4		
					C_5H_5N	0.149	7.7	kA	39	8.7	-5		
						0.248	7.7		39	1.00	-4		
						0.496	7.7		39	1.37	-4		
						$k = k' + k''[C_5H_5N]$			39	k'6.5	-5		
									39	k''1.4	-4		
.21		$C_6H_5C{:}OOPO_3H_2 + H_2O \longrightarrow C_6H_5COOH + H_3PO_4$	H_2O	A = 0.01	Na_2HPO_4 + glycine	0.033	7.4	kA	37	4.1	-5		([3])
						0.1	7.4		37	4.1	-5		

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.22		$(C_6H_5C{:}OO)_2PO_2H + 2H_2O \longrightarrow 2\,C_6H_5COOH + H_3PO_4$	H_2O		Na_2HPO_4 + glycine	0.033	7.4 (see .24)	$-dA/dt = kA$	37	4.3	-6	*	[3]
.23		$(C_6H_5C{:}OO)_2PO_2H + H_2O \longrightarrow C_6H_5COOH + C_6H_5C{:}OOPO_3H_2$	H_2O	A = 0.01	Na_2HPO_4	0.033	7.4	kA	37	4.3	-6	*	[3]
.24		$(C_6H_5C{:}OO)_2PO_2H + NH_2CH_2COOH \longrightarrow C_6H_5CONHCH_2COOH + C_6H_5C{:}OOPO_3H_2$	H_2O	A = 0.01; B = 0.1	Na_2HPO_4	0.033	7.4	kA	37	~4	-3	*	[3]

SOLVENTS

AnW50* (60, 70, 80, 90) — Acetone + weight % water indicated.

DiW* — Dioxane 75 vol % + H_2O 25 vol %.

COMMENTS

Reaction. (.2) First order rate law varied slightly with time. Value tabulated is from almost constant value at half time. (.3) Large number of electrolytes added by ([6]) to determine general acid and base catalysis. Slight variation of first order rate law with time observed by ([4]). Value tabulated is at half time. (.5) (.6) Reaction followed for about 25 % of course by ([8]). (.7) Reaction essentially complete in three minutes. (.8) Reaction followed for 25 % of course by ([3]). Slight variation of first order rate law with time observed by ([4]). Value is for half time. (.17) (.18) (.19) Reaction followed for about 25 % of course. (.20) Bicarbonate buffer used by ([7a]). Variety of buffers used by ([66]) covering pH from 0.6 to 11.5. Selected data tabulated. Ionic strength adjusted to 0.6 by added $NaClO_4$. Specific catalysis by Mg^{++} observed in neutral solution but shown to be absent in strongly acid region. Claimed by ([66]) that catalysis by pyridine changes mechanism of reaction from P-O bond split to C-O bond cleavage. (.22) Reaction proceeds in two steps (.23) and (.21) with second step approximately ten times as fast. Only initial rate observed. In presence of glycine first step is replaced by very rapid reaction (.24) to form equal moles of hippuric acid and monobenzoylphosphate. First step is complete in a few minutes. This is followed by (.21) at previously observed rate. (.23) First and rate determining step in reaction (.22). (.24) Value gives order of magnitude only. Replaces normal first step solvolysis of reaction (.22) in presence of glycine.

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([8]) D.E. Koshland, *ACS* 1951, **73**, 4103. ([9]) D.E. Koshland, *ACS* 1952, **74**, 2286. ([10]) M.W. Perrin, *TFS* 1938, **34**, 144. ([11]) F. Tynen, *BDC* 1940, **73**, 367. ([12]) S.E. Vles, *RTC* 1933, 52, 809. ([13]) E.G. Williams, M.W. Perrin, R.O. Gibson, *PRS* 1937, **A159**, 162.

SOLVOLYSIS
C-Si bond solvolysis

Liquid phase

Reaction type: $ArSiR_3 + H_2O \longrightarrow R_3SiOH + ArH$

Amounts are in M/l.
Rate constants are in M/l per sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$2,3\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$	CH_3COOH	A = 0.07; B = 3.2	$p\text{-}CH_3C_6H_4SO_3H$	0.80	k A	25	6.95	-5	*	(1)
.2	$2,4\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$	CH_3COOH	A = 0.07; B = 3.2	$p\text{-}CH_3C_6H_4SO_3H$	0.80	k A	25	4.10	-4	*	(1)
			6.0		0.80		25	1.05	-4		
.3	$2,5\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$	CH_3COOH	A = 0.06-0.07; B = 3.2	$p\text{-}CH_3C_6H_4SO_3H$	0.80	k A	25	5.15	-5	*	(1)
.4	$2,6\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$	CH_3COOH	A = 0.07; B = 6.0	$p\text{-}CH_3C_6H_4SO_3H$	0.80	k A	25	1.23	-3	*	(1)
.5	$3,4\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$	CH_3COOH	A = 0.03-0.07; B = 3.0	$p\text{-}CH_3C_6H_4SO_3H$	0.80	k A	25	6.06	-5	*	(1)
			3.2		0.80		25	4.95	-5		
			4.0		0.80		25	3.60	-5		
			6.0		0.80		25	1.98	-5		
			6.0	$p\text{-}CH_3C_6H_4SO_3H$ + $LiClO_4$	0.80 + 0.30		25	2.72	-5		
			6.0	$p\text{-}CH_3C_6H_4SO_3H$ + KCl	0.80 + 0.30		25	3.14	-5		
			6.0	$p\text{-}CH_3C_6H_4SO_3H$ + LiCl	0.80 + 0.30		25	3.92	-5		

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	Comments	Literature
.5	$3,4\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$ *(continued)*	CH_3COOH	A= 0.03-0.07; B= 6.0	$p\text{-}CH_3C_6H_4SO_3H$ LiCl	0.80 1.00	kA	25	4.16	-4	*	[1]
.6	$3,5\text{-}(CH_3)_2C_6H_3Si(CH_3)_3 + H_2O$	CH_3COOH	A = 0.06; B = 3.2	$p\text{-}CH_3C_6H_4SO_3H$	0.80	kA	25	5.10	-6	*	[1]
.7	$p\text{-}CH_3OC_6H_4Si(CH_3)_3 + H_2O$	CH_3OH	A = 0.018; B = 5	HCl	0.10	kA	50	2.3	-5		[2]
					0.21		50	5.5	-5		
					0.31		50	1.00	-4		
					0.39		50	1.40	-4		
					0.52		50	2.35	-4		
					0.70		50	3.75	-4		
					1.06		50	1.15	-3		
			A = 0.018; B = 15		0.31		50	8.5	-5		
					0.58		50	2.08	-4		
					0.70		50	2.83	-4		
			A = 0.018; B = 5	$HClO_4$	0.084		50	2.0	-5		
					0.20		50	6.7	-5		
					0.37		50	1.88	-4		
					0.52		50	3.34	-4		
		Dioxane	A = 0.018; B = 10	HCl	0.53		50	6.5	-5		
			15		0.79		50	1.05	-4		
			25		0.53		50	5.3	-6		
					0.79		50	1.27	-4		
					1.06		50	2.38	-4		

COMMENTS

Reactions. (.1) through (.6) Followed by rapid condensation of silanol to disiloxane, and pseudo first order rate law followed up to 4 or 5 half lives, except for reaction (.2). For (.2) after two half lives, (75 % reaction), upward curvature observed. Authors suggest this may be due to influence of the consecutive condensation to siloxane. Dilatometric method used by ([1]). **(.7)** Selected data. Plot of log k versus acidity function, H, gives straight line in water methanol solutions with slope of one. In dioxane-water solutions plot of log k/a_{H_2O} versus acidity function, H, gives straight line. Spectrophotometric method used by ([2]).

LITERATURE

([1]) R. A. Benkeser, H. R. Krysiak, *ACS* 1954, **76**, 6353. ([2]) E. Eaborn, *CSL* **1953**, 3148.

SOLVOLYSIS
C:N bond

Reaction type: $RR'C{:}NR'' + H_2O \longrightarrow RR'C{:}O + H_2NR''$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

*Coded solvents and comments at end of table.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	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
.10	$C_6H_5CH{:}NC_6H_5 + H_2O$	MW*		strong acid	$\mu = 0.110$	5.65	$k\,A$	10	5.18	-3				*	([3])
						6.00		10	3.88	-3					
						6.78		10	1.39	-3					
				strong acid		8.06		10	9.6	-5					
						8.24		10	6.15	-5					
						9.28		10	1.15	-5					
						10.23		10	4.45	-6					
			$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	$k\,A$	0	k' 4.49	+3					
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 3.80	-1					
					$(\mu = 0.110)$			10	k' 6.52	+3					
								10	k'' 7.66	-1					
								20	k' 8.79	+3	E' 5.3	8	7		
								20	k'' 1.76	0	E'' 13	9	9		
				phosphate		7.6	$k'\,A[H^+]$	10	1.11	+4					
				veronal		8.7		10	1.23	+4					
.11	$C_6H_5CH{:}NC_6H_4\text{-}p\text{-}CH_3 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	$k\,A$	0	k' 3.56	+3				*	([3])
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 2.76	-1					
					$(\mu = 0.110)$			10	k' 5.72	+3					
								10	k'' 4.91	-1					
								20	k' 8.64	+3	E' 7.0	1.4	9		
								20	k' 9.25	-1	E'' 9.9	2	7		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	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	p-$CH_3OC_6H_4CH{:}NC_6H_5 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	$k\,A$	0	k' 2.82	+3				*	(3)
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 1.88	-1					
					(μ = 0.110)			10	k' 4.56	+3					
								10	k'' 3.28	-1					
								20	k' 7.00	+3	E' 7.1	1.4	9		
								20	k'' 6.06	-1	E'' 9.8	1.2	7		
.13	$C_6H_5CH{:}NC_6H_4$-p-$OCH_3 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	$k\,A$	0	k' 2.00	+3				*	(3)
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 1.15	-1					
								10	k' 3.24	+3					
								10	k'' 2.34	-1					
								20	k' 4.72	+3	E' 6.8	6	8		
								20	k'' 5.06	-1	E'' 12.3	7	8		
			wt % B												
.14	$C_6H_5NHCH{:}NC_6H_5 + H_2O$	DW*	A = 0.01; 30.7	HCl	0.21		$k\,A$	35	1.64	-4				*	(1)
					0.084			35	1.66	-4					
			$10^3 A$ = 5-20;	CH_3COOH (HX)	0.01-0.08		$k\,A$	35	k' 1.3	+1					
			wt % B = 12.5	CH_3COONa	0.005-0.25	$k = k'[H^+] + k''[HX]$		35	k'' 1.68	-3					
			21.4					35	k' 3.5	+1					
								35	k'' 2.23	-3					
			30.7					35	k' 8.0	+1					
								35	k'' 2.89	-3					
			39.8					35	k' 2.0	+2					
								35	k'' 3.11	-3					
			48.9					35	k' 6.0	+2					
								35	k'' 2.78	-3					
			58.0					35	k' 2.0	+3					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Buffer ratio $[HX]/[X^-]$	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
.14	$C_6H_5NHCH{:}NC_6H_5 + H_2O$ *(continued)*	DW*	10^3A = 5–20; wt % B = 30.7	CH_3COOH (HX) CH_3COONa	0.01–0.08 0.005–0.25	$k = k'[H^+] + k''[HX]$	kA	35	k'8.0	+1				*	(1)
						0.533		35	k''5.0	-3					
						1.06		35	k''2.8	-3					
						1.60		35	k''2.1	-3					
						3.19		35	k''1.3	-3					
			10^3A = 5–20; wt % B = 30.7	p-$NO_2C_6H_4OH$ (p-$NO_2C_6H_4ONa$)	0.092	7.02	kA	35	2.37	-4					
					"	4.67		35	2.25	-4					
					"	2.58		35	2.22	-4					
					0.061	7.02		35	1.87	-4					
					"	4.67		35	1.79	-4					
					"	2.58		35	1.75	-4					
					0.031	7.02		35	1.36	-4					
					"	4.67		35	1.28	-4					
					"	2.58		35	1.32	-4					
				NaOH	0.01			35	6.0	-5					
						pH									
.15	p-$(CH_3)_2NC_6H_4CH{:}NC_6H_5 + H_2O$	MW*			μ = 0.110	6.39	kA	10	1.69	-2					(3)
				strong base	"	10.52		10	1.51	-5					
.16	p-$H(CH_3)_2N^+C_6H_4CH{:}NC_6H_5 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{–}6) \times 10^{-3}$	~6	$k'A[H^+]$	0	1.42	-1				*	(3)
				CH_3COONa	$(7\text{–}25) \times 10^{-3}$ (μ = 0.110)			20	6.03	-1	11.4	2	8		
.17	$C_6H_5CH{:}NC_6H_4$-p-$N(CH_3)_2 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{–}6) \times 10^{-3}$	~6	kA	0	k'1.66	+3				*	(3)
				CH_3COONa	$(7\text{–}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k''6.5	-2					
					(μ = 0.110)			20	k'3.92	+3	E'6.8	5	8		
								20	k''2.42	-1	E''12	3	8		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ 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	Literature
.18	p-$NO_2C_6H_4CH{:}NC_6H_5 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	kA	0	k' 1.96	+3				*	([3])
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 4.6	-2					
					(μ = 0.110)			10	k' 3.14	+3					
								10	k'' 7.7	-2					
								20	k' 4.65	+3	E' 6.8	6	8		
								20	k'' 2.42	-1	E'' 13	2	9		
.19	p-$ClC_6H_4CH{:}NC_6H_5 + H_2O$	MW*	$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	kA	0	k' 3.40	+3				*	([3])
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 1.07	-1					
					(μ = 0.110)			10	k' 4.80	+3					
								10	k'' 2.98	-1					
								20	k' 6.90	+3	E' 5.6	1.0	8		
								20	k'' 8.38	-1	E'' 16.6	2	12		
.20	$C_6H_5CH{:}NC_6H_4$-p-$Cl + H_2O$	MW*		strong acid	(μ = 0.110)	5.57	kA	10	3.36	-3				*	([3])
						5.98		10	2.06	-3					
				strong base		7.89		10	9.6	-5					
						9.96		10	2.96	-6					
			$A \sim 3 \times 10^{-4}$	CH_3COOH (HX)	$(2\text{-}6) \times 10^{-3}$	~6	kA	0	k' 3.56	+3					
				CH_3COONa	$(7\text{-}25) \times 10^{-3}$	$k = k'[H^+] + k''[HX]$		0	k'' 2.07	-1					
					(μ = 0.110)			10	k' 4.99	+3					
								10	k'' 4.64	-1					
								20	k' 6.95	+3	E' 5.3	6	7		
								20	k'' 1.13	0	E'' 14.2	4	10		

SOLVENTS

MW* 50 wt % CH_3OH + 50 wt % H_2O.

DW* Dioxane + wt % H_2O indicated under amount of reactant.

COMMENTS

Literature. (2) Values inconsistent with those of (3) perhaps due to rate of solution as limiting step. (3) All rate constants converted from original units in minutes and base 10 logarithms.

Reactions. **(.10)** Rate constant expression $k = k'[H^+] + k''[HX]$ is not valid at lowest buffer concentrations studied. Values of k' in unbuffered dilute strong acid and base not tabulated as they changed with changing pH. **(.11) (.12) (.13)** Rate constant expression $k = k'[H^+] + k''[HX]$ is not valid at lowest buffer concentrations studied. **(.14)** Independence of rate upon acid concentration in presence of dilute strong acids explained on basis of accumulation of A in unreactive acid form just balancing catalysis by acid. In buffered solution rate dependent upon acid concentration. In acetic acid, acetate buffer rate constants also dependent upon buffer ratio, $R = [CH_3COOH]/[CH_3COO^-]$. At 30.7 wt % H_2O and 35°C k may be expressed by: $k = [6 \times 10^{-5} + 4.8 \times 10^{-4}R + 0.013(CH_3COOH)]/(1 + 3.0R)$. **(.16) (.17) (.18) (.19)** Rate constant expression $k = k'[H^+] + k''[HX]$ is not valid at lowest buffer concentrations studied. **(.20)** Values of k' in unbuffered dilute strong acid and base not tabulated as they were a function of pH. Rate constant expression $k = k'[H^+] + k''[HX]$ is not valid at lowest buffer concentrations studied.

LITERATURE

(1) R.H. DeWolfe, R.M. Roberts, *ACS* 1953, **75**, 2942. (2) B.A. Porai-Koshits, E.M. Paznanskaya, V.S. Shevchenko, L.A. Pavlova, *ZhOKh* 1947, **17**: 10, 1774. (3) A.V. Willi, R.E. Robertson, *CJC* 1953, **31**, 361.

SOLVOLYSIS

CO-NHR′ bond (Acyl amide solvolysis)

Liquid phase

Reaction types: $RCONHR' + H_2O \longrightarrow RCOO^- + R'NH_3^+$

$RCONHR' + OH^- \longrightarrow RCOO^- + R'NH_2$

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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
.17	$HCONHC_6H_5 + H_2O$	B	A = 0.05	H_2SO_4	0.025	$k\,A[H^+]$	30	2.64	-3	14			*	(7)
					0.05		30	2.47	-3	15				
					0.125		30	2.46	-3	14				
					0.05		35	3.80	-3					
					0.05		40	5.18	-3					
					0.05		45	7.85	-3					
		EW50*	A = 0.05	H_2SO_4	0.125		20	8.76	-3					
					0.125		25	1.33	-2					
					0.025-0.15		30	1.60	-2					
					0.125		35	2.95	-2					
					0.125		40	4.13	-2					
					0.125		45	6.45	-2	12.7	3	7		
.18	$HCONHC_6H_4$-o-$CH_3 + H_2O$	B	A = 0.05	H_2SO_4	0.025-0.12	$k\,A[H^+]$	30	1.08	-3				*	(7)
					0.025		35	1.54	-3					
					0.025		40	2.28	-3					
					0.025		45	3.25	-3	14.6				
		EW50*	A = 0.05	H_2SO_4	0.125	$k\,A[H^+]$	20	3.9	-3					
					0.125		25	5.96	-3					
					0.025-0.15		30	8.0	-3					

No.	Reaction	Medium (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
.18	$HCONHC_6H_4$-o-$CH_3 + H_2O$ *(continued)*	EW50*	A = 0.05	H_2SO_4	0.125	$k\,A[H^+]$	35	1.26	-2				*	(7)
					0.125		40	1.76	-2					
					0.125		45	2.58	-2	13.6	6	7		
.19	$HCONHC_6H_4$-p-$CH_3 + H_2O$	B	A = 0.05	H_2SO_4	0.125	$k\,A$	40	1.02	-2				*	(7)
		EW50*	A = 0.05		0.125	$k\,A[H^+]$	20	5.85	-3					
					0.125		25	8.80	-3					
					0.025-0.12		30	1.17	-2					
					0.125		35	1.84	-2					
					0.125		40	2.69	-2					
					0.125		45	3.86	-2	13.0	3	7		
.20	$CH_3CONHC_6H_5 + H_2O$	B	A = 0.10	H_2SO_4	0.125	$k\,A$	65	1.44	-3				*	(7)
					0.125		70	2.01	-3					
					0.125		75	2.94	-3					
					0.125		80	4.12	-3					
					0.125		85	5.90	-3					
					0.125		90	8.30	-3					
					0.125		95	1.20	-2	17.9	5	8		
		EW50*	A = 0.050	H_2SO_4	0.125		60	8.7	-4					
			0.025		0.125		70	1.28	-3					
			0.050		0.125		70	1.20	-3	15	3	6		
			0.10		0.125		70	1.03	-3					
			0.15		0.125		70	9.4	-4					
			0.20		0.125		70	8.9	-4					

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
.21	$CH_3CONHC_6H_5 + \begin{cases} H_2O \\ C_2H_5OH \end{cases}$	B	A = 0.05; % H_2O = 0	H_2SO_4	0.125	k A	65	5.73	-4				*	([7])
			10		0.125		65	6.74	-4					
			20		0.125		65	7.28	-4					
			30		0.125		65	8.41	-4					
			40		0.125		65	8.67	-4					
			50		0.125		65	9.08	-4					
			60		0.125		65	9.25	-4					
			70		0.125		65	9.77	-4					
			80		0.125		65	1.12	-3					
			90		0.125		65	1.24	-3					
			100		0.125		65	1.44	-3					
.22	$CH_3CONHC_6H_5 + \begin{cases} H_2O \\ CH_3COOH \end{cases}$	CH_3COOH	A = 0.1	H_2SO_4	0.25	k A	70	3.97	-3				*	([7])
							80	8.05	-3					
							90	1.61	-2					
.23	$CH_3CONHC_6H_4$-o-$CH_3 + H_2O$	B	A = 0.1	H_2SO_4	0.125	k A	70	7.4	-4				*	([7])
							80	1.36	-3					
							90	2.46	-3	15.0	3	6		
		EW50*	A = 0.05	H_2SO_4	0.125		70	7.4	-4				*	
.24	$CH_3CONHC_6H_4$-m-$CH_3 + H_2O$	B	A = 0.05-0.1	H_2SO_4	0.125	k A	80	3.92	-3				*	([7])
							90	7.87	-3	18	6	8		
		EW50*	A = 0.05	H_2SO_4	0.125		70	1.61	-3					
.25	$CH_3CONHC_6H_4$-p-$CH_3 + H_2O$	EW50*	A = 0.05	H_2SO_4	0.125	k A	70	1.68	-3				*	([7])

No.	Reaction	Medium (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
.26	$CH_3CONHC_6H_4$-o-$NO_2 + H_2O$	B	A = 0.10	H_2SO_4	0.125	kA	80	7.62	-3				*	(7)
							85	1.05	-2					
							90	1.56	-2					
							95	2.11	-2	17.7	7	8		
		EW50*	A = 0.05		0.125		60	1.68	-3					
							70	3.55	-3	15	2	7		
.27	$CH_3CONHC_6H_4$-p-$NO_2 + H_2O$	EW50*	A = 0.05	H_2SO_4	0.125	kA	70	4.21	-3				*	(7)
.28	$CH_3CONHC_6H_4$-p-$Br + H_2O$	EW50*	A = 0.05	H_2SO_4	0.125	kA	70	1.65	-3				*	(7)
.29	CH_3CO-α-$NHC_{10}H_7 + H_2O$	EW50*	A = 0.05	H_2SO_4	0.125	kA	70	3.06	-3				*	(7)
.30	CH_3CO-β-$NHC_{10}H_7 + H_2O$	EW50*	A = 0.05	H_2SO_4	0.125	kA	70	1.88	-3				*	(7)
.31	$C_2H_5CONHC_6H_5 + H_2O$	EW50*	A = 0.05	H_2SO_4	0.125	kA	70	2.06	-3				*	(7)
.32	n-$C_4H_9CONH_2 + H_2O$	CH_3COOH	A = 0.25; B = 7	H_2SO_4	3.7	kA	90	5.58	-5				*	(12)
.33	$C_6H_5CONH_2 + H_2O$	B		HCl	1.0	kA	79	5.20	-5	21.7	1.6	9		(5) (14)
					4.0		79	1.75	-4	21.9	8	9		
					8.47		79	9.50	-5	22.6	1.0	10		
.34	$C_6H_5CONH_2 + OH^-$	H_2O	A~0.01; B=0.1-0.2			kAB	70	2.24	-4				*	(13)
			1.0				70	2.75	-4					
.35	$C_6H_5CONHC_6H_5 + C_2H_5OH$	B	A = 0.01	H_2SO_4	0.125	kA	65	3.91	-4				*	(7)
.36	$C_6H_5CONHC_6H_4$-o-$CH_3 + C_2H_5OH$	B	A = 0.012	H_2SO_4	0.125	kA	65	2.07	-4				*	(7)

No.	Reaction	Medium (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
.37	$C_6H_5CONHC_6H_4$-p-$CH_3 + C_2H_5OH$	B	A = 0.012	H_2SO_4	0.125	kA	65	2.52	-4				*	(7)
.38	$C_6H_5CH_2CONH_2 + H_2O$	CH_3COOH	A = 0.15; B = 7	H_2SO_4	3.7	kA	90	1.18	-4				*	(12)
							100	2.9	-4					
.39	p-$CH_3C_6H_4CONH_2 + OH^-$	H_2O	$A \simeq 0.01$; B = 0.2			kAB	70	1.55	-4				*	(13)
.40	p-$NO_2C_6H_4CONH_2 + OH^-$	H_2O	$A \simeq 0.01$; B = 0.2			kAB	70	2.34	-3				*	(13)
.41	$(CH_3)_3N^+CH_2CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.0}B^{1.5}$	35	8.85	-3				*	(11)
.42	$(C_2H_5)(CH_3)_2N^+CH_2CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.1}B^{1.5}$	35	5.82	-3				*	(11)
.43	$(CH_3)(C_2H_5)_2N^+CH_2CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.1}B^{1.6}$	35	3.18	-3				*	(11)
.44	$(C_2H_5)_3N^+CH_2CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.1}B^{1.8}$	35	1.19	-3				*	(11)
.45	$(p$-$CH_3C_6H_4)(CH_3)_2N^+CH_2CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.1}B^{1.7}$	35	3.46	-3				*	(11)
.46	$(CH_3)_3N^+CH(CH_3)CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5-1			$kA^{1.0}B^{1.1}$	0	2.22	-6				*	(11)
						$kA^{1.0}B^{1.3}$	25	2.10	-5					
							35	4.24	-5					
							55	1.64	-4					
							75	4.92	-4	13.3	1.4	5		
						$kA^{1.0}B^{1.2}$	95	1.37	-3					
.47	$(CH_3)(C_2H_5)_2N^+CH(CH_3)CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.0}B^{1.2}$	35	8.1	-6				*	(11)
.48	$(CH_3)_3N^+C(CH_3)_2CONH_2 + OH^-$	H_2O	A = 0.1; B = 0.5			$kA^{1.0}B^{0.9}$	35	4.1	-6				*	(11)

No.	Reaction	Medium (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
.49	2-$C_5H_4NCONH_2$ + H_2O (picolinamide)	H_2O	A = 0.030	HCl	8.08	k A	54	2.35	-5				*	([6])
			"		8.08		69	1.12	-4					
			"		8.08		85	5.35	-4	23.8	3.8	11		
			0.015		3.04		70	3.76	-5					
			"		3.04		85	1.48	-4					
			"		3.04		100	4.92	-4	22.2	8	9		
			0.005		1.0		85	4.05	-5					
			"		1.0		102	1.63	-4					
			"		1.0		113	3.66	-4	21.6	8	8		
					0.10		80	2.16	-6					
					0.10		90	8.36	-6					
					0.10		100	1.61	-5					
					0.10		120	7.25	-5					
					0.10		130	1.56	-4					
					0.10		140	2.73	-4	21.5	6.5	7		
.50	3-$C_5H_4NCONH_2$ + H_2O (nicotinamide)	H_2O	10^3A = 5-50	HCl	0.98	k A	71	2.17	-5				*	([6])
					0.98		76	3.35	-5					
					1.84		76	6.78	-5					
					3.00		76	1.29	-4					
					3.74		76	1.73	-4					
					4.94		76	2.75	-4					
					6.72		76	3.60	-4					
					8.61		76	5.12	-4					
					0.98		84	6.64	-4					
					0.98		92	1.31	-4					
					0.10		98	1.90	-5					
					0.05		108	1.49	-5					
					0.20		108	6.57	-5					

No.	Reaction	Medium (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
.50	$3\text{-}C_5H_4NCONH_2 + H_2O$ *(continued)* (nicotinamide)	H_2O	10^3A = 5-50	HCl	0.50	kA	108	1.98	-4				*	(6)
					0.98		108	4.20	-4	20.5	2.4	8		
					0.10		110	4.08	-5					
					0.10		119	6.87	-5					
					0.10		130	1.52	-4					
					0.10		138	2.43	-4	20.0	1.1	7		
				HCl	1.0		71	2.60	-5					
				NaCl	1.0									
.51	$4\text{-}C_5H_4NCONH_2 + H_2O$ (isonicotinamide)	H_2O	10^3A = 30	HCl	8.08	kA	41	2.96	-5				*	(6)
			15		3.04		56	3.80	-5					
			30		8.08		56	1.45	-4					
			5		0.10		68	2.0	-6					
					1.00		68	3.80	-5					
					1.96		68	7.75	-5					
			15		2.98		68	1.29	-4					
					3.91		68	1.83	-4					
					5.02		68	2.56	-4					
					5.80		68	3.18	-4					
			30		8.08		68	4.61	-4	21.7	7	10		
			5		0.1		80	5.87	-6					
			15		3.04		83	4.89	-4	21.1	8	9		
			5		1.0		90	2.23	-4					
					0.1		98	2.48	-5					
					1.0		100	5.00	-4					
					1.0		105	7.10	-4	20.9	9.2	8		
					0.1		120	1.23	-4					
					0.1		130	2.39	-4	20.5	2.7	7		

No.	Reaction	Medium (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
	Peptide linkage solvolysis													
.52	$CH_3CONHCH_2COOH + H_3O^+$	H_2O	$10^2A = 7\text{-}10$; $B \simeq 0.6$	KCl	2.8-B	k AB	54	1.09	-5					(9)
							70	5.00	-5					
							85	1.94	-4	21.9	4	9		
.53	$NH_3^+CH_2CONHCH_2COOH + H_3O^+$	H_2O	$10^2A = 7\text{-}10$; $B \simeq 0.6$	KCl	2.8-B	k AB	54	1.12	-6				*	(9)
			1-2 2.0				65	3.78	-6					(4)
			7-10 0.6		2.8-B		70	4.88	-6					(9)
			1-2 2.0				75	9.10	-6	20.5	7	7		(4)
			7-10 0.6		2.8-B		85	1.72	-5	20.5	5.6	7		(1) (9)
			7 0.6	$CoCl_2$ }	0.05		54	1.86	-6				*	(9)
				KCl }	2.8-B		70	6.93	-6					
							85	2.46	-5	20	5	7		
		AcW*		HCl	5	k A	37	2.9	-6				*	(15)
.54	$NH_2CH_2CONHCH_2COO^- + OH^-$	H_2O	$10^2A = 1\text{-}2$; $B = 2$			k A	20	4.12	-5					(4)
							30	9.60	-5	15	6	6		(4) (8)
			$10^2A = 5$; $B = 0.2$	KCl	2.8-B	k AB	54	5.14	-5					(9)
							70	1.83	-4					
							87	6.08	-4	17.6	3.0	7		(1) (9)
.55	$NH_3^+CH_2CONHCH_2COOC_2H_5 + C_2H_5OH$	B	$10^2A = 1.25$	HCl	0.17	k A	78	1.0	-5				*	(3)
					2.0		78	2.17	-4					
.56	$NH_3^+CH_2CONHCH(CH_3)COOH + H_2O$ (glycyl-dl-alanine)	AcW*		HCl	5	k A	37	1.8	-6				*	(15)

No.	Reaction	Medium (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
.57	*dl*-$CH_3(NH_3^+)CHCONHCH_2COOH + H_3O^+$ (dl-alanylglycine)	H_2O	10^2A = 7-10; B = 0.6-0.7	KCl	2.8-B	k AB	54	6.20	-7				*	(9)
							70	2.50	-6					
							85	1.01	-5	21.2	8	7		
		AcW*		HCl	5	k A	37	1.8	-6				*	(15)
.58	$NH_3^+CH_2CONHCH[CH(CH_3)_2]COOH + H_2O$ (glycyl-dl-valine)	AcW*		HCl	5	k A	37	8.9	-7				*	(15)
.59	*dl*-$(CH_3)_2CH(NH_3^+)CHCONHCH_2COOH + H_2O$ (dl-valylglycine)	AcW*		HCl	5	k A	37	4.2	-8				*	(15)
.60	$NH_3^+CH_2CONHCH(COOH)CH_2CH(CH_3)_2 + H_3O^+$ (glycyl-l-leucine)	H_2O	10^2A = 7-10; B = 0.6-0.7	KCl	2.8-B	k AB	54	5.30	-7				*	(9)
							70	2.16	-6					
							85	7.82	-6	20.5	2.6	7		
		AcW*		HCl	5	k A	37	1.2	-6				*	(15)
.61	*l*-$(CH_3)_2CHCH_2(NH_3^+)CHCONHCH_2COOH + H_3O^+ H_2O$ (l-leucylglycine)		10^2A = 7-10; B = 0.6-0.7	KCl	2.8-B	k AB	54	2.03	-7				*	(9)
							70	9.75	-7					
							85	3.80	-6	22.3	1.6	8		
		AcW*		HCl	5	k A	37	6.7	-7				*	(15)
.62	$NH_3^+CH_2CONHCH(COOH)CH_2C_6H_4OH + H_3O^+$ (glycyl-l-tyrosine)	H_2O	10^2A = 7-10; B = 0.6-0.7	KCl	2.8-B	k AB	54	5.66	-7				*	(9)
							70	2.40	-6					
							85	8.28	-6	20.4	2.4	7		
.63	$NH_3^+CH_2CONHCH(COOH)CH_2\overline{C{:}CHNHC_6H_4} + H_3O^+ H_2O$ (glycyl-l-tryptophan)		10^2A = 7-10; B = 0.6-0.7	KCl	2.8-B	k AB	54	4.90	-7				*	(9)
							70	2.08	-6					
							85	7.99	-6	20.9	4	7		
		AcW*		HCl	5	k A	37	1.0	-6				*	(15)

No.	Reaction	Medium (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
.64	dl-$(CH_3)_2CHCH_2(NH_3^+)CHCONHCH(COOH)CH_2CH(CH_3)_2 + H_2O$													
	(dl-leucyl-dl-leucine "A")	AcW*		HCl	5	k A	37	1.4	-7				*	(15)
.65	l-$(CH_3)_2CHCH_2(NH_3^+)CHCONHCH(COOH)CH_2C{:}CHNHC_6H_4 + H_2O$													
	(l-leucyl-l-tryptophan)	AcW*		HCl	5	k A	37	1.2	-7				*	(15)
.66	$NH_2CH_2CONHCH_2CONHCH_2COOH + H_2O \longrightarrow NH_2CH_2CONHCH_2COOH + NH_2CH_2COOH$	B	$10^3A = 8.3$	HCl	2.0	k A	65	4.12	-5				*	(4)
					2.0		75	9.34	-5					
				NaOH	2.0		20	1.63	-4					
	(diglycylglycine)				2.0		30	3.5	-4					
.67	$NH_2CH_2CONHCH_2CONHCH_2COOC_2H_5 + C_2H_5OH \longrightarrow NH_2CH_2CONHCH_2COOC_2H_5 + NH_2CH_2COOC_2H_5$	B	$10^3A = 8.3$	HCl	0.17	k A	78	7.0	-5				*	(3)
					2.0		78	9.0	-4					
.68	$NH_2CH_2CO(NHCH_2CO)_2NHCH_2COOH + H_2O \longrightarrow NH_2CH_2COOH,\ NH_2CH_2CONHCH_2COOH,\ NH_2(CH_2CONH)_2CH_2COOH$	B	$10^3A = 6.25$	HCl	2.0	k A	65	1.20	-4				*	(4)
					2.0		75	2.26	-4					
				NaOH	2.0		20	4.3	-4					
					2.0		30	1.10	-3					
.69	$NH_2CH_2CO(NHCH_2CO)_2NHCH_2COOH + H_2O \longrightarrow 2\,NH_2CH_2CONHCH_2COOH$	B	$10^3A = 6.25$	HCl	2.0	k A	65	3-5	-5				*	(4)
					2.0		75	7	-5					
				NaOH	2.0		20	3.0	-4					
.70	$NH_2CH_2CO(NHCH_2CO)_2NHCH_2COOH + H_2O \longrightarrow NH_2CH_2COOH + NH_2(CH_2CONH)_2CH_2COOH$	B	$10^3A = 6.25$	HCl	2.0	k A	65	7-9	-5				*	(4)
					2.0		75	1.6	-4					
				NaOH	2.0		20	1.3	-4					

No.	Reaction	Medium (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
.71	$NH_2CH_2CO(NHCH_2CO)_2NHCH_2COOC_2H_5 + C_2H_5OH \longrightarrow$ B $NH_2CH_2COOC_2H_5 + NH_2CH_2CONHCH_2COOC_2H_5$		$10^3A = 6.25$	HCl	0.17	kA	78	7.3	-5				*	[3]
					2.0		78	9.0	-4					
.72	$NH_2CH_2CO(NHCH_2CO)_3NHCH_2COOH + H_2O \longrightarrow$	B	$10^3A = 5$	HCl	2.0	kA	65	1.65	-4				*	[4]
					2.0		75	2.8	-4					
				NaOH	2.0		20	6.0	-4					
					2.0		30	1.43	-3					
.73	$NH_2CH_2CO(NHCH_2CO)_3NHCH_2COOC_2H_5 + C_2H_5OH \longrightarrow$ B		$10^3A = 5$	HCl	2.0	kA	78	6.7	-5				*	[3]
.74	$NH_2CH_2CO(NHCH_2CO)_4NHCH_2COOH + H_2O \longrightarrow$	B	$10^3A = 4.2$	HCl	2.0	kA	65	2.04	-4				*	[4]
					2.0		75	3.8	-4					
				NaOH	2.0		20	8.8	-4					
					2.0		30	2.12	-3					
.75	$NH_2CH_2CO(NHCH_2CO)_4NHCH_2COOC_2H_5 + C_2H_5OH \longrightarrow$ B		$10^3A = 4.2$	HCl	2.0	kA	78	1.8	-3				*	[3]

SOLVENTS

AcW* 50 vol % CH_3COOH + 50 vol % aqueous 10M HCl

EW* 50 % C_2H_5OH + 50 % H_2O (wt. or vol % not stated).

COMMENTS

Reference. (7) Time unit not stated and assumed to be the second. (9) $\Delta H^{\ddagger}$ of original converted to E by adding RT and A calculated with this value of E. (11) Determined order with respect to each reactant and actual rate but did not determine rate constants. Rate constants have been calculated from these rates and initial or instantaneous concentrations. (15) Time of half life in days converted to first order rate constants.

Reactions. (.23) (.24) (.25) (.26) (.27) (.28) (.29) (.30) (.31) Rate constants corrected for parallel (or consecutive) reaction leading to formation of ester in mixed water alcohol solvent. (.32) (.34) (.38) (.39) (.40) Reaction studied was the second of two consecutive reactions. First step was solvolysis of nitrile. See 242.453. Value of rate constant for (.32) and (.38) calculated from rate constant for solvolysis of nitrile and concentration of amide and nitrile at maximum amide concentration. (.49) (.50) (.51) Rate constants at higher temperatures corrected for volume expansion of solvent. (.55) Slight downward trend of rate constants with progress of reaction considered to be due to loss of HCl by reaction with solvent. (.66) Rate corrected for consecutive hydrolysis of diglycine and extrapolated to zero time. (.67) Slight downward trend of rate constant with course of reaction probably due to loss of HCl by reaction with solvent. (.68) Rate corrected for consecutive reaction of di- and tri-glycine. Reaction occurs at the three peptide linkages. Rate divided into total rate of two terminal linkages (.70) and solvolysis of center linkage (.69). (.69) (.70) Simultaneous reactions contributing to total reaction (.68). (.71) Rate constant calculated on basis that terminal glycine linkage is most reactive. Slight downward trend in rate constant probably due to loss of HCl by reaction with solvent. (.72) Initial rate to eliminate consecutive reactions of other linkages. (.73) Rate constant calculated on basis that terminal glycine linkage is most reactive. Slight downward trend in rate constant probably due to loss of HCl by reaction with solvent. (.74) Initial rate only. Solvolysis occurs to some extent at each peptide linkage and is followed by solvolysis of the fragments. Terminal linkages probably most reactive. (.75) Slight downward trend of rate constant with course probably due to loss of HCl by reaction with solvent. Calculations based upon principal reaction occuring at terminal peptide linkages.

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SOLVOLYSIS
C:N bond solvolysis

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Ionic strength	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
.16	$CH_3(CH_2)_3C{:}N + H_2O \longrightarrow CH_3(CH_2)_3CONH_2$	CH_3COOH	A = 0.25; B = 7	H_2SO_4	3.7		kA	60	2.25	-5				*	(1)
								70	5.50	-5					
								80	1.50	-4					
								90	4.25	-4	25	3	11		
.17	$C_6H_5CH_2C{:}N + H_2O \longrightarrow C_6H_5CH_2CONH_2$	CH_3COOH	A = 0.25; B = 7	H_2SO_4	3.7		kA	60	1.89	-5				*	(1)
								70	4.57	-5					
								80	1.25	-4					
								90	3.57	-4					
								100	8.97	-4	24	7	10		
.18	$CH_3(C_2H_5)_2N^+CH_2C{:}N + OH^- + H_2O \longrightarrow CH_3(C_2H_5)_2N^+CH_2COO^- + NH_3$	H_2O	A = 0.1; B = 0.455	NaI	0.099	0.6	$kA^{1.3}B^{1.6}$	35	1.59	-3				*	(3)
			0.455		0.508	1.0		35	1.19	-3					
			0.455		1.00	1.5		35	9.3	-4					
			0.550		0.402	1.0		35	1.37	-3					
			0.903		0.980	1.9		35	1.07	-3					
			A = B = 0.07-0.1	NaI	0.1		$kA^{2.4}$	25	9.59	-4					
								35	1.83	-3					
								45	3.54	-3					
								60	8.80	-3					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Ionic strength	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
.18	$CH_3(C_2H_5)_2\overset{+}{N}CH_2C{:}N + OH^- + H_2O \longrightarrow$ *(continued)*	H_2O	A = B = 0.07-0.1	NaI	0.1		$k\,A^{2.4}$	75	2.24	-2				*	(3)
								90	4.44	-2					
								100	7.71	-2					
								115	1.88	-1	13.2	4	6		
.19	$CH_3(C_2H_5)_2\overset{+}{N}CH(CH_3)C{:}N + OH^- + H_2O \longrightarrow$ $CH_3(C_2H_5)_2\overset{+}{N}CH(CH_3)COO^- + NH_3$	H_2O	A = 0.04-0.1; B = 1.0	NaI	0.10		$k\,A^{1.3}$	60	4.34	-5				*	(3)
					0.10			70	7.50	-5					
					0.10			80	1.25	-4					
					0.05			80	1.77	-4					
					0.10			90	1.92	-4					
					0.10			100	3.30	-4	12.6	8	3		
			A = B = 0.10	NaI	0.10		$k\,A^{2.4}$	120	5.45	-3					
.20	$CH_3(C_2H_5)_2\overset{+}{N}C(CH_3)_2C{:}N + OH^- + H_2O \longrightarrow$ $CH_3(C_2H_5)_2\overset{+}{N}C(CH_3)_2COO^- + NH_3$	H_2O	A = 0.035-0.04; B = 1.0	NaI	0.04		$k\,A^{1.4}$	80	5.34	-5				*	(3)
								90	1.12	-4					
								100	2.64	-4					
								110	5.10	-4	20.5	2.4	8		
Aryl-nitriles															
.21	$C_6H_5C{:}N + H_2O \longrightarrow C_6H_5CONH_2$	H_2O	A ≃ 0.01	NaOH	0.1-0.2		$k\,A[OH^-]$	70	2.17	-4				*	(2)
					1.0			70	2.60	-4					
.22	$C_6H_5C{:}N + 2H_2O_2 \longrightarrow$ $C_6H_5CONH_2 + O_2 + H_2O$	AW25*	A = 0.09; B = 0.09-0.18	buffers		pH 7.19	$-dA/dt = k\,AB$	40	1.5	-5				*	(4) (5)
						7.58		40	3.8	-5					
						8.07		40	1.23	-4					
		AW50*	A = 0.09; B = 0.18	boric acid buffer		8.6		40	3.6	-5					
		EW*	" "	phosphate buffer		8.08		40	1.63	-4					

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	pH	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
.23	$p\text{-}CH_3C_6H_4C{:}N + H_2O \longrightarrow p\text{-}CH_3C_6H_4CONH_2$	H_2O	$A \simeq 0.01$	NaOH	0.2		$k\,A[OH^-]$	70	1.43	-4				*	(2)
.24	$p\text{-}NO_2C_6H_4C{:}N + H_2O \longrightarrow p\text{-}NO_2C_6H_4CONH_2$	H_2O	$A \simeq 0.01$	NaOH	0.2		$k\,A[OH^-]$	70	2.25	-3				*	(2)
.25	$p\text{-}NO_2C_6H_4C{:}N + 2H_2O_2 \longrightarrow p\text{-}NO_2C_6H_4CONH_2 + O_2 + H_2O$	AW50*	A = 0.05; B = 0.18	buffer		8.6	$-dA/dt = k\,AB$	40	8.5	-4				*	(4) (5)
.26	$p\text{-}ClC_6H_4C{:}N + 2H_2O_2 \longrightarrow p\text{-}ClC_6H_4CONH_2 + O_2 + H_2O$	AW50*	A = 0.09; B = 0.18	buffer		8.6	$-dA/dt = k\,AB$	40	1.5	-4				*	(4) (5)

SOLVENTS

AW25* $(CH_3)_2CO$ 25 vol % + H_2O 75 vol %

AW50* $(CH_3)_2CO$ 50 vol % + H_2O 50 vol %

EW* C_2H_5OH 25 vol % + H_2O 75 vol %

COMMENTS

General. Reaction to amide usually followed by solvolysis of amide see 242.452. Rate law for each step obtained by treatment as consecutive reactions.

Reaction. **(.16) (.17)** Final product is ammonium salt as solvolysis of amide occurs with comparable rate constant. Authors state similar results obtained upon hydrolysis of aceto-, propio-, and butyro-nitrile but give no data. **(.18) (.19)** Fractional order maintained in presence or absence of I^- although actual value of rate constant changes. **(.20)** Secondary reaction produces small amount of tertiary amine. Order 1.4 compared to 1.3 observed for (.18) and (.19) considered not significant. **(.21)** Final product is ammonium salt produced by solvolysis of L with comparable rate constant. See 242.452. **(.22)** Reaction observed to be first order also in OH^-. $k = 1.0 \times 10^{-12} \times [OH^-]/K_W$, where K_W is ion product for water. $[OH^-]$ used in this calculation may be in error by factor of 2.5 as it was calculated from pH. In 50 % $(CH_3)_2CO$ solution pH is said to be 1.2 units high by (4). **(.23) (.24)** Final product is ammonium salt produced by solvolysis of L with comparable rate constant. See 242.452. **(.25) (.26)** pH is said to be 1.2 units high by (4).

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SOLVOLYSIS

N_2:C bond Solvolysis

Liquid phase

Reaction type: $RR'C{:}N_2 + R''OH \longrightarrow N_2 + RR'CHOR''$
(A) (B) (L) (M)

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
					(X)								
.12	.1	$C_2H_5OOCCH{:}N_2 + H_2O$	B	$A \simeq 10^{-4}$	$HClO_4$ +	$(1.4\text{-}10) \times 10^{-3}$	0.110	k AX	20	4.30	-1		[4]
					($NaClO_4$)	"	0.044		20	3.91	-1		
						"	0.022		20	3.82	-1		
			B + 50 wt % CH_3OH		$HClO_4$ + ($NaClO_4$) (X)	$10^{-5}\text{-}2 \times 10^{-4}$	0.110		20	8.1	-2		
.13	.4	$C_2H_5OOCCH{:}N_2 + C_2H_5OH$	B + H_2O (M/l) 0.0	$A \simeq 0.01$	p-$CH_3C_6H_4SO_3H$	0.00636		k AX	30	5.25	-1	*	[1]
			0.08						30	3.33	-1		
			0.15						30	2.17	-1		
			0.35						30	1.67	-1		
			0.47						30	1.33	-1		
			0.63						30	1.00	-1		
			B + 28.6 vol % C_6H_6	A = 0.016	p-$CH_3C_6H_4SO_3H$	0.00836			30	3.44	-1		
			B + 28.6 vol % $CHCl_3$	0.016	"	0.00836			30	2.94	-1		
			B + 28.6 vol % $(CH_3)_2CO$	0.016	"	0.00836			30	2.95	-1		
			C_2H_5OD						30	9.6	-1		
.14		$(C_6H_5)_2C{:}N_2 + C_2H_5OH$	B	10^3A = 1.93	p-$CH_3C_6H_4SO_3H$	5.0×10^{-5}		k AX	30	3.15	0	*	[2]
				2.96	"	7.54×10^{-5}			30	3.80	0		
				1.72	"	1.26×10^{-4}			30	4.56	0		
				1.4-3.8	"	$(2.5\text{-}7.5) \times 10^{-4}$			30	5.47	0		

No.	Supplementing 1951 No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	Ionic strength	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
					(X)								
.14		$(C_6H_5)_2C{:}N_2 + C_2H_5OH$	B	10^3A = 2.8	p-$CH_3C_6H_4SO_3H$	1.26×10^{-3}		k AX	30	5.64	0	*	(2)
		(continued)		1.6	"	3.3×10^{-4}	0.01		30	4.2	0		
				1.6	"	3.3×10^{-4}	0.03		30	4.7	0		
				1.6	"	3.3×10^{-4}	0.06		30	5.0	0		
				1.6	"	3.3×10^{-4}	0.13		30	5.8	0		
			B	2,4,6-$(NO_2)_3C_6H_2OH$ (XH)		10^4XH; 10^2XL1							
				+ 2,4,6-$(NO_2)_3C_6H_2OL1$ (XL1)		7.15 0	0.10	k_1A	30	3.74	-3		
						7.15 3-7	0.10		30	3.54	-3		
						7.15 10	0.10		30	3.52	-3		
			B + H_2O(M/l) 1.0	10^3A = 1.15	p-$CH_3C_6H_4SO_3H$	6.68×10^{-4}	0.0007	k AX	30	1.67	0		
			2.0	1.15	"	6.68×10^{-4}	0.0007		30	1.42	0		
			3.0	1.15	"	6.68×10^{-4}	0.0007		30	1.33	0		
			5.0	1.15	"	6.68×10^{-4}	0.0007		30	1.42	0		
			8.0	1.15	"	6.68×10^{-4}	0.0007		30	1.58	0		
						(X)							
			B + 28.6 vol % C_6H_6	10^3A = 2.3	p-$CH_3C_6H_4SO_3H$	0.000251		k AX	30	4.97	0		(1)
			B + 28.6 vol % $CHCl_3$	2.3	"	0.000251			30	6.87	0		
			B + 28.6 vol % $C_6H_5NO_2$	2.3	"	0.000251			30	6.87	0		
.15		$(C_6H_5)_2C{:}N_2$ + 2,4-$(NO_2)_2C_6H_3OH$	C_2H_5OH	10^3A= 3-4; 10^2B= 2-6				k AB	30	2.45	-2	*	(3)
					$LiClO_4$	0.10			30	3.8	-2		
					2,4-$(NO_2)_2C_6H_3OLi$	0.10			30	2.45	-2		
			C_2H_5OH + 28.6 vol % $C_6H_5NO_2$		"	0.10			30	3.00	-2		

COMMENTS

Reaction: **(.13)** Approximately linear relation between rate constant and concentration of water in range $[H_2O]$ = 0.15–0.63. Tabulated values taken from graph. **(.14)** No appreciable reaction in presence of C_2H_5ONa, $(C_2H_5)_2NH$ or p-$CH_3C_6H_4NH_2$. Replacement of 38 % of solvent OH bonds by OD bonds reduced rate of reaction to 69 % of rate in non-deuterium containing solvent. See (.13) where replacement by deuterium increases rate. Authors explain constant rate with varying concentration of lithium picrate on basis of catalytic constant of picric acid being 5.00 compared to 5.50 for $C_2H_5OH_2^+$, calculated from experiments with p-$CH_3C_6H_4SO_3H$. Depression of rate by H_2O taken as an indication of a smaller catalytic constant for H_3O^+. In presence of Cl^- a side reaction produces $(C_6H_5)_2CHCl$. **(.15)** Yields 61 % of L and 39 % benzhydrylethylether by parallel reaction with solvent. In presence of $LiClO_4$ product ratio of L drops to 43 % and total rate of reaction increases. Addition of 2,4-$(NO_2)_2C_6H_3OLi$ has no appreciable effect on product ratio or reaction rate. Addition of H_2O increases rate constant.

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SOLVOLYSIS

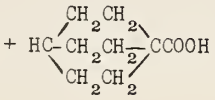
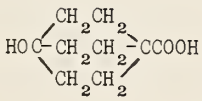
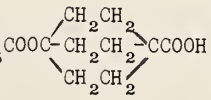
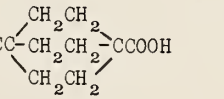
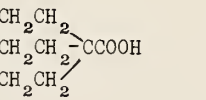
N_2:C bond by carboxylic acid

Liquid phase

Reaction type: $R_2C{:}N_2 + R'COOH \longrightarrow R'COOCHR_2 + N_2$
(A) (B) (L) (M)

Amounts are in M/l. Rate constants are in M/l and 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
	Solvolysis by aliphatic carboxylic acid										
.15	$(C_6H_5)_2C{:}N_2 + CH_3COOH$	C_2H_5OH	$10^3A = 2.2$; $10^2B = 3.4$			k AB	30	9.36	-3	*	(4)
			3.3 6.8				30	9.26	-3		
			5.5 14.7				30	9.64	-3		
			5.5 14.7	$LiClO_4$	0.033		30	1.04	-2		
			5.5 14.7		0.067		30	1.09	-2		
			5.5 14.7		0.100		30	1.15	-2		
			5.5 14.7	CH_3COONa	0.033		30	8.71	-3		
			5.5 14.7		0.067		30	8.21	-3		
			5.5 14.7		0.100		30	7.70	-3		
		C_2H_5OH + 17.5 vol % H_2O	5.2 15.4				30	3.54	-2		
		C_2H_5OH + 17.5 vol % D_2O	5.3 15.4				30	2.17	-2		
		C_2H_5OD	9.5 17.9				30	2.77	-3		
.16	$(C_6H_5)_2C{:}N_2 + CD_3COOD$	C_2H_5OH	$10^3A = 5.3$; $10^2B = 9.5$			k AB	30	9.22	-3		(4)
		C_2H_5OH + 17.5 vol % H_2O	5.3 9.5				30	3.54	-2		
		C_2H_5OH + 17.5 vol % D_2O	5.3 9.5				30	2.05	-2		
		C_2H_5OD	9.5 17.6				30	2.52	-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	Comments	Literature
	Solvolysis by aliphatic bicyclic carboxylic acid										
.17	$(C_6H_5)_2C{:}N_2$ + 	C_2H_5OH	$10^3B = 7.9$; $B \gg A$			k AB	30	3.94	-3		([3])
.18	$(C_6H_5)_2C{:}N_2$ + 	C_2H_5OH	$10^3B = 8.6$; $B \gg A$			k AB	30	6.16	-3		([3])
.19	$(C_6H_5)_2C{:}N_2 + C_2H_5COOC$- 	C_2H_5OH	$10^3B = 9.4$; $B \gg A$			k AB	30	6.26	-3		([3])
.20	$(C_6H_5)_2C{:}N_2 + N{:}C$- 	C_2H_5OH	$10^3B = 8.9$; $B \gg A$			k AB	30	9.86	-3		([3])
.21	$(C_6H_5)_2C{:}N_2 + Br$- 	C_2H_5OH	$10^3B = 7.4$; $B \gg A$			k AB	30	8.35	-3		([3])
	Solvolysis by aromatic carboxylic acid										
.22	$(C_6H_5)_2C{:}N_2 + C_6H_5COOH$	C_2H_5OH	$10^3A = 2.7\text{-}3.2$ $10^2B = 1.4\text{-}9.7$	$LiClO_4$	 0.017 0.033 0.067	k AB	30 30 30 30	1.77 1.87 1.90 1.98	-2 -2 -2 -2	* ([2]) ([5]) ([6]) ([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	Comments	Literature
.22	$(C_6H_5)_2C{:}N_2 + C_6H_5COOH$ *(continued)*	C_2H_5OH	10^3A = 2.7-3.2	$LiClO_4$	0.100	k AB	30	2.08	-2	*	(6)
				C_6H_5COOLi	0.07		30	1.62	-2		
			10^2B = 1.4-7	$C_6H_5COON(C_2H_5)_4$	0.10		30	1.47	-2		
					0.20		30	1.22	-2		
					0.30		30	1.12	-2		
		C_2H_5OH + 17 vol % H_2O	10^3A= 2.7; 10^2B= 1.4				30	6.37	-2		
				$LiClO_4$	0.067		30	7.59	-2		
					0.100		30	8.42	-2		
				LiCl	0.067		30	7.24	-2		
				C_6H_5COONa	0.100		30	5.58	-2		
		C_2H_5OH + 17 vol % D_2O	10^3A= 2.7; 10^2B= 1.4				30	3.92	-2		
		C_2H_5OH + 28.6 vol % $C_6H_5NO_2$	2.7 1.4				30	2.05	-2		
		C_2H_5OH + 28.6 vol % C_6H_6	2.7 1.4				30	2.10	-2		
		C_2H_5OH + 28.6 vol % $CHCl_3$	2.7 1.4				30	3.35	-2		
.23	$(C_6H_5)_2C{:}N_2 + p\text{-}CH_3C_6H_4COOH$	C_2H_5OH	10^2B = 2.9; A≪B			k AB	30	1.27	-2		(2)
.24	$(C_6H_5)_2C{:}N_2 + m\text{-}(CH_3)_3SiC_6H_4COOH$	C_2H_5OH	10^2B = 3-8; A≪B			k AB	30	1.80	-2		(2) (5)
.25	$(C_6H_5)_2C{:}N_2 + p\text{-}(CH_3)_3SiC_6H_4COOH$	C_2H_5OH	10^2B = 4-8; A≪B			k AB	30	1.92	-2	*	(2) (5)
.26	$(C_6H_5)_2C{:}N_2 + p\text{-}HOC_6H_4COOH$	C_2H_5OH	$10^2B \simeq 3$; A≪B			k AB	30	8.90	-3		(2)
.27	$(C_6H_5)_2C{:}N_2 + p\text{-}NH_2C_6H_4COOH$	C_2H_5OH	$10^2B \simeq 3$; A≪B			k AB	30	4.47	-3		(2)
.28	$(C_6H_5)_2C{:}N_2 + m\text{-}(CH_3)_3N^+C_6H_4COOH$	C_2H_5OH	$10^2B \simeq 3$; A≪B			k AB	30	1.30	-1		(1)
.29	$(C_6H_5)_2C{:}N_2 + p\text{-}(CH_3)_3N^+C_6H_4COOH$	C_2H_5OH	10^3B = 6-7; A≪B			k AB	30	8.18	-2		(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	Comments	Literature
.30	$(C_6H_5)_2C{:}N_2$ + m-$NO_2C_6H_4COOH$	C_2H_5OH	$10^2B \simeq 3$; $A \ll B$			k AB	30	8.60	-2		([2])
.31	$(C_6H_5)_2C{:}N_2$ + m-BrC_6H_4COOH	C_2H_5OH	$10^2B \simeq 3$; $A \ll B$			k AB	30	4.19	-2		([2])
.32	$(C_6H_5)_2C{:}N_2$ + p-BrC_6H_4COOH	C_2H_5OH	$10^2B \simeq 3$; $A \ll B$			k AB	30	3.14	-2		([2])
.33	$(C_6H_5)_2C{:}N_2$ + m-$F_3CC_6H_4COOH$	C_2H_5OH	$10^2B \simeq 3$; $A \ll B$			k AB	30	5.03	-2		([7])
.34	$(C_6H_5)_2C{:}N_2$ + p-$F_3CC_6H_4COOH$	C_2H_5OH	$10^2B \simeq 3$; $A \ll B$			k AB	30	4.82	-2		([7])

COMMENTS

General. Pseudo first order rate constant observed since acid in excess. First order dependence upon initial acid concentration observed, and second order rate constant calculated by dividing pseudo first order constant by initial concentration of acid. Spectrophotometric method used in preference to evolved nitrogen method of earlier investigators. Importance of solvent in mechanism shown by large effect on rate by replacing C_2H_5OH by C_2H_5OD. See (.15).

Reactions. **(.15)** Product is about 87 % benzhydrylacetate. Side reaction with solvent produces some benzhydrylethylether. See 242.455. **(.22)** Reaction leads to 55 % benzhydrylbenzoate and 32 % benzhydrylethylether by side reaction. See 242.455. Relative ratio of these two products is only slightly influenced by added salts or H_2O. LiCl and NaSCN have same effect on rate as $LiClO_4$. Rate constant observed to be almost linear function of H_2O concentration from 0 to 8 M/l. **(.25)** Value of rate constant tabulated is that of ([5]) which is about 10 % higher than earlier value reported by ([2]).

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SOLVOLYSIS
Alkyl Sulfonium Salts

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction types $R_2SR'^+ + OR''^- \longrightarrow R_2S + R'OR''$
$\longrightarrow RSR' + ROR''$

or $R_2SR'^+ + R''OH \longrightarrow R_2S + R'OR'' + H^+$
$\longrightarrow RSR' + ROR'' + H^+$

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	$(CH_3)_3S^+ + OH^-$	H_2O	A=B=0.1-0.3	k AB	100	3.70	-5				*	(3)
			A=0.1; B=0.35		100	3.3	-5					
.2	$(CH_3)_3S^+ + OH^-$	C_2H_5OH	A=B=0.06	k AB	100	7.43	-1				*	(3)
.3	$(CH_3)_3S^+ + OH^-$	Et80*	A~0.2; B=0.2-0.4	k AB	100	1.78	-2				*	(3)
		Et60*	A=0.2; B=0.2-0.4		100	1.51	-3					
		Et60*	10^3A=2; 10^3B=2-8		100	3.22	-3					
.4	$(CH_3)_3S^+ + OC_6H_5^-$	C_2H_5OH	A=0.09; B=0.14	k AB	100	1.35	-2					(3)
			A=0.13; B=0.26		100	1.00	-2					
.5	$2(CH_3)_3S^+ + OCO_2^= \longrightarrow 2(CH_3)_2S + (CH_3O)_2CO$	C_2H_5OH	A=0.04-0.2 B = or > A	$-dA/dt = k$ A	100	7.4	-5					(3)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$ 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	Literature
.6	$(CH_3)_2SC_2H_5^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	$-dA/dt =$	45	4.2	-4					(4)
	$\longrightarrow \begin{cases}(CH_3)_2S + (C_2H_5)_2O \\ CH_3SC_2H_5 + CH_3OC_2H_5\end{cases}$ (S)			$(k_S + k_E)AB = kAB$	64	3.89	-3	26	2	14		
	$\longrightarrow (CH_3)_2S + CH_2{:}CH_2 + C_2H_5OH$ (E)											
.6.1	$(CH_3)_2SC_2H_5^+ + OC_2H_5^-$	C_2H_5OH	A=0.05; B=0.095	k_SAB	45	3.7	-4					(4)
					64	3.3	-3	25	7	13		
.7	$(CH_3)_2SCH_2CH_2CH_3^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	$-dA/dt =$	64	3.81	-3					(4)
	$\longrightarrow \begin{cases}(CH_3)_2S + CH_3CH_2CH_2OC_2H_5$ (S) $\\ CH_3SCH_2CH_2CH_3 + CH_3OC_2H_5\end{cases}$			$(k_S + k_E)AB = kAB$								
	$\longrightarrow (CH_3)_2S + CH_3CH{:}CH_2 + C_2H_5OH$ (E)											
.7.1	$(CH_3)_2SCH_2CH_2CH_3^+ + OC_2H_5^-$	C_2H_5OH	A=0.05; B=0.095	k_SAB	64	3.54	-3					(4)
.8	$(CH_3)_2SCH(CH_3)_2^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	$-dA/dt =$	45	1.87	-3					(5)
	$\longrightarrow \begin{cases}(CH_3)_2S + (CH_3)_2CHOC_2H_5$ (S) $\\ CH_3SCH(CH_3)_2 + CH_3OC_2H_5\end{cases}$			$(k_S + k_E)AB = kAB$	64	1.58	-2	24	8	14		
	$\longrightarrow (CH_3)_2S + CH_2{:}CHCH_3 + C_2H_5OH$ (E)											
.8.1	$(CH_3)_2SCH(CH_3)_2^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	k_SAB	45	7.3	-4					(5)
	$\longrightarrow \begin{cases}(CH_3)_2S + (CH_3)_2CHOC_2H_5 \\ CH_3SCH(CH_3)_2 + CH_3OC_2H_5\end{cases}$				64	5.4	-3	22	2	12		

No.	Reaction	Solvent	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
.9	$(CH_3)_2SCH_2CH_2CH_2CH_3^+ + OC_2H_5^- \longrightarrow$ $\longrightarrow$ $\begin{cases}(CH_3)_2S + n\text{-}C_4H_9OC_2H_5 \\ n\text{-}C_4H_9SCH_3 + CH_3OC_2H_5\end{cases}$ (S) $\longrightarrow$ $CH_3CH_2CH{:}CH_2 + (CH_3)_2S + C_2H_5OH$ (E)	C_2H_5OH	A=0.05; B=0.095	$-dA/dt = \frac{(k_S + k_E)}{} AB = k\,AB$	64	3.94	-3						(4)
.9.1	$(CH_3)_2SCH_2CH_2CH_2CH_3^+ + OC_2H_5^- \longrightarrow$ $\longrightarrow$ $\begin{cases}(CH_3)_2S + n\text{-}C_4H_9OC_2H_5 \\ n\text{-}C_4H_9SCH_3 + CH_3OC_2H_5\end{cases}$	C_2H_5OH	A=0.05; B=0.095	$k_S AB$	64	3.77	-3						(4)
.10	$(CH_3)_2SCH_2CH(CH_3)_2^+ + OC_2H_5^- \longrightarrow$ $\longrightarrow$ $\begin{cases}(CH_3)_2S + i\text{-}C_4H_9OC_2H_5 \\ i\text{-}C_4H_9SCH_3 + CH_3OC_2H_5\end{cases}$ (S) $\longrightarrow$ $(CH_3)_2S + CH_2{:}C(CH_3)_2 + C_2H_5OH$ (E)	C_2H_5OH	A=0.05; B=0.095	$-dA/dt = \frac{(k_S + k_E)}{} AB = k\,AB$	64	5.93	-3						(4)
.10.1	$(CH_3)_2SCH_2CH(CH_3)_2^+ + OC_2H_5^- \longrightarrow$ $\longrightarrow$ $\begin{cases}(CH_3)_2S + i\text{-}C_4H_9OC_2H_5 \\ i\text{-}C_4H_9SCH_3 + CH_3OC_2H_5\end{cases}$	C_2H_5OH	A=0.05; B=0.095	$k_S AB$	64	5.79	-3						(4)
.11	$(CH_3)_2SCH(CH_3)C_2H_5^+ + OC_2H_5^- \longrightarrow$ $\longrightarrow$ $\begin{cases}(CH_3)_2S + s\text{-}C_4H_9OC_2H_5 \\ s\text{-}C_4H_9SCH_3 + CH_3OC_2H_5\end{cases}$ (S) $\longrightarrow$ $(CH_3)_2S + C_4H_8 + C_2H_5OH$ (E)	C_2H_5OH	A=0.05; B=0.095	$-dA/dt = \frac{(k_S + k_E)}{} AB = k\,AB$	64	1.20	-2						(5)

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
.11.1	$(CH_3)_2SCH(CH_3)C_2H_5^+ + OC_2H_5^- \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S + s\text{-}C_4H_9OC_2H_5\\ s\text{-}C_4H_9SCH_3 + CH_3OC_2H_5\end{cases}$	C_2H_5OH	A=0.05; B=0.095	$k_S AB$	64	5.1	-3					(5)
.12	$(CH_3)_2SC(CH_3)_3^+ + H_2O \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S + (CH_3)_3COH + H^+\\ CH_3SC(CH_3)_3 + CH_3OH + H^+\end{cases}$ (S) $(CH_3)_2S + (CH_3)_2C{:}CH_2 + H^+ + H_2O$ (E)	H_2O	A=0.059	$-dA/dt = (k_S + k_E)A = kA$	50	6.0	-6					(1)
					65	5.67	-5					(2)
					80	4.39	-4					(1)
					100	5.60	-3	33.0	1.2	17		(2)
.13	$(CH_3)_2SC(CH_3)_3^+ + C_2H_5OH \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S + (CH_3)_3COC_2H_5 + H^+\\ CH_3SC(CH_3)_3 + CH_3OC_2H_5 + H^+\end{cases}$ (S) $\longrightarrow (CH_3)_2S + (CH_3)_2C{:}CH_2 + H^+ + C_2H_5OH$ (E)	Et97*	A=0.02-0.034	$-dA/dt = (k_S + k_E)A = kA$	50	1.78	-5					(6)
.13.1	$(CH_3)_2SC(CH_3)_3^+ + C_2H_5OH \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S + (CH_3)_3COC_2H_5 + H^+\\ CH_3SC(CH_3)_3 + CH_3OC_2H_5 + H^+\end{cases}$	Et97*	A=0.02-0.034	$k_S A$	50	8.8	-6					(6)
.14	$(CH_3)_2SC(CH_3)_3^+ + \begin{cases}H_2O\\ C_2H_5OH\end{cases} \longrightarrow$ (see .12 and .13)	Et80*	A=0.059-0.064	$-dA/dt = kA$	50	1.24	-5					(1)
					65	1.18	-4					
					80	8.97	-4	32.7	1.6	17		

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
.15	$(CH_3)_2SC(CH_3)_3^+ + OC_2H_5^- \longrightarrow (CH_3)_2S + (CH_3)_2C{:}CH_2 + C_2H_5OH$	C_2H_5OH	(see 422.461)									
.16	$(CH_3)_2SC(CH_3)_2C_2H_5^+ + C_2H_5OH \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S + C_2H_5(CH_3)_2COC_2H_5 + H^+ \\ CH_3SC(CH_3)_2C_2H_5 + CH_3OC_2H_5 + H^+\end{cases}$ (S) $\longrightarrow (CH_3)_2S + C_5H_{10} + C_2H_5OH + H^+$ (E)	Et97*	A = 0.03-0.06	$-dA/dt = (k_S + k_E)A = kA$	50	1.50	-4					(6)
.16.1	$(CH_3)_2SC(CH_3)_2C_2H_5^+ + C_2H_5OH \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S + C_2H_5(CH_3)_2COC_2H_5 + H^+ \\ CH_3SC(CH_3)_2C_2H_5 + CH_3OC_2H_5 + H^+\end{cases}$	Et97*	A = 0.03-0.06	k_SA	50	5.3	-5					(6)
.17	$(CH_3)_2SC(CH_3)_2C_2H_5^+ + \begin{cases}H_2O \\ C_2H_5OH\end{cases} \longrightarrow$ $\longrightarrow \begin{cases}(CH_3)_2S,\ CH_3SC(CH_3)_2C_2H_5,\ CH_3OH, \\ C_2H_5(CH_3)_2COH,\ CH_3OC_2H_5,\ H^+, \\ C_2H_5(CH_3)_2COC_2H_5\end{cases}$ (S) $\longrightarrow (CH_3)_2S + C_5H_{10} + H^+$ (E)	C_2H_5OH + Vol % H_2O	A = 0.025-0.12	$-dA/dt = (k_S + k_E)A = kA$							*	(1) (2)
		3			50	1.50	-4					
		20			50	6.66	-5					
		20			65	6.18	-4					
		20			83	6.12	-3	31.6	1.5	17		
		50			65	4.54	-4					
.17.1	$(CH_3)_2SC(CH_3)_2C_2H_5^+ + \begin{cases}H_2O \\ C_2H_5OH\end{cases} \longrightarrow$ (see .17)	3	A = 0.025-0.12	k_SA	50	5.3	-5				*	(1) (2)
		20			50	3.52	-5					
		20			65	3.12	-4					
		20			83	2.83	-3					
		50			65	2.72	-4					

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
.18	$(CH_3)_2SCH_2CH_2C_6H_5^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	$-dA/dt =$	35	1.05	-2					(4)
	$\longrightarrow \begin{cases}(CH_3)_2S + C_6H_5CH_2CH_2OC_2H_5 \\ CH_3SCH_2CH_2C_6H_5 + CH_3OC_2H_5\end{cases}$ (S)			$(k_S + k_E)AB = k\,AB$	46	3.98	-2	24	1	15		
	$\longrightarrow (CH_3)_2S + C_6H_5CH{:}CH_2 + C_2H_5OH$ (E)											
.19	$(CH_3)_2SCH(CH_3)C_6H_5^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	$-dA/dt =$	20	2.75	-4					(5)
	$\longrightarrow \begin{cases}(CH_3)_2S + C_6H_5CH(CH_3)OC_2H_5 \\ CH_3SCH(CH_3)C_6H_5 + CH_3OC_2H_5\end{cases}$ (S)			$(k_S + k_E)AB = k\,AB$	45	9.61	-3	26.2	1.0	16		
					64	(9.8)	-2					
	$\longrightarrow (CH_3)_2S + C_6H_5CH{:}CH_2 + C_2H_5OH$ (E)											
.19.1	$(CH_3)_2SCH(CH_3)C_6H_5^+ + OC_2H_5^- \longrightarrow$	C_2H_5OH	A=0.05; B=0.095	$k_S AB$	64	(4.0)	-2				*	(5)
	$\longrightarrow \begin{cases}(CH_3)_2S + C_6H_5CH(CH_3)OC_2H_5 \\ CH_3SCH(CH_3)C_6H_5 + CH_3OC_2H_5\end{cases}$											
.20	$(C_2H_5)_3S^+ + OH^- \longrightarrow (C_2H_5)_2S + C_2H_5OH$ (S)	H_2O	A = 0.2-0.36	$-dA/dt =$	100	2.8	-5				*	(3)
	$\longrightarrow (C_2H_5)_2S + C_2H_4 + H_2O$ (E)		B = 0.2-0.66	$(k_S + k_E)AB = k\,AB$								
.20.1	$(C_2H_5)_3S^+ + OH^- \longrightarrow (C_2H_5)_2S + C_2H_5OH$	H_2O	A = 0.2-0.36 B = 0.2-0.66	$k_S AB$	100	4	-6				*	(3)
.21	$(i\text{-}C_3H_7)_2SCH_3^+ + OH^- \longrightarrow i\text{-}C_3H_7SCH_3 + i\text{-}C_3H_7OH$	H_2O	A = 0.003 B = 0.003-0.006	$k\,A$	100	2.2	-6				*	(3)

SOLVENTS

Et60*	C_2H_5OH 60 vol % + H_2O 40 vol %
Et80*	C_2H_5OH 80 vol % + H_2O 20 vol %
Et97*	C_2H_5OH 97 vol % + H_2O 3 vol %

COMMENTS

General. Reactants are listed in the order of increasing complexity. First are dimethyl sulfonium salts in the order of increasing numbers of C atoms of the third alkyl group. Straight-chain isomers precede the branched-chain isomers. The dimethyl sulfonium salts are followed by diethyl, etc. In all cases except $(CH_3)_3S^+$ solvolysis reactions are also accompanied by elimination reactions leading to olefin formation. In some cases elimination is the predominant reaction. Both reactions appear to be of the same order and are listed together with a rate constant $k = k_E + k_S$ where k_E is the reaction rate constant for the elimination reaction and k_S is the reaction rate constant for the solvolysis reaction. Where analysis of products has been made k_S has also been listed. For further information concerning k_E see 422.461. Unless otherwise stated rate law shows no drift in k from 10 to 80 % reaction.

Reactions. (.1) (.2) Small effect observed due to ionic strength but rate law valid from 12 to 75 % reaction. (.3) At higher concentrations of reactants slight increase in k with reaction observed. At low concentrations no drift in rate constant observed but value is almost double that at higher concentrations. (.17) (.17.1) Decrease in rate of olefin formation over the course of reaction noted and assumed to be due to consecutive reaction involving addition of solvent to previously formed olefin. (.19.1) Product separation showed predominant reaction to be formation of $(CH_3)_2S$ and $C_6H_5CH(CH_3)OC_2H_5$. (.20) (.21) Small variation in rate constant over course of reaction attributed by authors to neglect of effect of ionic strength upon ion activities. (.21) Reaction involved formation of $(CH_3)_2CHOH$ with no propylene or CH_3OH observed. Authors state that in 60 % C_2H_5OH and 40 % H_2O the reaction was second order and yielded $CH_2{:}CHCH_3$ with no $(CH_3)_2CHOH$ found in products.

LITERATURE

(1) K.A. Cooper, M.L. Dhar, E.D. Hughes, C.K. Ingold, B.J. MacNulty, *CSL* **1948**, 2043. (2) K.A. Cooper, E.D. Hughes, C.K. Ingold, G.A. Maw, B.J. MacNulty, *CSL* **1948**, 2049. (3) J.L. Gleave, E.D. Hughes, C.K. Ingold, *CSL* **1935**, 236. (4) E.D. Hughes, C.K. Ingold, G.A. Maw, *CSL* **1948**, 2072. (5) E.D. Hughes, C.K. Ingold, G.A. Maw, L.I. Woolf, *CSL* **1948**, 2077. (6) E.D. Hughes, C.K. Ingold, L.I. Woolf, *CSL* **1948**, 2084.

SOLVOLYSIS

Si-X(halogen) bond

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

Reaction types: $R_3SiX + H_2O \longrightarrow R_3SiOH + HX$

or $SiF_6^{=} + 4OH^- \longrightarrow 6F^- + H_2SiO_3 + H_2O$

No.	Reaction	Medium (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	$(C_6H_5)_3SiF + H_2O \longrightarrow (C_6H_5)_3SiOH + HF$	$(CH_3)_2CO$	A= 0.01; B= 2.2			kA	25	1.45	-6		*	(3)
			0.02 0.9				45	8.7	-7			
			0.02 1.8				45	4.0	-6			
			0.02 1.8	$NaClO_4$	0.52		45	4.8	-6			
			0.02 2.3				45	5.8	-6			
			0.01 2.8				45	1.17	-5			
			0.0008 2.8				45	1.20	-5			
			0.01 2.8	$NaClO_4$	0.26		45	1.52	-5			
			0.01 2.2				100	2.25	-4	15.5		
			0.01 2.2	$NaClO_4$	0.36		100	2.33	-4			
			0.01 2.8				100	2.88	-4	13.6		
.2	$(C_6H_5)_3SiF + OH^- \longrightarrow (C_6H_5)_3SiOH + F^-$	$(CH_3)_2CO + H_2O$	A ~ B ~ 0.001			kAB	25	> 2	+1		*	(3)
.3	$(p\text{-}CH_3C_6H_4)_3SiF + H_2O \longrightarrow (p\text{-}CH_3C_6H_4)_3SiOH + HF$	$(CH_3)_2CO$	A= 0.001; B= 2.8			kA	45	2.2	-6			(3)
			0.01 2.2				100	5.0	-5			
.4	$SiF_6^{=} + 4OH^- \longrightarrow H_2SiO_3 + 6F^- + H_2O$	H_2O	A= 0.04-0.2; B= 0.03-0.15			kA	0	3.85	-3		*	(1)
							15	2.4	-2			

No.	Reaction	Medium (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	$SiF_6^= + 4\,OH^- \longrightarrow H_2SiO_3 + 6\,F^- + H_2O$ *(continued)*	H_2O	$10^3A = 1.6\text{-}21$			kA	20	3.71	-2			(2)
							25	7.5	-2	44.2		(1)
			$10^3A = 6$	NaF	0.002-0.05		20	3.66	-2			(2)
			$10^3A = 1\text{-}10$	NaCl	0.005-0.2		20	3.66	-2			

COMMENTS

Reaction. (.1) Rate shown to be independent of pH in acid solutions. Approximate concentration of water calculated from %. (.2) Reaction too rapid to establish rate law. (.4) First order rate valid over course and independent of initial concentration of B. Reaction followed by using insufficient B and measuring time to disappearance of pink color of added phenolphthalein. Independence of rate upon B confirmed by using excess B and neutralizing excess with required acid just prior to expected disappearance of pink color. Rate measurements used by (1) as part of a quantitative method of determining A in hydrofluoric acid.

LITERATURE

(1) L.J. Hudleston, H. Bassett, *CSL* **1921,** 403.

(2) A.G. Rees, L.J. Hudleston, *CSL* **1936,** 1334.

(3) C.G. Swain, R.M. Esteve, R.H. Jones, *ACS* 1949, **71,** 965.

SOLVOLYSIS

Aliphatic acid halides

Liquid phase

Reaction types:

$$RCOX + R'OH \longrightarrow RCOOR' + HX$$
$$RCOX + R'O^- \longrightarrow RCOOR' + X^-$$
(A) (B) (L) (M)

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (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	$CH_3COF + H_2O$	$(CH_3)_2CO$ + B	10^3A= 3-9; B= 13.9			k A	25	1.1	-4					(2)
			27.8				0	2.2	-4					
			27.8	$LiClO_4$	0.1		0	2.0	-4					
			27.8	$HClO_4$	0.1		0	3.1	-4					
			27.8	H_3BO_3	0.02		0	4.10	-2					
				NaH_2BO_3	0.02									
.2	$CH_3COF + OH^-$	An50*	10^3A= 3-9; 10^4B= 1.6	H_3BO_3	0.02	k AB	0	2.5	+2				*	(2)
				NaH_2BO_3	0.02									
.3	$CH_3COCl + H_2O$	$(CH_3)_2CO$ + B	$10^3A \sim 7$; B= 13.9			k A	-30	4.1	-3					(2)
							-11	3.3	-2	13.9	1.3	10		
.4	$CH_3COCl + C_2H_5OH$	$(C_2H_5)_2O$ + B	10^3A= 2; B= 6.8			k A	0	2.4	-3				*	(1)
							25	1.64	-2	12.5	2	7		
.5	$ClCH_2COCl + C_2H_5OH$	$(C_2H_5)_2O$ + B	10^3A= 2; B= 6.8			k A	0	4.8	-2				*	(1)

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
.6	$Cl_2CHCOCl + C_2H_5OH$	$(C_2H_5)_2O + B$	$10^3A = 2$; $B = 6.8$				0	very fast						(1)
.7	$Cl_3COCl + C_2H_5OH$	$(C_2H_5)_2O + B$	$10^3A = 2$; $B = 6.8$				0	very fast						(1)

SOLVENTS

$(CH_3)_2CO + B$	$(CH_3)_2CO$ + second reactant 25-50 vol % amounts listed in M/l under "amount of reactant".
An50*	$(CH_3)_2CO$ 50 vol % + H_2O 50 vol %
$(C_2H_5)_2O + B$	$(C_2H_5)_2O$ + second reactant 40 vol %

COMMENTS

Reaction. (.2) Value calculated from pseudo first order constant in buffered solution after correcting for simultaneous reaction (.1). (.4) (.5) Final steady rate tabulated. Initial rate slower.

LITERATURE

(1) G.E.K. Branch, A.C. Nixon, *ACS* 1936, **58**, 2499. (2) C.G. Swain, C.B. Scott, *ACS* 1953, **75**, 246.

SOLVOLYSIS
Aromatic acyl halides

Liquid phase

Reaction types:

$ArCOX + ROH \longrightarrow ArCOOR + HX$

$ArCOX + RO^- \longrightarrow ArCOOR + X^-$

$ArSO_2X + ROH \longrightarrow ArSO_3R + HX$

$ArSO_2X + RO^- \longrightarrow ArSO_3R + X^-$

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

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Supplementing 1951 No.	Reaction	Medium (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
.49		$C_6H_5COF + H_2O$	$(CH_3)_2CO + B$	$10^3A = 1.6\text{-}4$; B = 27.8			$k\,A$	0	1.1	-5					[10]
				13.9				25	8.2	-6					
				A = 0.03; B = 5.06				30	5.7	-7					[3]
				8.33				30	2.16	-6					
				16.7				30	1.54	-5					
				20.8				30	2.84	-5					
				22.2				30	3.64	-5					
				27.8				30	7.92	-5					
				38.9				30	3.64	-4					
				$10^3A = 2$; B = 27.8	H_3BO_3	(0.01-0.02)	$k\,A$	0	3.2-3.6	-4					[10]
					NaH_2BO_3	(0.01-0.02)									
				A = 0.03; B = 5.06	HCl	0.05	$k\,A + k_H A[H^+]$		k_H						[3]
					LiCl	0.10		30	7.9	-5					
				8.33	"	"		30	9.5	-5					

No.	Supplementing 1951 No.	Reaction	Medium (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
.49		$C_6H_5COF + H_2O$ *(continued)*	$(CH_3)_2CO + B$	A = 0.03; B =	HCl	0.05 }	$k\,A + k_H A[H^+]$		k_H						(3)
				22.2	LiCl	0.10 }		30	2.34	-4					
				38.9	"	"		30	5	-4					
.50		$C_6H_5COF + OH^-$	An50*	~0.001			$k\,AB$	0	2.1	+1					(10)
.51		$C_6H_5SO_2F + H_2O$	An50*	10^3A = 5-7; B = 27.8			$k\,A$	25	< 5	-8				*	(10)
					$HClO_4$	0.1		25	< 5	-8					
					H_3BO_3	0.02 }		0	1.8	-5					
					NaH_2BO_3	0.02 }									
.52		$C_6H_5SO_2F + OH^-$	An50*	$10^3A \sim 5$; 10^4A = 1.6	"	"	$k\,AB$	0	1.1	-1				*	(10)
.53	.1	$C_6H_5COCl + H_2O$	$(CH_3)_2CO + B$	A = 0.001-0.04; B =	29.5		$k\,A$	0	7.3	-4					(5)
					38.6			0	3.88	-3					
					43.1			0	9.80	-3					
					2.81			15	2.6	-5					
					8.67			15	1.36	-4					
					14.5			15	2.93	-4					
					19.4			15	5.48	-4					
					23.3			15	9.40	-4					
					2.77			25	5.4	-5					
					8.52			25	3.00	-4					
					14.3			25	6.94	-4					
					19.2			25	1.41	-3					
					23.0			25	2.52	-3	16.9				
					2.73			35	1.05	-4	11.5				
					8.41			35	6.45	-4	13.9				
					14.2			35	1.61	-3	15.1				
					19.0			35	3.40	-3	16.2				

No.	Supplementing 1951 No.	Reaction	Medium (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
.53	.1	$C_6H_5COCl + H_2O$ *(continued)*	An50*	10^4A = 4-300	KNO_3	0.45	$k_1A + k_2A[OH^-]$								(7)
					NaOH	0-0.022		1	k_1 5.8	-4					
								1	k_2 1.3	-2					
								8	k_1 1.28	-3	16.1	3	9		
			$(CH_3)_2CO$ + B	10^3A = 8-35;											
				B = 2.77	LiBr	0.028	kA	25	1.53	-4					(2)
				8.52		0.013		25	3.25	-4					
				"		0.045		25	3.54	-4					
				"	KNO_3	0.010		25	3.34	-4					
				"		0.020		25	3.47	-4					
				"	KCl	0.020		25	3.03	-4					
				"	LiCl	0.037		25	2.97	-4					
				19.2	KNO_3	0.02		25	1.41	-3					
				"	HCl	0.01		25	1.43	-3					
			D1W*	10^2A= 2-3; B= 2.78			kA	15	3.9	-5					(5)
				5.55				15	1.06	-4					
				11.1				15	2.43	-4					
				18.5				15	6.01	-4					
				27.8				15	2.61	-3					
				2.78				25	7.7	-5					
				5.55				25	2.14	-4					
				11.1				25	5.60	-4					
				18.5				25	1.44	-3					
				2.78				35	1.48	-4	11.8				
				5.55				35	4.18	-4	12.1				
				11.1				35	1.22	-3	14.2				
				18.5				35	3.23	-3	14.8				
				27.8				35	>6	-3					

No.	Supplementing 1951 No.	Reaction	Medium (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
.54		$C_6H_5COCl + OH^-$	An50*	10^3A = 4-30; 10^3B = 6-22	KNO_3	0.45	k AB	1	1.27	-2				*	(7)
.55		$C_6H_5COCl + C_2H_5OH$	B	A ~ 0.1			k A	0	7.3	-5					(3a) (8)
								25	7.8	-4	15.3	1.4	8		
			$(C_2H_5)_2O$ + B	10^3A= 2; B= 6.9				0	1.17	-5					(4)
								25	1.08	-4	14.4	4	6		
				A = B = 1.0			k AB	25	2.3	-6				*	(9)
			$(C_4H_9)_2O$	A = B ~ 1			"	25	4.7	-6					
			$(CH_3)_2CO$	A = B ~ 1			"	25	8.6	-6					
			$C_6H_5CH_3$	A = B ~ 1			"	25	1.40	-5					
			C_6H_6	A = B ~ 1			"	25	1.51	-5					
			C_6H_5Cl	A = B ~ 1			"	25	1.70	-5					
			C_6H_{14}	A = B ~ 1			"	25	2.48	-5					
			$C_6H_5N(CH_3)_2$	A = B ~ 1			"	25	6.94	-5					
.56	.3	$C_6H_5SO_2Cl + H_2O$	An50*	A= 0.04; B= 27.8	H_2SO_4	0-0.26	k A	25	2.4	-4	14	8	6		(9a) (10)
.57		$C_6H_5SO_2Cl + OH^-$	An50*				k AB	0	6.8	-1					(10)
.58		$C_6H_5COBr + H_2O$	An50*	10^3A= 4-5; B= 27.8			k A	0	6.3	-2					(10)
					H_3BO_3	0.2		0	5.3	-2					
					NaH_2BO_3	0.2									
.59	.6	o-$CH_3C_6H_4COCl + C_2H_5OH$	B	A ≃ 0.1			k A	0	2.7	-4					(8)
								25	3.48	-3	16.5	4	9		

No.	Supplementing 1951 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
.60	.10	p-$CH_3C_6H_4COCl + H_2O$	$(CH_3)_2CO + B$	$10^2A = 2$; $B = 2.78$			kA	25	2.67	-5					(5)
				2.78				35	5.44	-5	13	6	4		
				27.8	KNO_3	0.45		0	1.92	-3					(7)
				27.8		0.45		8	4.2	-3	16	2	10		
			D1W*	$10^2A = 2$; $B = 2.78$				25	3.46	-5					(5)
.61	.12	p-$CH_3C_6H_4COCl + C_2H_5OH$	B	$A \simeq 0.1$			kA	0	5.6	-5					(3a) (8)
								25	6.0	-4	15.3	1.1	8		
			$(C_2H_5)_2O + B$	$10^3A = 2$; $B = 6.9$				0	5.5	-6				*	(4)
								25	6.44	-5	15.9	3	7		
.62	.13	2,4,6-$(CH_3)_3C_6H_2COCl + H_2O$	$(CH_3)_2CO + B$	$10^3A = 2$-3; $B = 2.78$			kA	-11	2.89	-4					(5)
				2.78				0	1.58	-3	22	6	14		
				5.55				-19	1.09	-3					
				5.55				-9	7.13	-3	24	5	17		
.63		p-$CH_3OC_6H_4COCl + H_2O$	$(CH_3)_2CO + B$	$10^2A = 2$; $B = 2.78$			kA	25	2.92	-5					(5) (6)
				2.78				35	6.54	-5	15	8	5		
				5.55				0	1.28	-5					
				5.55				15	6.39	-5					
				5.55				25	1.80	-4	17	4	8		
				8.34				0	4.29	-5					
				8.34				15	2.63	-4	19	6	10		
				$10^2A = 2$-3; $B = 11.1$				0	1.25	-4					
				11.1				12	4.94	-4	19	2	11		
				13.9				-14	4.95	-5					
				13.9				0	2.82	-4	18	7	10		
				16.6				0	7.03	-4					
.63.1		p-$(CH_3)_3CC_6H_4COCl + C_2H_5OH$	B				kA	0	5.26	-5					(3a)

No.	Supplementing 1951 No.	Reaction	Medium (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
.64		p-$CH_3OC_6H_4COCl + OH^-$	An25*	$10^3A \sim 2$; $10^3B \sim 6$			k AB	0	4.0	-1				*	(5)
.65		p-$CH_3OC_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			k A	0	5.9	-5					(8)
			$(C_2H_5)_2O$ + B	$10^3A = 2$; $B = 6.9$				0	3.0	-6				*	(4)
								25	5.33	-5	18.6	2	9		
.66	.20	o-$NO_2C_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			k A	0	1.62	-4					(8)
								25	1.22	-3	13.1	5	6		
.67		m-$NO_2C_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			k A	0	1.50	-3					(8)
.68	.23	p-$NO_2C_6H_4COCl + H_2O$	$(CH_3)_2CO$ + B	$10^3A = 2$-3; $B = 2.78$			k A	0	5.86	-4					(5) (6)
				2.78				15	1.23	-3					
				2.78				25	1.69	-3	6.7	1.3	2		
				8.34				0	1.26	-3					
				11.1				0	1.62	-3					
				14.4				0	2.03	-3					
				22.2				-16	1.06	-3					
				22.2				-10	1.88	-3					
				22.2				0	5.02	-3	13.7	4	8		
				$10^3A = 4$-30; $B = 27.8$	KNO_3	0.45		0	7.7	-3					(7)
								5	1.25	-2	16	2	10		
.69		p-$NO_2C_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			k A	0	1.58	-3					(8)
			$(C_2H_5)_2O$ + B	$10^3A = 2$; $B = 6.9$				0	3.7	-4				*	(4)
								25	2.04	-3	11.1	3	5		

No.	Supplementing 1951 No.	Reaction	Medium (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
.70		$2,4,6\text{-}(NO_2)_3C_6H_2COCl + H_2O$	$(CH_3)_2CO + B$	$10^2A \simeq 1$; B = 5.55			kA	0	4.02	-5					(5)
				5.55				20	2.82	-4	15.5	6	6		
				11.1				0	7.33	-5					
				16.6				0	1.03	-4					
.71		$p\text{-}FC_6H_4COCl + C_2H_5OH$	$(C_2H_5)_2O + B$	$10^3A = 2$; B = 6.9			kA	0	1.27	-5				*	(4)
								25	1.22	-4	14.6	6	7		
.72	.29	$o\text{-}ClC_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			kA	0	2.7	-4					(8)
								25	2.1	-3	13.3	1.2	7		
.73	.35	$p\text{-}ClC_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			kA	0	1.4	-4					(8)
								25	1.21	-3	14.0	2	7		
			$(C_2H_5)_2O + B$	$10^3A = 2$; B = 6.9				0	2.4	-5				*	(4)
								25	2.05	-4	13.8	3	6		
.74		$o\text{-}BrC_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			kA	0	2.5	-4					(8)
.75		$m\text{-}BrC_6H_4COCl + C_2H_5OH$	B	$A \sim 0.1$			kA	0	3.4	-4					(8)
.76	.40	$p\text{-}BrC_6H_4COCl + H_2O$	$(CH_3)_2CO + B$	$10^2A = 2$; B = 2.78			kA	0	3.1	-5					(5) (6)
				2.78				15	8.8	-5					
				2.78				25	1.54	-4					
				2.78				35	3.05	-4	11.0	2	3		
				10^3A = 4-30; B = 27.8	KNO_3	0.45		1	5.3	-4					(7)
				27.8		0.45		9	1.28	-3	17	8	9		

No.	Supplementing 1951 No.	Reaction	Medium (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
.77		p-$BrC_6H_4COCl + C_2H_5OH$	B	A ~ 0.1			kA	0	1.54	-4					(8)
			$(C_2H_5)_2O$ + B	10^3A= 2; B= 6.9				0	2.8	-5				*	(4)
								25	2.24	-4	13.4	2	6		
.78	.48	p-$IC_6H_4COCl + C_2H_5OH$	$(C_2H_5)_2O$ + B	10^3A= 2; B= 6.9			kA	0	2.6	-5				*	(4)
								25	2.10	-4	13.4	2	6		

SOLVENTS

An50*	$(CH_3)_2CO$ 50 vol % + H_2O 50 vol %.
$(CH_3)_2CO$ + B	$(CH_3)_2CO$ + H_2O 5-50 vol % with amount of H_2O listed in M/l under "amount of reactants".
B	The second reactant is the solvent (in great excess).
Diw*	Dioxane + H_2O 5-50 vol % with amount of H_2O listed in M/l under "amount of reactants".
$(C_2H_5)_2O$ + B	$(C_2H_5)_2O$ 60 vol % + C_2H_5OH 40 vol %.

COMMENTS

Reaction. **(.51)** Rate law not confirmed as less than 10 % reaction in 26 days in either acid or neutral solutions. **(.52)** Value of second order constant calculated by dividing pseudo first order constant in buffered solution by concentration of OH^-. **(.54)** Corrected for simultaneous reaction (.53), with H_2O. **(.55)** Selected data of [9] as wide variety of solvents used. **(.61)** Final steady rate tabulated. Initial rate slower. **(.64)** Corrected for simultaneous reaction (.63) with H_2O. **(.66) (.69) (.71) (.73) (.77) (.78)** Values of [4] refer to final steady rate in $(C_2H_5)_2O$. Initial rate slower.

LITERATURE

[1] B.L. Archer, R.F. Hudson, *CSL* **1950**, 3259. [2] B.L. Archer, R.F. Hudson, J.E. Wardill, *CSL* **1953**, 888. [3] C.W.L. Bevan, R.F. Hudson, *CSL* **1953**, 2187. [3a] C.W.L. Bevan, E.D. Hughes, C.K. Ingold, *Nature* 1953, **171**, 301. [4] G.E.K. Branch, A.C. Nixon, *ACS* 1936, **58**, 2499. [5] D.A. Brown, R.F. Hudson, *CSL* **1953**, 883, 3352. [6] D.A. Brown, R.F. Hudson, *Nature* 1951, **167**, 819. [7] R.F. Hudson, J.E. Wardill, *CSL* **1950**, 1729. [8] J.F. Norris, E.V. Fasce, C.J. Stand, *ACS* 1935, **57**, 1415. [9] J.F. Norris, E.C. Haines, *ACS* 1935, **57**, 1425. [9a] S.C.J. Olivier, G. Berger, *RTC* 1927, **46**, 609. [10] C.G. Swain, C.B. Scott, *ACS* 1953, **75**, 246.

SOLVOLYSIS
Oxime acetate

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.
* Coded solvents at the end of the table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n
.1	$C_6H_5C(CH_3):NOC:OCH_3 + OH^- \longrightarrow C_6H_5C(CH_3):NOH + CH_3COO^-$	Et90*	A = 0.025-0.10			k AB	25	3.85	-3			
			B = 0.065-0.13				35	1.08	-2	19	2	11
				L1Cl	0.05		25	3.85	-3			
		Et80*					25	7.65	-3			
		Et35*					25	4.44	-2			
.2	$p\text{-}CH_3C_6H_4C(CH_3):NOC:OCH_3 + OH^- \longrightarrow p\text{-}CH_3C_6H_4C(CH_3):NOH + CH_3COO^-$	Et90*	A = 0.025-0.10			k AB	25	5.80	-3			
			B = 0.065-0.13				35	1.15	-2	13	1	7
.3	$p\text{-}CH_3OC_6H_4C(CH_3):NOC:OCH_3 + OH^- \longrightarrow p\text{-}CH_3OC_6H_4C(CH_3):NOH + CH_3COO^-$	Et90*	A = 0.025-0.10			k AB	25	4.30	-3			
			B = 0.056-0.13				35	1.10	-2	17	1.4	10
.4	$m\text{-}NO_2C_6H_4C(CH_3):NOC:OCH_3 + OH^- \longrightarrow m\text{-}NO_2C_6H_4C(CH_3):NOH + CH_3COO^-$	Et90*	A = 0.025-0.10			k AB	25	2.10	-3			
			B = 0.056-0.13				35	5.40	-3	17	8	9
.5	$p\text{-}NO_2C_6H_4C(CH_3):NOC:OCH_3 + OH^- \longrightarrow p\text{-}NO_2C_6H_4C(CH_3):NOH + CH_3COO^-$	Et90*	A = 0.025-0.10			k AB	25	1.80	-3			
			B = 0.056-0.13				35	4.95	-3	18	6	10
.6	$p\text{-}BrC_6H_4C(CH_3):NOC:OCH_3 + OH^- \longrightarrow p\text{-}BrC_6H_4C(CH_3):NOH + CH_3COO^-$	Et90*	A = 0.025-0.10			k AB	25	3.00	-3			
			B = 0.056-0.13				35	7.75	-3	17	1.5	10

SOLVENT

Et X* C_2H_5OH X % + H_2O

COMMENTS

General. Selected Data. Rate law followed over course of all reactions.

LITERATURE

O.L. Brady, J. Miller, *CSL* **1953**, 4076.

SOLVOLYSIS
Amine sulfonates

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of catalyst	Addend (Salt)	$\mu^{\frac{1}{2}}$	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
.1	$HN(SO_3)_2^{=} + H_2O \longrightarrow HSO_4^{-} + H_2NSO_3^{-}$	B	10^2A = 1-5	HCl	0.01-0.2	NaCl or Na_2SO_4	0.141	$kA[H^+]$	25	7.96	-4		
							0.199		25	6.59	-4		
							0.300		25	3.15	-4		
							0.500		25	3.15	-4		
							1.00		25	1.70	-4		
							0.199		35	2.38	-3		
							0.250		35	1.95	-3		
							0.300		35	1.67	-3		
							0.199		45	7.99	-3		
							0.250		45	6.94	-3		
							0.300		45	5.9	-3		
							0		25	1.42	-3		
							0		35	5.35	-3		
							0		45	1.77	-2	23.5	21.3
			5		pH = 8			kA	25	1	-9		

COMMENTS

Selected data. Units converted from original minutes. Rate constants and order determined from initial rates. Confirmed over course by instantaneous rates as well as by a graphical method of integration. Beyond 50 % reaction rate constants

COMMENTS *(continued)*

decrease. Ionization of HSO_4^- included in rate expression. Dependence of rate constant upon ionic strength according to Brönsted theory indicates the rate determining step to involve oppositely charged ions with an ion product, $Z_1Z_2 = -2$: $\log k = \log k_o + [2AZ_1Z_2\mu^{\frac{1}{2}}/(1 + \mu^{\frac{1}{2}})] + B\mu$ where k_o is value of rate constant at $\mu = 0$ and $A = 0.506, 0.517, 0.528$ with $B = 0.092, -0.32, 0.13$ at 25, 35, and 45° respectively.

LITERATURE

G.J. Doyle, N. Davidson, *ACS* 1949, **71**, 3491.

SOLVOLYSIS

CN halides

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Literature
.3	$C{:}NCl + OH^- \longrightarrow C{:}NOH + Cl^-$	H_2O	$10^4A = 4; 10^3B = 1$	(X)	$\mu = 0.15$	$k\,AB$; $k = k_o$	0	1.33	0		(1)
							10	2.83	0		
							20	6.67	0		
							25	8.83	0		(1) (2)
							30	1.25	1		(1)
				$HOCl + Cl_2$	$0\text{-}4.5 \times 10^{-4}$	$k = k_o + k_1X$	0	k_1 = 1.2	7		
							10	k_1 = 1.6	7		
							20	k_1 = 1.8	7		
				Na_2HPO_4 } NaH_2PO_4 }	0.04-0.15	$k\,AB + k'\,AX$	25	k = 1.0	1		(2)
							25	k' = 5	-4		

LITERATURE

(1) G.E. Eden, A.B. Wheatland, *CIL* 1950, 69, 1640.

(2) C.C. Price, T.E. Larson, K.M. Beck, F.C. Harrington, L.C. Smith, I. Stephanoff, *ACS* 1947, 69, 1640.

SOLVOLYSIS

P - O bond

Liquid phase

Amounts are in M/l.
Rate constants are in M/l and sec.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Ionic strength	Defined mass-action law	Temperature	pH	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.6	.5	$Na_4P_2O_7 + H_2O \longrightarrow 2Na_2HPO_4$	H_2O	0.038			0.38	$k\,A$	60	1	1.77	-5				*	(4)
									60	4	2.05	-6					
					NaBr	2.65	3.0		60	1	9.58	-6					
									60	4	2.51	-6					
.7		$[N(CH_3)_4]_4P_2O_7 + H_2O \longrightarrow 2[N(CH_3)_4]_2HPO_4$	H_2O	0.021	$N(CH_3)_4Br$	0.65	0.86	$k\,A$	30	1	3.58	-7				*	(4)
									30	4	3.00	-8					
									60	1	1.12	-5					
									60	4	1.78	-6					
									60	7	2.77	-7					
									90	1	1.94	-4	22.7	9	9		
									90	4	5.25	-5	27.2	1.2	12		
									90	7	1.14	-5	29.8	1.0	13		
									90	10	1.86	-7					
									125	10	2.2	-5	40	2	17		
									125	13	1.4	-6					
.8	.5	$H_4P_2O_7 + H_2O \longrightarrow 2H_3PO_4$	H_2O	$(1\text{-}80)\times10^{-5}$	HCl, NaCl, or $HClO_4$		0.12	$k\,A[H^+]$	40	0.9	3.27	-5				*	(2)
							0.61		50	-0.2	1.70	-4					
							0.52		50	0.0	1.46	-4					
							0.50		50	0.3	1.28	-4					
							0.08		50	1.1	1.11	-4					
							0.01		50	2.0	2.13	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Ionic strength	Defined mass-action law	Temperature	pH	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.8	.5	$H_4P_2O_7 + H_2O \longrightarrow 2H_3PO_4$ *(continued)*	H_2O	$(1\text{-}80)\times10^{-5}$	HCl, NaCl, or $HClO_4$		0.15	$k\,A[H^+]$	50	2.0	1.59	-4				*	(2)
							0.15		50	2.5	3.30	-4					
							0.15		50	3.0	7.78	-4					
							0.15		50	3.3	1.60	-3					
							0.15		60	0.8-1.0	3.06	-4					
							0.15		60	1.7	4.09	-4					
							0.15		60	2.0	5.75	-4					
					HCl + buffers		0.15		60	2.5	1.27	-3					
							0.15		60	3.0	3.06	-3					
							0.15		60	3.3	6.25	-3					
						0.09-0.23			69	0.6-1	7.53	-4	22.3				
							0.006		69	2.3	3.46	-3					
							0.002		69	3.1	1.23	-2					
							0.15		69	1.4	9.20	-4					
							0.15		69	2.1	2.00	-3	27.5				
							0.15		69	2.3	2.88	-3	28.3				
							0.15		69	2.5	4.17	-3					
							0.15		69	3.0	1.02	-2	29.0				
							0.15		69	3.3	1.97	-2	29				
					CH_3COOH +	0.15											
					CH_3COONa	0.15	0.15	$k\,A$	50	4.6	6.23	-7					
									60	4.6	2.01	-6					
					CH_3COOH +	0.003-0.15											
					CH_3COONa	0.001-0.15	0.005-0.15		69	4.6-5	7.83	-6					
					HCOOH=HCOONa	0.15	0.15	$k\,A$	69	3.6	8.36	-6					
						0.10	0.15		69	3.6	8.46	-6					
						0.05	0.15		69	3.6	9.09	-6					
						0.005	0.15		69	3.6	9.14	-6					
						0.002	0.15		69	3.7	9.30	-6					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Ionic strength	Defined mass-action law	Temperature	pH	$k = k^\circ \times 10^n$ k°	n	E	$A = A^\circ \times 10^n$ A°	n	Comments	Literature
.8	.5	$H_4P_2O_7 + H_2O \longrightarrow 2H_3PO_4$ *(continued)*	H_2O	$(1\text{-}80)\times10^{-5}$	PBA*	0.0042	0.15	k A	69	3.7	9.15	-6				*	(2)
						0.0085	0.15		69	3.7	9.39	-6					
						0.0181	0.15		69	3.6	9.57	-6					
					NH_4Cl + NH_4OH	0.008											
						0.002	0.008		69	8.5	1.19	-6					
					NH_4Cl + NH_4OH	0.001											
						0.010	0.001		69	10	2.28	-7					
.9		$H_3P_2O_7^- + H_2O \longrightarrow$	(calculated from data of .8)				.15	k_2A	50		7.77	-7				*	(2)
									60		3.34	-6					
									70		1.12	-5	30	1	16		
.10		$H_3P_2O_7^- + H_3O^+ \longrightarrow$	(calculated from data of .8)				.15	k_2'AB	50		7.92	-5				*	(2)
									60		2.21	-4					
									70		6.39	-4	24	2	15		
.11		$H_2P_2O_7^{-2} + H_2O \longrightarrow$	(calculated from data of .8)				.15	k_3A	50		7.14	-7				*	(2)
									60		2.66	-6					
									70		9.25	-6	29	2	15		
.12		$H_2P_2O_7^{-2} + H_3O^+ \longrightarrow$	(calculated from data of .8)				.15	k_3'AB	50		8.75	-5				*	(2)
									60		3.29	-4					
									70		9.60	-4	27	5	17		
.13		$HP_2O_7^{-3} + H_2O \longrightarrow$	(calculated from data of .8)				0.008	k_4A	70		1.19	-6				*	(2)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Ionic strength	Defined mass-action law	Temperature	pH	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.14		$Na_3P_3O_9 + 3H_2O \longrightarrow 3NaH_2PO_4$	H_2O	0.1	NaOH	0.1		k A	65	13	1.7	-4				*(1)	(3)
									75		3.7	-4					
									85		7.0	-4					
									90		1.3	-3	20.0				
.15		$Na_5P_3O_{10} + H_2O \longrightarrow Na_4P_2O_7 + NaH_2PO_4$	H_2O	0.027			0.40	k A	60	4	6.64	-6				*	(4)
									60	7	1.25	-6					
									60	10	3.42	-7					
									90	4	2.13	-4	27.6	9	12		
									90	7	4.22	-5	28.0	3	12		
									90	10	5.95	-6	22.8	3	8		
					NaBr	0.65	1.0	k A	60	4	1.01	-5					
									60	7	1.56	-6					
									60	10	5.36	-7					
									90	4	2.38	-4	25.1	3	11		
									90	7	5.34	-5	28.1	4	12		
									90	10	1.39	-5	25.8	5	10		
									90	13	9.16	-6					
									125	10	1.7	-3					
.16		$[N(CH_3)_4]_5P_3O_{10} + H_2O \longrightarrow [N(CH_3)_4]_4P_2O_7 + N(CH_3)_4H_2PO_4$	H_2O	0.016			0.24	k A	30	1	9.09	-6				*	(4)
									60	4	6.48	-6					
									60	7	1.01	-6					
									60	10	8.80	-8					
									90	4	1.28	-4	23.8	3	10		
									90	7	4.09	-5	29.4	2	13		
									90	10	4.78	-6	31.7	6	13		
									90	13	9.05	-7					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Ionic strength	Defined mass-action law	Temperature	pH	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.16		$[N(CH_3)_4]_5P_3O_{10} + H_2O \longrightarrow [N(CH_3)_4]_4P_2O_7 + N(CH_3)_4H_2PO_4$ *(continued)*	H_2O	0.016	$N(CH_3)_4Br$	0.65	0.9	kA	30	1	3.11	-6				*	(4)
									30	4	1.11	-7					
									30	7	2.73	-8					
									60	1	1.14	-4					
									60	4	4.92	-6	23.8				
						1.30	1.5		60	4	3.50	-6					
				0.064		0.65	1.6		60	4	5.11	-6					
				0.016		0.65	0.9		90	1	1.50	-3	22.9	1.0	11		
									90	4	1.04	-4	24.8	9	10		
									90	7	3.00	-5	26.0	1.3	11		
									90	10	4.39	-6	30.3	6	12		
									90	13	8.47	-7	32.6	3	13		
									125	10	1.1	-4					
									125	13	6	-5					
.17		$Na_4P_4O_{12} + 4H_2O \longrightarrow 4NaH_2PO_4$	H_2O	0.1	NaOH	0.1		kA	75	13	2.2	-5					(1) (3)
									85		4.8	-5					
									95		1.7	-4					
									100		2.7	-4	26.4				
					H^+	0.1		kA	60	1	3.0	-5					(1)
									65		9.1	-5					
									75		2.0	-4					
									85		5.7	-4	25.3				

ADDEND

PBA* *p*-bromoaniline and *p*-bromoaniline hydrochloride in equal amounts as buffer.

COMMENTS

Reactions. (.6) Pseudo first order rate law in terms of total $P_2O_7^{-X}$ concentration in all forms from charge = 0 to -4. Authors observe that Na^+ inhibits reaction at pH below 4 and catalyzes reaction at pH > 4. (.7) Pseudo first order rate law in terms of total $P_2O_7^{-X}$ concentration in all forms, charge = 0 to -4. Authors note that rate is dependent upon ionic strength and the reaction shows hydrogen ion catalysis. (.8) Selected data. Authors observe first order rate over course for at least 3 half lives. In a few cases where drift of rate constants were observed the values were obtained by extrapolating to zero time. Authors used extremely dilute solutions by using isotope P^{32} and thus avoided large changes in pH over course of reaction. Adsorption on walls of reaction vessel limited the use of even lower concentrations. Many substances and types of glass tested for adsorption and it was found that none had any influence upon observed rate of reaction. (.9) (.10) (.11) (.12) (.14) Calculated from data for (.8) on the assumption that the general rate law may be expressed as:

$$-dA/dt = \{k_1 + k_1'[H^+]\}[H_4P_2O_7] + \{k_2 + k_2'[H^+]\}[H_3P_2O_7^-] + [k_3 + k_3'[H^+]\}[H_2P_2O_7^{-2}] + \{k_4 + k_4'[H^+]\}[HP_2O_7^{-3}] + k_5[P_2O_7^{-4}].$$

No quantitative data was available to evaluate k_1 or k_1' but they are probably greater than k_2 and k_2' respectively. k_5 was shown to be negligible as no reaction detected after 41 days at 70° with pH = 13. (.14) It is not clear whether k A = -dA/dt or -dB/dt. (.15) Pseudo first order rate law is in terms of total $P_3O_{10}^{-X}$ in all forms, charge = -x = 0 to -5. Catalysis by Na^+ at pH above 4 as well as H^+ catalysis observed. (.16) Pseudo first order rate law in terms of total $P_3O_{10}^{-X}$ in all forms, charge, -x = 0 to -5. (.17) It is not clear whether k A = -dA/dt or -dB/dt.

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SOLVOLYSIS
P-F bond solvolysis

Reaction types: $(RO)_2POF + H_2O \longrightarrow (RO)_2POOH + HF$

and $(RO)_2POF + OH^- \longrightarrow RO_2POO^- + HF$

Liquid phase

Amounts are in M/l. Rate constants are in M/l and sec.

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$(C_3H_7O)_2POF + H_2O$	B	$A \lesssim 0.04$	NaCl	0-0.17	7	kA	25	1.7	-6	*	(2)
				$CH_2ClCOOH$ / CH_2ClCOO^-		3		25	3.4	-6		
				HCl	0.02	1.7		25	2.8	-5		
					0.05	1.3		25	6.2	-5		
				NaOH					fast			
.2	$(i\text{-}C_3H_7O)_2POF + H_2O$	B	$A \simeq 0.01$	HCl, NaCl			kA; $k = k_W + k_H[H^+]$	25	k_W 2.0	-6		(1)
								30	k_W 2.8	-6		
				HCl =	NaCl =			35	k_W 4.2	-6		
				0.150	0			25	k_H 9.88	-4		
				0.149	0.351			25	k_H 1.02	-3		
				0.142	0.818			25	k_H 1.03	-3		
				0.177	0			25	k_H 9.45	-4		
				0.177	0.323			25	k_H 9.59	-4		
				0.177	0.823			25	k_H 9.77	-4		
				0.177	1.32			25	k_H 9.92	-4		
				0.177	1.82			25	k_H 1.01	-3		
				$C_2H_5NH_2$ / $C_2H_5NH_3Cl$			$k_{OH}A[OH^-]$	25	8.3	-1		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend (Catalyst)	Amount of addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.2	$(i\text{-}C_3H_7O)_2POF + H_2O$ *(continued)*	B	10^3A = 6-9	HPO_4 =	$H_2PO_4^-/HPO_4^-$	μ						
				0.0551	3.54	0.375	kA	25	3.42	-5		(1)
				0.0877	3.28	0.562		25	5.05	-5		
				0.118	3.23	0.750		25	6.30	-5		
				0.148	3.22	0.937		25	6.90	-5		
				0.180	3.18	1.125		25	8.25	-5		
				0.241	3.15	1.500		25	9.03	-5		

COMMENTS

Reaction. **(.1)** Autocatalysis observed in pure water or in absence of added acid, and rate constant calculated from initial rate. Pseudo first order over course in presence of buffer or strong acid.

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