NBS MONOGRAPH 34—Volume 2

Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

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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.

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Homogeneous Reactions

(Supplementary Tables)

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Preface

These tables have been prepared and organized as a supplement to the tables of chemical kinetics in National Bureau of Standards Circular 510, Supplement 1 to National Bureau of Standards Circular 510, and National Bureau of Standards Monograph 34. Code abbreviations for literature references, definitions of symbols and quantities used in the tables are given in the introduction of NBS Circular 510. A brief description of the method used in compiling these tables and the limitation of coverage are given in the preface to Supplement 1 of the NBS Circular 510. A description of the numbering system used in classifying reactions for the tables and an index are given in Supplement 2 of the NBS Circular 510.

The present volume contains information pertaining to substitution, exchange, and elimination reaction types and extends the material on these reaction types found in NBS Monograph 34, Volume I. The date on each page gives the year and month to which the literature had been surveyed. Significant omissions or errors should be reported to the Director of the Project: Dr. Charles H. Stauffer, Head, Department of Chemistry, St. Lawrence University, Canton, New York.

The Director of the Project and his associates gratefully acknowledge the financial assistance provided by the Office of Ordnance Research, Department of the Army, Office of Naval Research, Atomic Energy Commission, National Science Foundation, and the National Bureau of Standards to make the compilation of these data possible. The Director of the Project gratefully acknowledges the able assistance of his associates and collaborators in the review and analysis of the material in the chemical literature. He also acknowledges the assistance of the staff of the National Academy of Sciences and of the members of the Committee on Chemical Kinetics of the National Academy of Sciences, Division of Chemistry.

C. H. Stauffer

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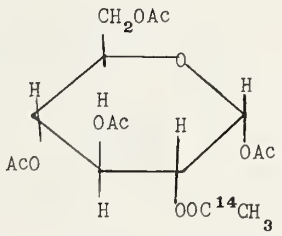
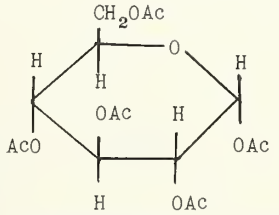
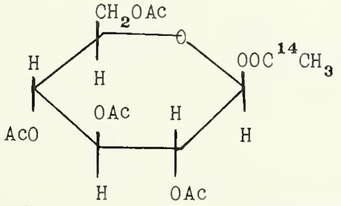
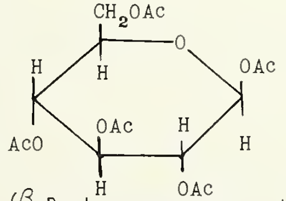
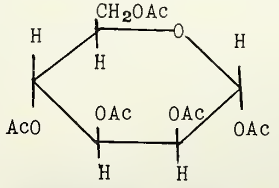
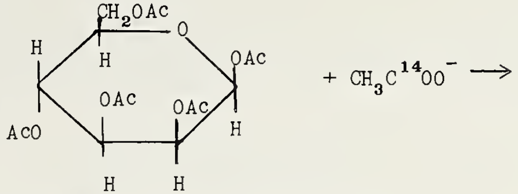
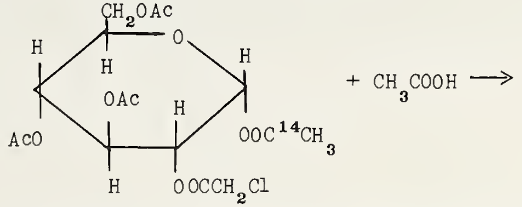
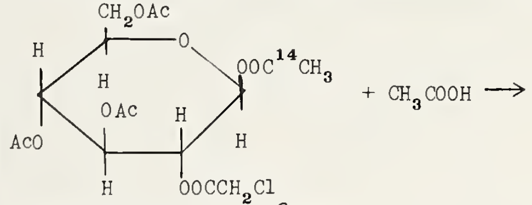
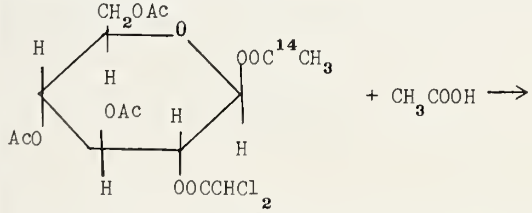
ISOTOPIC EXCHANGE
Carbon isotope exchange

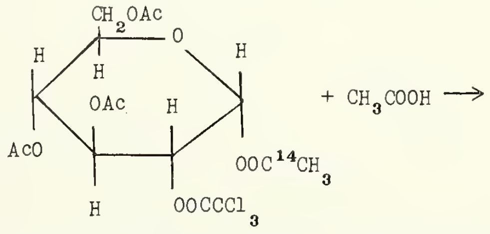
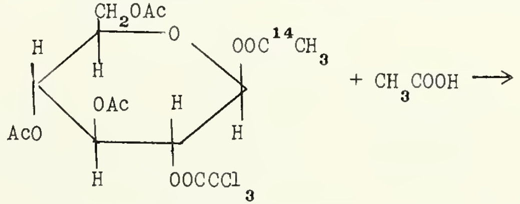
Liquid phase
Amounts are in M/l.
Rates and rate constants are in M/l and sec.

kF_E under rate law indicates rate constant is for measured pseudo first order rate of isotope equilibration.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$C^{13}O_2 + H_2CO_3 \longrightarrow CO_2 + H_2C^{13}O_3$	H_2O	$10^4A=1-200$	salts		kA	0	2.0	-3				*	(6)
							25	2.0	-2					
							40	1.4	-1	17	1	11		
.2	$C^{14}O(NH_2)_2 + CNO^- \longrightarrow CO(NH_2)_2 + C^{14}NO^-$	H_2O	$10^2A=5-10; 10^2B=5-25$			$k_1A + k_2AB$	80	$k_1=2.5$	-6				*	(1)
							80	$k_2\sim1$	-6					
.3	$4\text{-}C^{14}H_2{:}CHCH_2\text{-}2,6\text{-}(CH_3)_2C_6H_2OCH_2CH{:}CH_2 \longrightarrow 4\text{-}CH_2{:}CHCH_2\text{-}2,6\text{-}(CH_3)_2C_6H_2OCH_2CH{:}C^{14}H_2$	$C_6H_5N(C_2H_5)_2$	A=0-1.4			kA	140	2.2	-6				*	(3)
							150	5.4	-6					
							170	2.8	-5	31	6	10		
.4	 + $CH_3COOH \longrightarrow$ (α-D-glucopyranose pentaacetate)	$(CH_3CO)_2O + CH_3COOH$	A=0.1; B=50% of solvent	H_2SO_4	0.5	kA	25	9.3	-5					(5)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.5	 + $CH_3C^{14}OO^-$ $\longrightarrow$ (α-D-glucopyranose pentaacetate)	$CHCl_3$	A=B=0.05	$SnCl_3^+$ $SnCl_4$	= B = B	kF_E	40	1.6	-6		(4)
.6	 + CH_3COOH $\longrightarrow$ (β-D-glucopyranose pentaacetate)	$(CH_3CO)_2O$ + CH_3COOH	A=0.1; B=50% of solvent	H_2SO_4	0.5	kA	25	7.7	-3		(5)
.7	 + $CH_3C^{14}OO^-$ $\longrightarrow$ (β-D-glucopyranose pentaacetate)	$CHCl_3$	A=B=0.05	$SnCl_3^+$ $SnCl_4$	= B = B	kF_E	40	7.4	-4		(4)
.8	 + $CH_3C^{14}OO^-$ $\longrightarrow$ (α-D-mannopyranose pentaacetate)	$CHCl_3$	A=B=0.05	$SnCl_3^+$ $SnCl_4$	= B = B	kF_E	40	9.2	-5		(4)

<table>
<tr><th rowspan="2">No.</th><th rowspan="2">Reaction</th><th rowspan="2">Solvent</th><th rowspan="2">Amount of reactant</th><th rowspan="2">Addend</th><th rowspan="2">Amount of addend</th><th rowspan="2">Defined mass-action law</th><th rowspan="2">Temperature</th><th colspan="2">$k = k^o \times 10^n$</th><th rowspan="2">Literature</th></tr>
<tr><th>k^o</th><th>n</th></tr>
<tr><td>.9</td><td>
(β-D-mannopyranose pentaacetate)</td><td>$CHCl_3$</td><td>A=B=0.05</td><td>$SnCl_3^+$
$SnCl_4$</td><td>=B
=B</td><td>kF_E</td><td>40</td><td>1.3</td><td>-5</td><td>(4)</td></tr>
<tr><td>.10</td><td>
(2-O-monochloroacetyl-α-D-glucopyranose tetraacetate)</td><td>$(CH_3CO)_2O$ + CH_3COOH</td><td>A=0.1; B=50% of solvent</td><td>H_2SO_4</td><td>0.5</td><td>kA</td><td>25</td><td>3.1</td><td>-5</td><td>(5)</td></tr>
<tr><td>.11</td><td>
(2-O-monochloroacetyl-β-D-glucopyranose tetraacetate)</td><td>$(CH_3CO)_2O$ + CH_3COOH</td><td>A=0.1; B=50% of solvent</td><td>H_2SO_4</td><td>0.5</td><td>kA</td><td>25</td><td>8.3</td><td>-4</td><td>(5)</td></tr>
<tr><td>.12</td><td>
(2-O-dichloroacetyl-β-D-glucopyranose tetraacetate)</td><td>$(CH_3CO)_2O$ + CH_3COOH</td><td>A=0.1; B=50% of solvent</td><td>H_2SO_4</td><td>0.5</td><td>kA</td><td>25</td><td>7.7</td><td>-5</td><td>(5)</td></tr>
</table>

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.13	 (2-0-trichloroacetyl-α-D-glucopyranose tetraacetate)	$(CH_3CO)_2O$ + CH_3COOH	A=0.1; B=50% of solvent	H_2SO_4	0.5	kA	25	1.83	-6		(5)
.14	 (2-0-trichloroacetyl-β-D-glucopyranose tetraacetate)	$(CH_3CO)_2O$ + CH_3COOH	A=0.1; B=50% of solvent	H_2SO_4	0.5	kA	25	2.0	-5		(5)
.15	$(C_6H_5)_2CHC^{14}H(C_6H_5)OOCCH_3 \longrightarrow$ $CH_3COO(C_6H_5)CHC^{14}H(C_6H_5)_2$	CH_3COOH	10A=1.25	p-$CH_3C_6H_4SO_3H$	0.126	kF_E	55	6.2	-6	*	(2)
.16	$(C_6H_5)_2CHCH(C_6^*H_5)OOCCH_3 \longrightarrow$ $(C_6H_5)(C_6^*H_5)CHCH(C_6H_5)OOCCH_3$	CH_3COOH	10A=1.25	p-$CH_3C_6H_4SO_3H$	0.126	kF_E	55	6.0	-6	*	(2)
.17	$(C_6H_5)_2CHCH(C_6H_5)OOC^{14}CH_3 + CH_3COOH \longrightarrow$ $(C_6H_5)_2CHCH(C_6H_5)OOCCH_3 + CH_3C^{14}OOH$	CH_3COOH	10A=1.25	p-$CH_3C_6H_4SO_3H$	0.126 0.276	kF_E	55 55	6.4 1.33	-6 -5	*	(2)

COMMENTS

Reaction: **(.1)** Added salts $NaHCO_3$, NaCl, KCl, CH_3COONa and HCl and CH_3COOH had no effect on exchange so long as pH was low. **(.2)** Rate dependence upon CNO^- very slight so that value of k_2 is limited by experimental errors but authors consider it significant. **(.3)** Rate constant listed is one half observed rate constant for approach to equilibrium which is sum of rate constants for forward and reverse reactions. **(.15) (.16) (.17)** Equivalence of rates for all three reactions considered by authors to be consistent with rearrangement occuring by carbonium ion intermediate with lifetime long enough to permit equilibration. Exchange data indicates reaction is probably first order with respect to p-$CH_3C_6H_4SO_3H$ catalyst.

LITERATURE

(1) A.R. Amell, C.G. Houle, W.A. Cilley, *ACS* 1959, **81,** 4504. (2) W.A. Bonner, C.J. Collins, *ACS* 1955, **77,** 99. (3) F. Kalberer, H. Schmid, *H.C.A.* 1957, **40,** 13, 255. (4) R.U. Lemieux, C. Brice, *CJC* 1955, **33,** 109. (5) R.U. Lemieux, C. Brice, G. Huber, *CJC* 1955, **33,** 134.

ISOTOPIC EXCHANGE
Halogen on IVth group halide

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

No.	Supplementing 1959 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.2	.1	$SnCl_2 + Sn^*Cl_4 \longrightarrow Sn^*Cl_2 + SnCl_4$	H_2O	$10^3A=9-77; 10^3B=5-32$	HCl	10	*k* AB	0	1.74	-3					(1)
						9		25	6.3	-3					
						10		25	9.2	-3	11	4	7		
						11		25	1.22	-2					
			CH_3OH	$10^2A=3-9; 10^2B=3-13$			*k* AB	33	7.1	-5					(2)
								40	1.57	-4					
								47	3.2	-4	21	6	10		

COMMENTS

Reaction shown to proceed at same rate in presence of added glass surface and in presence and absence of light.

LITERATURE

(1) C.I. Browne, R.P. Craig, N. Davidson, *ACS* 1951, **73**, 1946.

(2) E.G. Meyer, M.A. Melnick, *JPC* 1957, **61**, 367.

ISOTOPIC EXCHANGE

Halogen isotope exchange between IVth group and Vth group atoms

Liquid phase

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

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$(CH_3)_3SiCl + SbCl_3^* \longrightarrow (CH_3)_3SiCl^* + SbCl_3$	hexane, C_6H_{14}	10^2A=2-74; 10^3B=5-57	kAB	20	1.4	-5				*	(^{2})
					30	3.0	-5					
					40	9.1	-5	18	2	8		
		(unlabeled reactants pre-equilibrated)			40	6.3	-4					
		C_6H_6	10^2A=1.8; 10^2B=1.6	kAB	25	9	-3					
			4.0 9.5		25	3.8	-5					
			11 27		25	4.3	-5					
			11 2.2		25	2.3	-4					
			11 2.2		40	1.6	-3	24	1	14		
.2	$(CH_3)_3SiCl + (C_2H_5)_4NCl^* \longrightarrow (CH_3)_3SiCl^* + (C_2H_5)_4NCl$	CH_3NO_2+Dioxane 50%			25	very fast					*	(^{1})
.3	$[(CH_3)_2CH]_3SiCl + (C_2H_5)_4NCl^* \longrightarrow [(CH_3)_2CH]_3SiCl^* + (C_2H_5)_4NCl$	CH_3NO_2	10^3A=8-9; 10^2B=1-2	kAB	25	7	0				*	(^{1})
		CH_3NO_2+Dioxane 25%	6-8 0.6-2		25	1.1	+1					
		" " 50%	8 0.6-1		25	1.7	+1					
		" " 75%	8 0.6-1		25	1.6	+1					
.4	$(cyclo\text{-}C_6H_{11})_3SiCl + (C_2H_5)_4NCl^* \longrightarrow (cyclo\text{-}C_6H_{11})_3SiCl^* + (C_2H_5)_4NCl$	CH_3NO_2+Dioxane 50%	10^3A=4; 10^3B=2-9	kAB	25	5.0	0					(^{1})
.5	$(C_6H_5)_3SiCl + (C_2H_5)_4NCl^* \longrightarrow (C_6H_5)_3SiCl^* + (C_2H_5)_4NCl$	CH_3NO_2+Dioxane 50%			25	very fast					*	(^{1})
.6	$(1\text{-}C_{10}H_7)_3SiCl + (C_2H_5)_4NCl^*$ $(1\text{-}C_{10}H_7)_3SiCl^* + (C_2H_5)_4NCl$	CH_3NO_2+Dioxane 50%	10^3A=6-7; 10^3B=6-12	kAB	25	4.2	+1					(^{1})
		" " 75%	4-7 7-8		25	2.0	+1					

COMMENTS

Reaction: (.1) Initial rate only as usual plot of log(1-F) versus time was not linear. In hexane all curves were concave downward and in benzene at 25° curves were concave downward but at 40° they were concave upward. In one case where unlabeled reactants were pre-equilibrated in hexane at 40° the plot was linear over 90% of exchange with an exchange rate about seven times that for freshly mixed reactants. (.2) Exchange complete within 0.3 seconds. (.3) Addition of $(C_2H_5)_4NClO_4$ at 0.1M had no measureable effect on rate of exchange. (.5) Exchange complete within 0.3 seconds.

LITERATURE

(1) A.D. Allen, G. Modena, *CSL* **1957**, 3671. (2) A.F. Reid, R. Mills, *CSL* **1960**, 703, 708.

ISOTOPIC EXCHANGE

Exchange of oxygen on Vth group element

Liquid phase

Amounts are in M/l. Rates and rate constants are in M/l and sec.

R listed under defined mass action law is isotopic exchange rate in M/l and sec. See (9).

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$HNO_2 + H_2O^{18} \longrightarrow$	H_2O	10^4A=7-14; $[NO_2^-]$=.01-.1	H^+	$3-6\times10^{-5}$	$kA[H^+]$	0	2.3	+2				*	(8)
	$HNOO^{18} + H_2O$		10^2A=1-10; $[NO_2^-]$=0.5-2		$1-10\times10^{-5}$	kA^2	0	5.1	-1					(5)
							25	6	0					
			$[NO_2^-]$=.025-.165	CH_3COOH	.05-.2	$kA[H^+][CH_3COO^-]$	0	3	+3					(6)
			pH=4.6-6.0	CH_3COONa	.17-.8									
					pH									
			$[NO_2^-]$=.005-0.5	phosphate	8.0	$kA[H^+]$	25	8	+4					(1)
			ionic strength=1.0	buffer	6.3		25	5	+3					
					5.7		25	3.8	+3					
					4.4		25	2.2	+3					
				phthalate	5.7		25	1.2	+4					
.2	$HNO_3 + H_2O^{18} \longrightarrow$	H_2O	A = 14.8; B = 25.8			R	0	3.3	-5				*	(7)
	$HNO_2O^{18} + H_2O$		15.4 24.4				0	6.9	-5					
			15.8 23.4				0	1.11	-4					(2)
			17.1 20.2				0	5.2	-4					
			18.2 16.7				0	3.2	-3					
			18.7 15.6				0	6.2	-3					
			19.3 13.6				0	1.6	-2					
			19.9 12.3				0	4.3	-2					
			4.30 48.1	HNO_2	.0016		0	2.0	-4					(3) (4)
			4.30 48.1		.0026		0	3.3	-4					
			5.40 46.0		.0012		0	3.4	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2	$HNO_3 + H_2O^{18} \longrightarrow$ *(cont.)*	H_2O	A = 5.40; B = 46.0	HNO_2	.0026	R	0	8.8	-4				*	(3) (4)
			7.88 41.4		.0010		0	1.5	-3					
			7.88 41.4		.0026		0	6.8	-3					
			10.9 35.3		.0012		0	1.8	-2					
			10.9 35.3		.0024		0	5.6	-2					
			12.5 31.7		.0010		0	3.1	-2					
			12.5 31.7		.0022		0	7.9	-2					
.3	$H_3PO_4 + H_2O^{18} \longrightarrow$ $H_3PO_3O^{18} + H_2O$	H_2O	A = 17.8; B = 2.81			R	25	1.48	-6				*	(10)
			17.8 2.81				40	7.0	-6					
			15.1 9.9				40	1.37	-4					
			17.8 2.81				60	4.6	-5					
			15.1 9.9				60	1.06	-5					
			12.2 19.7				60	2.9	-6					
			17.8 2.81				80	2.0	-4					
			15.1 9.9				80	6.7	-5					
			12.2 19.7				80	2.2	-5					
			17.8 2.81				90	4.5	-4					
			15.1 9.9				90	1.59	-4					
			12.2 19.7				90	5.1	-5					
			8.8 30.0				90	1.41	-5					
			17.8 2.81				100	9.5	-4	19.7				
			15.1 9.9				100	3.4	-4					
			12.2 19.7				100	1.14	-4					
			8.8 30.0				100	3.4	-5					
			15.1 9.9				110	8.6	-4	23.1				
			12.2 19.7				110	2.6	-4	24.0				
			8.8 30.0				110	7.8	-5	26.5				

COMMENTS

General: For general treatment of isotopic exchange reactions see ([9]). Where rate constant for chemical process responsible for exchange has not been explicitly determined the value listed under k will be indicated under the defined mass-action law as either R, the rate of the chemical process responsible for exchange, or kF_X a pseudo first order constant for rate of isotopic equilibration. R is calculated from the equation $R=-\frac{m\cdot n\,\underline{A}\cdot\underline{B}}{(m\underline{A}+n\underline{B})\,t}\ln(1-x)$; m and n are the number of exchangeable atoms of the labeled species in A and B respectively. $\underline{A}$ represents the sum [A] + [L] and $\underline{B}$ represents the sum [B] + [M]· X is the fractional extent of isotopic equilibration at time *t*. The pseudo first order rate constant kF_X for isotopic equilibration is calculated from the expression $kF_X=-\frac{1}{t}\ln(1-x)$ where x and t are the same as defined above.

Reaction: (.1) At low concentrations of $NO_2^- < .05$ M rate law is first order in A and first order in $[H^+]$. At higher concentrations of NO_2^- rate law is second order in A and mechanism is thought to involve N_2O_3 formation. Rate constants of ([1]) converted from form $k'[NO_2^-][H^+]^2$ to $k[HNO_2][H^+]$ by multiplying by $K_a=5.0\times10^{-4}$ used by ([1]) to correct total nitrite for HNO_2 formed. $[H^+]$ calculated from pH. ([6]) studied catalysis of exchange by acetate buffer, and corrected exchange rate for uncatalyzed reaction. At most concentrations correction less than 10% of rate. On basis of: $R/[NO_2^-]=k\,K_{HNO_2}^{-1}\,[H^+]^2[OAc^-]$ found $k\simeq5\times10^3$ while on basis of $R/[NO_2^-]=k\,K_{HOAc}K_{HNO_2}^{-1}\,[H^+][HOAc]$ calculated $k\simeq3\times10^3$. Latter value favored as salt effect on the HOAc and HNO_2 equilibria should cancel. (.2) Exchange rates and concentrations converted from Mol % of authors to moles/liter but densities not corrected to 0°C. HNO_2 shown to be a catalyst for the exchange with an apparent order varying between 1 and 2. (.3) Authors show that rate of oxygen exchange is approximately equal to rate of $H_4P_2O_7$ hydrolysis under same conditions. Suggest rate law probably involves three simultaneous paths and suggest that the expression $R=k_1[H_3PO_4][H_2O] + k_2[H_3PO_4]^2 + k_3[H_3PO_4]^3[H_2O]^{-1}$ fits the data well.

LITERATURE

([1]) M. Anbar, H. Taube, *ACS* 1954, **76**, 6243. ([2]) C.A. Bunton, E.A. Halevi, D.R. Llewellyn, *CSL* **1952**, 4913. ([3]) C.A. Bunton, E.A. Halevi, D.R. Llewellyn, *CSL* **1952**, 4917. ([4]) C.A. Bunton, E.A. Halevi, D.R. Llewellyn, *CSL* **1953**, 2653. ([5]) C.A. Bunton, D.R. Llewellyn, G. Stedman, *CSL* **1959**, 568. ([6]) C.A. Bunton, M. Masui, *CSL* **1960**, 304. ([7]) C.A. Bunton, G. Stedman, *CSL* **1958**, 2420. ([8]) C.A. Bunton, G. Stedman, *CSL* **1959**, 3466. ([9]) G.M. Harris, *T.F.S.* 1951, **47**, 716. ([10]) B. Keisch, J.W. Kennedy, A.C. Wahl, *ACS* 1958, **80**, 4778.

ISOTOPIC EXCHANGE

Halogen exchange between Vth group halides

Liquid phase

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

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$PCl_3^* + PCl_5 \longrightarrow PCl_3 + PCl_5^*$	CCl_4	10^3A=5-60; 10^3B=5-20	kB	0	2.5	-7				*	(1)
					25	2.9	-6					
					50	2.3	-5	16	1.2	6		

COMMENTS

(.1) Exchange rate and rate law in gram atoms/l was identical for chlorine exchange and phosphorous exchange using Cl^{36} and P^{32} for labeling. See 302.590.1. Rate of exchange was unaffected by increasing glass surface, illumination or small amounts of O_2. Addition of HCl or H_2O increased rate of exchange of halogen but had no measurable effect on rate of exchange of phosphorous.

LITERATURE

(1) W.E. Becker, R.E. Johnson, *ACS* 1957, **79**, 5157.

ISOTOPIC EXCHANGE
Vth group element between oxidation states

Liquid phase

Amounts are in M/l. Rates and rate constants are in gram atoms/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$P^*Cl_3 + PCl_5 \longrightarrow PCl_3 + P^*Cl_5$	CCl_4	$10^3A=5-60; 10^3B=5-20$			kB	0	2.5	-7				*	(2)
							25	2.9	-6					
							50	2.3	-5	16	1.2	6		
.2	$Sb^{*+3} + Sb^{+5} \longrightarrow Sb^{+3} + Sb^{*+5}$	H_2O	$10^2A=2-30; 10^2B=2$	HCl	2.3	kAB	25	~1.5	-1				*	(6)
					5.8		25	2.7	-2					
					8.8		25	1.3	-2					
					10.8		25	7.5	-3					
					11.7		25	6.0	-3					
			2.1 2.1	HCl, NaCl	5.9	$k'A^{.6}B^{1.1}[H^+]^4[Cl^-]^9$	10	2.0	-15					(3)
			0.8-2 0.08-4		5-6		25	2.5	-14					
			2.1 2.1		5.9		35	9.7	-14	27				
.3	$Sb^*Cl_3 + SbCl_5 \longrightarrow SbCl_3 + Sb^*Cl_5$	CCl_4	$10^2A=1.5-10;$ $10^3B=5-70$			$k_1B + k_2AB^2$	50	k_1 1.6	-7				*	(1)
							50	k_2 1.8	-4					
							68	k_1 7.5	-7					
							68	k_2 6.0	-4					
							81	k_1 2.1	-6	19	1	6		
							81	k_2 1.5	-3	15	4	6		
.4	$V^{*+2} + V^{+3} \longrightarrow V^{+2} + V^{*+3}$	H_2O	$10^2A=4-13; 10^2B=4-12$ $\mu=2.0$	$HClO_4$	1.00	kAB	25	1.4	-2					(5)
					0.198		25	3.2	-2		$\Delta S^\ddagger$			
					0.5-0.12	$k = k_1 + k_2[H^+]^{-1} + k_3[Cl^-]$	25	k_1 1.0	-2	13.	-25			
							25	k_2 3.5	-3					
							25	k_3 ~1.4	+1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.5	$V^{+3} + V^{*}O^{+2} \longrightarrow V^{*+3} + VO^{+2}$	H_2O	$10^2A=1-5; 10^2B=1-5$ $\mu=2.5$	$HClO_4$	0.5-2	$k\,AB[H^+]^{-1}$	25	2.6	-3					(4)
							32	8.0	-3					
							40	1.44	-2	21	5	12		
.6	$VOH^{+2} + V^{*}O^{+2} \longrightarrow V^{*}OH^{+2} + VO^{+2}$	H_2O	$[V^{+3}]=.01-.05; 10^2B=1-5$	$HClO_4$	0.5-2	$k\,AB$	25	~1	0	11	1	8	*	(4)

COMMENTS

Reaction: **(.1)** Exchange rate and rate law in gram atoms per liter was identical for phosphorous exchange using P^{32} and chlorine exchange using Cl^{36} for labeling. See 302.575.1. Addition of small amounts of molecular oxygen, illumination or increased glass surface had no measurable effect on either exchange rate. Addition of HCl or H_2O had no measurable effect on phosphorous exchange rate but definite catalytic effect on chlorine exchange rate. **(.2)** Rate law empirically determined by (3) considered to have no fundamental significance. (6) determines exchange rate under non-equilibrium conditions by preparing stock $SbCl_5$ and $SbCl_3$ solutions in concentrated HCl and diluting at start of reaction. Under these conditions exchange is found to be more rapid in the more dilute HCl solutions. The complex kinetics is attributed to different rate controlling steps in dilute acid and concentrated acid. It is suggested that in dilute acid the rate controlling step is the rate of formation of the $SbCl_6^-$ ion, while in concentrated acid the rate controlling step is the reaction of the $SbCl_6^-$ ion with the $SbCl_3$ species capable of exchanging with it. Experiments performed with either reactant isotopically labelled. Reaction vessel packed with glass beads gave no change in exchange rate. **(.3)** Light said to accelerate exchange reaction. Packing with glass beads had no observable effect. **(.4)** No observable effect on exchange rate by light, glass surface, doubling ionic strength or replacing $NaClO_4$ by $LiClO_4$ as added salt. **(.6)** Assumed to be rate determining step for (.5) and calculated from constant for (.5) on basis of rapid reversible hydrolysis of V^{+3} using $K_h = 2 \times 10^{-3}$.

LITERATURE

(1) F. Barker, M. Kahn, *ACS* 1956, **78**, 1317. (2) W. E. Becker, R. E. Johnson, *ACS* 1957, **79**, 5157. (3) N. A. Bonner, *ACS* 1949, **71**, 3909. (4) S. C. Furman, C. S. Garner, *ACS* 1952, **74**, 2336. (5) K. V. Krishnamurty, A. C. Wahl, *ACS* 1958, **80**, 5921. (6) H. M. Neumann, H. Brown, *ACS* 1956, **78**, 1843.

ISOTOPE EXCHANGE

O_2 exchange with H_2O and H_2O_2

Amounts are in M/l. Rates and rate constants are in M/l and sec. Half times are in sec.

kF_E under rate law indicates that rate constant is for pseudo first order rate of isotopic equilibration.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		$t_{\frac{1}{2}}$	Comments	Literature
								k^o	n			
.1	$H_2O + OO^{18} \longrightarrow H_2O^{18} + O_2$	H_2O	B sat. at 0.5 atm.	$S_2O_8^=$ buffer	.00625 pH 2-11	kF_E	60	2	-4		*	(1)
				$S_2O_8^=$ NaOH	.001-.006 0.03	$k[S_2O_8^=]^{-1}$	60	3.2	0			
				$S_2O_8^=$ NaOH	.00625 >0.2	kF_E	60	2.3	-2			
.2	$H_2O_2 + O_2^{18} \longrightarrow H_2O_2^{18} + O_2$	H_2O	$10^4A=1.79$; $10^3B=1.19$	NaOH	pH 11.75		25			9,000		(2)

COMMENTS

Reaction: **(.1)** Oxygen exchange catalyzed by persulfate generated free radicals. Below pH=11 chain length of free radical reaction approximately 4. Above pH=11 chain length increases rapidly then levels off to about 450 at $[OH^-] = 0.2$. Pseudo first order exchange rate constant corrected for the fraction of oxygen in the gas phase.

LITERATURE

(1) C.R. Guiliano, N. Schwartz, W.K. Wilmarth, *J.P.C.* 1959, **63**, 353.
(2) E.J. Hart, S. Gordon, D.A. Hutchinson, *ACS* 1953, **75**, 6165.

ISOTOPIC EXCHANGE

Hydrogen, D_2 exchange with water

Liquid phase

Amounts are in M/l. Rates and rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
								k^o	n			
.1	$H_2 + OD^- \longrightarrow HD + OH^-$	D_2O	sat. with A at 1 atm.	K^+	= B			% exchanged		time		(^{2})
			and room temp.									
			B = 0.1				100	7.2		1.8×10^5		
			0.2				100	12.0		1.8×10^5		
			0.5				100	7.4		4×10^4		
			1.0				100	12.8		4×10^4		
.2	$HD + OH^- \longrightarrow H^2 + OD^-$	H_2O	D_2 +up to 50 vol. % HD sat.; B = .1246	K^+	= B	kAB	100.4	3.2	-3		*	(^{1})
			.534				100.4	3.3	-3			
			.882				100.4	3.9	-3			
.3	$D_2 + OH^- \longrightarrow HD + OD^-$	H_2O	sat. with D_2;								*	(^{1})
			B = .1246	K^+	= B	kAB	94	5.1	-3			
			.534				101	6.1	-3			
			.882				105	5.4	-3			

COMMENTS

Reaction: **(.1)** Data gives little more than order of magnitude of exchange rate. Authors observed exchange rate in 1N KOH to be about 8 times faster than in 1N HCl and 25 times faster than in neutral D_2O. **(.2) (.3)** Rate constant calculated from integrated form of differential rate equation for two consecutive first order reactions, (.3) and (.2).

LITERATURE

(^{1}) W.K. Wilmarth, J.C. Dayton, J.M. Flournoy, *ACS* 1953, **75**, 4549. (^{2}) K. Wirtz, K.F. Bonhoeffer, *ZPC*^{A} 1936, **177**, 1.

ISOTOPIC EXCHANGE

VIth group cyanide complex with CN^-

Liquid phase

Amounts are in M/l.
Rates and rate constants are in M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$Cr(CN)_6^{-3} + C^{14}N^- \longrightarrow Cr(CN)_5(C^{14}N)^{-3} + CN^-$	H_2O	$10^2A=2.5$; $10^2B=1-2.5$	KOH	10.4	kA	~25	1	-6	*	(2)
.2	$Cr(CN)_6^{-4} + 6C^{14}N^- \longrightarrow Cr(C^{14}N)_6^{-4} + 6CN^-$	H_2O	A=B=0.025	KOH	11.3		~25	very fast		*	(2)
.3	$W(CN)_8^{-3} + C^{14}N^- \longrightarrow W(CN)_7(C^{14}N)^{-3} + CN^-$	H_2O	$10^2A=1-2$; $10B=1.5-3$		9.5-11	kA	25	<6	-8	*	(1)
.4	$W(CN)_8^{-4} + C^{14}N^- \longrightarrow W(CN)_7(C^{14}N)^{-4} + CN^-$	H_2O	$10^2A=1-2$; $10B=1.5-3$		9.5-11	kA	25	<5	-8	*	(1)

COMMENTS

Reaction: **(.1)** Exchange rate independent of [B] over range studied. Rate of exchange increased 1000 times in sun light over dark reaction. **(.2)** Exchange complete in less than 35 seconds in diffuse sun light. **(.3) (.4)** Rate law not verified and value given represents probable maximum. Reaction much faster in light and rate of light reaction independent of [A] or [B] over range studied.

LITERATURE

(1) E.L. Goodenow, C.S. Garner, *ACS* 1955, **77**, 5268.

(2) A.C. MacDiarmid, N.F. Hall, *ACS* 1954, **76**, 4222.

ISOTOPIC EXCHANGE

VIth group NH_3 complex with NH_3

Liquid phase

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

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
						k^o	n		
.1	$Cr(N^{15}H_3)_6(NO_3)_3 + 6NH_3 \longrightarrow Cr(NH_3)_6(NO_3)_3 + 6N^{15}H_3$	NH_3	A = 0.013	kAB	25	1.3	-6	*	(1)

COMMENTS

Reaction: **(.1)** Rate law not verified as B in very large excess and concentration of A not varied. Value gives only order of magnitude of exchange as mass-spectrometer analyses were erratic.

LITERATURE

(1) H.U.D. Weisendanger, W.H. Jones, C.S. Garner, *J.C.P.* 1957, **27**, 668.

ISOTOPIC EXCHANGE

Exchange involving VIth group element as central atom in both reactants

Liquid phase

Amounts are in M/l. Rates and rate constants are in M/l and sec.

R under rate law indicates that constant listed is the rate of the chemical process responsible for exchange ([10]).

kF_E under rate law indicates rate constant is for measured pseudo first order rate of isotopic equilibration.

Isotopically labeled atom indicated with *.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$H_2SO_4 + H_2O^* \longrightarrow H_2SO_3O^* + H_2O$	H_2O	A=14.0; B=19.8			R	10	2.41	-3				*	([12])
			14.5 18.2				10	3.60	-3					
			15.0 16.6				10	7.77	-3					
			15.5 15.0				10	1.40	-2					
			16.0 13.1				10	2.06	-2					
			3.00 49.1				25	2.16	-8					
			4.00 46.7				25	1.40	-7					
			5.00 44.4				25	3.58	-7					
			6.00 41.9				25	1.62	-6					
			7.00 39.2				25	5.72	-6					
			8.00 36.5				25	2.70	-5	24.6				
			9.00 33.9				25	8.53	-5					
			10.0 31.0				25	2.08	-4					
			11.0 28.2				25	6.25	-4					
			11.8 26.0				25	2.42	-3					
			13.0 22.5				25	6.53	-3	20.4				
			13.8 19.8				25	1.41	-2					
			15.0 16.0				25	4.56	-2					
			1.04 51.2				100	5.28	-5					
			1.72 49.6				100	2.25	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$H_2SO_4 + H_2O^* \longrightarrow$ *(cont.)*	H_2O	A=2.85; B=46.9			R	100	7.49	-3				*	(12)
			3.52 45.3				100	1.43	-3	31.3				
			4.40 43.2				100	3.30	-3					
.2	$S_2O_3^{-2} + S^*O_3^{-2} \longrightarrow SO_3^{-2} + SS^*O_3^{-2}$	H_2O	10A~1; 10^2B=2-20	NaCl, HCl	pH=5.0	kAB	62	6.2	-4				*	(1)
				μ= 2.0			70	1.05	-3					
				"			80	1.65	-3					
				"			89	3.3	-3					
				"			96	4.8	-3					
				NaCl, NaOH	pH=12.7		60	7.5	-4					
				μ= 2.0			70	1.77	-3					
							79	2.8	-3					
							89	4.2	-3					
			10^2A=20				89	3.3	-3					
			12				89	3.8	-3					
			6.3				89	5.0	-3					
			2.1				89	7.9	-3					
			~10				98	7.4	-3	14.5	2	6		
.3	$H_2S^*O_4 + SO_2 \longrightarrow H_2SO_4 + S^*O_2$	A	10^2B=1-10			R	101	1.2	-3				*	(21)
							136	5.5	-2					
							160	2.5	-1					
							211	1.2	+1					
.4	$S_2O_4^{=} + S_2^*O_3^{=}$	H_2O	A=B=0.015	NaOH	pH=13	no exchange							*	(6)
.5	$S_4O_6^{=} + S^*O_4^{=}$	H_2O	A=B=0.015	buffer	pH=6	no exchange							*	(6)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$S^*OCl_2 + SO_2 \longrightarrow SOCl_2 + S^*O_2$	SO_2	10^3A=5-90			kF_E	61	<2	-8					(^{9}) (^{17})
			A=2.0; B=18-19	HCl	.08	R	0	<1	-7					(^{20})
					1.04		25	<5	-8					
			A=1.18; B=21.3	RbCl	0.01	kAB[RbCl]	-22	6.1	-7					
			1.15 20.6		.002-.015		0	8.4	-6					(^{20}) (^{22})
			1-2 18-20		.009-.017		25	8.1	-5	13.6	5	6		(^{20})
			1-2 19-21	$(CH_3)_4NCl$	.04-.67	kAB[$(CH_3)_4NCl$]	-21	1.50	-6					
			2-8 9-20		.004-.6		0	1.74	-5					(^{20}) (^{22})
			1.1 19.6		0.04		25	1.36	-4	14.7	1.1	7		
		$SOCl_2$	14 0.8		0.016		-21	7.9	-6					(^{20})
			10-14 0.8-6		.003-.05		0	6.0	-5					(^{20}) (^{22})
			13 0.8		0.015		25	5.5	-4	14.7	5	6		
		SO_2	1-2 19-20	$AlCl_3$	0.65	kAB[$AlCl_3$]	0	6	-9					(^{3}) (^{10})
			2 19		0.63		23	8	-8	18	3	6		(^{20})
			1.1 20.9	$SbCl_5$	0.051	R	-15	4.4	-8					(^{3})
			1.1 20.5		0.214		-15	2.1	-7					
			1.1 19.7		0.497		-15	4.3	-7					
			1-12 0.5-20		.02-2.8	kB[A·$SbCl_5$]	0	4.1	-7					
			1-12 0.5-20		.3-2		15	1.11	-6					
			1-12 0.6-19		.2-.6		23	1.75	-6					
			1-12 0.6-18		.4-.6		30	2.9	-6	10.4	1	2		
			1.1 20.6	$\left\{\begin{matrix}(CH_3)_4NCl \\ AlCl_3\end{matrix}\right\}$	$\left.\begin{matrix}0.11 \\ 0.06\end{matrix}\right\}$	R	0	~4	-5				*	(^{4})
					$\left.\begin{matrix}0.05 \\ 0.04\end{matrix}\right\}$		0	1.4	-6					
					$\left.\begin{matrix}0.081 \\ 0.079\end{matrix}\right\}$		0	5.5	-7					
					$\left.\begin{matrix}0.048 \\ 0.108\end{matrix}\right\}$		0	7.8	-8					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		E	$A = A^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		A°	n		
.6	$S^{*}OCl_2 + SO_2 \longrightarrow$ *(continued)*	SO_2	A=1.0-1.1; B=19-20	$(CH_3)_4NCl$ $SbCl_5$	0.104 0.018	R	0	2.9	-5				*	(4)
					0.118 0.041		0	3.7	-5					
					0.092 0.079		0	5.1	-6					
					0.092 0.086		0	2.8	-6					
					0.086 0.089		0	2.2	-7					
					0.086 0.115		0	1.4	-7					
					0.085 0.207		0	5.9	-7					
					0.083 0.327		0	1.12	-6					
					0.080 0.632		0	2.2	-6					
					0.08 0.1-0.6	$kB[A \cdot SbCl_5]$	0	5.2	-7					
.7	$S^{*}OCl_2 + SO_2Cl_2 \longrightarrow SOCl_2 + S^{*}O_2Cl_2$	SO_2Cl_2	$A \simeq 0.1$				0	$t_{\frac{1}{2}} > 6 \times 10^{6}$						(16)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.8	$S^*OBr_2 + SO_2 \longrightarrow SOBr_2 + S^*O_2$	SO_2	$A \simeq 0.1$				25	$t_{\frac{1}{2}} \simeq 6 \times 10^7$					*	(17)
			$A \simeq 2$			k_o	25	$\lesssim 1$	-6					(11)
			2	KCl	sat.	$k[KCl]$	25	1.2	-2					
			1-4	KBr	sat.	$k[KBr]$	0	~5	-4					
			2	RbBr	0.01-0.3	$k[RbBr]$	0	6	-5					(11) (22)
			1-4	$(CH_3)_4NBr$	0.1-2	$k[(CH_3)_4NBr]$	-21	1.6	-5					
							0	1.0	-4					
							25	1.0	-3	13.2	4	6		
.9	$S^*OBr_2 + SOCl_2 \longrightarrow SOBr_2 + S^*OCl_2$	SO_2	A~4; B~1				-50	$t_{\frac{1}{2}} < 120$						(16)
			A~1; B~4				-50	$t_{\frac{1}{2}} < 300$						
		A	B~1				-50	$t_{\frac{1}{2}} < 180$						
		B	A~1				-50	$t_{\frac{1}{2}} < 4800$						
							-18	$t_{\frac{1}{2}} < 480$						
.10	$SSCl_2 + S_7S^* \longrightarrow S^*SCl_2 + S_8$	A	$10^2B=1-5$			kB	25	1.2	-5					(5)
							98	2	-2					
.11	$CH_3SSO_3^- + S^*O_3^= \longrightarrow CH_3SS^*O_3^- + SO_3^=$	H_2O	not stated	$\mu = 0.5$	pH=7.9	kAB	25	2.2	-1					(7)
.12	$C_2H_5SSO_3^- + S^*O_3^= \longrightarrow C_2H_5SS^*O_3^- + SO_3^=$	H_2O	$10^3A=3-5; 10^3B=3-5$	phosphate buffer	pH=7.3 μ=0.1	kAB	7	2.1	-2				*	(8)
							17	4.1	-2					
							27	6.2	-2					
							41	1.6	-1	10.3	2	6		
			phosphate buffer + NaCl	μ = .03	pH=7.4		25	4.6	-2					
				.07			25	6.6	-2					
				.18			25	1.0	-1					
				.5	7.9		25	1.1	-1					(7)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.13	$(CH_3)_2CHSSO_3^- + S^*O_3^= \longrightarrow (CH_3)_2CHSS^*O_3^- + SO_3^=$	H_2O	not stated	$\mu = 0.5$	pH=7.9	kAB	25	1.5	-3				*	(7)
.14	$(CH_3)_3CSSO_3^- + S^*O_3^= \longrightarrow (CH_3)_3CSS^*O_3^- + SO_3^=$	H_2O	not stated	$\mu = 0.5$	pH=7.9	kAB	25	1.3	-6				*	(7)
.15	$CH_2{:}CHCH_2SSO_3^- + S^*O_3^= \longrightarrow CH_2{:}CHCH_2SS^*O_3^- + SO_3^=$	H_2O	10^3A=3-5; 10^3B=3-5	phosphate buffer	pH=7.3 μ=0.1	kAB	7	2.3	-3					(8)
							16	4.5	-3					
							26	5.8	-3					
							36	9.6	-3	8.5	9	3		
.16	$C_6H_5CH_2SSO_3^- + S^*O_3^= \longrightarrow C_6H_5CH_2SS^*O_3^- + SO_3^=$	H_2O	10^3A=3-5; 10^3B=3-5	phosphate buffer	pH=7.3 μ=0.1	kAB	18	1.9	-2					(8)
							25	2.5	-2					
							37	5.3	-2					
							50	1.1	-1	9.7	3	5		
.17	$CH_3OOCCH_2SSO_3^- + S^*O_3^= \longrightarrow CH_3OOCCH_2SS^*O_3^- + SO_3^=$	H_2O	10^3A=2-20; 10^3B=2-20	phosphate buffer	pH=8.0 μ=0.4	kAB	25	1.3	-2					(8)
					μ=0.1 pH=7.3		25	3.5	-3					
							33	4.9	-3					
							40	6.7	-3					
							50	1.1	-2	9.3	2	4		
			$10^3A=10^3B$=5		pH=8.4		50	4.4	-2					
					7.2		50	3.8	-2					
					6.2		50	1.6	-2					
					5.8		50	8.4	-3					
					5.3		50	3.6	-3					
					4.1		50	6.8	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	Comments	Literature
								k^o	n			
.18	$(CH_2SSO_3^-)_2 + S^*O_3^= \longrightarrow$ $^-SO_3SCH_2CH_2SS^*O_3^- + SO_3^=$	H_2O	$10^3A=3\text{-}5$; $10^3B=3\text{-}5$	phosphate buffer	pH=7.3 $\mu=0.1$	kAB	12	2.8	-2		*	(8)
							25	5.8	-2			
							33	8.4	-2			
							43	1.4	-1			
	Chromium ion complex, no change in valence											
.19	$Cr(H_2O)_3F_3 + Cr^*(H_2O)_6^{+3} \longrightarrow$ $Cr^*(H_2O)_3F_3 + Cr(H_2O)_6^{+3}$	H_2O	(A+L) =0.16; (B+M) = 0.10	HNO_3 $NaNO_3$	0.01 $\mu=0.5$	kF_E	22	1.5	-6			(18)
				HNO_3 $NaNO_3$	0.1 $\mu=0.5$		22	6	-7			
.20	$Cr(H_2O)_6^{+3} + H_2O^* \longrightarrow$ $Cr(H_2O)_5(H_2O^*) + H_2O$	H_2O	A=0.05-0.1	$HClO_4$	0.1-0.5	kA	27	3.3	-6		*	(13) (15)
					$\mu=0.4\text{-}1$		27	3.4	-6			
					$\mu=2$		27	3.6	-6			
					$\mu=4.3$		27	5.0	-6			
			2.40; B=36.1	NaCl	$\mu=22.2$	kAB	30	4.0	-7			(19)
			2.40 36.1		$\mu=22.2$		35	1.00	-6			
			2.40 36.1		$\mu=22.2$		40	1.67	-6			
			2.40 36.1		$\mu=22.2$		45	5.0	-6	31		
			2.20 37.7		$\mu=19.6$		45	3.5	-6			
			2.13 38.8		$\mu=18.3$		45	3.2	-6			
			2.02 40.4		$\mu=16.7$		45	2.7	-6			
			1.71 42.8		$\mu=13.3$		45	2.3	-6			
			1.9 38-39	NaCl, $NaNO_3$, Na_2SO_4, or $K_3Fe(CN)_6$	$\mu=18.3$		45	3.3	-6			(23)
			A=0.5-1.5; $[H^+]=0.4$	ClO_4^-	1.5-5	$kA[ClO_4^-]$	27	1.3	-6			
			0.35	NO_3^-	2.7-4.4	$kA[NO_3^-]$	27	2.2	-6			
			0.38	Br^-	2.3	$kA[Br^-]$	27	1.2	-6			

COMMENTS

General: For general treatment of isotopic exchange reactions see ([10]). In those cases where rate constant for the chemical process responsible for exchange has not been explicitly determined the value listed under k will be indicated in the "Defined mass-action law" column by either R or kF_E. R, the rate of the chemical process responsible for exchange: is calculated from the equation: $R=-\frac{m\cdot n\cdot \underline{A}\cdot \underline{B}}{(m\cdot \underline{A}+n\cdot \underline{B})}\ln(1-x)$, m and n are the number of exchangeable atoms of the labeled species in A and B respectively. $\underline{A}$ represents the sum of [A] + [L] and $\underline{B}$ represents the sum of [B] + [M]. X is the fractional extent of isotopic equilibration having taken place at time t. The pseudo first order rate constant k for the defined mass-action law kF_E is calculated from the expression $k=-\frac{1}{t}\ln(1-x)$ where X and t have the same significance as above.

Reaction: **(.1)** Selected data. Authors show that at 25° from 3 to 10M H_2SO_4 R is proportional to $a^{0.8}_{H_2SO_4}$ and at 100° from 1 to 4 M, R is proportional to $a^{0.72}_{H_2SO_4}$. At three fixed HSO_4^- concentrations, 1.1, 2.2, and 4.4 it was shown that R was proportional to $[H^+]$. At two fixed $[H^+]$=2.2 and 4.4 it was shown that R was proportional to $[HSO_4^-]$. **(.2)** Selected data. Calculated second order rate constant decreases more than 50% with a ten fold increase in [A]. Increasing pH from 5-14 increased exchange rate less than 50%. Activation energy and A-factor calculated by least squares using all data pH=5-12.7. **(.3)** Exchange rate corrected for fraction of exchanging atoms in gas phase. **(.4)** **(.5)** No measurable exchange in 44 hrs. **(.6)** In absence of halide salts rate of exchange immeasurably slow. Sulfur atom labeled in either SO_2 or $SOCl_2$ by ([20]). Third order rate law observed by ([20]) with specific constants for each halide salt. ([20]) also observed about a three fold increase in the calculated rate constants when $SOCl_2$ was in excess over rate constants when SO_2 was solvent. ([3]) calculates a second order rate law assuming rapid equilibrium $SOCl_2+SbCl_5 \rightleftarrows SbCl_5\cdot SOCl_2$ with a temperature dependent equilibrium constant, $K=\frac{[SbCl_5\cdot SOCl_2]}{[SbCl_5][SOCl_2]}$, with K=0.8 at 0°, 0.9 at 15°, 1.4 at 23° and 2.0 at 30°. With $SbCl_5$ as catalyst ([3]) did not observe any large increase in rate constants with $SOCl_2$ in excess. With mixed salts $(CH_3)_4NCl$ and $AlCl_3$ catalytic effect of $(CH_3)_4NCl$ is cancelled by formation of a 1 to 1 complex $AlCl_3\cdot(CH_3)_4NCl$. With mixed salts $SbCl_5$ and $(CH_3)_4NCl$ an inactive 1 to 1 complex also is formed but either salt in excess is observed to have its normal catalytic effect. HCl showed no appreciable effect upon catalytic activity of either $(CH_3)_4NCl$ or $SbCl_5$.

(.8) Reaction found to be zero order with respect to A on fourfold variation of concentration. Order with respect to B not determined as concentration not varied. Units of zero order constant converted from mmoles min^{-1} to $Ml^{-1}sec.^{-1}$. Constant gives order of magnitude only. First order catalytic constants estimated using solubilities of salts in pure B. Identical results obtained using labeled SO_2 or $SOBr_2$. **(.12)** Selected values. Variation of rate constants observed with change in ionic strength as well as with specific salts. pH maintained with phosphate buffers. **(.13)** Rate constant calculated from rate of (.11) and rate constant ratio. **(.14)** Rate constant calculated from rate of (.11) and

COMMENTS *(continued)*

rate constant ratio. Value extrapolated by authors from data, (not given), between 60° and 90°. **(.18)** Rate constant is for exchange per sulfite. Authors list this value divided by two for comparison with compounds containing a single $-SSO_3^-$ group per molecule. **(.20)** No dependence upon $[H^+]$ observed by (15) up to concentrations 1.5M. Values of (15) about four times faster than those of (19). Both show evidence of decrease in rate constants with decrease in ionic strength. (19) observed that simultaneous hydrogen exchange is immeasurably fast. (23) observed a slight anion catalysis in acid solution and calculated catalytic constants for ClO_4^-, NO_3^-, Br^- and Cl^-. This was not observed by (19) in neutral solutions. Rate constants of (13)(23) are for exchange of all six H_2O while constants listed by (15) and (19) are for individual H_2O exchange all six being assumed identical.

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ISOTOPIC EXCHANGE

VIth Group Central Element complexed with exchanging VIIth Group ions.

Liquid phase

Amounts are in M/l. Rates and rate constants in M/l and secs.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$SOCl_2 + Cl^{*-} \longrightarrow SOCl_2^* + Cl^-$	$SOCl_2$	B=0.25-0.32	$(CH_3)_4N^+$	= B	$t_{\frac{1}{2}} < 10^3$ $t_{\frac{1}{2}} < 500$	0 25				(2)
			B=0.12-0.17	Sb^{+3}	$= \frac{1}{3}$ B	$t_{\frac{1}{2}} < 700$	0				
.2	$SeOCl_2 + Cl^{*-} \longrightarrow SeOCl_2^* + Cl^-$	$SeOCl_2$	B=0.5	K^+	= B	$t_{\frac{1}{2}} < 500$ $t_{\frac{1}{2}} < 400$	21 48				(2)
			B=0.6-1	Fe^{+++}	$= \frac{1}{3}$ B	$t_{\frac{1}{2}} < 6 \times 10^3$ $t_{\frac{1}{2}} < 1.5 \times 10^4$	40 45				
.3	$CrCl^{++} + Cl^{*-} \longrightarrow CrCl^{*++} + Cl^-$	H_2O	$10^2A=4.8;$ $10^2B=2.4-10$	$HClO_4$ Cr^{++}	1.0 0.0053	$k\,AB[Cr^{++}]$	0	5.2	-1	*	(3)
.4	$W_2Cl_9^{-3} + Cl^{*-} \longrightarrow W_2Cl_8Cl^{*-3} + Cl^-$	H_2O	A=0.11-1.1; B=9.9-12.6			$k\,AB$	25	2.1	-4	*	(1)

COMMENTS

Reaction: (.3) Rate law with respect to A or Cr^{++} based upon only two determinations. (.4) Rate law with respect to B not verified as variation in concentration of B small since its concentration always large with respect to A. Authors state all 9 Cl appeared to be kinetically equivalent inspite of fact that three are considered to be bridge atoms.

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ISOTOPIC EXCHANGE
VIth group element between oxidation states

Liquid phase

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

kF_A under defined mass action law indicates rate constant listed is for pseudo first order isotopic equilibration only.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Cr^{*+3} + Cr^{+2} \longrightarrow Cr^{+3} + Cr^{*+2}$	H_2O	$10^4(A+L) = 6\text{-}360$; $10^2(B+M) = 1\text{-}7$	$HClO_4$	1.0	kAB	0	4.0	-6				*	(1)
					1.0		24	1.22	-4					
					0.51		24	2.06	-4					
					0.37		24	2.95	-4					
					0.28		24	4.5	-4					
					0.21		24	5.2	-4					
					1.0		34	3.7	-4	22	2	12		
					0.2-1.0	$kAB[H^+]^{-1}$	24	1.15	-4					
.2	$Cr^{*+3} + Cr_2O_7^{=} \longrightarrow$	H_2O	$10^2A = 1$; $10^3B = 5$	$HClO_4$	0.05	kF_A	25	< 2	-8				*	(2)
							45	1	-7					

COMMENTS

Reaction: (.1) No measurable change in rate constant in presence of HCl 0.01f or 0.23 f. In 1f HCl rate constant about 10% larger than in presence of 1f $HClO_4$. (.2) Pseudo first order constant for fractional exchange calculated from half time given by authors.

LITERATURE

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ISOTOPIC EXCHANGE

VIth group element involving complexed valence states

Liquid phase

Amounts are in M/l.
Rates and rate constants are in M/l and sec.

kF_x under defined mass action law indicates constant tabulated is pseudo first order isotopic equilibration constant.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		$\Delta H^\ddagger$	$\Delta S^\ddagger$	Comments	Literature
								k^o	n				
.1	$CrF^{+2} + Cr^{*+2} \longrightarrow Cr^*F^{+2} + Cr^{+2}$	H_2O	$10^3A=6$; $10^3B=7$	$HClO_4$	0.93	kAB	0	2.5	-3				(^{1})
			3 3		0.97		27	2.6	-2				
			0.5-5 0.9-7		0.1-0.9		43	9.0	-2	14	-20		
.2	$CrCl^{+2} + Cr^{*+2} \longrightarrow Cr^*Cl^{+2} + Cr^{+2}$	H_2O	$10^5A=5-47$; $10^5B=7-51$	$HClO_4$	0.05-0.9	kAB	0	9	0				(^{1})(^{3})
.3	$CrBr^{+2} + Cr^{*+2} \longrightarrow Cr^*Br^{+2} + Cr^{+2}$	H_2O	$10^4A=4$; $10^3B=1$	$HClO_4$	1.0	kAB	0	>6	+1			*	(^{1})
.4	$CrN_3^{+2} + Cr^{*+2} \longrightarrow Cr^*N_3^{+2} + Cr^{+2}$	H_2O	$10^3A=1.8$; $10^3B=3.8$	$HClO_4$	1.0	kAB	0	>1	0			*	(^{1})
.5	$CrNSC^{+2} + Cr^{*+2} \longrightarrow Cr^*NSC^{+2} + Cr^{+2}$	H_2O	$10^3A=9$; $10^3B=5$	$HClO_4$	1.0	kAB	27	1.8	-4				(^{1})
.6	$CrF_3 + Cr^{*+3} \longrightarrow Cr^*F_3 + Cr^{+3}$	H_2O	A=0.16; B=0.10	HNO_3	.01	kF_x	22	1.5	-6				(^{2})
				μ= 1.6	.5		22	6	-7				
				1.6	1.0		22	4	-7				
.7	$Mo^*(CN)_8^{-4} + Mo(CN)_8^{-3} \longrightarrow Mo(CN)_8^{-4} + Mo^*(CN)_8^{-3}$	H_2O	$10^5A=5-5000$; $10^5B=4-1500$		pH=2-11	kAB	2	>1	+3				(^{4})

COMMENTS

Reaction: (.3) Calculated rate constant represents lower limit based upon at least 90% exchange in sampling time of 25 seconds. (.4) Calculated rate constant represents lower limit based upon at least 90% exchange in sampling time of 330 seconds. (.7) Calculated rate constant represents lower limit based upon assumed second order exchange reaction.

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Homogeneous Reactions
302.740

ISOTOPIC EXCHANGE
Cyanide ion with VIIth group cyanide complex

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

No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Mn(CN)_6^{-3} + C^*N^- \longrightarrow Mn(C^*N)_6^{-3} + CN^-$	H_2O	$10^2(A+L)=1-2$; $10^2(B+M)=6-12$ $\mu=0.18-1.2$	KOH	9-10.8	kA	0	4.4	-4	~8			*	(2)
			$10^2(A+L)=6.2$; $10^2(B+M)=11$	KOH	~11		25	~2	-3					(1)
.2	$Mn(CN)_6^{-4} + C^*N^- \longrightarrow Mn(C^*N)_6^{-4} + CN^-$	H_2O	$(A+L)=(B+M)=0.025$	KOH	11.8		~25	$t_{\frac{1}{2}}$ = 400 sec.						(3)

COMMENTS

Reaction. (.1) Rate constant calculated from time and % exchange data of (1) using rate law demonstarted by (2). Value gives order of magnitude only. (3) reported complete exchange in 4 min. under similar conditions. (.2) Half time of exchange varied from 340 to 410 seconds with no appreciable effect due to illumination.

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ISOTOPIC EXCHANGE

Exchange of oxygen attached to VIIth group element

Liquid phase

Amounts are in M/l.
Rates and rate constants are in gram atoms/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$ClO^- + H_2O^{18} \longrightarrow ClO^{18-} + H_2O$	H_2O	A=0.2-0.7	NaH_2PO_4 NaCl	pH=8.5-12.5 .01-.1	$k_1A[OH^-]^{-1} +$ $k_2A[Cl^-]/[OH^-]$	25 25	$k_1 = 6$ $k_2 = 5$	-8 -5				*	(1)
.2	$BrO^- + H_2O^{18} \longrightarrow BrO^{18-} + H_2O$	H_2O	A ~ 0.5	NaH_2PO_4 NaCl NaBr	pH=12-14	$k_1A[OH^-]^{-1} +$ $k_2A[Cl^-][OH^-]^{-1} +$ $k_3A[Br^-]/[OH^-]$	25 25 25	$k_1 = 9$ $k_2 = 4$ $k_3 \sim 3$	-5 -2 -2				*	(1)
.3	$ClO_2^{18-} + H_2O \longrightarrow$	H_2O	not stated	$HClO_4$	0.09-9		100	(no measurable exchange)						(3)
.4	$ClO_3^{18-} + H_2O \longrightarrow ClO_3^- + H_2O^{18}$	H_2O	A=0.1-0.5	$HClO_4$	0.09-.8	$kA[H^+]^2$	100	8.9	-4	27	1	11	*	(3)
.5	$ClO_4^{18-} + H_2O \longrightarrow$	H_2O	A=6-9				100	(no measurable exchange)						(3)
.6	$BrO_3^{18-} + H_2O \longrightarrow BrO_3^- + H_2O^{18}$	H_2O	A=0.04-0.1	HNO_3 μ =	0.01-1 0.9	$kA[H^+]^2$	30	6.6	-3	14	1	8	*	(2)
.7	$IO_3^{18-} + H_2O \longrightarrow IO_3^- + H_2O^{18}$	H_2O						(exchange complete in 1 minute)						(2)

COMMENTS

Reaction. (.1) (.2) Experimentally measured exchange rates varied by as much as a factor of 2 but rate constants calculated from average over wide range of pH considered to be reliable ±30% except for k_3 of reaction (.2). $[OH^-]$ calculated from measured pH. Units converted to seconds from minutes. (.4) Activation energy determined for temperature range 85 to 100° but only data at 100° given. Exchange also studied in H_2O-D_2O mixtures up to 89.3% D. At $0.96=[H^+]$ and $[ClO_3^-]=0.25$, $10^4R=4.8N^2+0.7N+3.0$ where N=atom fraction of D. Also $R_{D_2O}/R_{H_2O}=2.8$. (.6) Activation energy calculated from rate constants at 20°, 25°, 30° and 35° but only data at 30° given. $R_{D_2O}/R_{H_2O}=1.7$.

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ISOTOPIC EXCHANGE

VIIth group element between oxidation states

Liquid phase
Amounts are in M/l.
Rates and rate constants are in gram atoms/l and sec.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.1	$Cl^- + Cl^*O^- \longrightarrow Cl^{*-} + ClO^-$	H_2O	A=0.002-5; B=0.002-0.7	phosphate buffer	pH=9.6-13.3	$k\,AB[H^+]^2$	27	1.6	+19		*	(2)
			A=1; B=0.05	OH^- +	0.1							
				$(CH_3)_3COH$	0	$k\,AB$	27	1.3	-7			
				"	0.2		27	1.8	-7			
				"	1.0		27	2.7	-7			
				"	2.0		27	4.8	-7			
				"	3.0		27	7.4	-7			
				OH^- +	0.5							
				$(CH_3)_3COH$	0.0	$k\,AB$	27	4.2	-9			
				"	1.0		27	4.2	-7			
				"	2.0		27	7.5	-7			
				CH_3OH	1.0		27	4.3	-8			
				C_2H_5OH	1.0		27	4.3	-8			
				Dioxane	2.0		27	1.5	-8			
.2	$Cl^- + Cl^*OC(CH_3)_3 \longrightarrow$ $Cl^{*-} + ClOC(CH_3)_3$	$(CH_3)_3COH$	$10^2A=7;\ 10^3B=50$	$(CH_3)_3CO^-$	.05	$k\,AB$	27	5.2	-3		*	(2)
			7 50		.025		27	4.4	-3			
			7 50		.0125		27	3.4	-3			
			7 50		.005		27	2.8	-3			
			6 2.5-250		.0035		27	2	-3			
			0.7-35 40		.0025		27	5	-3			
			7 50		.0005		27	7	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
.2	$Cl^- + Cl^*OC(CH_3)_3 \longrightarrow$ *(cont.)*	$(CH_3)_3COH$	$10^2A=6$; $10^3B=40$	$(CH_3)_3CO^-$	.00023	kAB	27	5	-4				*	(2)
			6 40		.000077		27	2	-4					
			6 40		.000037		27	9	-5					
.3	$Br^{*-} + BrO^- \longrightarrow Br^- + Br^*O^-$	H_2O	$10^3A=1-50$; $10^2B=1-10$	$NaOH+Cl^-$	0.5-4.0	$kAB[OH^-]^{-1}$	27	5.5	-2				*	(3)
					0.2		27	3	-2					
.4	$Br^*_2 + BrO_3^- \longrightarrow Br_2 + Br^*O_3^-$	H_2O	$10^3A{\sim}2$; $10^2B=4-8$	$HClO_4$	1.65	$kA^{0.3}B^{1.7}[H^+]^{1.1}$	25	6.4	-6				*	(4)
.5	$I_2^* + IO_3^- \longrightarrow I_2 + I^*O_3^-$	H_2O	$10^4A=2-10$; $10^2B=2-100$	$HClO_4$	0.02-1	$kA^{0.6}B^{1.8}[H^+]^{1.8}$	25	1.4	-3					(7)
						$k'A^{0.6}B^{1.8}[H^+]^{1.8}\gamma_{\pm}^{3.6}$	25	2.1	-3	~20			*	(8)
				ClO_4^-	$A^{0.6}B^{0.8}[H^+]^{1.8}[k'B+k''(ClO_4^-)]\Gamma$		25	k'2.1	-3					
							25	k''4	-4					
.6	$Mn^{*+2} + MnO_4^- \longrightarrow Mn^{+2} + Mn^*O_4^-$	H_2O	$10^4A=2-14$; $10^3B=2-16$	$HClO_4$	1.6-3.2	$kA^{4/3}B^{1/3}[H^+]^{4/3}$	25	~7	-4				*	(1)
			$10^4A=8.9$; $10^4B=5.7$	HNO_3	1.0	R	25	4.4	-9					(6)
			8.9 3.6		2.0		25	5.6	-9					
			13.5 2.7		1.0		25	3.9	-9					
.7	$Mn^*O_4^{=} + MnO_4^- \longrightarrow MnO_4^{=} + Mn^*O_4^-$	H_2O	$10^5A=1-200$; $10^5B=5-380$	LiOH	0.16	kAB	0	7.0	+2				*	(10)
					0.57		0	1.1	+3					
				NaOH	0.08		0	6.0	+2					
					0.16		0	7.2	+2				(5) (9)	(10)
					0.32		0	9.2	+2					(10)
					0.57		0	1.2	+3					
				KOH	0.08		0	6.1	+2					
					0.16		0	8.0	+2					
					0.32		0	1.5	+3					
					0.57		0	2.2	+3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.7	$Mn^*O_4^= + MnO_4^- \longrightarrow$ *(continued)*	H_2O	$10^5A=1-200$; $10^5B=5-380$	CsOH	0.08	kAB	0	1.7	+3				*	(^{5}) (^{10})
				NaOH	0.16		11	1.8	+3					
					0.16		22	3.1	+3	10.5	2	11		
				NaOH +	$AB\{k_o+k'(Cs)\}$		0	k_o 7.0	+2					(^{5})
				CsOH	0-0.16		0	k' 1.2	+4					

COMMENTS

Reaction. (.1) Rate constant listed for the empirical rate law $k AB[H^+]^{-2}$ is average of 23 experiments some of which differed by a factor of five. Effect of acetate ion also determined but results were less reproducible. (.2) Reproducibility of data limited due to effect of traces of water. (.3) Value listed is average of 14 experiments some of which deviate by as much as 33% from the mean. (.4) Reaction studied in the dark as rates increased in light. Authors state reaction is actually complex and linear first order exchange plots were obtained only when tracer was added 100 hours after mixing $NaBrO_3$, $HClO_4$ and NaBr. They suggest this is due to accumulation of HOBr by reaction: $2H_2O + BrO_3^- + 2Br_2 \longrightarrow 5HOBr$, and data indicates exchange rate is inversely proportional to $[HOBr]$. (.5) $\gamma_\pm$ in rate law is mean ionic activity coefficient of $HClO_4$ at ionic strength of reaction medium. Γ in rate law indicates that the activity coefficients of the reactants and transition states are to be introduced with the appropriate power. Exchange studied after system IO_3^-, I^- and H^+ had reached equilibrium. See reaction (.4).

(.6) Exchange rates observed by (^{6}) lower than those predicted by rate law of (^{1}) but agree within a factor of two. (^{6}) suggests that concentrations of intermediates may be changing and that pseudo first order exchange plot may not be linear. (.7) Exchange rate dependent upon cation but no noticeable effect observed for following anions, $SO_4^=$, PO_4^{-3}, $P_2O_7^{-4}$, Cl^-, $Co(CN)_6^\equiv$. Catalysis observed by $Fe(CN)_6^{-3}$ with 0.16 NaOH $k = 1.2 \times 10^3$ at 0°C. probably due to rapid reversible electron transfer, $MnO_4^- + Fe(CN)_6^{-4} \rightleftarrows MnO_4^{-2} + Fe(CN)_6^{-3}$.

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ISOTOPIC EXCHANGE
N-bonded complex exchanging on VIIIth group element

Liquid phase
Amounts are in M/l.
Rates and rate constants are in gram atoms/l and sec.

R under defined mass action law indicates value listed under k is rate of isotopic exchange and kF_x indicates value is first order isotopic equilibration constant.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Co(phen^*)_3^{+2} + phen \longrightarrow Co(phen)_3^{+2} + phen^*$	H_2O	$10^4A=8-16$; $10^3B=2.8$	NO_3^-	=2A	kA	0	8.1	-3					(1)
	$phen^*$ = 1,10-phenanthroline with C^{14} tracer						7	2.0	-2					
	phen = 1,10-phenanthroline without tracer						11	3.6	-2	21	1.4	16		
.2	$Co(phen)_3^{+2} + Co^{60}(phen)_2Cl^{+2} \longrightarrow Co^{60}(phen)_3^{+2} + Co(phen)_2Cl^{+2}$	H_2O				kA	0	9	-3					(1)
.3	$Co(N^{15}H_3)_6(NO_3)_3 + NH_3 \longrightarrow Co(NH_3)_6(NO_3)_3 + N^{15}H_3$	NH_3	$10^3A=3-6$				25	$t_{\frac{1}{2}}$ = 7,000-40,000						(6)
.4	$Co(phen)_3^{+3} + phen^* \longrightarrow Co(phen^*)_3^{+3} + phen$	H_2O	$10^3A=1.2$; $10^3B=5.6$			R	20	3.3	-7				*	(2)
			1.2 5.8	Co^{+2}	.031		20	5.1	-7					
			1.2 5.7		.045		20	5.8	-7					
			1.2 5.7			$kA[Co^{++}]$	20	5	-2					
			1.6 9.1			R	35	1.2	-7					
			1.3 9.4				45	1.2	-6					
			4.0 .08	HCl	2		~100	no exchange in 17 hrs.						
.5	$Co(dipyr)_3^{+3} + dipyr^* \longrightarrow Co(dipyr^*)_3^{+3} + dipyr$	H_2O	$10^3A=4$; $10^2B=1-2$			R	45	4	-7				*	(2)
	$dipyr^*$ = dipyridyl with C^{14} tracer		4 1	Co^{+2}	.015		45	1.5	-6					
	dipyr = dipyridyl without tracer		4 1		.031		45	2.6	-6					
			4 1		.01-.03	$kA[Co^{++}]$	45	2	-2					
			4 .08	HCl	2		~100	no exchange in 15 hrs.						

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$Ni(NH_3)_6(NO_3)_2 + N^{15}H_3 \longrightarrow Ni(N^{15}H_3)_6NO_3 + NH_3$	NH_3	$10^2A=9.0$			kF_x	-50	3	+1				*	(5)
.7	$Ni(NH_2CH_2CH_2NH_2)_3^{+2} + NH_2CH_2C^{14}H_2NH_2 \longrightarrow$ $Ni(NH_2CH_2C^{14}H_2NH_2)_3^{+2} + NH_2CH_2CH_2NH_2$	H_2O	$10^3A=5\text{-}50$; $10^2B=1.6\text{-}15$	$SO_4^{=}$	pH~11	kA	0	2	-1				*	(4)

COMMENTS

General: For general treatment of isotopic exchange reactions see (3). Where rate constant for chemical process responsible for exchange has not been explicitly determined the value listed under k will be indicated under the defined mass action law as either R, the rate of the chemical process responsible for exchange or, kF_x a pseudo first order constant for rate of isotopic equilibration. R is calculated from the equation: $R = -\frac{m \cdot n\ \underline{A} \cdot \underline{B}}{(m\underline{A}+n\underline{B})t} \ln(1-X)$; m and n are the number of exchangeable atoms of the labeled species in A and B respectively. $\underline{A}$ represents the sum of $[A]+[L]$ and $\underline{B}$ represents the sum of $[B]+[M]$. X is the fractional extent of isotopic equilibration having taken place at time t. The pseudo first order rate constant kF_x is calculated from the expression $kF_x = -(1/t)\ln(1-X)$ where X is the fractional extent of isotopic equilibration at time t.

Reaction: **(.3)** Exchange in both stainless steel and pyrex with some catalysis by stainless steel. **(.4) (.5)** No measurable exchange in acid solution. In basic solution exchange is thought to be due to unknown trace amounts of Co^{++}. A rate constant for the Co^{++} catalyzed reaction calculated from difference in exchange rate with and without added Co^{++} divided by $[Co^{++}]$ and A. **(.6)** Half time of exchange of the order of 0.025 seconds determined by flow method, reliable only with regard to order of magnitude. **(.7)** Exchange very fast and rate constants only give order of magnitude.

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Homogeneous Reactions
302.858

ISOTOPIC EXCHANGE
VIIIth group ion exchange with N-bonded complex

Liquid phase

Amounts are in M/l.
Rates and rate constants are in gram atoms/l and sec.

R under defined mass action law indicates value listed under k is rate of isotopic exchange and kF_X indicates value is first order isotopic equilibration constant.

No.	Reaction	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
.1	$Fe^*(Phen)^{+2} + Fe^{+2} \longrightarrow Fe(Phen)^{+2} + Fe^{*+2}$ Phen = 1, 10-phenanthroline	H_2O	$10^3A=2.5$; $10^2B=1$	HCl	0.005	R	30	5.9	-5				*	(^{8})
			5.0 1		0.005		30	8.2	-5					
			7.5 1		0.005		30	8.6	-5					
			10 1		0.005		30	8.3	-5	19				
.2	$Fe(EDTA)^{-1} + Fe^{*+3} \longrightarrow Fe^*(EDTA)^{-1} + Fe^{+3}$ EDTA = ethylene diamine tetraacetate	H_2O	$10^3A=6-20$; $10^3B=6-20$	$HClO_4$ $NaClO_4$	$\left.\begin{array}{l}0.005\text{-}0.3\\ \mu = 1.1\end{array}\right\}$	$k_1A[H^+]^3 + k_2AB + k_3AB[H^+]^{-1}$							*	(^{6})
							25	k_1 7.8	-3					
							25	k_2 2.5	-4					
							25	k_3 1.5	-6					
.3	$Co^*(Phen)_3^{+2} + Co^{+2} \longrightarrow Co(Phen)^{+2} + Co^{*+2}$ Phen = 1, 10-phenanthroline	H_2O	$10^2A=1.5-3$; $B=0.1-1.3$			kA	0	1.1	-3					(^{4})
							11	4.5	-3					
							15	7.3	-3	19	2	14		
		pyridine	A=B=0.005			kF_X	~25	>2	-2				*	(^{7})
.4	$Co(5\text{-}M\text{-}Phen)_3^{+2} + Co^{*+2} \longrightarrow Co^*(5\text{-}M\text{-}Phen)^{+2} + Co^{+2}$ 5-M-Phen = 5-methyl-1, 10-phenanthroline	pyridine	A=B=0.005			kF_X	~25	>2	-2				*	(^{7})
.5	$Co(5\text{-}N\text{-}Phen)_3^{+2} + Co^{*+2} \longrightarrow Co^*(5\text{-}N\text{-}Phen)^{+2} + Co^{+2}$ 5-N-Phen = 5-Nitro-1, 10-phenanthroline	pyridine	A=B=0.005			kF_X	~25	>3	-2				*	(^{7})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$Co(tripyridyl)_2^{+2} + Co^{*+2} \longrightarrow Co^*(tripyridyl)_2^{+2} + Co^{+2}$	pyridine	A=B=0.005			$k F_x$	~25	7	-6				*	(7)
.7	NN'-disalicylidine-ethylene diamine cobaltII + $Co^{*+2} \longrightarrow$	pyridine	$10^5A=9$; $10^5B=8.5$			$k F_x$	15	6	-4				*	(7)
.8	NN'-disalicylidene-*o*-phenylenediamine cobalt II + $Co^{*+2} \longrightarrow$	pyridine	A=B=0.0017-0.017			$k AB$	15	7.3	-3				*	(7)
							25	1.1	-2					
							35	5.7	-2	~18	~5	11		
.9	$Ni^*(EDTA)^{-2} + Ni^{+2} \longrightarrow Ni(EDTA)^{-2} + Ni^{*+2}$ EDTA= ethylenediaminetetraacetate ion	H_2O	$10^4A=4-18$; $10^4B=9-36$	HCl KCl	$(5-400)\times10^{-6}$ $\mu=0.028$	$k_1AB+k_2AB[H^+]+k_3A[H^+]+k_4[HA^-][H^+]+k_5[H^+]^2[HA^-]$	25	k_1 5.2	-5				*	(2)
							25	k_2 3.0	0					
							25	k_3 2.2	-3					
							25	k_4 3.5	-3					
							25	k_5 not determined						
			$10^5A=9-90$; $10^4B=4-19$	HCl KCl	$(4-1000)\times10^{-4}$ $\mu=0.10$		25	k_1 not determined						
							25	k_2 1.7	0					
							25	k_3 1.3	-3					
							25	k_4 3.2	-3					
							25	k_5 1.1	-1					
			$10^4A=9-90$; $10^3B=2-18$	$HClO_4$ $KClO_4$	$(3-300)\times10^{-4}$ $\mu=1.25$		25	k_1 8	-7					
							25	k_2 3.8	-1					
							25	k_3 8	-4					
							25	k_4 2.0	-3					
							25	k_5 2.1	-1					
.10	$Ni(dipyr)^{+2}+Ni^{*+2} \longrightarrow Ni^*(dipyr)^{+2} + Ni^{+2}$ dipyr = 2, 2'-dipyridyl	H_2O	$10^2A=3.5$; B=0.16			kA	14	1.1	-5					(3)
			3.5-7 .16-.3		pH=4-6		25	5.4	-5					
			3.5 .16				30	1.1	-4					
							35	2.0	-4	24	2	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.11	$Ni(diMP)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(diMP)^{+2} + Ni^{+2}$	H_2O	$10^2A=3.9; B=0.16$			k A	25	1.8	-5					(3)
	diMP = 4,4'-dimethyl-2,2'-dipyridyl						40	1.3	-4	24	8	12		
.12	$Ni(phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(phen)^{+2} + Ni^{+2}$	H_2O	$10^3A=3.6; 10^2B=1.6$			k A	25	1.0	-5					(3) (9)
	phen = 1,10-phenanthroline						30	2.4	-5					
							40	7.0	-5	24.5	1.1	13		
.13	$Ni(2\text{-}M\text{-}Phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(2\text{-}M\text{-}Phen)^{+2} + Ni^{+2}$	H_2O	$10^2A=6; B=0.29$	NO_3^-	=2(A+B)	k A	0	2.2	-5					(3)
	2-M-Phen = 2-Methyl-1,10-phenanthroline		5 0.24				8	6.5	-5					
			5 0.24				16	1.6	-4					
			6 0.3-0.47				25	4.8	-4	20	3	11		
.14	$Ni(5\text{-}M\text{-}Phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(5\text{-}M\text{-}Phen)^{+2} + Ni^{+2}$	H_2O	$10^2A=3.5; B=0.16$	NO_3^-	=2(A+B)	k A	25	7.3	-6					(3)
	5-M-Phen = 5-Methyl-1,10-phenanthroline		3.5 0.16				35	2.7	-5					
			3.5 0.16				40	5.3	-5					
			3.5-3.7 0.16-.19				45	1.02	-4					
			3.5 0.16				50	1.6	-4	24.4	7	12		
.15	$Ni(47\text{-}MM\text{-}Phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(47\text{-}MM\text{-}Phen)^{+2} + Ni^{+2}$	H_2O	$10^2A=2; 10^2B=8$	Cl^-	=2(A+B)	k A	40	1.4	-5					(3)
	47-MM-Phen = 4,7-Dimethyl-1,10-phenanthroline		1.5-1.9 6-8				60	1.6	-4	26	1	13		
.16	$Ni(5\text{-}N\text{-}Phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(5\text{-}N\text{-}Phen)^{+2} + Ni^{+2}$	H_2O	$10^2A=4.3; B=0.15$	NO_3^-	=2(A+B)	k A	0	1.5	-6					(3)
	5-N-Phen = 5-Nitro-1,10-phenanthroline		4.3 0.15				20	3.0	-5					
			4.3 0.15				30	1.16	-4	23.5	1	13		
.17	$Ni(2\text{-}C\text{-}Phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(2\text{-}C\text{-}Phen)^{+2} + Ni^{+2}$	H_2O	$10^2A=6.8; B=0.29$	NO_3^-	=2(A+B)	k A	0	7.8	-4					(3)
	2-C-Phen = 2-chloro-1,10-phenanthroline		6.8 0.29				5	1.4	-3	17	3	10		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.18	$Ni(5\text{-}C\text{-}Phen)^{+2} + Ni^{*+2} \longrightarrow Ni^{*}(5\text{-}C\text{-}Phen)^{+2} + Ni^{+2}$	H_2O	$10^2A=1.8$; $10^2B=8$	NO_3^-	=2(A+B)	kA	25	2.5	-5					(3)
	5-C-phen = 5-chloro-1,10-phenanthroline		1.8 8				35	9.0	-5					
			1.8 8				40	1.8	-4	24	1	13		
.19	$Ni(CN)_4^{-2} + Ni^{*}(OOCCH_2NH_2)_2 \longrightarrow$ (nickel glycinate)	H_2O	$10^3A=6-23$; $10^3B=6-23$	NaOH $NaClO_4$	pH=11	kAB	5	2.0	-3				*	(1)
							15	4.0	-3					
							25	1.6	-2					
							45	8.3	-2	17.3	8	10		
			10 10		pH=9		25	4.6	-1					
				$NaClO_4$	3; pH=9		25	6.9	-1					
.20	$Ni(CN)_4^{-2} + Ni^{*}(OOCCHNH_2CH_2OH)_2 \longrightarrow$ (nickel serinate)	H_2O	$10^3A=6-23$; $10^3B=6-23$	NaOH $NaClO_4$	pH=11	kAB	5	1.4	-3				*	(1)
							15	2.4	-3					
							25	1.2	-2					
							45	5.6	-2	18.2	3	11		
			10 10		pH=9		25	8.3	-1					
			10 10	$NaClO_4$	0.2; pH=9		25	6.8	-1					
.21	$Ni(CN)_4^{-2} + Ni^{*}(OOCCH_2CH_2CHNH_2OO)_2^{-2} \longrightarrow$ (nickel glutamate complex)	H_2O	$10^3A=6-23$; $10^3B=6-23$	NaOH $NaClO_4$	pH=11	kAB	5	2.3	-3				*	(1)
							15	4.0	-3					
							25	2.1	-2					
							45	1.0	-1	18.6	9	11		
			10 10		pH=9		25	5.0	-1					
			10 10	$NaClO_4$	3; pH=9		25	7.4	-1					
.22	$Ni(CN)_4^{-2} + Ni^{*}(NH_2CH_2CH_2CH_2CH_2CHNH_2COOH)_2^{+?} \longrightarrow$ (nickel lysinate)	H_2O	$10^3A=6-23$; $10^3B=6-23$	NaOH $NaClO_4$	pH=11	kAB	5	3.3	-3				*	(1)
							15	5.9	-3					
							25	3.4	-2	19	2	11		
			10 10		pH=9		25	8.1	-1					
			10 10	$NaClO_4$	3; pH=9		25	5.9	-1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		Comments	Literature
								k°	n		
.23	$Ni(Y)^{-2} + Ni^{*}(NH_3)_4{}^{+2} \longrightarrow Ni^{*}(Y)^{-2} + Ni(NH_3)_4{}^{+2}$ (Y = Versenate ion)	H_2O	$10^2A=1; 10^2B=1$	NaOH	pH=9	kAB	25	8.4	-1	*	(^{1})
.24	$Ni(Y)^{-2} + Ni^{*}(NH_2CH_2CH_2NH_2)_3{}^{+2} \longrightarrow$ (Y = Versenate ion)	H_2O	$10^2A=1; 10^2B=1$	NaOH	pH=9	kAB	25	5.3	-1	*	(^{1})
.25	$Ni(Y)^{-2} + Ni^{*}(OOCCH_2CH_2NH_2)_2 \longrightarrow$ (Y = Versenate ion)(nickel glycinate)	H_2O	$10^2A=1; 10^2B=1$	NaOH	pH=9	kAB	25	3.8	-1	*	(^{1})
.26	$Ni(Y)^{-2} + Ni^{*}(OOCCH_2CH_2CHNH_2COO)_2{}^{-2} \longrightarrow$ (Y = Versenate ion)(nickel glutamate complex)	H_2O	$10^2A=1; 10^2B=1$	NaOH	pH=9	kAB	25	1.7	-1	*	(^{1})
.27	$Ni(Y)^{-2} + Ni^{*}(NH_2CH_2CH_2CH_2CH_2CHNH_2COO)_2 \longrightarrow$ (Y = Versenate ion)(nickel lysinate)	H_2O	$10^2A=1; 10^2B=1$	NaOH	pH=9	kAB	25	9.9	-1	*	(^{1})

COMMENTS

General: For general treatment of isotopic exchange reactions see (^{5}). Where rate constant for chemical process responsible for exchange has not been explicitly determined the value listed under k will be indicated under the defined mass-action law as either R, the rate of the chemical process responsible for exchange or, kF_X, a pseudo first order constant for rate of isotopic equilibration. R is calculated from the equation $R = -\frac{m \cdot n \cdot \underline{A} \cdot \underline{B}}{(m\underline{A} + n\underline{B})\, t} \ln(1-x)$; where m and n are the number of exchangeable atoms of the labeled species in A and B respectively. $\underline{A}$ represents the sum $[A] + [L]$ and $\underline{B}$ represents the sum $[B]+[M]$· X is the fractional extent of isotopic equilibration having taken place at time t. The pseudo first order rate constant kF_X is calculated from the expression $kF_X = -\frac{1}{t} \ln(1-x)$ where X is the fractional extent of isotopic equilibration at time t.

Reaction: (.1) Authors state that exchange rate increases linearly with $[H^+]$ and that the increase is greater with the 2,2'-dipyridyl complex but no data is given. Temperature range over which activation energy was calculated is not given. Activation energy for 2,2'-dipyridyl complex stated to be 15 k.cals. (.2) At low ionic strength the first term shows no salt effect and the second and third terms both show a large negative salt effect. Order of second term with respect to H^+ very uncertain and expression of the form $k'_2AB[H^+]$ could equally well fit data. (.3) In pyridine (^{7}) finds $t_{\frac{1}{2}}$ for exchange <28 sec. (.4) $t_{\frac{1}{2}}<36$ sec. (.5) $t_{\frac{1}{2}}<25$ sec. (.6) $t_{\frac{1}{2}}=1.0\times10^5$ sec. (.7) $t_{\frac{1}{2}}=1,170$ sec. at 15° at concentration listed and at 30° with $10^2A=1.2$ and $10^3B=5.7$ $t_{\frac{1}{2}}<360$ sec. (.8) Order with respect to A and B individually not confirmed as A=B in all experiments. (.9) Rate equation of authors related to a suggested

COMMENTS *(continued)*

mechanism for exchange involving nine separate reactions. Reliability of each of the specific constants is not high but equation does fit data over range studied. **(.19)-(.27)** Authors calculate R correctly by formula $R = \frac{AB}{A+B} \times \frac{\ln 2}{t_{\frac{1}{2}}}$ not by formula stated which omitted ln2. Values at 45° not weighted heavily due to possible inaccuracy.

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Homogeneous Reactions
302.860

ISOTOPIC EXCHANGE

O-bonded complex exchanging on VIIIth group element

Liquid phase

Amounts are in M/l.
Rates and rate constants are in M/l and sec.

R listed under defined mass action law indicates value listed is rate of exchange reaction and kF_X indicates value is for pseudo first order isotopic equilibration constant.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.1	$Co(NH_3)_5H_2O^{+3} + H_2O^* \longrightarrow$ $Co(NH_3)_5H_2O^{*+3} + H_2O$	H_2O	$10^2A=2-10$	$HClO_4$	0.008-0.07	kA	25	5.9	-6				*	(5)(6) (5)
							35	2.6	-5					
							45	9.3	-5	27	2	14		
			2.5	NaOH	0.009		25	3.8	-6					
					0.018		25	1.8	-6					
			pressure		0.027		25	1.4	-7					
			2,080 atm.	$HClO_4$	0.008-0.07		25	4.8	-6					
			7,000 atm.				35	1.9	-5					
		CH_3OH	$10^3A=5$; B=2.22	$HClO_4$	0.01		25	1.8	-6					
			4.44				25	2.1	-6					
			6.66				25	2.4	-6					
.2	$Co(NH_3)_4CO_3^+ + C^*O_3^= \longrightarrow$ $Co(NH_3)_4C^*O_3^+ + CO_3^=$	H_2O	$10^3A=5-90$; $10^3B=8-36$	$NaNO_3$	pH=9.5-9.7	$k'AB[H^+]$ + $k'A[H^+]$	20	k' 7.5	+5				*	(3)(7)
							20	k''1.4	+4					
.3	$Co(NH_3)_5CO_3^+ + C^*O_3^= \longrightarrow$ $Co(NH_3)_5C^*O_3^+ + CO_3^=$	H_2O	$10^3A=6-40$; $10^3B=6-40$	$NaNO_3$	pH=8.8-9.9	$k'AB[H^+]$ + $k''A[H^+]$	0	k' 1.45	+5				*	(8)
							0	k'' 1.3	+4					
							25	k' 1.67	+6	16	6	17		
							25	k''2.5	+5	20	1	20		
.4	$Co(NH_2CH_2CH_2NH_2)_2CO_3^+ + C^*O_3^= \longrightarrow$ $Co(NH_2CH_2CH_2NH_2)_2C^*O_3^+ + CO_3^=$	H_2O	$10^2A=1-6$; $10^3B=6-35$	Borate buffer	pH=9.3-9.9	$kAB+k'A[H^+]$	25	k 2.5	-4	~25			*	(1)(4)
							25	k' 1.25	-6	~0				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	Comments	Literature
.5	$Co(NH_2CH_2CH_2CH_2NH_2)_2CO_3^+ + C^*O_3^= \longrightarrow$ $Co(NH_2CH_2CH_2CH_2NH_2)_2C^*O_3^+ + CO_3^=$	H_2O	$10^2A\sim4$; $10^2B\sim2$	Borate buffer	pH~9.1	$kAB + k'A$	25	k 1.2	-3		*	(1)
							25	k'3.3	-5			
							50	k 5.8	-4	25		
							50	k'1.5	-5	25		

COMMENTS

Reaction: **(.1)** Slight decrease in exchange rate observed by (6) in presence of $[Na_2SO_4]$=0.33, $[NaHSO_4]$=0.5. Rate constant in presence of 0.027 M NaOH considered by (5) to be limiting value for exchange involving $Co(NH_3)_5OH^{+2}$ as this was predominant species. Value gives only order of magnitude as only 2% exchange had taken place at last sampling. $\Delta V^{\ddagger}$=1.2 and was independent of pressure over range studied. O^{18} used as tracer. **(.2)** (7) calculates with exchange rate equation which accounts for isotope equilibrium constant ϵ=0.89. Uses equation $\frac{1}{t}\ \ln(1-\alpha) = (\epsilon k'A + \epsilon k''AB^{-1} + k'B + k'')[H^+]$ to calculate k' and k''. B represents total $CO_3^=$ and HCO_3^- concentration. C^{14} used as tracer. **(.3)** Exchange rate law valid after aquation equilibrium attained. Aquation equilibrium attained in less than one exchange half time. No influence of light, glass surface, N_2 or O_2. **(.4)** Exchange studied after aquation equilibrium attained which required 12 hrs. at room temperature or 2-3 hrs. at 50°C. Exchange does not follow racemization rate law. Borate used as buffer reduces exchange rate by a factor of about 0.8. (1) reports no measureable effect of borate buffer. **(.5)** Values at 25° extrapolated by authors. No appreciable effect of changing $[H^+]$ or ionic strength up to μ= 1.5 and $[H^+]$ up to 9×10^{-10}. C^{14} used as tracer.

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ISOTOPIC EXCHANGE

Halogen ion exchange on VIIIth group complex

Liquid phase

Amounts are in M/l. Rate and rate constants are in M/l and sec. Time is in seconds.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	*cis*-Co $en_2\ Cl_2^+ + Cl^{*-} \longrightarrow$ *cis*-Co $en_2\ ClCl^{*+} + Cl^-$ en = ethylene-diamine, $NH_2CH_2CH_2NH_2$	CH_3OH	$10^3A=1.8$; $10^2B=4$	Li^+	=B	kA	36	1.4	-4				*	(1)
.2	*trans*-Co $en_2\ Cl_2^+ + Cl^{*-} \longrightarrow$ *trans*-Co $en_2\ ClCl^{*+} + Cl^-$ en = ethylene-diamine, $NH_2CH_2CH_2NH_2$	CH_3OH	$10^3A=2-5$; $10^3B=9-70$	ClO_4^- Li^+	=A =B	kA	25	5.3	-6				*	(6)
.3	*trans*-Co $pn_2\ Cl_2^+ + Cl^{*-} \longrightarrow$ *trans*-Co $pn_2\ ClCl^{*+} + Cl^-$ pn = propylene-diamine, $NH_2CH_2CHNH_2CH_3$	CH_3OH	$10^3A=2-5$; $10^2B=2.1$	ClO_4^- Li^+	=A =B	kA	25	7.3	-6				*	(6)
.4	*trans*-Co(N-meen)$_2\ Cl_2^+ + Cl^{*-} \longrightarrow$ *trans*-Co(N-meen)$_2\ ClCl^{*+} + Cl^-$ N-meen = N-methylethylene diamine, $CH_3NHCH_2CH_2NH_2$	CH_3OH	$10^3A=2-5$; $10^2B=2.6$	ClO_4^- Li^+	=A =B	kA	25	7.2	-7				*	(6)
Pt(II) halide complexes														
.5	$PtCl_4^= + Cl^{*-} \longrightarrow PtCl^*Cl_3^= + Cl^-$	H_2O	$10^2A=1.25$; $10^2B=3.42$			kA	0	~1	-5				*	(7)
			$B \simeq 4A$				~20	3.2	-5					(4)
			$10^2A=1.25$; $10^2B=3.42$	Ce^{+4}	5.5×10^{-4}			% exchange	time					(7)
								62	30					
								87	240					
								95	8400					
.6	$Pt(H_2O)Cl_3^- + Cl^{*-} \longrightarrow Pt(H_2O)Cl^*Cl_2^- + Cl^-$	H_2O	$10^2A \simeq 1$; $10^2B=3.42$			kA	15	9.2	-6				*	(3)
							25	4.4	-5					
							30	7.8	-5	25	9	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.7	$Pt(NH_3)Cl_3^- + Cl^{*-} \longrightarrow Pt(NH_3)Cl^*Cl_2^- + Cl^-$	H_2O	$10^3A=4-17$; $10^2B=1-27$	HCl + KCl or H_2SO_4 + K_2SO_4	pH=4.5-5 $\mu=0.318$	kA	0	1.1	-6				*	(2)
							15	6.5	-6					
							20	1.2	-5					
							25	2.5	-5					
							30	4.1	-5	20	1.1	10		
.8	$Pt(NH_3)(H_2O)Cl_2^- + 2Cl^{*-} \longrightarrow$ $Pt(NH_3)(H_2O)Cl_2^{*-} + 2Cl^-$	H_2O	$10^3A=7$; $10^2B=1.7$			$-dB/dt=kA$	0	6.9	-6				*	(2)
							20	8.9	-5					
							30	2.0	-4	18	2	9		
.9	*trans*-$Pt(NH_3)_2Cl_2 + Cl^{*-} \longrightarrow$ *trans*-$Pt(NH_3)_2Cl_2^* + Cl^-$	H_2O	$10^3A\simeq1$			kA	25	3.5	-5					(5)
.10	*trans*-$Pt(Py)_2Cl_2 + Cl^{*-} \longrightarrow$ *trans*-$Pt(Py)_2Cl_2^* + Cl^-$	CH_3NO_2	$10^3A\simeq1$; $10^2[R_4NCl]=1-7$			kA	25	3.2	-5				*	(5)
	pY = pyridine		$10^3[R_4NCl]=1.1$	CH_3COOH	2.2		25	4.0	-4					
	(unless otherwise stated Cl^- introduced as R_4NCl where R_4NCl is *n*-octadecylbenzyl dimethyl ammonium chloride)		3.8		2.2		25	5.0	-4					
			3.5		4.4		25	2.5	-3					
			3.8	CH_3COOH CH_3COONa	2.2 0.012		25	6	-5					
			$10^3[HCl]=1$				25	1.1	-5					
			3				25	3.4	-5					
			7.5				25	3.3	-5					
		C_2H_5OH	$10^3A\simeq1$; $10^4[R_4NCl]=8-76$				25	1.42	-5					
		n-C_3H_7OH	$10^3A\simeq1$; $10^3[R_4NCl]=1-3$				25	4.2	-6					
		$(CH_3)_2SO$	$10^3A\simeq1$; $10^4[R_4NCl]=8-25$				25	3.8	-4					
		H_2O 10% + C_2H_5OH	$10^3A\simeq1$; $10^3[R_4NCl]=6-10$	H_3BO_3	0.075		25	5.3	-5					
				+NaOH	0.075 0.2		25	2.4	-5					
		$(CH_3)_3COH$	6 $10^3A\simeq1$; $10^3[R_4NCl]=1-3$			$kA[R_4NCl]^{\frac{1}{2}}$	25	7	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.10	*trans*-$Pt(Py)_2Cl_2 + Cl^{*-} \longrightarrow$ *(continued)* Py = pyridine (unless otherwise stated Cl^- introduced as R_4NCl where R_4NCl is octadecylbenzyl dimethyl ammonium chloride)	CCl_4	$10^3A \simeq 1$; $10^4[R_4NCl]=8-16$			$kA[R_4NCl]^{\frac{1}{2}}$	25	4.7	-4				*	(^{5})
			$10^4[HCl]=5-25$			kA	25	1.4	-7					
		C_6H_6	$10^3A \simeq 1$; $10^3[R_4NCl]=1.6-8.5$			$kA[R_4NCl]^{\frac{1}{2}}$	25	1.06	-4					
			$10^3[HCl]=1$			kA	25	1.15	-6					
			5				25	3.12	-6					
		CH_3CN	$10^3A \simeq 1$; $10^4[R_4NCl]=8-24$			$kA[R_4NCl]$	25	1.25	-2					
			$10^4[HCl]=8$			kA	25	1.27	-5					
			24				25	4.1	-5					
		$HCON(CH_3)_2$	$10^3A \simeq 1$; $10^3[R_4NCl]=1.0$			kA	25	1.53	-5					
			3.0				25	2.8	-5					
		$(CH_3)_2CO$	$10^3A \simeq 1$; $10^4[R_4NCl]=5-60$			$kA[R_4NCl]^{\frac{1}{2}}$	25	1.7	-4					
		$CH_3COOC_2H_5$	$10^3A \simeq 1$; $10^3[R_4NCl]=1-5$			$kA[R_4NCl]^{\frac{1}{2}}$	25	2.2	-5					
		CH_2ClCH_2Cl	$10^3A \simeq 1$; $10^4[R_4NCl]=8-38$			$kA[R_4NCl]^{\frac{1}{2}}$	25	3.8	-4					
		m-$CH_3C_6H_4OH$	$10^3A \simeq 1$; $10^3[R_4NCl]=2-5$			$kA[R_4NCl]^{\frac{1}{2}}$	25	9.3	-5					
.11	*cis*-$Pt(4\text{-ampy})_2Cl_2 + Cl^{*-} \longrightarrow$ *cis*-$Pt(4\text{-ampy})_2Cl_2^* + Cl^-$ (4-ampy = 4-amylpyridine) (Cl^- introduced as R_4NCl = *n*-octadecylbenzyldimethylammonium chloride)	C_2H_5OH	$10^3A \simeq 1$; $10^3[R_4NCl]=5$			kA	25	1.09	-5					(^{5})
		$C_2H_5OH + H_2O$	10% 6-10	H_3BO_3	0.075		25	3.0	-5					
			6	$+NaOH$	0.2		25	1.5	-5					
.12	*cis*-$Pt(\alpha\text{-pic})_2Cl_2 + Cl^{*-} \longrightarrow$ *cis*-$Pt(\alpha\text{-pic})_2Cl_2^* + Cl^-$ (α-pic = α-picoline)	C_2H_5OH	$10^3A \simeq 1$; $10^3[HCl]=1.43$			kA	25	4.8	-7					(^{5})
.13	$PtBr_4^{=} + Br^{*-} \longrightarrow PtBr^*Br_3^{=} + Br^-$	H_2O	$B \simeq 4A$			kA	~20	7.6	-4					(^{4})
.14	$PtI_4^{=} + I^{*-} \longrightarrow PtI^*I_3^{=} + I^-$	H_2O	$B \simeq 4A$			kA	~20	1.6	-3					(^{4})
.15	$Pt(CN)_4^{=} + C^*N^- \longrightarrow Pt(C^*N)_4^{=} + CN^-$	H_2O	$B \simeq 4A$			kA	~20	1.5	-2					(^{4})

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
Pt(IV) halide complex														
.16	$PtCl_6^= + Cl^{*-} \longrightarrow PtCl^*Cl_5^= + Cl^-$	H_2O	$10^2A=4.8$; $10B=1.06$	HCl	0.095		 25 25	% exchange 62 97		time 3,600 83,000			*	(7)

COMMENTS

Reaction: **(.1)** Rate constant is for initial rate only as complications arise due to exchange of second chloride. Exchange rate identical to loss of optical activity and substitution by nitrate ion, bromide ion and thiocyanate ion all of which are first order in A and zero order in other substituent. **(.2) (.3)** Rate constant is for initial rate, about one half life. Exchange rate agrees with substitution rate by thiocyanate ion within experimental uncertainty. **(.4)** Initial rate, about one half life. **(.5)** Exchange law not verified by (7) and rate constant calculated from original data of 1.2% exchange in 30 minutes to compare with data of (4). (3) shows that exchange involves equilibrium aquation, $PtCl_4^= + H_2O \rightleftarrows PtCl_3H_2O^- + Cl^-$ and isotope exchange of $PtCl_3H_2O^- + Cl^{*-}$ see (.6). **(.6)** Reaction considered by (3) to be responsible for majority of reaction (.5). Rate constant measured in aged solutions so that equilibrium concentration of $Pt(H_2O)Cl_3^-$ could be established. **(.7)** Authors show relation between rate of exchange and rate of hydrolysis of A. Rate constant measured as initial rate in freshly prepared solutions before aquation equilibrium established.

(.8) Rate constant is for exchange of both chlorine. These appear not to be equivalent and data gives best fit to equation for which one chlorine exchanges four times as fast as other chlorine. **(.10)** Exchange observed to be first order in complex in all solvents studied and zero order with respect to chloride ion in CH_3NO_2, C_2H_5OH, n-C_3H_7OH and $(CH_3)_2SO$. In other solvents studied pseudo first order rate constant versus $[R_4NCl]^{\frac{1}{2}}$ gave a straight line (R_4NCl=n-octadecylbenzyl dimethyl ammonium chloride which was the form in which Cl^- was introduced.) This is interpreted to indicate a first order dependence on Cl^- in each of these solvents with the R_4NCl predominantly existing as ion pairs. **(.16)** Exchange inhibited by $IrCl_6^=$ (impurity in commercial product), $Fe(CN)_6^{-3}$, Cl_2 and some reducing agents. Exchange catalyzed by $PtCl_4^=$, Pt^{+3} and initiated by light.

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ISOTOPIC EXCHANGE
VIIIth group element between oxidation states

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

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Fe^{+2} + Fe^{*+3} \longrightarrow Fe^{*+2} + Fe^{+3}$	H_2O	$10^4A = 1-5$; $10^4B = 1-10$	$HClO_4$ $NaClO_4$	0.01-0.5 $\mu = 0.5$	$k\,AB$; $k = k_1 + k_2K[H^+]^{-1}$ $K = 2.6 \times 10^{-4}$	0	k_1 8.7	-1	9.9	7	7	*	(5) (14)
							0	k_2 1.01	+3	7.4	9	8		
				$HClO_4$	0.0967 $\mu = 0.5$	$k\,AB$	0	3.10	0					(11)
							10	8.5	0					
							25	3.46	0					
		D_2O	$10^3A = 1$; $10^4B = 5$	$DClO_4$ $NaClO_4$	0.06-0.5 $\mu = 0.55$	$k\,AB$; $k = k_1 + k_2K[D^+]^{-1}$ $K = 1.2 \times 10^{-3}$	7	k_1 7	-1					(8)
							7	k_2 7.7	+2					
		$(CH_3)_2CHOH$	$10^2A = 7-9$; $10^2B = 3-5$ $HClO_4 < 0.01$	H_2O	0.53	$k\,AB$	25	9.4	-5					(17)
					0.88		25	1.3	-4					
					2.02		25	2.5	-4					
.2	$Fe^{+2} + Fe^{*}(OH)^{+2} \longrightarrow Fe^{*+2} + Fe(OH)^{+2}$	H_2O	$10^4A = 1-4$; $10^4[Fe^{+3}] = 1-4$	$HClO_4$ $NaClO_4$	0.01-0.5 $\mu = 0.5$	$k\,AB$	0	1.01	+3	7.4	9	8	*	(14)
		D_2O		$DClO_4$ $NaClO_4$	0.06-0.5 $\mu = 0.55$		7	7.7	+2					(11)
.3	$Fe^{+2} + Fe^{*}F^{+2} \longrightarrow Fe^{*+2} + FeF^{+2}$	H_2O	$10^4A = 1-5$; $10^4[Fe^{+3}] = 1-10$ $10^4[F^-] = 4-7000$	$HClO_4$	0.02-0.5	$k\,AB$	0	9.7	0				*	(9)
							10	1.9	+1					
							17	2.5	+1	9.1	2	8		
.4	$Fe^{+2} + Fe^{*}F_2^{+} \longrightarrow Fe^{*+2} + FeF_2^{+}$	H_2O	$10^4A = 1-5$; $10^4[Fe^{+3}] = 1-10$ $10^4[F^-] = 4-7000$	$HClO_4$	0.02-0.5	$k\,AB$	0	2.5	0				*	(9)
							25	1.1	+1	9.5	1.0	8		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.5	$Fe^{+2} + Fe^{*}F_3 \longrightarrow Fe^{*+2} + FeF_3$	H_2O	$10^4A = 1$-5; $10^4[Fe^{+3}] = 1$-10 $10^4[F^-] = 4$-7000	$HClO_4$	0.02-0.5	k AB	0	~5	-1				*	(9)
							10	~1	0					
							25	~3	0					
.6	$Fe^{+2} + Fe^{*}Cl^{+2} \longrightarrow Fe^{*+2} + FeCl^{+2}$	H_2O	$10^4A = 1$-4; $10^4[Fe^{+3}] = 1$-4 $[Cl]^-$ = up to 0.5	$HClO_4$ $NaClO_4$	0.016-0.5 0.55	k AB	0	9.7	0				*	(14)
							10	1.6	+1					
							20	2.9	+1	8.8	1.1	8		
.7	$Fe^{+2} + Fe^{*}Cl_2{}^{+} \longrightarrow Fe^{*+2} + FeCl_2{}^{+}$	H_2O	$10^4A = 1$-4; $10^4[Fe^{+3}] = 1$-4 $[Cl^-]$ = up to 0.5	$HClO_4$ $NaClO_4$	0.016-0.5 0.55	k AB	0	1.5	+1				*	(14)
							10	3.2	+1					
							20	5.1	+1	9.7	9	7		
.8	$Fe^{+2} + Fe^{*}N_3{}^{+2} \longrightarrow Fe^{*+2} + FeN_3{}^{+2}$	H_2O	not given			k AB	7	4	+3	13.7	2	14		(4)
		D_2O					7	2.7	+3					
.9	$Fe^{+2} + Fe^{*}SCN^{+2} \longrightarrow Fe^{*+2} + FeSCN^{+2}$	H_2O	$10^4A = 2$-4; $10^4[Fe^{+3}] = 1.5$-4 $10^4[SCN^-] = 2$-880	$HClO_4$	$\left.\begin{matrix}0.0967\\ \mu = 0.5\end{matrix}\right\}$	k AB	0	1.22	+1				*	(11)
							10	2.02	+1					
							25	4.2	+1	7.9	3	7		
.10	$Fe^{+2} + Fe^{*}(SCN)_2{}^{+} \longrightarrow Fe^{*+2} + Fe(SCN)_2{}^{+}$	H_2O	$10^4A = 2$-4; $10^4[Fe^{+3}] = 1.5$-4 $10^4[SCN^-] = 2$-880	$HClO_4$	$\left.\begin{matrix}0.0967\\ \mu = 0.5\end{matrix}\right\}$	k AB	0	2.0	0				*	(11)
							10	3.5	0					
							25	7.6	0	9	2	7		
.11	$Fe^{+2} + Fe^{*}(C_2O_4)^{+} \longrightarrow Fe^{*+2} + Fe(C_2O_4)^{+}$	H_2O	$10^4A = 1$; $10^5[Fe^{+3}] = 6.5$ $[H_2C_2O_4] = 0$-0.09	$HClO_4$	0.548 $\mu = 0.55$	k AB	0	7.0	+2				*	(8)
							10	1.10	+3					
							20	2.14	+3	9	1	10		
.12	$Fe^{+2} + Fe^{*}(C_2O_4)_2{}^{-} \longrightarrow Fe^{*+2} + Fe(C_2O_4)_2{}^{-}$	H_2O	$10^4A = 1$; $10^5[Fe^{+3}] = 6.5$ $[H_2C_2O_4] = 0$-0.09	$HClO_4$	0.548 $\mu = 0.55$	k AB	0	3	+3				*	(8)
							10	3	+3					
							20	4	+3					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
	Cobalt exchange between oxidation states													
.13	$Co^{+3} + Co^{*+2} \longrightarrow Co^{*+3} + Co^{+2}$	H_2O	$10^4A=6-15$; $10^4B=1-15$	$HClO_4$	1.0	kAB	0	7.7	-1				*	(3)
.14	$Co(NH_3)_5H_2O^{+3}+Co^{*+2} \longrightarrow Co^*(NH_3)_5H_2O^{+3} + Co^{+2}$	H_2O	$10^2A=4$; $10^5B=5-14$	NH_3 salts	0.33 $\mu=2.28$	$kAB[NH_3]^5$	16	1.3	+2				*	(1)
							25	1.8	+2					
							44	3.3	+2					
							55	5.1	+2	6	6	6		
.15	$Co(NH_3)_5(OH)^{+2} + Co^*(NH_3)_5^{+2} \longrightarrow Co^*(NH_3)_5(OH)^{+2} + Co(NH_3)_5^{+2}$	H_2O	not given		$\mu=1.0$	kAB	25	5.9	-5	13.5	5	5	*	(2)
							64	8.3	-4					
.16	$Co(NH_3)_5(NH_2)^{+2} + Co^*(NH_3)_5^{+2} \longrightarrow Co^*(NH_3)_5(NH_2)^{+2} + Co(NH_3)_5^{+2}$	H_2O	not given		$\mu=1.0$	kAB	25	3.1	-6	13.5	3	4	*	(2)
							64	4.5	-5					
.17	$Co(NH_3)_6^{+3} + Co^*(NH_3)_5^{+2} \longrightarrow Co^*(NH_3)_6^{+3} + Co(NH_3)_5^{+2}$	H_2O	not given		(see .16)								*	(2)
			$10^2A=9$; $10^2B=5$	NH_4OH NH_4Cl pH=10.7	5.7 0.174 $\mu=1$	kAB	45	<6.4	-7					(12)
		NH_3	$10^3A=10^3B=2-4$			kAB	25	6	-5					
							45	7	-4	23	4	12		(7)
.18	$Co(NH_3)_6^{+3} + Co^*(NH_2CH_2CH_2NH_2)_3^{+2} \longrightarrow Co^*(NH_2CH_2CH_2NH_2)_3^{+3} + Co(NH_3)_6^{+2}$	H_2O	$10^2A=10^2B=9$	$NH_2CH_2CH_2NH_2$	0.3-1	kAB	25	2.0	-2				*	(12)
.19	$Co(NH_2CH_2CH_2NH_2)_3^{+3} + Co^*(NH_3)_6^{+2} \longrightarrow Co^*(NH_3)_6^{+3} + Co(NH_2CH_2CH_2NH_2)_3^{+2}$	H_2O	$10^2A=9$; $10^2B=5$	NH_4OH NH_4Cl	5.7 0.174 $\mu=1$	kAB	45	<1	-7				*	(12)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.20	$Co(NH_2CH_2CH_2NH_2)_3^{+3} + Co^*(NH_2CH_2CH_2NH_2)_3^{+2} \longrightarrow$ $Co^*(NH_2CH_2CH_2NH_2)_3^{+3} + Co(NH_2CH_2CH_2NH_2)_3^{+2}$	H_2O	$10^2A=2\text{-}9;\ 10^2B=2\text{-}9$	ClO_4^-	$\mu=1$	kAB	25	5.2	-5				*	(12) (13)
					$\mu=2$		25	1.02	-4					
					$\mu=1$		45	2.4	-4	14				
					$\mu=2$		45	5.4	-4	16				
.21	$Co(C_{10}H_8N_2)_3^{+3} + Co^*(C_{10}H_8N_2)_3^{+2} \longrightarrow$ $Co^*(C_{10}H_8N_2)_3^{+3} + Co(C_{10}H_8N_2)_3^{+2}$ $C_{10}H_8N_2$ = dipyridyl	H_2O	not stated			kAB	45	1.9	+1				*	(6)
.22	$Co(C_{12}H_8N_2)_3^{+3} + Co^*(C_{12}H_8N_2)_3^{+2} \longrightarrow$ $Co^*(C_{12}H_8N_2)_3^{+3} + Co(C_{12}H_8N_2)_3^{+2}$ $C_{12}H_8N_2$ = phenanthroline	H_2O	not stated	NO_3^-		kAB	0	3.6	0				*	(6)
							20	4.5	0					
	Iridium exchange between oxidation states													
.23	$Na_3IrCl_6 + Na_2Ir^*Cl_6 \longrightarrow Na_3Ir^*Cl_6 + Na_2IrCl_6$	H_2O	$10^4A=10^4B=1$	HCl	1.0	kAB	1	>3	+2				*	(16)
	Platinum exchange between oxidation states													
.24	$PtCl_6^{-2} + Pt^*Cl_4^{-2} \longrightarrow Pt^*Cl_6^{-2} + PtCl_4^{-2}$	H_2O	$10^3A=10^3B=5$	HCl	0.01		25	$t_{\frac{1}{2}} = 3600$					*	(15)

COMMENTS

Reaction: **(.1)** Reaction considered by (8), (14) and (17) to proceed through simultaneous reactions (.1) and (.2) with individual rate constants k_1 and k_2. At constant $[H^+]$ a combined second order constant is measured where: $k=k_1+k_2K[H^+]^{-1}$ and $K=[Fe(OH)^{+2}][H^+]/[Fe^{+3}]=2.6\times10^{-4}$ at 0°C with $\Delta H=12.5$ in H_2O and $K=1.2\times10^{-3}$ at 21°C in D_2O. For exchange in presence of addends see (.3) (.4) (.5) (.6) (.7) (.8) (.9) (.10) (.11) (.12). **(.2)** One of the simultaneous reactions considered to be responsible for exchange in H_2O or D_2O solutions. Calculated from hydrogen ion dependence of total exchange rate and equilibrium constant for formation of $Fe(OH)^{+2}$ see (.1). **(.3) (.4) (.5)** Simultaneous reactions considered partially responsible for exchange in solutions containing fluoride ion. Rate constants calculated using the following equilibrium constants and enthalpies of reaction: $[FeF^{+2}][Fe^{+3}]^{-1}[F^-]^{-1}=9.7\times10^4$, $\Delta H=3.3$ k.cals.; $[FeF_2^{+}][FeF^{+2}]^{-1}[F^-]^{-1}=7.8\times10^3$, $\Delta H=900$ cals.; $[FeF_3][FeF_2^{+}]^{-1}[F^-]^{-1}=1\times10^3$, $\Delta H=-4.8$ k.cals. **(.6) (.7)** Simultaneous reactions to (.1) and (.2) considered partially responsible for exchange in presence of chloride ion. Rate constants calculated using the following equilibrium constants and enthalpies of reaction: $[FeCl^{+2}][Fe^{+3}]^{-1}[Cl^-]^{-1}=1.03$, $\Delta H=8.6$; $[FeCl_2^{+}][FeCl^{+2}]^{-1}[Cl^-]^{-1}=0.32$, $\Delta H=(8.6)$. The enthalpy change for the latter equilibrium not determined and assumed the same as for the former equilibrium. Rate constants calculated for (.7) are therefore less accurate. **(.9) (.10)** Simultaneous reactions to (.1) and (.2) considered partially responsible for exchange in presence of thiocyanate ion. Equilibrium constants for formation of complexes used in calculating the specific rate constants listed. Values of these equilibrium constants not stated.

(.11) (.12) Simultaneous reactions to (.1) and (.2) considered partially responsible for exchange in presence of oxalic acid. Equilibrium constants for formation of complexes and ionization constants of oxalic acid used to calculate the second order specific reaction rate constants for the ion species listed. **(.13)** Authors observe no appreciable effect of light or glass surface upon exchange rate. **(.14)** Selected data. Authors state rate is independent of acidity for $[NH_3]=0.16-0.47$ in which range it is 5th order in NH_3. At lower $[NH_3]$ apparent order with respect to NH_3 is between 1 and 2. Solution contained added salts $NaNO_3$, NH_4NO_3 and $NaClO_4$. Activation energy listed is an average value. Rate constant at highest temperature deviates toward higher E. **(.15)** Temperature range and concentrations not given. **(.16)** Temperatures range and concentrations not given. Reaction considered to be rate determining step for reaction (.17). **(.17)** Proceeds through a preequilibrium forming $Co(NH_3)_5(NH_2)^{+2}$ followed by (.16) as rate determining step according to (2) with $K_{64.50}=3.5\times10^{-11}=\dfrac{[Co(NH_3)_5(NH_2)^{+2}][H^+]}{[Co(NH_3)_6^{+3}]}$. Catalysis by O_2 observed by both (7) and (12) and rate data was not accurately reproducible. **(.18)** Followed by rapid reaction of $Co(NH_3)_6^{+2}+3NH_2CH_2CH_2NH_2 \longrightarrow Co(NH_2CH_2CH_2NH_2)_3^{+2}+6NH_3$ so that all Co^{+2} was in diamine complex at end of reaction.

COMMENTS *(continued)*

(.19) Only 0.15% exchange in 27 hours. No correction for possible catalysis by O_2. **(.20)** Exchange catalyzed by O_2, powdered silica, powdered glass, nickel wire, polystyrene and parafin, Catalysis by surface of glass vessel estimated to be about 4%. **(.21) (.22)** Rate constant gives order of magnitude only and rate law not verified. Results are from a personal communication to authors from Neumann and Baker. **(.23)** Lower limit of exchange rate based on at least 90% exchange in 42 seconds with assumed second order rate law provided exchange was not separation-induced. **(.24)** Exchange catalyzed by UV light giving 100% exchange in 300 seconds. Light catalyzed reaction inhibited by $IrCl_6^{-2}$.

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HYDROGEN SUBSTITUTION

Hydrogen substitution by oxygen (alkoxy)(phenoxy) on boron hydrides

Liquid phase

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

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$B_{10}H_{14} + 30 CH_3OH \longrightarrow 10B(OCH_3)_3 + 22H_2$	C_6H_6	A≃0.1; B≃0.1			$-dA/dt=kAB$	25	7.3	-7	32	1	17	*	(1)
.2	$B_{10}H_{14} + 30 C_2H_5OH \longrightarrow 10B(OC_2H_5)_3 + 22H_2$	C_6H_6	A≃0.1; B≃0.1			$-dA/dt=kAB$	25	5.2	-7	26	3	12	*	(1) (2)
.3	$B_{10}H_{14} + 30 n\text{-}C_3H_7OH \longrightarrow 10B(OC_3H_7)_3 + 22H_2$	C_6H_6	A≃0.1; B≃0.1			$-dA/dt=kAB$	25	5.4	-7	24	5	11	*	(1)
.4	$B_{10}H_{14} + 30 (CH_3)_2CHOH \longrightarrow 10 B[OCH(CH_3)_2]_3 + 22H_2$	C_6H_6	A≃0.1; B≃0.1			$-dA/dt=kAB$	25	2.0	-7	16	9	4	*	(1)
.5	$B_{10}H_{14} + 30 n\text{-}C_4H_9OH \longrightarrow 10 B(OC_4H_9)_3 + 22H_2$	C_6H_6	A≃0.1; B=0.1-3			$-dA/dt=kAB$	25	6.7	-7	25	3	12	*	(1)
			0.08 ≃5				25	6.2	-7					(2)
			" "	I_2	0.25×[A]		25	1.9	-6					
			" "		0.5×[A]		25	3.6	-6					
			" "		=[A]		25	4.7	-6					
			" "		1.5×[A]		25	5.9	-6					
			" "		2.0×[A]		25	6.8	-6					
			" "		2.5×[A]		25	7.3	-6					
			" "		3.0×[A]		25	8.1	-6					
		$C_6H_5CH_3$	0.1 0.1				25	6.7	-7					(1)
		CCl_4	" "				25	6.0	-7					
		cyclo-C_6H_{12}	" "				25	6.0	-7					
		$B(OC_4H_9)_3$	" "				25	6.0	-7					
		CS_2	" "				25	5.4	-7					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.5	$B_{10}H_{14} + 30\,n\text{-}C_4H_9OH \longrightarrow$ *(continued)*	Dioxane	$A \simeq 0.1; B = 0.1$			$-dA/dt = kAB$	25	5.4	-7				*	(1)
		$C_6H_5NO_2$	" "				25	3.7	-7					
		$n\text{-}C_7H_{16}$	" "				25	3.4	-7					
		$CH_3COOC_2H_5$	" "				25	2.7	-7					
		Dimethylcellosolve	" "				25	2.7	-7					
.6	$B_{10}H_{14} + 30\,n\text{-}C_4H_9OD \longrightarrow 10\,B(OC_4H_9)_3 + 22(H_2, HD, D_2)$	C_6H_6	$A \simeq 0.08; B \simeq 5$			$-dA/dt = kAB$	25	2.8	-7	27	2	13	*	(2)
.7	$B_{10}D_{14} + 30\,n\text{-}C_4H_9OH \longrightarrow 10\,B(OC_4H_9)_3 + 22(H_2, HD, D_2)$	CCl_4	$A \simeq 0.1; B \simeq 0.1$			$-dA/dt = kAB$	25	3.4	-7				*	(1)
.8	$B_{10}H_{14} + 30\,(CH_3)_2CHCH_2OH \longrightarrow 10\,B[OCH_2CH(CH_3)_2]_3 + 22H_2$	C_6H_6	$A \simeq 0.1; B \simeq 0.1$			$-dA/dt = kAB$	25	4.8	-7	21	8	8	*	(1)
.9	$B_{10}H_{14} + 30\,C_2H_5(CH_3)CHOH \longrightarrow 10\,B[OCH(CH_3)C_2H_5]_3 + 22H_2$	C_6H_6	$A \simeq 0.1; B \simeq 0.1$			$-dA/dt = kAB$	25	3.8	-7	16	3	5	*	(1)
.10	$B_{10}H_{14} + 30\,(CH_3)_3COH \longrightarrow 10\,B[OC(CH_3)_3]_3 + 22H_2$	C_6H_6	$A \simeq 0.1; B \simeq 0.1$			$-dA/dt = kAB$	25	9	-9				*	(1)
.11	$B_{10}H_{14} + 30\,n\text{-}C_5H_{11}OH \longrightarrow 10\,B(OC_5H_{11})_3 + 22H_2$	C_6H_6	$A \simeq 0.08; B \simeq 5$			$-dA/dt = kAB$	25	7.4	-7	25	2	12	*	(2)
		CCl_4	.1 .1				25	7.4	-7					(1)
.12	$B_{10}H_{14} + 30\,(CH_3)_2CHCH_2CH_2OH \longrightarrow 10\,B[OCH_2CH_2CH(CH_3)_2]_3 + 22H_2$	C_6H_6	$A \simeq 0.08; B \simeq 5$			$-dA/dt = kAB$	25	7.6	-7	23	1	9	*	(2)
.13	$B_{10}H_{14} + 30\,CH_3CH_2(CH_3)CHCH_2OH \longrightarrow 10\,B[OCH_2CH(CH_3)CH_2CH_3]_3 + 22H_2$	C_6H_6	$A \simeq 0.08; B \simeq 5$			$-dA/dt = kAB$	25	9.5	-7	18	1	7	*	(2)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.14	$B_{10}H_{14} + 30\,C_2H_5(CH_3)_2COH \longrightarrow 10\,B[OC(CH_3)_2C_2H_5]_3 + 22H_2$	$CH_3COOC_2H_5$	$A \simeq 0.1; B \simeq 0.1$	$-dA/dt = k\,AB$	25	2	-9				*	(1)
.15	$B_{10}H_{14} + 30\,C_6H_5CH_2OH \longrightarrow 10\,B(OCH_2C_6H_5)_3 + 22H_2$	C_6H_6	$A \simeq 0.1; B \simeq 0.1$ 0.08 5	$-dA/dt = k\,AB$	25 25	8.0 2.9	-7 -7	 25	 7	 11	*	(1) (2)
.16	$B_{10}H_{14} + 30\,C_6H_5CH_2OD \longrightarrow 10\,B(OCH_2C_6H_5)_3 + 22\,(H_2, HD, D_2)$	C_6H_6	$A \simeq 0.08; B \simeq 5$	$-dA/dt = k\,AB$	25	1.7	-7	27	9	12	*	(2)
.17	$B_{10}H_{14} + 30\,cyclo\text{-}C_5H_9OH \longrightarrow 10\,B(OC_5H_9)_3 + 22H_2$	C_6H_6	$A \simeq 0.08; B \simeq 5$	$-dA/dt = k\,AB$	25	3.4	-7	27	3	13	*	(2)
.18	$B_{10}H_{14} + 30\,C_6H_5OH \longrightarrow 10\,B(OC_6H_5)_3 + 22H_2$	$CH_3COOC_2H_5$ C_6H_6	$A \simeq 0.1; B \simeq 0.1$ 4 5	$-dA/dt = k\,AB$	25 48	3 7.0	-9 -10				*	(1) (2)
.19	$B_{10}H_{14} + 30\,m\text{-}CH_3C_6H_4OH \longrightarrow 10\,B(OC_6H_4CH_3)_3 + 22H_2$	C_6H_6	$A \simeq 4; B \simeq 5$	$-dA/dt = k\,AB$	48	1.9	-9				*	(2)
.20	$B_{10}H_{14} + 30\,p\text{-}CH_3C_6H_4OH \longrightarrow 10\,B(OC_6H_4CH_3)_3 + 22H_2$	C_6H_6	$A \simeq 4; B \simeq 5$	$-dA/dt = k\,AB$	48	1.5	-9				*	(2)
.21	$B_{10}H_{14} + 30\,CH_3OCH_2CH_2CH_2CH_2OH \longrightarrow$ $10\,B(OCH_2CH_2CH_2CH_2OCH_3)_3 + 22H_2$	C_6H_6	$A \simeq 0.08; B \simeq 5$	$-dA/dt = k\,AB$	25	7.6	-7	24	7	11	*	(2)
.22	$B_{10}H_{14} + 30\,HC{:}OCH_2(C_2H_5)CHOH \longrightarrow 10\,B[OCH(C_2H_5)CH_2CH{:}O]_3 + 22H_2$	CCl_4	$A \simeq 0.1; B \simeq 0.1$	$-dA/dt = k\,AB$	25	2	-9				*	(1)
.23	$B_{10}H_{14} + 30\,CH_2FCH_2OH \longrightarrow 10\,B(OCH_2CH_2F)_3 + 22H_2$	CH_2FCH_2OH	$A \simeq 0.08$	$-dA/dt = k\,AB$	25	4.0	-7				*	(2)
.24	$B_{10}H_{14} + 30\,CH_2ClCH_2OH \longrightarrow 10\,B(OCH_2CH_2Cl)_3 + 22H_2$	CH_2ClCH_2OH C_6H_6	$A \simeq 0.08;$ $A \simeq 0.08; B \simeq 5$	$-dA/dt = k\,AB$	25 25 37	9.6 8.8 2.5	-8 -8 -7	 19	 1	 7	*	(2)
.25	$B_{10}H_{14} + 30\,CH_2BrCH_2OH \longrightarrow 10\,B(OCH_2CH_2Br)_3 + 22H_2$	C_6H_6	$A \simeq 0.08; B \simeq 5$	$-dA/dt = k\,AB$	25	8.0	-8				*	(2)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.26	$B_{10}H_{14} + 30\ CH_2ICH_2OH \longrightarrow 10\ B(OCH_2CH_2I)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	25	1.8	-8				*	(2)
.27	$B_{10}H_{14} + 30\ CHCl_2CH_2OH \longrightarrow 10\ B(OCH_2CHCl_2)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	37	8.1	-10				*	(2)
.28	$B_{10}H_{14} + 30\ CCl_3CH_2OH \longrightarrow 10\ B(OCH_2CCl_3)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	37	1.0	-10				*	(2)
.29	$B_{10}H_{14} + 30\ CH_2ClCH_2CH_2CH_2OH \longrightarrow 10\ B(OCH_2CH_2CH_2CH_2Cl)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	25	8.2	-7	25	2	12	*	(2)
.30	$B_{10}H_{14} + 30\ CH_3CHClCH_2CH_2OH \longrightarrow 10\ B(OCH_2CH_2CHClCH_3)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	25	4.2	-7	27	3	13	*	(2)
.31	$B_{10}H_{14} + 30\ CH_3CH_2CHClCH_2OH \longrightarrow 10\ B(OCH_2CHClCH_2CH_3)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	25	1.8	-7	18	3	6	*	(2)
.32	$B_{10}H_{14} + 30\ CH_2ClCH_2CHClCH_2OH \longrightarrow 10B(OCH_2CHClCH_2CH_2Cl)_3 + 22H_2$	C_6H_6	$A \simeq 0.08$; $B \simeq 5$	$-dA/dt = kAB$	25	1.7	-7				*	(2)
.33	$B_{10}H_{14} + 30\ o\text{-}ClC_6H_4OH \longrightarrow 10\ B(OC_6H_4Cl)_3 + 22H_2$	C_6H_6	$A \simeq 4$; $B \simeq 5$	$-dA/dt = kAB$	48	3.0	-10				*	(2)
.34	$B_{10}H_{14} + 30\ m\text{-}ClC_6H_4OH \longrightarrow 10\ B(OC_6H_4Cl)_3 + 22H_2$	C_6H_6	$A \simeq 4$; $B \simeq 5$	$-dA/dt = kAB$	48	5.0	-10				*	(2)
.35	$B_{10}H_{14} + 30\ p\text{-}ClC_6H_4OH \longrightarrow 10\ B(OC_6H_4Cl)_3 + 22H_2$	C_6H_6	$A \simeq 4$; $B \simeq 5$	$-dA/dt = kAB$	48	2.0	-10				*	(2)
.36	$B_{10}H_{12}I_2 + 30\ n\text{-}C_4H_9OH \longrightarrow 10\ B(OC_4H_9)_3 + 20H_2 + 2HI$	CCl_4	$A \simeq 0.1$; $B \simeq 0.1$	$-dA/dt = kAB$	25	1.8	-6				*	(1)

COMMENTS

Literature: (1) followed rate of evolution of H_2 only for first 5 to 10% reaction. Calculated rate of decrease of A on basis of 1 A per 22 H_2. Measured rate constants at 25.20, 27.34, 29.89 and 32.20 but only values at 25.2 were listed. Values of E and A of limited accuracy since only 7° temperature range used for calculations. Concentrations of reactants not clearly stated. (2) followed rate of evolution of H_2 only for first 5% reaction after an induction period of one to five minutes. Calculated rate of decrease of [A] on basis of one mole A per 22 mole H_2. Temperature range used for calculating E not indicated so accuracy of values uncertain. (3) observed strong monoprotic acid nature of $B_{10}H_{14}$ in alcohols and aqueous solutions. Measured rate of acid formation in aqueous dioxane mixture by conductimetric method and found rate law first order in $B_{10}H_{14}$ with E=14 kcal. but gave no time units for constants calculated.

LITERATURE

(1) H.C. Beachell, T.R. Meeker, *ACS* 1956, **78**, 1796. (2) H.C. Beachell, W.C. Schar, *ACS* 1958, **80**, 2943. (3) G.A. Guter, G.W. Schaeffer, *ACS* 1956, **78**, 3546.

HYDROGEN SUBSTITUTION
Hydrogen replacing IVth group element on aromatic C

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	2,6-$(CH_3)_2C_6H_3COCH_3 + H_2O \longrightarrow (CH_3)_2C_6H_4 + CH_3COOH$	72.5% H_2SO_4	$A \sim 0.3$			kA	40	3.48	-6				*	(2)
		75.0					40	9.3	-6					
		77.5					40	2.35	-5					
		80.0					40	5.25	-5					
		82.5					40	1.13	-4					
		85.0					40	2.18	-4					
		87.5					40	3.68	-4					
		90.0					40	5.10	-4					
		96.0					40	6.89	-4					
.2	2,4,6-$(CH_3)_3C_6H_2COCH_3 + H_2O \longrightarrow (CH_3)_3C_6H_3 + CH_3COOH$	80.4% H_2SO_4	$A \sim 0.3$			kA	30	2.78	-3					(2)
							40	6.33	-3	16	4	8		
		83.5					30	5.16	-3					
		87.1					30	8.0	-3					
		90.4% CH_3HSO_4					20	5.46	-5					
		99.0					20	4.60	-4					
.3	$C_6H_5Si(CH_3)_3 + H^+ \longrightarrow C_6H_6 + Si(CH_3)_3^+$	CH_3COOH	$A \sim 0.4$; B=2.35	H_2O	7.23	kA	25	6.4	-5				*	(1)
.4	*m*-$CH_3C_6H_4Si(CH_3)_3 + H^+ \longrightarrow CH_3C_6H_5 + Si(CH_3)_3^+$	CH_3COOH	$A \sim 0.4$; B=2.35	H_2O	7.23	kA	25	1.38	-4				*	(1)
.5	*m*-$C_2H_5C_6H_4Si(CH_3)_3 + H^+ \longrightarrow C_2H_5C_6H_5 + Si(CH_3)_3^+$	CH_3COOH	$A \sim 0.4$; B=2.35	H_2O	7.23	kA	25	1.42	-4				*	(1)
.6	*m*-$(CH_3)_2CHC_6H_4Si(CH_3)_3 + H^+ \longrightarrow (CH_3)_2CHC_6H_5 + Si(CH_3)_3^+$	CH_3COOH	$A \sim 0.4$; B=2.35	H_2O	7.23	kA	25	1.51	-4				*	(1)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.7	$m\text{-}(CH_3)_3CC_6H_4Si(CH_3)_3 + H^+ \longrightarrow (CH_3)_3CC_6H_5 + Si(CH_3)_3^+$	CH_3COOH	$A \simeq 0.4$; B=2.35	H_2O	7.23	kA	25	1.80	-4				*	(1)
.8	$C_6H_5Si(C_2H_5)_3 + H^+ \longrightarrow C_6H_6 + Si(C_2H_5)_3^+$	CH_3COOH	$A \simeq 0.4$; B=2.35	H_2O	7.23	kA	25	2.7	-6				*	(1)
.9	$m\text{-}CH_3C_6H_4Si(C_2H_5)_3 + H^+ \longrightarrow CH_3C_6H_5 + Si(C_2H_5)_3^+$	CH_3COOH	$A \simeq 0.4$; B=2.35	H_2O	7.23	kA	25	6.4	-5				*	(1)
.10	$m\text{-}C_2H_5C_6H_4Si(C_2H_5)_3 + H^+ \longrightarrow C_2H_5C_6H_5 + Si(C_2H_5)_3^+$	CH_3COOH	$A \simeq 0.4$; B=2.35	H_2O	7.23	kA	25	7.8	-5				*	(1)
.11	$m\text{-}(CH_3)_2CHC_6H_4Si(C_2H_5)_3 + H^+ \longrightarrow (CH_3)_2CHC_6H_5 + Si(C_2H_5)_3^+$	CH_3COOH	$A \simeq 0.4$; B=2.35	H_2O	7.23	kA	25	8.6	-5				*	(1)
.12	$m\text{-}(CH_3)_3CC_6H_4Si(C_2H_5)_3 + H^+ \longrightarrow (CH_3)_3CC_6H_5 + Si(C_2H_5)_3^+$	CH_3COOH	$A \simeq 0.4$; B=2.35	H_2O	7.23	kA	25	9.8	-5				*	(1)

COMMENTS

Reaction. **(.1)** At H_2SO_4 concentrations greater than 85% parallel sulfonation reaction occurs. See 312.462. **(.3)-(.12)** Reactions carried out in glacial acetic acid to which had been added aqueous HCl sufficient to make solution 2.35M in HCl and 7.23M in H_2O. Units converted to seconds from original minutes. Reaction pseudo first order over course but, dependence upon B not determined.

LITERATURE

(1) R.A. Benkeser, R.A. Hickner, D.I. Hoke, *ACS* 1958, **80**, 2279. (2) W.M. Schubert, H.K. Latourette, *ACS* 1952, **74**, 1829.

HYDROGEN SUBSTITUTION
H on aliphatic C with group I metal

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

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$C_2H_5Li + CH_3OC_6H_5 \longrightarrow C_2H_6 + o\text{-}CH_3OC_6H_4Li$	C_6H_6	10A=2-5; B=2-7	kA^2B^2/B_o^2	30	2.45	-6				*	(²)
					40	7.6	-6	21	5	9		
.2	$(p\text{-}NO_2C_6H_4)_3CNa + C_2H_5OH \longrightarrow (p\text{-}NO_2C_6H_4)_3CH + C_2H_5ONa$	85% C_2H_5OH, 15% $C_6H_5CH_3$ by vol.	10^6A=3-13; 10^2B=1-40	kA	-78	7.0	-5					(¹)
					-70	2.2	-4					
					-60	8.6	-4					
					-50	3.0	-3					
					-40	8.5	-3					
					-30	2.3	-2					
					-20	5.3	-2	11.3	4	8		
.3	$(p\text{-}NO_2C_6H_4)_3CH + C_2H_5ONa \longrightarrow (p\text{-}NO_2C_6H_4)_3CNa + C_2H_5OH$	85% C_2H_5OH, 15% $C_6H_5CH_3$ by vol.	10^6A=3-13; 10^2B=1-40	kAB	-78	8.3	-4					(¹)
					-70	3.0	-3					
					-60	1.21	-2					
					-50	4.6	-2					
					-40	1.50	-1					
					-30	4.4	-1					
					-20	1.5	0					

COMMENTS

Reaction: (.1) B_o in rate law represents initial concentration of B in any run. Authors consider true rate law may be kAB^2 but observed complexity may be due to variation of dielectric constant of solvent with concentration changes and linear dependence of simple rate constant with dielectric constant. Also reaction followed by evolution of ethane which is partially soluble in reaction medium.

LITERATURE

(¹) E. F. Caldin, J. C. Trickett, *TFS* 1953, **49**, 772. (²) T. F. Fagley, E. Klein, *ACS* 1955, **77**, 786.

HYDROGEN SUBSTITUTION

Hydrogen replacing halogen on aliphatic C

Liquid phase

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
.1	$n\text{-}C_4H_9Br + LiAlH_4 \longrightarrow n\text{-}C_4H_{10}, LiBr, [(AlH_3)_x]$	$(C_2H_5)_2O$	A=1-3; 10B=4-5	k AB	25	1.3	-4
.2	$n\text{-}C_4H_9Br + [(AlH_3)_x] \longrightarrow n\text{-}C_4H_{10}$	$(C_2H_5)_2O$	A=1-3; 10B=4-5	k AB	25	4.5	-6
.3	$n\text{-}C_5H_{11}Br + LiAlH_4 \longrightarrow n\text{-}C_5H_{12}, LiBr, [(AlH_3)_x]$	$(C_2H_5)_2O$	10A=6-25; 10B=5-6	k AB	25	1.23	-4
.4	$n\text{-}C_5H_{11}Br + [(AlH_3)_x] \longrightarrow n\text{-}C_5H_{12}$	$(C_2H_5)_2O$	10A=6-25; 10B=5-6	k AB	25	2.7	-6

COMMENTS

Reaction of first hydrogen of $LiAlH_4$ much more rapid than second. Rate constants calculated assuming reaction (.2) consecutive to (.1) and (.4) consecutive to (.3). Form of aluminum hydride after loss of first hydrogen postulated as $[(AlH_3)_x]$ but not verified.

LITERATURE

D.J. Malter, J.H. Wotiz, C.A. Hollingsworth, *ACS* 1956, **78**, 1311.

HYDROGEN SUBSTITUTION
H on aromatic C replaced by C
Aromatic alkylation

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	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$CH_2{:}CH_2 + C_6H_6 \longrightarrow CH_3CH_2C_6H_5$	B	A=1-1.5	$AlBr_3$	0.06-0.1	$k\,A[AlBr_3]$	9	1.4	-3	*	(27)
.2	$C_6H_5CH{:}CH_2 + C_6H_5OH \longrightarrow C_6H_5CH(CH_3)C_6H_4OH(o+p)$	CH_3COOH	10A=2.8-4.2; 10B=8-9	$HClO_4$	0.025	$k\,AB$	25	1.1	-5	*	(17)
			6.4		0.05		25	3.0	-5		
			8-9		0.05		25	2.4	-5		
			11		0.05		25	2.2	-5		
			14.5		0.05		25	1.6	-5		
			8-9		0.075		25	3.9	-5		
			8-9		0.10		25	5.1	-5		
	Aldehyde alkylating agent										
.3	$CH_2O + 1,3,5\text{-}(CH_3)_3C_6H_3 + HCl \longrightarrow 2,4,6\text{-}(CH_3)_3C_6H_2CH_2Cl + H_2O$	AW90*	10A=2; 10B=2; 10C=4			$k\,AB$	60	5.9	-4	*	(37)
			4 2 4				60	5.6	-4		
			4 4 4				60	5.1	-4		
			2 2 0	H_2SO_4	0.6		60	2.23	-3		
			2 2 1.5		0.6		60	2.17	-3		
			2 2 2		0		60	1.7	-4		
			2 2 6				60	1.28	-3		
			2 2 8				60	1.88	-3		
			2 2 10				60	3.2	-3		
.4	$CH_2O + C_6H_5OH \longrightarrow 2\text{-}HOC_6H_4CH_2OH$	H_2O	A=6; B=1.8	NaOH	1.8	$k\,AB$	30	1.05	-5	*	(18)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
.5	$CH_2O + C_6H_5OH \longrightarrow 4\text{-}HOC_6H_4CH_2OH$	H_2O	A=6; B=1.8	NaOH	1.8	k AB	30	6.2	-6		*	(18)
.6	$CH_2O + 2\text{-}HOC_6H_4CH_2OH \longrightarrow 2,4\text{-}(HOCH_2)_2C_6H_3OH$	H_2O	A=3.2; B=1.6	NaOH	1.6	k AB	30	7.3	-6		*	(18)
.7	$CH_2O + 2\text{-}HOC_6H_4CH_2OH \longrightarrow 2,6\text{-}(HOCH_2)_2C_6H_3OH$	H_2O	A=3.2; B=1.6	NaOH	1.6	k AB	30	8.7	-6		*	(18)
.8	$CH_2O + 4\text{-}HOC_6H_4CH_2OH \longrightarrow 2,4\text{-}(HOCH_2)_2C_6H_3OH$	H_2O	A=2.1; B=1.2	NaOH	1.2	k AB	30	7.5	-6		*	(18)
.9	$CH_2O + 2,4\text{-}(HOCH_2)_2C_6H_3OH \longrightarrow 2,4,6\text{-}(HOCH_2)_3C_6H_2OH$	H_2O	10A=9; 10B=8	NaOH	0.8	k AB	30	9.1	-6			(18)
.10	$CH_2O + 2,6\text{-}(HOCH_2)_2C_6H_3OH \longrightarrow 2,4,6\text{-}(HOCH_2)_3C_6H_2OH$	H_2O	A=1.3; B=1.2	NaOH	1.2	k AB	30	4.2	-5			(18)
Carbinol alkylating agent												
								time		% reacted		
.11	$C_6H_5CH_2OH + C_6H_6 \longrightarrow C_6H_5CH_2C_6H_5 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.128		83	4,800		50	*	(40)
							83	10,600		90		
.12	$C_6H_5CH_2OH + C_6H_5CH_3 \longrightarrow C_6H_5CH_2C_6H_4CH_3 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.064		113	5,100		50	*	(40)
					0.064		113	8,600		90		
					0.128		113	650		50		
					0.128		113	1,300		90		
.13	$C_6H_5CH_2OH + C_6H_5OCH_3 \longrightarrow C_6H_5CH_2C_6H_4OCH_3 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.032	k A	158	9.2	-5			(40)
					0.064		158	3.8	-4			
								time		% reacted		
.14	$C_6H_5CH_2OH + 1,4\text{-}(CH_3)_2C_6H_4 \longrightarrow C_6H_5CH_2C_6H_3(CH_3)_2 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.064		140	970		50	*	(40)
								1,800		90		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	Comments	Literature
								k^o	n			
								time		% reacted		
.15	$C_6H_5CH_2OH + 1,3,5\text{-}(CH_3)_3C_6H_3 \longrightarrow C_6H_5CH_2C_6H_2(CH_3)_3 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.064		166	290		50	*	(40)
								540		90		
.16	$p\text{-}CH_3C_6H_4CH_2OH + C_6H_5OCH_3 \longrightarrow p\text{-}CH_3C_6H_4CH_2C_6H_4OCH_3 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.016	kA	158	3.8	-4			(14)
.17	$p\text{-}CH_3OC_6H_4CH_2OH + C_6H_5OCH_3 \longrightarrow p\text{-}CH_3OC_6H_4CH_2C_6H_4OCH_3 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.00025	kA	158	4.3	-4			(14)
.18	$p\text{-}ClC_6H_4CH_2OH + C_6H_5OCH_3 \longrightarrow p\text{-}ClC_6H_4CH_2C_6H_4OCH_3 + H_2O$	B	10A=2.5	$p\text{-}CH_3C_6H_4SO_3H$	0.032	kA	158	3.9	-5			(14)
.19	$(C_6H_5)_2CHOH + C_6H_6 \longrightarrow (C_6H_5)_3CH + H_2O$	CH_3COOH	10^2A=1.5; B=0.29; M=0.55	H_2SO_4	3.75	kAB	25	3.6	-6			(3)
					3.89		25	4.7	-6			
					4.89		25	2.63	-5			
.20	$(C_6H_5)_2CHOH + C_6H_5OCH_3 \longrightarrow (C_6H_5)_2CHC_6H_4OCH_3 + H_2O$	CH_3COOH	10^3A=3; 10^2B=3; M=0	H_2SO_4	0.306	kAB	25	1.53	-4		*	(1)
			0.55		0.377		25	9.0	-5			
			2.2 2.6		0.633		25	5.5	-4			(3)
			3 3		0.909		25	1.18	-3			(1)
			0		0.919		25	3.27	-3			
			2.2 2.6 0.55		1.15		25	4.2	-3			(3)
			3 3 0		1.43		25	1.25	-2			(1)
			0.28		1.43		25	1.02	-2			
			0.55		1.43		25	8.0	-3			
			1.11		1.43		25	4.8	-3			
			2.78		1.43		25	3.5	-4			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.20	$(C_6H_5)_2CHOH + C_6H_5OCH_3 \longrightarrow$ *(continued)*	CH_3COOH	$10^3A=2.2;\ 10^2B=2.6;\ M=0.55$	H_2SO_4	1.59	kAB	25	1.11	-2	*	(3)
					1.77		25	1.56	-1		
			4.2 4.1 0	BF_3	0.23		25	1.23	-4		(19)
					0.46		25	5.7	-4		
					0.57		25	9.2	-4		
					0.80		25	2.27	-3		
					1.03		25	4.5	-3		
					1.16		25	6.9	-3		
			6.2		1.16		25	6.5	-3		
			8.3		1.16		25	6.3	-3		
			4.1		1.39		25	1.15	-2		
.21	$(C_6H_5)_2CHOH + 4\text{-}DC_6H_4OCH_3 \longrightarrow (C_6H_5)_2CHC_6H_4OCH_3 + HOD$	CH_3COOH	$10^3A=3;\ 10^2B=2$	H_2SO_4	0.919	kAB	25	3.4	-3		(1)
					1.22		25	8.7	-3		
					1.48		25	1.41	-2		
.22	$(C_6H_5)_2CHOH + o\text{-}C_6H_4(OCH_3)_2 \longrightarrow (C_6H_5)_2CHC_6H_3(OCH_3)_2 + H_2O$	CH_3COOH	$10^4A=9.5;\ 10^3B=9.3;\ M=0.55$	H_2SO_4	0.476	kAB	25	1.56	-3		(3)
					0.641		25	3.3	-3	*	
					0.864		25	8.1	-3		
			7.9		0.993		25	1.02	-2		
			9.5		1.10		25	1.41	-2		
					1.29		25	1.99	-2		
			7.9		1.39		25	2.22	-2		
					1.59		25	4.08	-2		
			9.5		1.66		25	4.04	-2		
			5.8 6.2 0	BF_3	0.805		25	1.49	-2		(19)

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
.23	$(C_6H_5)_2CHOH + m\text{-}C_6H_4(OCH_3)_2 \longrightarrow (C_6H_5)_2CHC_6H_3(OCH_3)_2 + H_2O$	CH_3COOH	$10^3A=1.5$; $10^2B=1.5$; $M=0.55$	H_2SO_4	0.102	kAB	25	2.81	-3		(3)
			2.0 2-4 0		0.107		25	3.6	-3		
			1.5 1.5 0.55		0.153		25	5.4	-3		
					0.204		25	9.8	-3		
					0.224		25	1.30	-2		
					0.407		25	4.5	-2		
			1.4 0	BF_3	0.173		25	3.7	-2		(19)
.24	$(C_6H_5)_2CHOH + p\text{-}C_6H_4(OCH_3)_2 \longrightarrow (C_6H_5)_2CHC_6H_3(OCH_3)_2 + H_2O$	CH_3COOH	$10^3A=1.3$; $10^2B=1.5$; $M=0.55$	H_2SO_4	1.18	kAB	25	2.77	-3	*	(3)
			1.6 1.6		1.24		25	2.90	-3		
					1.39		25	4.9	-3		
			1.3 1.5		1.73		25	7.5	-3		
			1.6 1.6		1.74		25	1.05	-2		
			1.3 1.5		2.07		25	1.58	-2		
			1.6 1.6		2.23		25	1.94	-2		
			1.3 1.5		2.48		25	2.86	-2		
			1.3	BF_3	0.805		25	1.70	-3		(19)
.25	$(C_6H_5)_2CHOH + 1,3,5\text{-}(CH_3)_3C_6H_3 \longrightarrow$ $2,4,6\text{-}(CH_3)_3C_6H_2CH(C_6H_5)_2 + H_2O$	CH_3COOH	$10^3A=5$; $10^2B=3$	H_2SO_4	0.729	kAB	25	2.59	-4	*	(1)
			3-7		0.981		25	6.3	-4		
					1.16		25	1.12	-3		
					1.36		25	1.83	-3		
					1.7		25	3.8	-3		
.26	$(p\text{-}ClC_6H_4)_2CHOH + 1,3,5\text{-}(CH_3)_3C_6H_3 \longrightarrow$ $(p\text{-}ClC_6H_4)_2CHC_6H_2(CH_3)_3 + H_2O$	CH_3COOH	$10^2A=1$; $B=0.1$; $M=0.55$	H_2SO_4	0.886	kAB	25	1.87	-4		(1)
					1.19		25	4.87	-4		
					1.58		25	1.25	-3		
					1.91		25	2.72	-3		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-ac ion law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
					wt. %									
.27	$(C_6H_5)_3COH + 2\text{-}CH_3C_6H_4OH \longrightarrow 2\text{-}CH_3\text{-}4\text{-}(C_6H_5)_3CC_6H_3OH + H_2O$	CH_3COOH	$10^2A=2.5$; $B=0.1$; $M \simeq 2.8$	H_2SO_4	12.4	k AB	25	8.1	-5					(^{4})
			2-20; 0.02-0.2		14.7		25	1.93	-4					
					17.2		25	3.7	-4					
					21.0		25	5.3	-4					
					4.9		55	5.2	-5					
					10		55	6.5	-4					
					12.4		55	1.52	-3					
					15		55	3.0	-3					
					20-22		55	4.8	-3					
					25		55	4.6	-3					
					30		55	3.6	-3					
					40		55	1.7	-3					
						$k_o[(C_6H_5)_3C^+]B$	25	7.4	-4					
							55	6.2	-3	13.5	1.0	7		
	Ether alkylating agent													
								time		% reacted				
.28	$(C_6H_5CH_2)_2O + 2C_6H_6 \longrightarrow 2C_6H_5CH_2C_6H_5 + H_2O$	B	A=0.125	$p\text{-}CH_3C_6H_4SO_3H$	0.128		83	4,300		50				(^{42})
								8,600		90				
.29	$(C_6H_5CH_2)_2O + 2C_6H_5CH_3 \longrightarrow 2C_6H_5CH_2C_6H_4CH_3 + H_2O$	B	A=0.125	$p\text{-}CH_3C_6H_4SO_3H$	0.064		113	5,000		50				(^{40})
								10,000		90				
.30	$(C_6H_5CH_2)_2O + 2C_6H_5OCH_3 \longrightarrow 2C_6H_5CH_2C_6H_4OCH_3 + H_2O$	B	A=0.125	$p\text{-}CH_3C_6H_4SO_3H$	0.128		158	2,060		50				(^{40})
								5,500		90				
.31	$[(C_6H_5)_2CH]_2O + 2C_6H_6 \longrightarrow 2(C_6H_5)_3CH + H_2O$	B	A=0.125	$p\text{-}CH_3C_6H_4SO_3H$	0.256		83	830		50				(^{40})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Literature
								k^o	n		A^o	n	
								time		% reacted			
.32	$[(C_6H_5)_2CH]_2O + 2C_6H_5CH_3 \longrightarrow 2(C_6H_5)_2CHC_6H_5CH_3 + H_2O$	B	A=0.125	p-$CH_3C_6H_4SO_3H$	0.064		113	430		20			(40)
							113	1,260		30			
							113	16,300		40			
							113	28,000		50			
							113	37,400		60			
							113	46,000		70			
							113	50,000		80			
							113	52,000		90			
							113	56,000		100			
.33	$[(C_6H_5)_2CH]_2O + 2C_6H_5OCH_3 \longrightarrow 2(C_6H_5)_2CHC_6H_4OCH_3 + H_2O$	B	A=0.125	p-$CH_3C_6H_4SO_3H$	0.004		158	3,700		50			(40)
							158	6,900		90			
Ester alkylating agent													
.34	$(C_6H_5)_2CHOOCCH_3 + C_6H_5OCH_3 \longrightarrow$ $(C_6H_5)_2CHC_6H_4OCH_3 + CH_3COOH$	CH_3COOH	$10^3A=3$; $10^2B=3$	H_2SO_4	0.612	k AB	25	1.16	-3				(1)
					1.122		25	6.3	-3				
			27 46	$ZnCl_2$	0.351		25	3.5	-6				(2)
					0.70		25	4.2	-5				
					1.05		25	1.71	-4				
					1.40		25	5.0	-4				
.35	$CH_3COOHgCH_2CH_2OOCCH_3 + C_6H_5OCH_3 \longrightarrow$ $CH_3COOHgCH_2CH_2C_6H_4OCH_3 + CH_3COOH$	Ac86.5*	10A=1-2; B=1	$HClO_4$	1.60	k AB	25	1.54	-4				(28)
			2 1		0.995		25	7.7	-6				
					1.60		25	4.6	-5				
					2.03		25	1.90	-4				
		Ac75*	2 1		1.00		25	3.7	-6				
					1.32		15	2.45	-6				
					1.32		25	9.9	-6				
					1.32		35	3.4	-5	23.3	1.2	12	

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.35	$CH_3COOHgCH_2CH_2OOCCH_3 + C_6H_5OCH_3 \longrightarrow$ *(continued)*	Ac75*	10A=5.3; B=1	$HClO_4$	1.60	kAB	25	1.48	-5					(^{28})
			3.5		1.60		25	1.92	-5					
			0.4-2 0.5-1		1.60		25	2.37	-5					
			2 1		1.99		25	8.4	-5					
					2.40		25	3.21	-4					
		Ac67.4*	0.5 0.05		1.60		25	1.14	-5					
		Ac61.4*	0.5 0.1		1.60		25	7.6	-6					
		Ac50*	0.5 0.1		1.60		25	4.0	-6					
		Ac40*	0.5 0.1		1.60		25	2.0	-6					
	Alkyl-aryl sulfonate alkylating agent													
.36	$\underset{(A)}{C_6H_5CH_2OSC_2C_6H_5} + \underset{(B)}{C_6H_6} \longrightarrow \underset{(L)}{(C_6H_5)_2CH_2} + \underset{(M)}{C_6H_5SO_3H}$	B	10^2A=1-5;			kAM^2	30	7.0	-2					(^{36})
			10^3M=5-50				40	9.7	-2					
							50	1.41	-1					
							60	1.92	-1	6.8	6	3		
.37	$\underset{(A)}{p\text{-}CH_3C_6H_4CH_2OSO_2C_6H_5} + \underset{(B)}{C_6H_6} \longrightarrow \underset{(L)}{p\text{-}CH_3C_6H_4CH_2C_6H_5} + \underset{(M)}{C_6H_5SO_3H}$	B	10^3A=4-8;			kAM^2	36	7.4	-1					(^{36})
			10^3M=2-3				42	7.7	-1					
							50	9.7	-1	3.9	4	2		
.38	$\underset{(A)}{m\text{-}NO_2C_6H_4CH_2OSO_2C_6H_5} + \underset{(B)}{C_6H_6} \longrightarrow \underset{(L)}{m\text{-}NO_2C_6H_4CH_2C_6H_5} + \underset{(M)}{C_6H_5SO_3H}$	B	10^2A=3-7;			kAM^2	50	1.61	-4					(^{36})
			10^2M=1.7-4				55	2.79	-4					
							60	5.16	-4	25	1	13		
.39	$\underset{(A)}{p\text{-}ClC_6H_4CH_2OSO_2C_6H_5} + \underset{(B)}{C_6H_6} \longrightarrow \underset{(L)}{p\text{-}ClC_6H_4CH_2C_6H_5} + \underset{(M)}{C_6H_5SO_3H}$	B	10^2A$\simeq$1;			kAM^2	40	3.45	-2					(^{36})
			10^3M=3-7				50	7.0	-2					
							60	1.45	-1	15	8	8		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
Alkyl halide alkylating agent														
.40	$CH_3Br + C_6H_6 \longrightarrow CH_3C_6H_5 + HBr$	B	A$\simeq$0.4	(X) $GaBr_3$	0.03-0.04	kX^2	15	2.3	-3				*	(47)
							25	5.0	-3					
							40	1.31	-2	12.5	6	6		
		1, 2, 4-$Cl_3C_6H_3$	10A=1-2.5; 10B=3-7	Al_2Br_6	0.01-0.036	kABX	25	3.7	-3					(33)
							35	8.9	-3					
							45	1.35	-2	14.7	2	8		
.41	$CH_3Br + C_6H_5CH_3 \longrightarrow C_6H_4(CH_3)_2 + HBr$ (55.7%*o*, 9.9%*m*, 34.4%*p*)	B	A=0.3 0.4-0.47	$GaBr_3$	0.03 0.022-.025	kX^2	0	2.78	-3				*	(16) (47)
							15	1.43	-2					
							25	2.8	-2					
							40	7.7	-2	12.1	3	8		
		1, 2, 4-$Cl_3C_6H_3$	A=0.18; B=0.70	Al_2Br_6	0.035	kABX	25	1.82	-2					(33)
.42	$CH_3I + C_6H_5CH_3 \longrightarrow C_6H_4(CH_3)_2 + HI$ (49%*o*, 11%*m*, 40%*p*)	B	A$\simeq$1.2	Al_2Br_6	~1.2	kA	0	~5	-4				*	(11)
.43	$C_2H_5Br + C_6H_6 \longrightarrow C_2H_5C_6H_5 + HBr$	B	A$\simeq$0.4 0.2-0.8	$GaBr_3$	0.02-0.03 0.01-0.04	kX^2	15	7.5	-2				*	(46) (47)
							25	1.56	-1					(5) (46) (47)
							40	4.25	-1	12.4	2	8		(46) (47)
		1, 2, 4-$Cl_3C_6H_3$	A=0.1-0.15; B=0.2-0.5	Al_2Br_6	0.013-0.017	kABX	25	2.32	-1					(33)
							35	4.5	-1					
							45	6.1	-1	11	2	7		
.44	$C_2H_6Br + C_6H_5CH_3 \longrightarrow C_2H_6C_6H_4CH_3 + HBr$	B	A=0.40-0.42	$GaBr_3$	0.018-0.027	kX^2	15	1.92	-1				*	(47)
							25	3.9	-1					
							40	1.02	0	12	2	8		
		1, 2, 4-$Cl_3C_6H_3$	A=0.13; B=0.25-0.4	Al_2Br_6	0.017	kABX	25	6.5	-1					(33)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
				(X)										
.45	$n\text{-}C_3H_7Br + C_6H_6 \longrightarrow n\text{-}C_3H_7C_6H_5 + HBr$	B	A=0.41	$GaBr_3$	0.042-0.047	kX^2	15	1.57	-1				*	(47)
							25	3.3	-1	13	1	9		
.46	$n\text{-}C_3H_7Br + C_6H_5CH_3 \longrightarrow$	B	A=0.4	$GaBr_3$	0.024-0.027	kX^2	15	2.37	-1				*	(47)
	$n\text{-}C_3H_7C_6H_4CH_3 + HBr$						25	4.5	-1					
							40	1.22	0	11.8	2	8		
.47	$(CH_3)_2CHBr + C_6H_6 \longrightarrow (CH_3)_2CHC_6H_5 + HBr$	B	A~0.4	$GaBr_3$	~0.01	kX^2	25	~4	+3				*	(16) (47)
.48	$(CH_3)_2CHBr + C_6H_5CH_3 \longrightarrow$	B	A~0.6	$GaBr_3$	0.01	kX^2	-78	3.5	-1					(16)
	$(CH_3)_2CHC_6H_4CH_3 + HBr$		0.3-0.7		0.003-0.03		-64	1.46	0					
			0.3-0.5		0.006-0.01		-45	8.0	0	8.3	7	8		
			0.4		0.05		+25	~7	+3					(47)
.49	$(CH_3)_3CCl + C_6H_5CH_3 \longrightarrow$	B	A=0.42	HF	402 mm.		25	$t_{\frac{1}{2}}$ 14,000					*	(20)
	$(CH_3)_3CC_6H_4CH_3 + HCl$													
.50	$(CH_3)_3CCl + C_6H_5OH \longrightarrow$	B	10 A=3-5; B=10.5-10.8			kA	45	1.39	-4				*	(26)
	$(CH_3)_3CC_6H_4OH + HCl$		5 10.5				50	2.08	-4					(25) (26)
							55	3.3	-4	17.1				(26)
			5-7 8.7	$\phi(CH_3)_2C_6H_4$	1.27		45	5.5	-5					
			7.6		2.00		45	2.1	-5					
			5 9	$CH_2(CH_2)_4O$	1.37		50	7.9	-5					(25)
			9.9		0.556		50	9.7	-5					
			9.4		1.09		50	4.3	-5					
			9.1	dioxane	1.46		50	2.7	-5					
			10.3		0.295		50	1.09	-4					
			9.9		0.616		50	6.5	-5					
			9.5		1.07		50	2.5	-5					
			9.1		1.52		50	7.7	-6					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.50	$(CH_3)_3CCl + C_6H_5OH \longrightarrow$ *(continued)*	B	10A=6; B=7.9	1, 2-$Cl_2C_2H_4$	2.18	kA	45	6.1	-5				*	(26)
			5 9.9	1, 4-$Cl_2C_4H_8$	0.58		45	1.19	-4					
			8.9		1.25		45	8.5	-5					
			7.6		2.18		45	3.6	-5					
			5.3		4.11		45	7.6	-6					
			7 8.0	$C_6H_5NO_2$	2.38		35	6.2	-5					
			8.6		1.42		45	1.27	-4					
			7.6		2.41		45	1.12	-4					
			5.4		4.31		45	4.3	-5					
.51	$(CH_3)_3CCl + p\text{-}CH_3C_6H_4OH \longrightarrow$ $2\text{-}(CH_3)_3C\text{-}4\text{-}CH_3C_6H_3OH + HCl$	B	A=0.5			kA	45	3.2	-5					(26)
.52	$(CH_3)_3CBr + C_6H_5CH_3 \longrightarrow (CH_3)_3CC_6H_4CH_3 + HBr$	B	A=0.4	(X) $GaBr_3$	0.047	kX^2	25	~2	+4					(47)
.53	$C_2H_5(CH_3)_2CCl + C_6H_5OH \longrightarrow$ $p\text{-}C_2H_5(CH_3)_2CC_6H_4OH + HCl$	B	A=0.5; B=11			kA	45	9.6	-5					(26)
							50	1.62	-4					
							55	1.80	-4	15	1	6		
.54	$(CH_3)_2CH(CH_3)_2CCl + C_6H_5OH \longrightarrow$ $p\text{-}(CH_3)_2CH(CH_3)_2CC_6H_4OH + HCl$	B	10A=5-7; B=11			kA	45	2.7	-5					(26)
							50	3.8	-5					
							55	6.6	-5	16	2	6		
.55	$C_6H_5CH_2Cl + C_6H_6 \longrightarrow (C_6H_5)_2CH_2 + HCl$	B	10^2A=5	(X) $C_6H_5SO_3H$	0.36	kAX^2	80	1.39	-5					(36)
					0.50		80	1.41	-5					
					0.65		80	1.45	-5					
.56	$C_6H_5CH_2Cl + C_6H_5CH_3 \longrightarrow C_6H_5CH_2C_6H_4CH_3 + HCl$	B	A=0.8; $10^3[AlCl_3]$=4.4	(X) $FeCl_3$	9×10^{-8}	kA	30	4.9	-3				*	(34)
			0.5 3.0		4×10^{-7}		30	1.6	-2					
			0.8 4.0		1×10^{-5}		30	2.3	-2					
			4.1		1×10^{-4}		30	1.3	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.57	$p\text{-}NO_2C_6H_4CH_2Cl + C_6H_6 \longrightarrow p\text{-}NO_2C_6H_4CH_2C_6H_4 + HCl$	$C_6H_5NO_2$	A=0.334; B=1.0	(X) $AlCl_3$	0.334	kA	25	1.59	-6				*	(^{8})
						kABX	25	4.78	-6					
			B=50 vol.%				25	2.4	-6					
			83 vol.%				25	1.9	-6					
		B	A≃0.3				30	8.5	-5				(^{8}) (^{38})	
.58	$p\text{-}NO_2C_6H_4CH_2Cl + m\text{-}(CH_3)_2C_6H_4 \longrightarrow p\text{-}NO_2C_6H_4CH_2C_6H_3(CH_3)_2 + HCl$	$C_6H_5NO_2$	A=0.334; B=1.0	$AlCl_3$	0.33	kA	25	8.0	-6				*	(^{8})
						kABX	25	2.4	-5					
.59	$3,4\text{-}Cl_2C_6H_3CH_2Cl + C_6H_6 \longrightarrow 3,4\text{-}Cl_2C_6H_3CH_2C_6H_5 + HCl$	$C_6H_5NO_2$	A=0.11-1; B=0.335	$AlCl_3$	0.333	kABX	15	5.3	-4				*	(^{8})
			0.335		0.1-0.67		25	2.4	-3					
			0.333 0.5-1		0.333		25	1.75	-3					
			1.67		0.333		25	1.40	-3					
			0.11-1 0.335		0.333		35	5.5	-3	20	6	10		
		$C_6H_5NO_2$+10 vol.% *cyclo*-$C_6H_{11}CH_3$	0.333 0.335		0.333		25	2.3	-3					
		40	0.335		0.333		25	1.54	-3					
		60	0.335		0.333		25	1.19	-3					
.60	$3,4\text{-}Cl_2C_6H_3CH_2Cl + C_6H_5CH_3 \longrightarrow 3,4\text{-}Cl_2C_6H_3CH_2C_6H_4CH_3 + HCl$	$C_6H_5NO_2$	A=0.33; B=6.5	$AlCl_3$	0.33	kA	25	4.3	-4				*	(^{8})
						kABX	25	2.6	-3					
.61	$3,4\text{-}Cl_2C_6H_3CH_2Cl + m\text{-}(CH_3)_2C_6H_4 \longrightarrow 3,4\text{-}Cl_2C_6H_3CH_2C_6H_3(CH_3)_2 + HCl$	$C_6H_5NO_2$	A=0.33; B=1.0	$AlCl_3$	0.33	kA	25	1.01	-3				*	(^{8})
			0.33		0.33		25	4.7	-4					
			0.11		0.33		25	2.5	-4					
.62	$3,4\text{-}Cl_2C_6H_3CH_2Cl + C_6H_5Cl \longrightarrow 3,4\text{-}Cl_2C_6H_3CH_2C_6H_4Cl + HCl$	$C_6H_5NO_2$	A=0.33; B=1.0	$AlCl_3$	0.33	kABX	25	7.4	-4				*	(^{8})
			0.33		0.33		25	9.1	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.63	$3,4\text{-}Cl_2C_6H_3CH_2Cl + 3,4\text{-}Cl_2C_6H_3CH_2C_6H_5 \longrightarrow (3,4\text{-}Cl_2C_6H_3CH_2)_2C_6H_4 + HCl$	$C_6H_5NO_2$	A=0.33; B=1.0	(X) $AlCl_3$	0.333	kA	25	3.0	-4		(^{8})
						kABX	25	9	-4		
.64	$(C_6H_5)_2CHCl + C_6H_5OCH_3 \longrightarrow (C_6H_5)_2CHC_6H_4OCH_3 + HCl$ (A) (B) (L) (M)	CH_3COOH	10^2A=2.7; B=0.46; M=0	$ZnCl_2$	0.046	kAB	25	4.1	-5		(^{2})
					0.092		25	8.9	-5		
					0.184		25	2.25	-4		
					0.351		25	2.64	-4		
			M=0.022		0.351		25	7.7	-4		
			0		0.922		25	2.8	-4		
					1.20		25	5.4	-4		
					1.48		25	9.1	-4		
.65	$(p\text{-}CH_3OC_6H_4)_2CHCl + C_6H_5OCH_3 \longrightarrow (p\text{-}CH_3OC_6H_4)_3CH + HCl$ (A) (B) (L) (M)	CH_3COOH	10^2A=1; B=0.213	$ZnCl_2$	0.011		25	1.36	-4		(^{2})
					0.022		25	2.6	-4		
					0.054		25	7.5	-4		
					0.108		25	1.03	-3		
					0.162		25	5.1	-4		
					0.216		25	1.40	-4		
					0.323		25	1.11	-4		
					0.398		25	1.90	-4		
					0.597		25	5.8	-4		
					0.796		25	1.21	-3		
.66	$(C_6H_5)_3CCl + C_6H_5OH \longrightarrow p(C_6H_5)_3CC_6H_4OH + HCl$	$o\text{-}Cl_2C_6H_4$	A$\sim$0.6; B=0.315	$dP_M/dt=k_2AB+k_3ABP_M$			88	$k_2$3.4	-3	*	(^{24})
							88	$k_3$2.9	-5		
			0.61				88	$k_2$7.2	-3		
							88	$k_3$9.0	-5		
			0.91				88	$k_2$1.31	-2		
							88	$k_3$1.36	-4		
			1.18				88	$k_2$1.81	-2		
							88	$k_3$2.2	-4		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.67	$(C_6H_5)_3CCl + o\text{-}CH_3C_6H_4OH \longrightarrow$ $2\text{-}CH_3\text{-}4\text{-}(C_6H_5)_3CC_6H_3OH + HCl$	$o\text{-}Cl_2C_6H_4$	A=0.35-0.6; B=1.3 M=0-117 mm of Hg.	$dP_M/dt = k_2AB + k_3ABP_M$			88 88	$k_2$5.7 $k_3$1.68	-3 -4				*	(^{24})
Acyl-halide alkylating agent														
.68	$CH_3COCl + C_6H_6 \longrightarrow CH_3COC_6H_5 + HCl$	$ClCH_2CH_2Cl$	A=0.02-0.2; B=0.1-0.4	(X) $AlCl_3$	0.2	$k[A\cdot X]B$	0	3.4	-4				*	(^{14})
							25	2.65	-3	13.3	2	7		
.69	$CH_3COCl + C_6H_5CH_3 \longrightarrow CH_3COC_6H_4CH_3 + HCl$ (o=1.17%: m=1.25%; p=97.6%)	$ClCH_2CH_2Cl$	10^2A=5; B=0.1-0.2	$AlCl_3$	0.05	$k[A\cdot X]B$	25	3.40	-1				*	(^{14})
.70	$CH_3COCl + C_6H_5C_2H_5 \longrightarrow CH_3COC_6H_4C_2H_5 + HCl$	$ClCH_2CH_2Cl$	10^2A=7.5; B=0.1	$AlCl_3$	0.075	$k[A\cdot X]B$	25	3.43	-1				*	(^{13})
.71	$CH_3COCl + C_6H_5CH(CH_3)_2 \longrightarrow$ $CH_3COC_6H_4CH(CH_3)_2 + HCl$	$ClCH_2CH_2Cl$	10^2A=6; 10^2B=8	$AlCl_3$	0.06	$k[A\cdot X]B$	25	3.40	-1				*	(^{13})
.72	$CH_3COCl + C_6H_5C(CH_3)_3 \longrightarrow$ $CH_3COC_6H_4C(CH_3)_3 + HCl$	$ClCH_2CH_2Cl$	10^2A=7.5; B=0.1-0.15	$AlCl_3$	0.075	$k[A\cdot X]B$	25	3.04	-1				*	(^{13})
.73	$CH_3COCl + C_6H_5Cl \longrightarrow CH_3COC_6H_4Cl + HCl$	B	A$\simeq$0.5	$AlCl_3$	= A	$k[A\cdot X]B$	20	2.65	-5					(^{44})
							35	8.3	-5					
							45	1.82	-4					
							55	3.3	-4	13.5	4	5		
.74	$CH_3COCl + C_6H_5Br \longrightarrow CH_3COC_6H_4Br + HCl$	B	A$\simeq$0.5	$AlCl_3$	= A	$k[A\cdot X]B$	25	2.8	-5					(^{44})
							35	5.9	-5					
							45	1.29	-4					
							55	2.6	-4	14.3	9	5		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.75	$C_2H_5COCl + C_6H_6 \longrightarrow C_2H_5COC_6H_5 + HCl$	B	not stated	(X) $AlCl_3$	= A	$k[A \cdot X]B$	0	>1	-2					$(^{44})$
.76	$C_2H_5COCl + C_6H_5CH_3 \longrightarrow C_2H_5COC_6H_4CH_3 + HCl$	B	not stated	$AlCl_3$	= A	$k[A \cdot X]B$	0	>1	-2					$(^{44})$
.77	$C_2H_5COCl + C_6H_5Cl \longrightarrow C_2H_5COC_6H_4Cl + HCl$	B	A≃0.5	$AlCl_3$	= A	$k[A \cdot X]B$	45	1.05	-4					$(^{44})$
							60	2.6	-4					
							70	5.1	-4	12.9	9	4		
.78	$C_2H_5COCl + C_6H_5Br \longrightarrow C_2H_5COC_6H_4Br + HCl$	B	A≃0.5	$AlCl_3$	= A	$k[A \cdot X]B$	35	3.5	-5					$(^{44})$
							45	7.8	-5					
							55	1.64	-4					
							65	3.2	-4	14.8	1.2	6		
.79	$n\text{-}C_3H_7COCl + C_6H_6 \longrightarrow n\text{-}C_3H_7COC_6H_5 + HCl$	B	not stated	$AlCl_3$	= A	$k[A \cdot X]B$	0	>1	-2					$(^{44})$
.80	$n\text{-}C_3H_7COCl + C_6H_5CH_3 \longrightarrow n\text{-}C_3H_7COC_6H_4CH_3 + HCl$	B	not stated	$AlCl_3$	= A	$k[A \cdot X]B$	0	>1	-2					$(^{44})$
.81	$n\text{-}C_3H_7COCl + C_6H_5Cl \longrightarrow n\text{-}C_3H_7COC_6H_4Cl + HCl$	B	A≃0.5	$AlCl_3$	= A	$k[A \cdot X]B$	35	5.9	-5					$(^{44})$
							50	1.51	-4					
							60	2.6	-4					
							70	5.0	-4	12.9	9	4		
.82	$n\text{-}C_3H_7COCl + C_6H_5Br \longrightarrow n\text{-}C_3H_7COC_6H_4Br + HCl$	B	A≃0.5	$AlCl_3$	= A	$k[A \cdot X]B$	50	8.7	-5					$(^{44})$
							60	1.74	-4					
							70	3.2	-4					
							80	5.6	-4	14.0	3	5		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.83	$(CH_3)_3CCOCl + C_6H_6 \longrightarrow (CH_3)_3CC_6H_5 + CO + HCl$	B	$10^2A=2.5-30$	(X) $AlCl_3$	0.0315	kA	19.4	1.6	-5				*	(^{23})
					0.0158		20.4	5	-6					
					0.0315		20.4	1.8	-5					
					0.050		20.4	3.7	-5					
					0.100		20.4	1.2	-4					
					0.150		20.4	2.4	-4					(^{22}) (^{23})
					0.200		20.4	4.1	-4					(^{23})
					0.250		20.4	6.1	-4					
					0.0315		22.4	3.0	-5					
					0.125		22.4	3.4	-4					
		CS_2	A=0.32; B=0.32	$AlCl_3$	0.32	kA	20	2.5	-3					(^{41})
.84	$(CH_3)_3CCOCl + C_6H_5CH_3 \longrightarrow (CH_3)_3CC_6H_4CH_3 + CO + HCl$	CS_2	A~0.3; B~0.3	$AlCl_3$	~0.3	kA	20	~2.5	-3				*	(^{42})
.85	$(CH_3)_3CCOCl + C_6H_5OCH_3 \longrightarrow p\text{-}(CH_3)_3CC_6H_4OCH_3 + CO + HCl$	B	A=0.314;	$AlCl_3$	~0.025	kA	20	7.7	-6				*	(^{42})
		CS_2	0.315; B=0.315	$AlCl_3$	~0.022		20	7.0	-6					
			0.063 0.063		~0.027		20	8.5	-6					
.86	$C_6H_5COCl + C_6H_6 \longrightarrow (C_6H_5)_2CO + HCl$	A	B=0.45;	$AlCl_3$	0.231	kBX	25	5.0	-5				*	(^{9}) (^{10})
					0.231		40	1.67	-4					(^{9})
					0.231		50	3.8	-4	15.8	2	7		
		A+25% *cyclo*C_6H_{12}			0.231		50	9.5	-5					
		51%	0.46		0.239		50	3.0	-5					
		74%	0.48		0.245		50	1.75	-5					
		$C_6H_5NO_2$	10A=2-6; 10B=2-8		0.40	kABX	25	5.7	-5					(^{15})
			A=B=0.4		0.2		25	8.3	-5					
			0.4		0.8		25	3.5	-5					
			0.2		0.2	kA$^{3.5}$	25	2.4	-4					(^{6})
			0.4		0.4		25	1.03	-4					(^{6}) (^{7})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.86	$C_6H_5COCl + C_6H_6 \longrightarrow$ *(continued)*	CH_2ClCH_2Cl	A=B=0.222	(X) $AlCl_3$	0.222	$k[A\cdot X]B$	25	8.6	-6				*	(31)
			0.3		0.3		25	9.3	-6					(12)
		B	$A\simeq 0.5$	$AlCl_3$	= A	$k[A.X]B$	40	4.1	-5					(44)
							50	6.8	-5					
							60	1.35	-4					
							68	2.1	-4	13.4	9	4		
.87	$C_6H_5COCl + C_6H_5CH_3 \longrightarrow C_6H_5COC_6H_4CH_3 + HCl$	A	B=0.38	BCl_3	0.38	$k\,BX$	25	3.5	-6				*	(30)
			1.1		0.38		25	2.8	-6					
			A=7.4-8; 0.2-0.9	$SnCl_4$	0.2-0.9	$k\,ABX_o$	25	2.06	-6					
			0.4		0.15		40	4.9	-6					
			0.6		0.3		50	8.0	-6	10.9	2	2		
			10B=2-9	$AlCl_3$	0.2-0.9	$k\,BX$	0	7.2	-4					(10)
							15	2.38	-3					
							25	5.4	-3	13.3	3	7	(10)	(32)
		B	$A\simeq 0.5$	$AlCl_3$	= A	$k[A\cdot X]B$	15	2.14	-4					(44)
							20	4.4	-4					
							30	8.5	-4					
							35	1.29	-3					
							40	2.1	-3	15.0	6	7		
		B	$A\simeq 0.2$		0.09	$k\,A$	25	1.9	-3					(34)
			0.1		0.05		30	1.5	-3					
			0.5		0.26		30	3.2	-3					
			1.0		0.51		30	5.9	-3					
			0.2	$FeCl_3$	0.07		25	1.3	-3					
		$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$k\,A^{3.5}$	25	8.2	-2					(7)
			0.2		0.2		25	3.5	-2				(6) (7)	(15)
			0.4		0.4		25	$\underline{1.61}$	-2					
		CH_2Cl_2	0.097; B=0.3		0.097	$k(A\cdot X)B$	25	6.3	-4					(32)
			.3-5 0.3-0.7		0.31		25	8.0	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
				(X)										
.87	$C_6H_5COCl + C_6H_5CH_3 \longrightarrow$ *(continued)*	CH_2ClCH_2Cl	A=0.3 B=0.1	$AlCl_3$	0.1	$k(A\cdot X)B$	0	8.7	-5				*	(32)
			0.1-0.3; 0.1-0.3		0.1		25	7.7	-4					
			0.4 0.1-0.2		0.2		25	9.6	-4					
			.222 .222		.222		25	1.13	-3				(29)	(31)
			0.5 0.1-0.3		0.3		25	1.09	-3					(32)
			0.3 0.1		0.1		35	1.59	-3	13.9	1.2	7		
		$1,2\text{-}Cl_2C_6H_4$	0.095 0.3		0.095		25	4.3	-4					
			0.29		0.29		25	4.9	-4					
			0.68		0.68		25	7.8	-4					
		$1,2,4\text{-}Cl_3C_6H_3$	0.09 0.1-0.3		0.09		25	1.8	-4					
			0.3-0.5		0.27		25	3.0	-4					
			0.64 0.28		0.64		25	5.0	-4					
.88	$C_6H_5COCl + C_6H_5C_2H_5 \longrightarrow C_6H_5COC_6H_4C_2H_5 + HCl$	$C_6H_5NO_2$	A=B=0.2	$AlCl_3$	0.2	$kA^{3.5}$	25	3.1	-2				*	(6)
		CH_2ClCH_2Cl	A=B=0.1		0.1	$k(A\cdot X)B$	25	6.6	-4					(13)
.89	$C_6H_5COCl + C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5COC_6H_4CH(CH_3)_2 + HCl$	$C_6H_5NO_2$	A=B=0.2	$AlCl_3$	0.2	$kA^{3.5}$	25	3.0	-2				*	(6)
		CH_2ClCH_2Cl	A=B=0.1		0.1	$k(A\cdot X)B$	25	6.1	-4					(13)
.90	$C_6H_5COCl + C_6H_5C(CH_3)_3 \longrightarrow C_6H_5COC_6H_4C(CH_3)_3 + HCl$	A	10B=2-9	$AlCl_3$	0.2-0.9	kBX	25	3.6	-3				*	(10)
		C_6H_5NO	A=B=0.2		0.2	$kA^{3.5}$	25	2.58	-2					(6)
		CH_2ClCH_2Cl	0.1		0.1	$k(A\cdot X)B$	25	4.6	-4					(13)
.91	$C_6H_5COCl + 1,2\text{-}(CH_3)_2C_6H_4 \longrightarrow$	A	10B=2-9	$AlCl_3$	0.2-0.9	kBX	25	5.6	-2				*	(10)
	$C_6H_5COC_6H_3(CH_3)_2 + HCl$	$C_6H_5NO_2$	A=B=0.2		0.2	$kA^{3.5}$	25	3.27	-1					(7)
		CH_2ClCH_2Cl	0.1		0.1	$k(A\cdot X)B$	25	9.1	-3					(12)
			0.2		0.2		25	1.51	-2					(31)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.92	$C_6H_5COCl + 1,3\text{-}(CH_3)_2C_6H_4 \longrightarrow C_6H_5COC_6H_3(CH_3)_2 + HCl$	A	B=0.2–0.9	(X) $AlCl_3$	0.2–0.9	kBX	25	1.95	-1	*	(10)
		$C_6H_5NO_2$	A=B=0.1		0.1	$kA^{3.5}$	25	2.12	0		(7)
			0.2		0.2		25	9.2	-1		
		CH_2ClCH_2Cl	0.1		0.1	$k(A\cdot X)B$	25	2.58	-2		(12)
.93	$C_6H_5COCl + 1,4\text{-}(CH_3)_2C_6H_4 \longrightarrow C_6H_5COC_6H_3(CH_3)_2 + HCl$	$C_6H_5NO_2$	A=B=0.2	$AlCl_3$	0.2	$kA^{3.5}$	25	3.4	-2	*	(7)
		CH_2ClCH_2Cl	0.1		0.1	$k(A\cdot X)B$	25	1.59	-3		(12)
			0.22		0.22		25	2.1	-3		(29)
.94	$C_6H_5COCl + 1,2\text{-}(CH_2)_2C_6H_4 \longrightarrow C_6H_5COC_6H_3(CH_2)_2 + HCl$	CH_2ClCH_2Cl	A=B=0.2	$AlCl_3$	0.2	$k(A\cdot X)B$	25	4.1	-2		(31)
.95	$C_6H_5COCl + 1,2\text{-}(CH_2)_3C_6H_4 \longrightarrow C_6H_5COC_6H_3(CH_2)_3 + HCl$	CH_2ClCH_2Cl	A=B=0.2	$AlCl_3$	0.2	$k(A\cdot X)B$	25	2.86	-2		(31)
.96	$C_6H_5COCl + 1,2\text{-}(CH_2)_4C_6H_4 \longrightarrow C_6H_5COC_6H_3(CH_2)_4 + HCl$	CH_2ClCH_2Cl	A=B=0.2	$AlCl_3$	0.2	$k(A\cdot X)B$	25	3.4	-2		(31)
.97	$C_6H_5COCl + 1,2,3\text{-}(CH_3)_3C_6H_3 \longrightarrow C_6H_5COC_6H_2(CH_3)_3 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	7.0	0	*	(7)
.98	$C_6H_5COCl + 1,2,4\text{-}(CH_3)_3C_6H_3 \longrightarrow C_6H_5COC_6H_2(CH_3)_3 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	4.0	0	*	(7)
.99	$C_6H_5COCl + 1,3,5\text{-}(CH_3)_3C_6H_3 \longrightarrow C_6H_5COC_6H_2(CH_3)_3 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	6.7	+1	*	(7)
.100	$C_6H_5COCl + 1,2,3,4\text{-}(CH_3)_4C_6H_2 \longrightarrow C_6H_5COC_6H(CH_3)_4 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	1.88	+1	*	(7)
.101	$C_6H_5COCl + 1,2,3,5\text{-}(CH_3)_4C_6H_2 \longrightarrow C_6H_5COC_6H(CH_3)_4 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	1.12	+2	*	(7)
.102	$C_6H_5COCl + 1,2,4,5\text{-}(CH_3)_4C_6H_2 \longrightarrow C_6H_5COC_6H(CH_3)_4 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	5.8	0	*	(7)
.103	$C_6H_5COCl + (CH_3)_5C_6H \longrightarrow C_6H_5COC_6(CH_3)_5 + HCl$	$C_6H_5NO_2$	A=B=0.1	$AlCl_3$	0.1	$kA^{3.5}$	25	7.3	+1	*	(7)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
				(X)										
.104	$C_6H_5COCl + C_6H_5Cl \longrightarrow p\text{-}C_6H_5COC_6H_4Cl + HCl$	A	10B=2-9	$AlCl_3$	0.2-0.9	$k(A \cdot X)B$	70	3.08	-5				*	(10)
			1-3	$GaCl_3$	0.1-0.5	kX^2B/X_o	25	2.45	-4					(30)
							40	8.1	-4					
							52	2.16	-3	15.4	5	7		
			~2	$SbCl_5$	~0.2		25	6.4	-4					
			3-5	$FeCl_3$	0.3-0.5		25	2.83	-4					
		B	A≃0.5	$AlCl_3$	= A	$k[A \cdot X]B$	90	2.37	-5					(44)
							100	5.2	-5					
							110	1.13	-4					
							120	2.24	-4	20.4	5	7		
.105	$C_6H_5COCl + C_6H_5Br \longrightarrow C_6H_5COC_6H_4Br + HCl$	B	A≃0.5	$AlCl_3$	= A	$k[A \cdot X]B$	100	4.6	-5					(44)
							110	9.1	-5					
							120	1.74	-4					
							130	3.2	-4	19.4	1.1	7		
.106	$C_6H_5COCl + C_{10}H_8 \longrightarrow \alpha\text{-}C_6H_5COC_{10}H_7 + HCl$ $\searrow \beta\text{-}C_6H_5COC_{10}H_7 + HCl$	CH_2ClCH_2Cl	A=0.222; B=0.222	$AlCl_3$	0.222	$k(A \cdot X)^2B$	25	3.6	-1					(29)
			0.272		0.222		25	2.5	-1					
			0.322		0.222		25	2.2	-1					
			0.444		0.222		25	1.9	-1					
			0.522		0.222		25	1.7	-1					
			0.622		0.222		25	1.6	-1					
			0.222		0.222	$k = k_\alpha + k_\beta$	25	k_α 2.9	-1					
					0.222		25	k_β 7.2	-2					
			0.444		0.222		25	k_α 1.3	-1					
					0.222		25	k_β 6.5	-2					
			0.622		0.222		25	k_α 1.0	-1					
					0.222		25	k_β 6.1	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.107	$C_6H_5COBr + C_6H_5CH_3 \rightarrow C_6H_5COC_6H_4CH_3 + HBr$	1,2,4-$Cl_3C_6H_3$	10^2A=2.42;B=0.3	(X) $AlBr_3$	0.0242	k(A·X)B	25	2.00	-4				*	(^{32})
			5.26		0.0526		25	2.28	-4					
			10.5		0.105		25	2.68	-4					
			31 0.1-0.6		0.31		25	4.1	-4					
			67.6 0.3		0.676		25	6.8	-4					
			102		1.02		25	9.1	-4					
			31 0.3		0.46		25	6.0	-3					
			31		0.62	k(A·X)^{2}B	25	1.28	-1					
			31		0.77		25	2.25	-1					
			31		0.93		25	3.3	-1					
.108	$C_6H_5CH_2COCl + C_6H_6 \rightarrow C_6H_5CH_2COC_6H_5 + HCl$	B	not stated	$AlCl_3$	=A	k[A·X]B	0	> 1	-2					(^{44})
.109	$C_6H_5CH_2COCl + C_6H_5CH_3 \rightarrow C_6H_5CH_2COC_6H_4CH_3 + HCl$	B	not stated	$AlCl_3$	=A	k[A·X]B	0	> 1	-2					(^{44})
.110	$C_6H_5CH_2COCl + C_6H_5Cl \rightarrow C_6H_5CH_2COC_6H_4Cl + HCl$	B	A≃0.5	$AlCl_3$	=A	k[A·X]B	15	4.0	-5					(^{44})
							25	9.4	-5					
							35	1.74	-4					
							45	3.5	-4	12.8	2	5		
.111	$C_6H_5CH_2COCl + C_6H_5Br \rightarrow C_6H_5CH_2COC_6H_4Br + HCl$	B	A≃0.5	$AlCl_3$	=A	k[A·X]B	35	1.32	-4					(^{44})
							45	2.6	-4					
							55	5.2	-4	13.5	5	5		
.112	$C_6H_5CH{:}CHCOCl + C_6H_6 \rightarrow C_6H_5CH{:}CHCOC_6H_5 + HCl$	B	A≃0.5	$AlCl_3$	=A	k[A·X]B	55	4.1	-5					(^{44})
							60	5.4	-5					
							64	6.8	-5	13	1	4		
.113	$C_6H_5CH{:}CHCOCl + C_6H_5CH_3 \rightarrow C_6H_5CH{:}CHCOC_6H_4CH_3 + HCl$	B	A≃0.5	$AlCl_3$	=A	k[A·X]B	15	5.7	-5					(^{44})
							25	1.48	-4					
							35	3.3	-4	15	3	7		

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	Literature
.114	$C_6H_5CH{:}CHCOCl + C_6H_5Cl \longrightarrow C_6H_5CH{:}CHCOC_6H_4Cl + HCl$	B	not stated	(X) $AlCl_3$	= A	$k[A{\cdot}X]B$	100	< 2	-5					$(^{44})$
.115	$C_6H_5CH{:}CHCOCl + C_6H_5Br \longrightarrow C_6H_5CH{:}CHCOC_6H_4Br + HCl$	B	not stated	$AlCl_3$	= A	$k[A{\cdot}X]B$	100	<2	-5					$(^{44})$
.116	$\underset{(A)}{(C_6H_5)_2CHCOCl} + \underset{(B)}{C_6H_6} \longrightarrow \underset{(L)}{(C_6H_5)_3CH} + \underset{(M)}{CO} + \underset{(N)}{HCl}$	B 11*	$10^2A=5$	$AlCl_3$	0.25	$dM/dt=kA$	20	1.00	-4				*	$(^{21})$
.117	$\underset{(A)}{(C_6H_5)_2CHCOCl} + \underset{(B)}{C_6H_6} \longrightarrow \underset{(L)}{(C_6H_5)_2CHCOC_6H_5} + \underset{(M)}{HCl}$	B 11*	$10^2A=5$	$AlCl_3$	0.25	$dL/dt=kA$	20	8	-5				*	$(^{21})$
.118	$\underset{(A)}{(C_6H_5)(p\text{-}CH_3C_6H_4)CHCOCl} + \underset{(B)}{C_6H_6} \rightarrow \underset{(L)}{(C_6H_5)_2(p\text{-}CH_3C_6H_4)CH} + \underset{(M)}{CO} + \underset{(N)}{HCl}$	B 11*	$10^2A=5$	$AlCl_3$	0.05 0.25	$dM/dt=kA$	20 20	5.3 8.8	-5 -4					$(^{21})$
.119	$(C_6H_5)(p\text{-}CH_3C_6H_4)CHCOCl + C_6H_6 \longrightarrow$ $CO, HCl, + (C_6H_5)_2(p\text{-}CH_3C_6H_4)CH, (C_6H_5)(p\text{-}CH_3C_6H_4)CHCOC_6H_5$	B 11*	A=0.1	$AlCl_3$	0.063	$-dA/dt=kA$	20	7.7	-5				*	$(^{21})$
.120	$\underset{(A)}{(C_6H_5)(p\text{-}ClC_6H_4)CHCOCl} + \underset{(B)}{C_6H_6} \rightarrow \underset{(L)}{(C_6H_5)_2(p\text{-}ClC_6H_4)CH} + \underset{(M)}{CO} + \underset{(N)}{HCl}$	B 11*	$10^2A=5$	$AlCl_3$	0.25	$dM/dt=kA$	20	1.95	-5				*	$(^{21})$
.121	$\underset{(A)}{(C_6H_5)(p\text{-}ClC_6H_4)CHCOCl} + \underset{(B)}{C_6H_6} \rightarrow (C_6H_5)_2(p\text{-}ClC_6H_4)CH + CO + HCl$ $\searrow (C_6H_5)(p\text{-}ClC_6H_4)CHCOC_6H_5 + HCl$	B 11*	A=0.1	$AlCl_3$	0.063	$-dA/dt=kA$	20	5.7	-6					$(^{21})$
.122	$\underset{(A)}{(C_6H_5)(p\text{-}BrC_6H_4)CHCOCl} + \underset{(B)}{C_6H_6} \rightarrow \underset{(L)}{(C_6H_5)_2(p\text{-}BrC_6H_4)CH} + \underset{(M)}{CO} + \underset{(N)}{HCl}$	B 11*	$10^2A=5$	$AlCl_3$	0.25	$dM/dt=kA$	20	1.55	-5					$(^{21})$
.123	$\underset{(A)}{(C_6H_5)(p\text{-}BrC_6H_4)CHCOCl} + \underset{(B)}{C_6H_6} \rightarrow (C_6H_5)_2(p\text{-}BrC_6H_4)CH + CO + HCl$ $\longrightarrow (C_6H_5)(p\text{-}BrC_6H_4)CHCOC_6H_5 + HCl$	B 11*	A=0.1	$AlCl_3$	0.063 0.126	$-dA/dt=kA$	20 20	5.8 3.1	-6 -5					$(^{21})$

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
.124	$(p\text{-}CH_3C_6H_4)(p\text{-}ClC_6H_4)CHCOCl + C_6H_6 \rightarrow (p\text{-}CH_3C_6H_4)(p\text{-}ClC_6H_4)(C_6H_5)CH + CO + HCl$ (A) (B) (L) (M) (N)	B 11*	$10^2A=5$	$AlCl_3$	0.05 0.25	$dM/dt=kA$	20 20	9.2 9.1	-6 -5	*	(21)
.125	$(p\text{-}CH_3C_6H_4)(p\text{-}ClC_6H_4)CHCOCl + C_6H_6 \rightarrow$ (A) (B) $\rightarrow (p\text{-}CH_3C_6H_4)(p\text{-}ClC_6H_4)(C_6H_5)CH + CO + HCl$ $\rightarrow (p\text{-}CH_3C_6H_4)(p\text{-}ClC_6H_4)CHCOC_6H_5 + HCl$	B 11*	$A=0.1$	$AlCl_3$	0.063	$-dA/dt=kA$	20	2.08	-5		(21)

CODED SOLVENTS

AW90*	90% CH_3COOH + 10% H_2O by volume
Ac 86.5*(80) (75) (67.4) (50) (40)	CH_3COOH wt % indicated + H_2O
B 11*	89 vol % C_6H_6 + 11% $C_6H_5NO_2$

COMMENTS

General: Reactions are listed with alkylating agents first. Order of alkylating agents: olefins (.1)(.2), aldehydes (.3)-(.10), carbinols (.11)-(.27), ethers (.28)-(.33), esters (.34)-(.35), alkyl aryl sulfonates (.36)-(.39), alkyl halide (.40)-(.67), acyl halide and aromatic acyl halide (.68)-(.125). For each alkylating agent the aromatic compounds undergoing substitution are then listed in order of complexity.

Reaction: **(.1)** Second order rate constant calculated by dividing initial pseudo first order constant by concentration of $AlBr_3$. Reaction becomes heterogeneous upon formation of Friedel-Crafts oil. **(.2)** Less than 0.1% H_2O reduced rate constant by about one half. Acetic anhydride added to remove traces of H_2O. Excess acetic anhydride gave high and erratic values. **(.3)** Rate constants are for less than 50% reaction as calculated constants decrease as reaction proceeds. **(.4) (.5)** Reactions simultaneous and are followed by (.6)(.7)(.8)(.9) and (.10). Kinetics are complex and rate constants calculated by trial and error solution of simultaneous differential equations. **(.6) (.7)** Reactions simultaneous and are followed by (.9) and (.10) respectively. Kinetics are complex and rate constants calculated by solution of simultaneous differential equations. **(.8)** Reaction followed by (.9). **(.11) (.12) (.14) (.15)** No simple order as reaction procedes partially through formation of ether, $(C_6H_5CH_2)_2O$ which reacts see (.28)-(.30). **(.20)** Selected data. Values of (2) and (3) differ slightly from those reported in earlier paper by same authors.

COMMENTS *(continued)*

(.22) (.24) Selected data of (3). **(.25)** Selected data. **(.40) (.41)** With $GaBr_3$ as catalyst and B in excess rate law pseudo zero order with respect to each reactant, and second order with respect to catalyst. Units converted to seconds from original minutes of (49). Rate constants of (34) are for initial rate as calculated constants decrease with course of reaction. **(.42)** Authors calculate first order rate constant, however for the two points given zero order would give better fit with $k_o \simeq 4.5\times10^{-4}$ m/l sec. **(.43) (.44)** With $GaBr_3$ as catalyst and B in excess rate law is pseudo zero order with respect to each reactant, and second order with respect to catalyst. Units converted to seconds from original minutes of (48) (49). Rate constants of (34) are for initial rate as calculated constants decrease with course of reaction. **(.45) (.46)** Units converted to seconds from original minutes. **(.47)** Rate constant estimated using rate ratio $C_6H_5CH_3$ to C_6H_6 measured by (16) and approximate rate for $C_6H_5CH_3$ measured by (49).

(.49) Authors give a great deal of data which fits an integrated equation of the form $t=a+b\cdot\log(P_\infty-P)+c\cdot\log[d-(P_\infty-P)]$ where a, b, c and d, are individual constants for each run and P is pressure of HCl+HF. Constants not directly related to simple rate constants. Reaction also studied by (41) but data not easily reduced to significant reaction rate constants. **(.56)** Rate constant calculated by treating data as from two consecutive first order processes. The first is the reaction listed and the second is the sweeping of the HCl into standard base using H_2 gas. **(.57)** Third order rate constant calculated by dividing pseudo first order constant by concentration of B and $AlCl_3$. Data of (40) calculated in this form by (8). **(.58)** Third order rate constant calculated by dividing pseudo first order constant by concentration of B and $AlCl_3$. Order with respect to B not verified. **(.59) (.60)** Third order constant calculated by dividing pseudo first order constant by concentration of B and $AlCl_3$. Reaction pseudo first order with respect to A and zero order with respect to B over course of reaction since L reacts almost as rapidly with A as B in a consecutive reaction see (.63).

(.61) Pseudo first order with respect to A and zero order over course with respect to B considered due to almost equal reactivity of L and B with A. **(.62)** Third order constant calculated by dividing pseudo first order constant by concentration of B and $AlCl_3$ each of which show zero order over course of reaction. **(.66) (.67)** Reaction shows induction period and auto catalysis by M. Units of k_2 are mm. $l.^2 M.^{-2}$ sec^{-1}. Units of k_3 are $l^2 M^{-2}$ sec^{-1}. k_2 would be conventional second order rate constant if divided by Henry's constant for HCl in reaction medium in mm. l./M. **(.68)** Second order rate law is first order with respect to complex $CH_3COCl\cdot AlCl_3$ and first order with respect to B. **(.69)** Rate constant calculated from measured relative rate (.69) to (.68) and observed rate constant for (.68). **(.70) (.71) (.72)** Rate constant calculated from measured relative rate to (.69) and calculated rate constant for (.69).

(.83) Rate constants about 20% larger than reported earlier by (43). First order rate constant at 20°C expressed quite well by $k=9.8\times10^{-3}[AlCl_3]^2+1.41\times10^{-5}$. **(.84)** Rate constant estimated from time for 10% and 25% change given for (.83) and (.84). **(.85)** Reaction produces some ketone by initial rapid reaction which ties up some $AlCl_3$. Rate

COMMENTS *(continued)*

constant measured was for the slow alkylation reaction and the concentration of free $AlCl_3$ estimated. **(.86)** Rate law with respect to individual reactants not determined by (6)(7) and (32) as concentrations of each reactant and catalyst were kept equal. **(.87)** Selected data of (35). Additional data shows effect of mixed catalyst $FeCl_3$+$AlCl_3$. With $SnCl_4$ as catalyst rate is proportional to initial concentration of catalyst. Rate law with respect to individual reactants not determined by (6)(7)(15) and (32) as concentrations of reactants and catalyst were kept equal. **(.88) (.89) (.90) (.91) (.92) (.93)** Rate law in $C_6H_5NO_2$ with respect to individual reactants and catalyst not determined as concentration of reactants and catalyst were kept equal. Overall 3.5 order gave best fit to data.

(.97) - (.103) Rate law with respect to individual reactants and catalyst not determined as concentrations of reactants and catalyst were kept equal. Overall 3.5 order gave best fit to data. **(.104)** With $GaCl_3$, $SbCl_5$ and $FeCl_3$ as catalysts reaction obeys third order rate law over course, first order with respect to B and second order with respect to catalyst. Calculated third order constants are inversely proportional to initial catalyst concentration. Constants listed are the third order constant multiplied by initial catalyst concentration. **(.107)** Reaction second order over course except with excess $AlBr_3$ when third order rate law is followed. **(.116) (.117)** Simultaneous reactions, (.116) was followed by rate of CO evolution and (.117) from overall reaction. **(.119)** Overall rate of two simultaneous reactions one of which is (.118). **(.120)** One of two simultaneous reactions see (.121). Yield 62% ketone and 18% CO. **(.124)** With $[AlCl_3]=0.25$ 10-20% ketone produced simultaneously to 50% CO.

LITERATURE

(1) D. Bethell, V. Gold, *CSL* **1958**, 1905. (2) D. Bethell, V. Gold, *CSL* **1958**, 1931. (3) D. Bethell, V. Gold, T. Riley, *CSL* **1959**, 3134. (4) T.G. Bonner, J.M. Clayton, G. Williams, *CSL* **1957**, 2867. (5) H.C. Brown, B.A. Bolto, *ACS* 1959, **81**, 3320. (6) H.C. Brown, B.A. Bolto, F.R. Jensen, *JOC* 1958, **23**, 414. (7) H.C. Brown, B.A. Bolto, F.R. Jensen, *JOC* 1958, **23**, 417. (8) H.C. Brown, M. Grayson, *ACS* 1953, **75**, 6285. (9) H.C. Brown, F.R. Jensen, *ACS* 1958, **80**, 2291. (10) H.C. Brown, F.R. Jensen, *ACS* 1958, **80**, 2296.

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HYDROGEN SUBSTITUTION

H on nitrogen replaced by NO_2

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	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$2,4\text{-}(NO_2)_2C_6H_3NHCH_3 + HNO_3 \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3N(CH_3)NO_2 + H_2O$	CH_3NO_2	10^2A=5; B=3.0			k	25	2.13	-5	*	(1)
			10-14 4.0				25	7.2	-5		
.2	$2,4,6\text{-}(NO_2)_3C_6H_2NHCH_3 + HNO_3 \longrightarrow 2,4,6\text{-}(NO_2)_3C_6H_2N(CH_3)NO_2 + H_2O$	CH_3NO_2	10^2A=3-16; B=2.0			k	25	6.8	-6	*	(1)
			2.5				25	1.41	-5		
			3.0				25	2.89	-5		
			3.5				25	6.0	-5		
			4.0				25	9.6	-5		
			4.5				25	1.49	-4		
			5 2.0	H_2SO_4	0.0030		25	1.89	-5		
					0.0047		25	3.3	-5		
					0.0069		25	5.5	-5		
					0.0092		25	7.8	-5		
			5 3.0	$NaClO_4$	0.0032		25	3.2	-5		
					0.0064		25	3.5	-5		
					0.0072		25	3.8	-5		
			5 3.0	$NaNO_3$	0.0032		25	2.03	-5		
					0.0078		25	1.53	-5		
					0.0120		25	1.42	-5		
					0.0177		25	1.31	-5		
			5 3.0	H_2O	0.149		25	3.29	-5		
					0.228		25	3.23	-5		
					0.47		25	~1.8	-5		

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
.2	$2,4,6\text{-}(NO_2)_3C_6H_2NHCH_3 + HNO_3 \longrightarrow$ *(continued)*	CH_3NO_2	$10^2A=5; B=3.0$	H_2O	0.61	k	25	~1	-5	*	(^{1})
					0.79	k_1A	25	~2.6	-5		
					0.82		25	1.96	-5		
					0.97		25	1.40	-5		
					1.02		25	1.34	-5		
.3	$2,4,6\text{-}(NO_2)_3C_6H_2NHC_2H_5 + HNO_3 \longrightarrow 2,4,6\text{-}(NO_2)_3C_6H_2N(C_2H_5)NO_2 + H_2O$	CH_3NO_2	$10^2A=5; B=3.0$			k	25	~2.8	-5	*	(^{1})
.4	$2,4,6\text{-}(NO_2)_3C_6H_2NH(n\text{-}C_3H_7) + HNO_3 \longrightarrow 2,4,6\text{-}(NO_2)_3C_6H_2N(n\text{-}C_3H_7)NO_2 + H_2O$	CH_3NO_2	$10^2A=5; B=3.0$			k	25	~2.8	-5	*	(^{1})
.5	$2,4,6\text{-}(NO_2)_3C_6H_2NH[CH(CH_3)_2] + HNO_3 \longrightarrow$ $2,4,6\text{-}(NO_2)_3C_6H_2N[CH(CH_3)_2]NO_2 + H_2O$	CH_3NO_2	$10^2A=5; B=3.0$			k	25	1.65	-5	*	(^{1})
.6	$2,4,6\text{-}(NO_2)_3C_6H_2NH(n\text{-}C_4H_9) + HNO_3 \longrightarrow 2,4,6\text{-}(NO_2)_3C_6H_2N(n\text{-}C_4H_9)NO_2 + H_2O$	CH_3NO_2	$10^2A=5; B=3.0$			k	25	~2.8	-5	*	(^{1})

COMMENTS

Reaction: **(.1)** Zero order with respect to A and order with respect to B not determined. Product formed by this reaction is further nitrated by a slower step to produce N-methyl-N,2,4,6-tetranitroaniline as a final product. **(.2)** Reaction zero order over course of reaction when $[H_2O]<0.2$. Reaction first order with respect to A at $[H_2O]>0.8$. At intermediate $[H_2O]$ the order changes with course of reaction, confirming the nitronium ion mechanism. **(.3)** **(.4)** **(.5)** **(.6)** All reactions zero order in A and react at same speed as (.2) except (.5) which reacts at 0.6 times the common rate. Order with respect to B not determined.

LITERATURE

(^{1}) E.D. Hughes, C.K. Ingold, R.B. Pearson, *CSL* **1958**, 4357.

EXCHANGE OF SUBSTITUENTS
IInd group metal on aliphatic C exchange

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

No.	Reaction	Solvent	Amount of reactant		Amount of Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$	
									k^o	n
.1	$[CH_3CH_2(CH_3)CH]_2Hg + (CH_3COO)_2Hg \longrightarrow 2[CH_3CH_2(CH_3)CH]Hg(OOCCH_3)$	C_2H_5OH	$10^4A=2-20$; $10^4B=2-4$				kAB	0	5.4	0
.2	$[CH_3CH_2(CH_3)CH]_2Hg + Hg(NO_3)_2 \longrightarrow 2[CH_3CH_2(CH_3)CH]HgNO_3$	C_2H_5OH	$10^4A=4$; $10^4B=4$				kAB	-47	7.6	0
.3	$[CH_8CH_2(CH_3)CH]_2Hg + HgBr_2 \longrightarrow 2[CH_3CH_2(CH_3)CH]HgBr$	C_2H_5OH	$10^3A=2$; $10^3B=2$				kAB	25	3.9	-1
		$(CH_3)_2CO$	$10^5A=8-100$; $10^5B=8-100$					25	2.4	0
			40	40	LiBr	0.0002		25	9	-1
			80	40		0.0004		25	1.0	0
			100	100		0.0005		25	1.0	0
			400	400		0.0040		25	1.0	-1
			400	400		0.0080		25	4.5	-2
			40-100	40-100		$<B$	$kA(B-[LiBr])$	25	2.3	0

COMMENTS

Exchange occurs by a configuration retaining, bimolecular, electrophylic, S_{E2} mechanism.
(.3) effect of LiBr is to reduce concentration of B by formation of $LiHgBr_3$ complex.

LITERATURE

H.B. Charman, E.D. Hughes, C. Ingold, *CSL* **1959**, 2530.

EXCHANGE OF SUBSTITUENTS
IInd group metal on aromatic-C replaced by N

Liquid phase
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
.1	$C_6H_5HgNO_3 + N_2O_4 \longrightarrow C_6H_5NO + Hg(NO_3)_2$	20% HNO_3 in H_2O	$10^3 A \simeq 1$; $[HNO_2]$=0.075	k A	0	5	-5
			0.15		0	1.0	-4
			0.30		0	3.3	-4
			0.45		0	8.8	-4
			0.15		25	8	-4
			0.30		25	1.1	-3
		30% HNO_3 in H_2O	0.30		0	3.7	-3
		40% HNO_3 in H_2O	0.30		0	2.3	-2

COMMENTS

Reaction immediately followed by diazotization and rate constant calculated from overall rate and independent measurement of diazotization reaction.

LITERATURE

F.H. Westheimer, E. Segel, R. Schramm, *ACS* 1947, **69**, 773.

EXCHANGE OF SUBSTITUENTS
IInd group metal on aliphatic C replaced by acid radical

Reaction types:
$RHgZ \longrightarrow RZ + Hg$
$RHgZ + HgZ_2 \longrightarrow RZ + Hg_2Z_2$

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$C_6H_5CH_2HgOOCCH_3 \longrightarrow C_6H_5CH_2OOCCH_3 + Hg$	50 HAc*	10^2A=5-10 ~5	$HClO_4$	3.18	kA	25	2.23	-5				*	(1)
					3.97		25	5.7	-5					
					4.73		25	1.27	-4					
					5.15		25	2.25	-4					
					5.55		25	4.22	-4					
					3.17		35	9.87	-5					
					4.73		35	6.45	-4					
					3.17		45	4.18	-4					
					4.73		45	2.84	-3	29.3	4	17		
					3.19		60	3.13	-3	27.7	5	15		
				$HClO_4$ + $NaClO_4$	3.19 0.80		25	3.97	-5					
				"	1.60		25	6.67	-5					
				"	2.00		25	8.40	-5					
		63.9 HAc*	10^2A~5	$HClO_4$	3.22		25	3.93	-5					
					3.62		25	6.23	-5					
					4.02		25	1.09	-4					
					4.42		25	1.73	-4					
					4.83		25	2.82	-4					
		78.1 HAc*	10^2A=2-9	$HClO_4$	3.22		25	1.10	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2	$C_6H_5CH_2HgOOCCH_3 + Hg(OOCCH_3)_2 \longrightarrow$ $C_6H_5CH_2OOCCH_3 + Hg_2(OOCCH_3)_2$	50 HAc*	$10^2A\sim5$; $10^2B\sim10$	$HClO_4$	0.79	kAB	25	5	-6				*	(^{1})
					1.58		25	2.03	-5					
			2-5 5-20		2.38		25	8.2	-5					
			~5 ~10		2.78		25	1.34	-4					
				HNO_3	0.56		25	9	-6					
					1.13		25	4	-5					
					1.58		25	8	-5					
				$HClO_4$	1.58		35	6.3	-5					
					1.58		45	1.90	-4	21	5	12		
		65 HAc*	$10^2A\sim5$; $10^2B\sim10$	$HClO_4$	1.58		25	3.8	-5					
				HNO_3	1.13		25	6.2	-5					
.3	$p\text{-}CH_3OC_6H_4CH_2CH_2HgOOCCH_3 \longrightarrow$ $p\text{-}CH_3OC_6H_4CH_2CH_2OOCCH_3 + Hg$	50 HAc*	$10^2A\sim5$	$HClO_4$	3.17	kA	35	2.19	-5				*	(^{1})
					3.17		45	8.7	-5					
					3.17		55	3.04	-4	26	1	14		
		60 HAc*	$10^2A\sim5$		2.79		35	2.72	-5					
					3.19		35	4.7	-5					
					3.59		35	7.8	-5					
					3.99		35	1.30	-4					
					4.39		35	2.04	-4					
			2-14		4.79		35	3.23	-4					
				$HClO_4$+ $NaClO_4$	2.79									
			~5		0.63		35	4.5	-5					
					1.26		35	7.0	-5					
					1.61		35	8.9	-5					
		63.9 HAc*	$10^2A\sim5$	$HClO_4$	3.22		25	1.23	-5					
					4.83		25	9.1	-5					

COMMENTS

Reaction: **(.1)** As much as 18% of reacted substrate converted to mercurous salt instead of to free mercury. **(.2)** Reaction followed by determining decrease in A as well as by increase in M. Good agreement between both methods obtained at higher concentrations of $HClO_4$ and at lower initial concentration of B. Differences considered to be due to mercuration of ring. **(.3)** As much as 18% of reacted substrate converted to mercurous salt instead of to free mercury.

CODED SOLVENTS

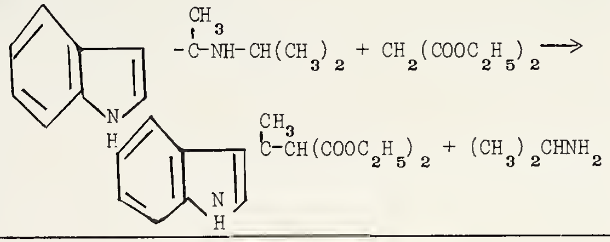
50 HAc*(60, 63.9, 65, 78.1) vol. % CH_3COOH indicated with H_2O.

LITERATURE

(1) K. Ichikawa, H. Ouchi, *ACS* 1960, **82**, 3876.

EXCHANGE OF SUBSTITUENTS
Vth group element on aliphatic C replaced by C

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
.1		xylene	10^2A=8; B=0.33	CH_3ONa	0.046	kA	94	1.9	-5
			12				94	3.4	-5
			19				94	5.6	-5
			25				94	7.3	-5

COMMENTS

Reaction first order with respect to course of reaction but calculated pseudo first order constants are also linear with respect to initial concentration of A. This is attributed to catalysis by both A and L. Doubling concentration of B increases rate about 25%. M also is catalyst for reaction as rate gradually increases if M not removed by passing N_2 through solution.

LITERATURE

J.D. Albright, H.R. Snyder, *ACS* 1959, **81**, 2239.

EXCHANGE OF SUBSTITUENTS
$NO_2(NO_3)$ replaced by N on aliphatic or aromatic C

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$C_6H_5CH_2ONO_2 + H_2NNH_2 \longrightarrow C_6H_5CH_2NHNH_2 + HNO_3$	60 vol % $C_2H_5OH + H_2O$	10A=1-2; 10B=3			kAB	29	6.5	-5				*	(²)
							40	1.78	-4					
							52	5.60	-4	18.1	8	8		
		90 vol % $C_2H_5OH + H_2O$	1 2-3				29	3.9	-5					
							40	1.04	-4					
							52	3.07	-4	17.3	1	8		
		60 vol % $C_3H_7OH + H_2O$					29	5.0	-5					
							52	3.5	-4	17	1	8		
.2	$1,2,4\text{-}(NO_2)_3C_6H_3 + 2C_5H_{10}NH \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3NC_5H_{10} + C_5H_{10}NH_2NO_2$	CH_3OH	$10^3A \simeq 1$; $10^2B \simeq 4$	$C_5H_{10}NH_2Cl$	0.02	dL/dt= kAB	0	4.0	-1				*	(¹)

COMMENTS

Reaction: (.1) Rate law valid over course of reaction when H_2NNH_2 in excess. If $C_6H_5CH_2ONO_2$ in excess calculated second order constants increased with course of reaction possibly due to further alkylation of $C_6H_5NHNH_2$. (.2) Units converted to seconds from original minutes. Second order constant calculated from pseudo first order constant by dividing by concentration of piperidine. In absence of $C_5H_{10}NH_2Cl$ yield of L was only 98% attributed to side reaction involving CH_3O^-.

LITERATURE

(¹) J.F. Bunnett, E.W. Garbisch, K.M. Pruitt, *ACS* 1957, **79**, 385. (²) R.T. Merrow, *ACS* 1956, **78**, 1297.

EXCHANGE OF SUBSTITUENTS
$ROSO_2$ on aliphatic C replaced by R'S

Reaction type: $R_1OSO_2R + R'SNa \longrightarrow R_1SR' + RSO_3Na$

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

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
						k^o	n		
.1	$n\text{-}C_4H_9OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow n\text{-}C_4H_9SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=4-7; 10^2B=2-11	k AB	25	8.4	-3	*	(1)
.2	$C_2H_5(CH_3)CHOSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow C_2H_5(CH_3)CHSC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=6-11; 10^2B=5-10	k AB	25	1.55	-3	*	(1)
.3	$cyclo\text{-}C_6H_{11}OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow cyclo\text{-}C_6H_{11}SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	$10A$=1-2; 10^2B=9-20	k AB	25	1.01	-4	*	(1)
.4	$cis\text{-}3\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow$ $3\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=7-10; 10^2B=6-12	k AB	25	2.41	-5	*	(1)
.5	$trans\text{-}3\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow$ $3\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=8-11; 10^2B=7-15	k AB	25	3.24	-4	*	(1)
.6	$cis\text{-}4\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow$ $4\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=7-10; 10^2B=9-27	k AB	25	1.82	-4	*	(1)
.7	$trans\text{-}4\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow$ $4\text{-}CH_3\text{-}cyclo\text{-}C_6H_{10}SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	$10^2A \simeq 8$; $10B$=1-2	k AB	25	2.58	-5	*	(1)
.8	$cis\text{-}4\text{-}(CH_3)_3C\text{-}cyclo\text{-}C_6H_{10}OSO_2C_6H_4\text{-}p\text{-}CH_3 + C_6H_5SNa \longrightarrow$ $trans\text{-}4\text{-}(CH_3)_3C\text{-}cyclo\text{-}C_6H_{10}SC_6H_5 + p\text{-}CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=4-10; 10^2B=6-12	k AB	25	3.6	-4	*	(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		Comments	Literature
						k^{o}	n		
.9	*trans*--4-$(CH_3)_3$C-*cyclo*-$C_6H_{10}OSO_2C_6H_4$-*p*-CH_3 + C_6H_5SNa ⟶ *cis*-4-$(CH_3)_3$C-*cyclo*-$C_6H_{10}SC_6H_5$ + *p*-$CH_3C_6H_4SO_3Na$	87% $C_2H_5OH + H_2O$	10^2A=4-7; 10^2B=7-22	*k* AB	25	1.95	-5	*	(¹)

COMMENTS

General: Solvent 87% ethanol prepared to density d_4^{20} = 0.8258 ± 0.0015.

Reaction: (.1) (.2) No measureable parallel elimination reaction. (.3) For parallel elimination reaction see 422.463. Rate constant calculated from rate for total reaction and rate for elimination, k_S/k_E=1.22. (.4) No measureable parallel elimination reaction. (.5) (.6) For parallel elimination reaction see 422.463. Rate constant calculated from rate for total reaction and rate for elimination, k_S/k_E=1.20 and 0.65 respectively. (.7) No measureable parallel elimination reaction. (.8) For parallel elimination reaction see 422.463. Rate constant calculated from rate for total reaction and rate for elimination, k_S/k_E=1.06. (.9) No measureable parallel elimination reaction.

LITERATURE

(¹) E.L. Eliel, R.S. Ro, *ACS* 1957, **79**, 5995.

EXCHANGE OF SUBSTITUENTS
SO_3^- on aromatic C replaced by halogen

Reaction type: $RSO_3^- + X_2 \longrightarrow RX + SO_3 + Br^-$

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	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$4\text{-}CH_3OC_6H_4SO_3Na + Br_2 \longrightarrow 4\text{-}CH_3OC_6H_4Br + SO_3 + NaBr$	H_2O	10^4A=5; 10^4B=3; 10^3N=0	$HClO_4$	0.0023	k AB	0	4.3	-1	*	(2)
			2.5	$\mu=0.15$	0.0023		0	4.0	-1		
			10		0.0023		0	2.9	-1		
			50		0.0023		0	9.9	-2		
			100		0.0023		0	4.5	-2		
			150		0.0023		0	2.5	-2		
			10 5 5		0.01		0	3.2	-1		
			2.5-10 5 20		0.01		0	1.80	-1		
			10 5 50		0.01		0	9.6	-2		
.2	$3,5\text{-}(NO_2)_2\text{-}4\text{-}NaOC_6H_2SO_3Na + Br_2 \longrightarrow 3,5\text{-}(NO_2)_2\text{-}4\text{-}NaOC_6H_2Br + SO_3 + NaBr$	H_2O	10^4A=5; 10^4B=3; 10^3N=2.5	$HClO_4$	0.1	k AB	0	3.0	0	*	(2)
			2.5	$\mu=0.17$	0.02		0	1.31	+1		
			2-20 2-6 10		0.02		0	2.34	0		
			5 3 150		0.02		0	5.3	-2		
.3	$3,5\text{-}Br_2\text{-}4\text{-}HOC_6H_2SO_3Na + Br_2 \longrightarrow 2,4,6\text{-}Br_3C_6H_2OH + SO_3 + NaBr$	H_2O	10^4A=5; 10^4B=3; 10^3N=2.5	$HClO_4$	0.0023	k B	0	3.3	-6	*	(1)
			2.5	$\mu=0.16$	0.0023		0	2.1	-6		
			10-50 3-5 0		0.01		25	9.1	-5		
			10 5 0		0.03		25	9.5	-5		
			20 20		0.01		25	8.9	-5		
			10 150		0.01		25	5.5	-5		
			0		0		25	1.23	-4		
			1-2 5-10 0		0.01	k A	25	1.41	-4		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.4	$3,5\text{-}Br_2\text{-}4\text{-}H_2NC_6H_2SO_3Na + Br_2 \longrightarrow 2,4,6\text{-}Br_3C_6H_2NH_2 + SO_3 + NaBr$	H_2O	$10^4A=5;\ 10^4B=3;\ 10^3N=0$	$HClO_4$	0.0023	k AB	0	1.53	+2	*	(²)
			2.5		0.0023		0	2.6	+1		
			10		0.0023		0	6.0	0		
			2.5-25 2-6 50		0.002-0.1		0	7.2	-1		
		$\mu\simeq 0.15$	5 3		0.0023		0	2.4	-1		
					0.0023		0	1.16	-1		
.5	$4\text{-}CH_3C_{10}H_6\text{-}1\text{-}SO_3K + Br_2 \longrightarrow 4\text{-}CH_3C_{10}H_6\text{-}1\text{-}Br + SO_3 + KBr$	H_2O	$10^4A=5;\ 10^4B=3;\ 10^3N=2.5$	$HClO_4$	0.0023	k AB	0	1.34	-1	*	(²)
			2-12 1-5 20		0.0023		0	9.5	-2		
			10 2 20		0.10		0	1.05	-1		
			5 3 150		0.0023		0	2.7	-2		

COMMENTS

Reaction: (.1) Pseudo second order constants valid for 93% reaction if $A_o=4B_o$ but to only 60% reaction if $A_o=2B_o$ and to only 35% reaction if $B_o > A_o$. Beyond this calculated constants increase with time probably due to bromination of product. Correction for $Br^-+Br_2=Br_3^-$ equilibrium not sufficient to account for rate dependence upon Br^-. $NaClO_4$ added to make ionic strength about 0.15. (.2) Pseudo second order constants observed to be almost inversely dependent upon $[H^+]$. Dependence upon Br^- greater than can be accounted for by $Br_2+Br^-=Br_3^-$ equilibrium. (.3) Pseudo first order kinetics observed with reaction first order in B when A in excess and first order in A when B in excess. Behavior is attributed to very rapid equilibrium reaction between A and B forming intermediate which undergoes first order conversion to product. In excess B reaction is further complicated by a similar reaction of B with first product which forms at least two additional products. Authors treat this as two consecutive first order reactions with rate constants 9.2×10^{-5} and 3.7×10^{-4} respectively at 25°C. They propose that decrease in apparent rate constant with added NaBr is due to shift in rapid equilibrium reducing concentration of intermediate. Activation energy calculated to be 23 kcals/mole.

(.4) Pseudo second order rate constants show greater dependence upon concentration of NaBr than can be accounted for by the $Br_2+Br^-=Br_3^-$ equilibrium. (.5) Pseudo second order rate constant dependence upon NaBr almost accounted for effect of $Br_2+Br^-=Br_3^-$ equilibrium.

LITERATURE

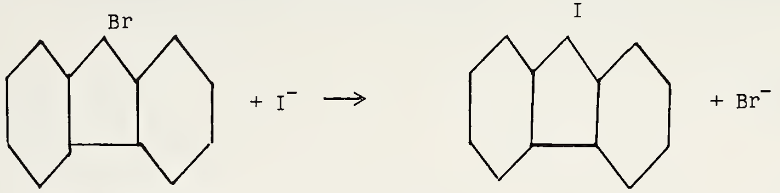
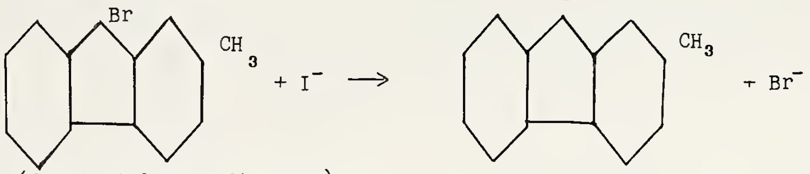
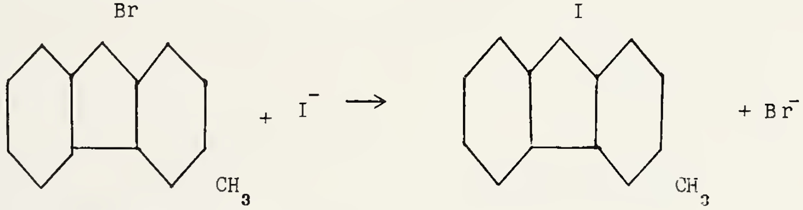
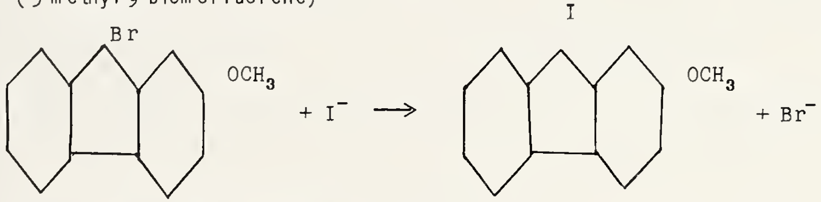
(¹) L. G. Cannell, *ACS* 1957, **79**, 2927. (²) L. G. Cannell, *ACS* 1957, **79**, 2932.

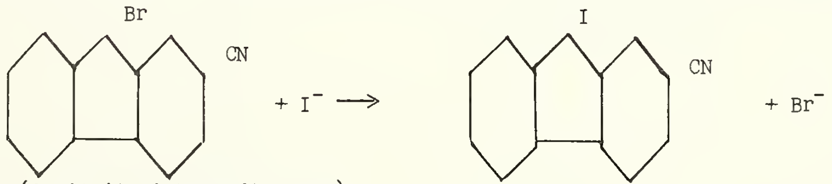
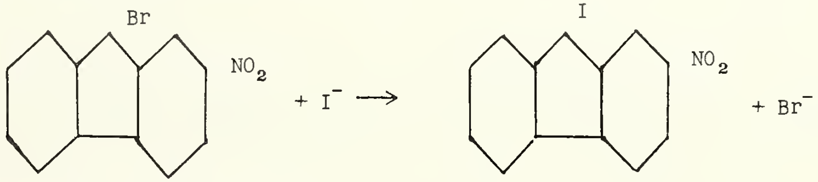
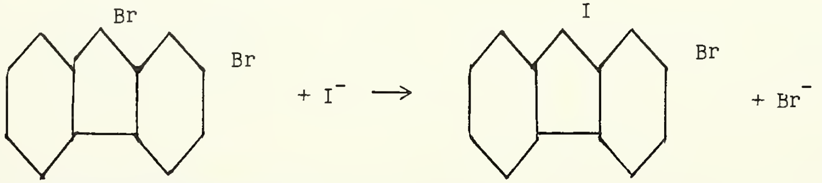
EXCHANGE OF SUBSTITUENTS
Halogen for halogen on aromatic carbon

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

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.4	2,4-$(NO_2)_2C_6H_3F + KI \longrightarrow$ 2,4-$(NO_2)_2C_6H_3I + KF$	$(CH_3)_2CO$	$10^2A \simeq 2$; $10^2B \simeq 1$	kAB	109	2	-5				*	(1)
.5	2,4-$(NO_2)_2C_6H_3Cl + KI \longrightarrow$ 2,4-$(NO_2)_2C_6H_3I + KCl$	$(CH_3)_2CO$	$10^2A \simeq 2$; $10^2B \simeq 1$	kAB	81	2.39	-5					(1)
					90	6.4	-5					
					99	1.21	-4					
					109	2.94	-4	23.6	9	9		
.6	2,4-$(NO_2)_2C_6H_3Br + KI \longrightarrow$ 2,4-$(NO_2)_2C_6H_3I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 2.5$; $10^2B \simeq 1.5$	kAB	48	1.09	-4				*	(3)
					60	3.63	-4					
					73	1.53	-3					
					80	2.93	-3	23.6	1	12		
.7	2,6-$(NO_2)_2C_6H_3Br + KI \longrightarrow$ 2,6-$(NO_2)_2C_6H_3I + KBr$	$(CH_3)_2CO$	$10^2A = 3-4$; $10^2B \simeq 1$	kAB	75	1.49	-4					(4)
					86	4.4	-4					
					95	8.5	-4					
					102	1.48	-3	21.7	7	9		
	Tri-substituted aryl halides											
.8	2,4-$(NO_2)_2$-6-$CH_3C_6H_2F + KI \longrightarrow$ 2,4-$(NO_2)_2$-6-$CH_3C_6H_2I + KF$	$(CH_3)_2CO$	$10^2A \simeq 2.4$; $10^2B \simeq 1.2$	kAB	109	8	-6				*	(1)
.9	2,4-$(NO_2)_2$-6-$CH_3C_6H_2Cl + KI \longrightarrow$ 2,4-$(NO_2)_2$-6-$CH_3C_6H_2I + KCl$	$(CH_3)_2CO$	$10^2A \simeq 4$; $10^2B \simeq 1$	kAB	90	9.3	-6					(1)
					104	3.2	-5					
					110	6.3	-5	25.6	2	10		

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		
.10	$2,4\text{-}(NO_2)_2\text{-}6\text{-}CH_3C_6H_2Br + KI \longrightarrow 2,4\text{-}(NO_2)_2\text{-}6\text{-}CH_3C_6H_2I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 2.3$; $10^2B \simeq 1.4$	kAB	60	9.0	-5				*	(3)
					80	6.6	-4					
					90	1.39	-3					
					100	3.36	-3	22.3	4	10		
.11	$2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3C_6H_2Br + KI \longrightarrow 2,6\text{-}(NO_2)_2\text{-}4\text{-}CH_3C_6H_2I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 3.5$; $10^2B \simeq 1.4$	kAB	74	1.70	-5					(4)
					90	7.7	-5					
					104	2.33	-4					
					110	3.71	-4	22.8	4	9		
.12	$2,4\text{-}(NO_2)_2\text{-}6\text{-}C_2H_5C_6H_2Br + KI \longrightarrow 2,4\text{-}(NO_2)_2\text{-}6\text{-}C_2H_5C_6H_2I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 2.2$; $10^2B \simeq 1.4$	kAB	60	5.5	-5				*	(3)
					80	3.78	-4					
					90	8.7	-4					
					100	1.88	-3	21.9	1.2	10		
.13	$2,4\text{-}(NO_2)_2\text{-}6\text{-}(CH_3)_2CHC_6H_2Br + KI \longrightarrow$ $2,4\text{-}(NO_2)_2\text{-}6\text{-}(CH_3)_2CHC_6H_2I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 2.3$; $10^2B \simeq 1.4$	kAB	60	6.4	-5				*	(3)
					80	4.4	-4					
					90	1.06	-3					
					100	2.21	-3	22.1	2	10		
.14	$2,4\text{-}(NO_2)_2\text{-}6\text{-}(CH_3)_3CC_6H_2Br + KI \longrightarrow$ $2,4\text{-}(NO_2)_2\text{-}6\text{-}(CH_3)_3CC_6H_2I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 2.2$; $10^2B \simeq 1.3$	kAB	90	1.17	-5				*	(3)
					100	2.70	-5					
					110	6.1	-5	23	6	8		
.15	$2,6\text{-}(NO_2)_2\text{-}4\text{-}(CH_3)_3CC_6H_2Br + KI \longrightarrow$ $2,6\text{-}(NO_2)_2\text{-}4\text{-}(CH_3)_3CC_6H_2I + KBr$	$(CH_3)_2CO$	$10^2A \simeq 3$; $10^2B \simeq 1.3$	kAB	86	6.9	-5					(4)
					90	1.02	-4					
					105	3.7	-4	23.7	2	10		

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.16	 (9-bromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	5.34 2.12	-4 -3	19	6	12	*	(^{2})
.17	 (2-methyl-9-bromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	5.20 1.64	-4 -3	16	1	10	*	(^{2})
.18	 (3-methyl-9-bromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	5.54 2.00	-4 -3	18	5	11	*	(^{2})
.19	 (2-methoxy-9-bromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	4.52 1.42	-4 -3	16	9	9	*	(^{2})

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.20	 (2-nitrile-9-bromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	3.64 1.64	-3 -2	21	1	15	*	(^{2})
.21	 (2-nitro-9-bromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	6.15 2.48	-3 -2	20	1	14	*	(^{2})
.22	 (2,9-dibromofluorene)	$(CH_3)_2CO$	$10^2A \simeq 1.8$; $10^3B \simeq 5$	kAB	-10 0	1.95 7.6	-3 -3	19	1	13	*	(^{2})

COMMENTS

Reaction: **(.4)** Rate constant calculated for first 8% reaction only, due to experimental complications involving inclusion of KI in precipitating KF, formation of free I_2 and etching of conductivity cell by HF. **(.6)** Reaction followed to about 25% completion. **(.8)** Rate constant calculated for first 8% reaction only, due to experimental complications involving inclusion of KI in precipitating KF, formation of free I_2 and etching of conductivity cell by HF. **(.10) (.12) (.13) (.14)** Reaction followed to about 25% completion. **(.16) - (.22)** Rate constants measured at only two temperatures ten degrees apart so E and A are given with considerable uncertainty.

LITERATURE

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(2) J.D. Dickinson, C. Eaborn, *CSL* **1959**, 3574. (3) P.J.C. Fierens, A. Halleux, *Bull. Soc.
Chim. Belg*. 1955, **64**, 696. (4) A. Pinguair, P.J.C. Fierens, A. Frennet, A. Halleux,
Bull. Soc. Chim. Belg. 1955, **64**, 704.

EXCHANGE
Halogen exchange for halogen on IVth group element

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		$\Delta S^\ddagger$	Comments	Literature
								k^o	n		A^o	n			
.1	$(C_5H_5)_2TiCl_2 + 2LiBr \longrightarrow (C_5H_5)_2TiBr_2 + 2LiCl$ (bis-(cyclopentadienyl)-titanium(IV)chloride)	$\overline{CH_2CH_2CH_2CH_2O}$	$10^4A=2-4; 10^2B\simeq1$			kA	16	8	-5					*	(^{1})
							25	2.0	-4						
							39	4.3	-4	14	3	6	-30		
.2	$(C_5H_5)_2TiBr_2 + 2LiCl \longrightarrow (C_5H_5)_2TiCl_2 + 2LiBr$ (bis-(cyclopentadienyl)-titanium(IV)chloride)	$(CH_3)_2CO$	$10^4A\simeq4; 10^3B=4.1$			kA	16	1.8	-3					*	(^{1})
			4.1				25	3.2	-3						
			10				25	4.2	-3						
			4.2	H_2O	0.56		25	1.5	-2						
			4.2	CH_3OH	0.56		25	3.5	-3						
			4.2	C_6H_5OH	0.56		25	2.0	-3						
			4.1		0		39	6.3	-3	9.2	1.8	4	-39		
		$\overline{CH_2CH_2CH_2CH_2O}$	$\simeq4$ 3.7			kA	16	2.2	-4						
			1.0				25	3.5	-4						
			3.7				25	3.8	-4						
			10.0				25	6.3	-4						
			40				25	8.3	-4						
			100				25	9.2	-4						
			3.9	H_2O	0.56		25	4.7	-3						
			3.9	CH_3OH	0.56		25	9.8	-4						
			3.9	C_6H_5OH	0.56		25	5.0	-4						
			3.9	LiBr	0.10		25	4.2	-4						
			3.7		0		39	6.5	-4	8.4	5	2	-46		

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	$\Delta S^\ddagger$	Comments	Literature
.3	$(C_5H_5)_2TiBr_2 + 2(CH_3)_4NCl \longrightarrow (C_5H_5)_2TiCl_2 + 2(CH_3)_4NBr$ (bis-(cyclopentadienyl)-titanium(IV)bromide)	CH_3NO_2	$10^4A \simeq 4$; $10^3B = 4.4$			kA	16	1.8	-3						(1)
			4.4				25	3.3	-3						
			1.1				25	1.4	-3						
			4.4				39	6.5	-3	9.9	6	4	-37		
.4	$(C_5H_5)_2TiBr_2 + 2(C_6H_5CH_2)(CH_3)_2(C_{18}H_{37})NCl \longrightarrow (C_5H_5)_2TCl_2 + 2(C_6H_5CH_2)(CH_3)_2(C_{18}H_{37})NBr$ (bis-(cyclopentadienyl)-titanium(IV)bromide and benzyldimethyloctadecylammonium chloride)	C_6H_6	$10^4A \simeq 2$; $10^3B = 1.0$			kA	25	4.3	-3					*	(1)
			2.0				25	9.7	-3						
			4.0				25	1.7	-2						
		$\overline{CH_2CH_2CH_2CH_2O}$	$\simeq 2$ 1.0				25	2.7	-3						
			$\simeq 4$ 2.0				25	4.8	-3						
			4.0				25	8.8	-3						
			10				25	2.0	-2						
			20				25	>3	-2						
.5	$(C_5H_5)_2ZrBr_2 + 2LiCl \longrightarrow (C_5H_5)_2ZrCl_2 + 2LiBr$ (bis-(cyclopentadienyl)-zirconium(IV)bromide)	$\overline{CH_2CH_2CH_2CH_2O}$	$10^3A \sim 1$; $10^3B = 3.7$				15	very fast						*	(1)

COMMENTS

Reaction: **(.1)** Initial rate of reaction as reverse reaction important and equilibrium represents about 50% conversion of the chloride to bromide. See reactions (.2)-(.4). **(.2)** Rate dependence with respect to LiCl appears to be about one quarter order. **(.3)** Rate dependence with respect to $(CH_3)_4NCl$ appears to be about one half order. **(.4)** Rate dependence with respect to $(C_6H_5CH_2)(CH_3)_2(C_{18}H_{37})NCl$ appears to be about first order. At concentration of B=0.02 M/l reaction too fast to measure by spectrophotometric method used. **(.5)** Reaction complete within two minutes.

LITERATURE

(1) A. Jensen, F. Basolo, *ACS* 1959, **81**, 3813.

COORDINATIVE EXCHANGE
H_2O replaced by N-compound in Group I complex
(H_2O not always shown in equation)

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	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.1	$2Cu^{+2} + 6CN^- \longrightarrow 2Cu(CN)_2{}^- + (CN)_2$	H_2O	$10^5A=1$; $10^3B=1.6-2.4$	CH_3COONa CH_3COOH	pH=4.75 5.05	kA^2B^6	25 25	3.2 2.3	+17 +18	*	(1)
.2	$2Cu^{+2} + 8CN^- \longrightarrow 2Cu(CN)_3{}^{-2} + (CN)_2$	H_2O	$10^3A=1-6$; $10^3B=6-15$	NH_3	10.5-12.5 $\mu=1$	$-dA/dt=kAB^4$; $k=k_1/(k_2[NH_3]^4+k_3[NH_3]^5)$	0 0 0	$k_1=2.9$ $k_2=2.4$ $k_3=1.5$	+26 +15 +15	*	(2)

COMMENTS

Reaction: **(.1)** Units converted to seconds from original minutes. Eighth order over all could be explained by rapid equilibrium formation of $Cu(CN)_3{}^-$ followed by slow rate determining bimolecular reaction, $2Cu(CN)_3{}^- \longrightarrow 2Cu(CN)_2{}^- + (CN)_2$.

(.2) Concentrations in rate expression are total analytical. Data presented by authors insufficient to verify units or calculations.

LITERATURE

(1) J.H. Baxendale, D.T. Wescott, *CSL* **1959**, 2347.

(2) F.R. Duke, W.G. Courtney, *J.P.C.* 1952, **56**, 19.

COORDINATIVE EXCHANGE

H_2O solvent replacing N compound on Group I complex
(solvent not always shown in equation)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Cu(H_2NCH_2CH_2NH_2)_2^{+2} \longrightarrow Cu(H_2NCH_2CH_2NH_2)^{+2} + H_2NCH_2CH_2NH_2$	CH_3OH		acid		kA	0	> 7	-1	~14			*	(2)(3)
.2	$Cu(H_2NCH_2CH_2NH_2)^{+2} \longrightarrow Cu^{+2} + H_2NCH_2CH_2NH_2$	CH_3OH		acid		kA	0	4	-1	17	1	14	*	(2)(3)
.3	$Cu[H_2N(CH_3)_2CC(CH_3)_2NH_2]_2^{+2} \longrightarrow Cu[H_2N(CH_3)_2CC(CH_3)_2NH_2]^{+2} + H_2N(CH_3)_2CC(CH_3)_2NH_2$	H_2O	$10^2A = 1$	pH = 6.8–7.0		kA	0	2.5	-3	17	1.3	11	*	(3)
				HCl	0.10		0	3.3	-1					
.4	$Cu[H_2N(CH_3)_2CC(CH_3)_2NH_2]^{+2} \longrightarrow Cu^{+2} + H_2N(CH_3)_2CC(CH_3)_2NH_2$	H_2O	$10^2A=1$	HCl	0.10	kA	0	4.0	-2				*	(3)
.5	$Cu(ETM)_2^{+2} \longrightarrow Cu(ETM)^{+2} + ETM$ $ETM = H_2N(CH_3)_2CC(CH_3)(C_2H_5)NH_2$	H_2O	$10^2A=1$	HCl	0.10	kA	0	1.0	-1				*	(3)
.6	$Cu[H_2N(CH_3)_2CC(CH_3)(C_2H_5)NH_2]^{+2} \longrightarrow Cu^{+2} + H_2N(CH_3)_2CC(CH_3)(C_2H_5)NH_2$	H_2O	$10^2A=1$	HCl	0.10	kA	0	2.0	-2				*	(3)
.7	$Cu(DEM)_2^{+2} \longrightarrow Cu(DEM)^{+2} + DEM$ $DEM = H_2N(C_2H_5)(CH_3)CC(C_2H_5)(CH_3)NH_2$	H_2O	$10^2A=1$	HCl	0.10	kA	0	2.5	-2				*	(3)
.8	$Cu(DEM)^{+2} \longrightarrow Cu^{+2} + DEM$ $DEM = H_2N(C_2H_5)(CH_3)CC(C_2H_5)(CH_3)NH_2$	H_2O	$10^2A=1$	HCl	0.10	kA	0	1.0	-2				*	(3)
.9	$Cu(Etio) + H_2SO_4 \longrightarrow Cu^{+2} + H_2Etio + SO_4^{=}$ Etio = Etioporphyrin II	CH_3COOH	$10^6A=6$; $10B=2.16$			kA^2	30	1.19	+1				*	(1)
			2.67				30	3.4	+1					
			2.87				30	4.6	+1					
			3.12				30	7.4	+1					
			3.28				30	8.3	+1					

COMMENTS

Reactions: **(.1) (.2)** Values listed are work of (2) as listed in (3). **(.3)-(.8)** Units converted from original minutes. Rate constants determined in acid solutions are semiquantitative because of limitations of visual method used in following course of reactions. **(.9)** Units converted from original minutes. Rate appears to be fifth order with respect to B but this probably has no real significance. Plot of log *k* versus Hammett's acidity function yields straight line with slope of 4.

LITERATURE

(1) W. S. Caughey, A. H. Corwin, *ACS* 1955, **77**, 1509. (2) J. Bjerrum, K. G. Poulsen, I. Poulsen, *Proceedings of the Symposium on Coordination Chemistry, Danish Chemical Society* **1954**, 51. (3) R. G. Wilkins, *CSL* **1957**, 4521.

COORDINATIVE EXCHANGE
H_2O replacing halogen on Group I complex

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
.1	$AuCl_4^- + 4H_2O \longrightarrow Au(H_2O)_4^{+3} + 4Cl^-$	H_2O	$10^4A=9$	HCl, KNO_3	0.0007, 0.087 $\mu = 0.088$	kA	0	2.8	-3

COMMENTS

Units converted from minutes. Rate constant calculated from measurement of initial rate in order to avoid complications due to reverse reaction.

LITERATURE

R.L. Rich, H. Taube, *JPC* 1954, **58**, 1.

COORDINATIVE EXCHANGE

H_2O replacing N compound in Group II complex
(H_2O not always shown in equation)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$ZnY^= + Pb^{++} \longrightarrow Zn^{++} + PbY^=$ $Y = (OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{-4}$	H_2O	$10^4A = 1-47$; $10^4B = 1.2$	Acetate buffer + KNO_3	$CH_3COONa = 0.1$, $10^6[H^+] = 2.48$ $\mu = 1.00$	$AB(k_1 + k_2[H^+] + k_3[H^+]/L)$	25	$k_1 = 3.4$	-1				*	(¹)
							25	$k_2 = 2$	+4					
							25	$k_3 = 1.2$	+3					
.2	$CdY^= + Cu^{++} \longrightarrow Cd^{++} + CuY^=$ $Y = (OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{-4}$	H_2O	$10^4A = 1-8$; $10^4B = 1.9$	Acetate buffer + KNO_3	$CH_3COONa = 0.1$, $10^6[H^+] = 2.54$, $\mu = 1.00$	$AB(k' + k_3[H^+]/L)$	25	$k' = 2.1$	0				*	(¹)
							25	$k_3 = 1.2$	+3					
.3	$Hg(CN)_2 + Hg^{++} \longrightarrow 2HgCN^+$	H_2O	$10^3A = 1-3$; $10^4B = 6-26$	$NaClO_4$	$\mu = 0.12$	kAB	0	1.67	-2				*	(²)
					1.0		15	8.1	-2					
					pH=2.6 0.01		25	2.62	-1					
					0.12		25	2.50	-1					
					1.0		25	2.30	-1					
					1.0		36	6.1	-1	17	7	11		
.4	$2Hg(CN)^+ \longrightarrow Hg^{++} + Hg(CN)_2$	H_2O	$10^4L = 6-26$; $10^3M = 1-3$	$NaClO_4$	$\mu = 0.12$ pH = 2.6	kA^2	0	8	-4				*	(²)
							25	1.2	-2	17	3	10		

COMMENTS

Reaction: (.1) (.2) Rate constants based on initial rates. Constants probably correct to within 20%. (.3) Rate constant is for initial rate unless combined with constant for reverse reaction, (.4). (.4) Rate constant calculated from equilibrium constant and rate constant of reverse reaction, (.3).

LITERATURE

(¹) K. Bril, S. Bril, P. Krumholz, *JPC* 1956, **60**, 251. (²) R.L. Wolfgang, R.W. Dodson, *ACS* 1954, **76**, 2004.

COORDINATIVE EXCHANGE

$H_2O(OH^-)$ exchange with halogen on Group V complex

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

No.	Reaction	Solvent	Amount of reactant	Salt added	Amount of salt	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	Comments	Literature
.1	$SbCl_6^- + H_2O \longrightarrow HOSbCl_5 + HCl$	H_2O	$10^4A=4; M=1.0$	LiCl	5	kA	25	8.0	-5	*	(1)
			2.0		4		25	9.0	-5		
			4.0		2		25	1.20	-5		
			6.0		0		25	1.43	-5		
			1-6		5-0	$k_1A+k_2A[H^+]$	25	$k_1=6.5$	-5		
							25	$k_2=1.3$	-5		
			.01		9	kA	25	8.8	-5		
			1.0		8		25	1.07	-4		
			2.0		7		25	1.38	-4		
			4.0		6		25	2.00	-4		
			6.0		3		25	2.42	-4		
			9.0		0		25	3.50	-4		
			.01-9		9-0	$k_1A+k_2A[H^+]$	25	$k_1=8.8$	-5		
							25	$k_2=2.7$	-5		
			$10^2A=1-2; M=6.17$	$SbCl_3$	0.0385	kA	25	1.80	-4		
			5.35		0.0385		25	2.60	-4		
			4.55		0.0385		25	5.0	-4		
			3.51		0.0385		25	1.45	-3		
			2.63		0.0385		25	3.67	-3		
			1.78		0.0385		25	5.8	-3		
			2.2		0.00038		25	9.5	-5		
			2.2		0.00188		25	2.97	-4		
			2.2		0.00376		25	5.2	-4		
			2.2		0.00934		25	1.27	-3		
			2.2		0.0185		25	2.35	-3		
			2.2		0.0004-.02	$k_1A+k_2A[SbCl_3]$	25	$k_1=4.5$	-5		
								$k_2=2.2$	-3		

No.	Reaction	Solvent	Amount of reactant	Salt added	Amount of salt	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.2	$HOSbCl_5^- + HCl \longrightarrow SbCl_6^- + H_2O$	H_2O	10^4L=4; B=1.0	LiCl	8	kA	25	3.7	-5	*	(^{1})
			2.0		7		25	7.8	-5		
			3.0		6		25	2.0	-4		
			6.0		3		25	5.5	-4		
			8.0		1		25	9.3	-4		
			9.0		0		25	1.3	-3		

COMMENTS

Reaction: (.1) At high chloride concentration reverse reaction (.2) becomes important. Under these conditions, rate constant was calculated from difference between actual absorbance and calculated absorbance for hypothetical 100% conversion of A. Rate constant extrapolated to zero time. (.2) Rate constant calculated from difference between observed rate constant for approach to equilibrium and initial rate constant of reverse reaction, (.1).

LITERATURE

(¹) H.M. Neumann, R.W. Ramette, *ACS* 1956, **78**, 1848.

COORDINATIVE EXCHANGE
C compound replacing H_2O in Group VI complex

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Cr(H_2O)_6^{+3} + CH_3COO^- \longrightarrow Cr(H_2O)_4(OH)OOCCH_3 + H^+ + H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=4.20	kA	25	1.1	-4				*	(2)
					4.62		25	2.7	-4					
					4.75		25	3.8	-4					
					4.2-4.75	$kA[H^+]^{-1}$	25	7	-9	21				
.2	$Cr(H_2O)_6^{+3} + HOCH_2COO^- \longrightarrow Cr(H_2O)_4(OH)OOCCH_2OH + H^+ + H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=4.34	kA	25	2.2	-4				*	(2)
					4.52		25	4.0	-4					
					4.78		25	8.3	-4					
					5.09		25	1.4	-3					
					4.3-5.1	$kA[H^+]^{-1}$	25	1.2	-8					
.3	$Cr(H_2O)_6^{+3} + C_2O_4^{-2} \longrightarrow Cr(H_2O)_4(C_2O_4)^+ + 2H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=4.25	kA	25	1.4	-4					(2)
					4.59		25	3.5	-4					
					5.04		25	9.1	-4					
					4.2-5.0	$kA[H^+]^{-1}$	25	9	-9					
			$10^3A=1; 10^3B=1-100$	HNO_3 $NaNO_3$	$\mu=0.3$									
					pH=4.42	kA	25	7.4	-5					(1)
					4.73		25	1.41	-4					
					5.10		25	2.95	-4					
					5.30		25	4.7	-4					
					5.49		25	6.2	-4					
					5.71		25	1.10	-3					
					4.4-5.7	$k=\frac{k'K}{K+[H^+]}$	25	k'=2.82	-3	23.2	3	14		
							25	K=1.0	-6					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.4	$Cr(H_2O)_4(C_2O_4)^+ + C_2O_4^{-2} \longrightarrow Cr(H_2O)_2(C_2O_4)_2^- + 2H_2O$	H_2O	$10^3A=1; 10^2B=1$	HNO_3 $NaNO_3$	$\mu=0.3$ pH=4.2-6.2	kA	25	3.1	-4	24	7	13		(1)
.5	$Cr(H_2O)_2(C_2O_4)_2^- + C_2O_4^{-2} \longrightarrow Cr(C_2O_4)_3^{-3} + 2H_2O$	H_2O	$10^3A=1; B=0.1$	HNO_3 $NaNO_3$	pH=4-9	kA	40	1.05	-4	23.2	8	12	*	(3)
.6	$Cr(H_2O)_6^{+3} + CH_3CHOHCOO^- \longrightarrow Cr(H_2O)_4(OH)(CH_3CHOHCOO)^+ + H^+ + H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=4.45	kA	25	3.7	-4				*	(2)
					4.78		25	6.3	-4					
					4.98		25	1.12	-3					
					5.17		25	1.8	-3					
					4.4-5.2	$kA[H^+]^{-1}$	25	1.2	-8					
.7	$Cr(H_2O)_6^{+3} + CH_2(COO)_2^{-2} \longrightarrow Cr(H_2O)_4[CH_2(COO)_2]^+ + 2H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=3.67	kA	25	4.5	-5				*	(2)
					4.01		25	8.9	-5					
					4.79		25	5.2	-4					
					5.49		25	2.5	-3					
					3.7-5.5	$kA[H^+]^{-1}$	25	9	-9					
			$10^3A=1; B=0.1$	$NaNO_3$ HNO_3	$\mu=0.3$									(3)
					pH=4.83	kA	26	1.33	-4					
					5.22		26	2.90	-4					
					5.39		26	4.32	-4					
					5.62		26	6.6	-4					
					5.77		26	9.7	-4					
					4.8-5.8	$k=\frac{k'K}{K+[H^+]}$	26	$k'=2.2$	-3	23.0	1	14		
							26	K=1.0	-6					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.8	$Cr(H_2O)_4[CH_2(COO)_2]^+ + CH_2(COO)_2^{-2} \longrightarrow$ $Cr(H_2O)_2[CH_2(COO)_2]_2^- + 2H_2O$	H_2O	$10^3A=1; B=0.1$	$NaNO_3$ HNO_3	pH=4.81	kA	26	5.0	-5				*	([3])
					5.09		26	1.29	-4					
					5.63		26	2.24	-4					
					6.15		26	4.0	-4					
					4.8-6.1	$k=\frac{k'K}{K+[H^+]}$	26	$k'=9$ K=1	-4 -6	23.7	2	14		
.9	$Cr(H_2O)_2[CH_2(COO)_2]_2^- + CH_2(COO)_2^{-2} \longrightarrow$ $Cr[CH_2(COO)_2]_3^{-3} + 2H_2O$	H_2O	$10^3A=1; B=0.1$	$NaNO_3$ HNO_3	pH=5.5-8	kA	40	4.0	-5	26.6	1	14	*	([3])
.10	$Cr(H_2O)_6^{+3} + OOCCHOHCHOHCOO^{-2} \longrightarrow$ (*tartrate*) $Cr(H_2O)_4(OOCCHOHCHOHCOO)^+ + 2H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=4.18	kA	25	1.6	-4				*	([2])
					4.68		25	5.0	-4					
					5.28		25	2.0	-3					
					4.2-5.3	$kA[H^+]^{-1}$	25	1.0	-8					
.11	$Cr(H_2O)_6^{+3} + C_6H_5O_7^{-3} \longrightarrow Cr(H_2O)_4C_6H_5O_7 + 2H_2O$ (*citrate*)	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=3.83	kA	25	6.1	-5				*	([2])
					4.45		25	2.5	-4					
					4.87		25	5.6	-4					
					5.44		25	1.6	-3					
					3.8-5.4	$kA[H^+]^{-1}$	25	8	-9					
.12	$Cr(H_2O)_6^{+3} + o\text{-}C_6H_4(COO)_2^{-2} \longrightarrow$ $Cr(H_2O)_4[C_6H_4(COO)_2]^+ + 2H_2O$	H_2O	$10^3A=2; B=0.1$	HNO_3	pH=4.39	kA	25	1.8	-4				*	([2])
					5.19		25	1.0	-3					
					4.4-5.2	$kA[H^+]^{-1}$	25	7	-9	23.0				

COMMENTS

Reaction: **(.1) (.2) (.3)** Activation energy based upon rate constants at 25 and 46°C but values at 46° not listed. Rate constants increase by a factor of five on increasing ionic strength by factor of eight. Rate constants for (.1)(.2)(.3)(.6)(.7)(.10)(.11)(.12) may be identical within accuracy of measurements. **(.4)** Only rate constant at 25°C listed. E probably measured for range from 25 to 40°C. Rate constant is independent of ionic strength. **(.5)** Temperature range 10 to 40°C but value of rate constant given only at 40°C. Rate constant independent of ionic strength and pH over range studied. **(.7)** Rate constants observed by (3) identical within experimental accuracy with rate constants for (.1)(.2)(.3)(.6)(.10)(.11)(.12). Temperature range 10 to 40°C used for calculating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ by (4) but values of rate constants at other temperatures not listed. Ionic strength not specifically stated by (4) and rate constant is dependent upon ionic strength. **(.8)** Ionic strength not stated but probably $\mu \sim 0.3$. Rate constant increases with increase in ionic strength. Temperature range 10 to 40°C used but only values at 26°C. listed. **(.9)** Ionic strength and its effect not stated. Temperature range 10 to 40°C but only value at 40°C given.

(.10) (.11) (.12) No added salts to adjust ionic strength. HNO_3 added to obtain desired pH starting with solutions of sodium tartrate, citrate and potassium acid phthalate respectively. Rate constants almost identical for reactions (.1)(.2)(.3)(.6)(.7)(.10)(.11)(.12). Rate constants increase by a factor of about five on increasing ionic strength by a factor of eight.

LITERATURE

(1) R.E. Hamm, R.E. Davis, *ACS* 1953, **75**, 3085. (2) R.E. Hamm, R.L. Johnson, R.H. Perkins, R.E. Davis, *ACS* 1958, **80**, 4469. (3) R.E. Hamm, R,H. Perkins, *ACS* 1955, **77**, 2083.

COORDINATIVE EXCHANGE
N-compound replacing H_2O on Group VI complex
(H_2O not always shown in formula of complex)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Cr(H_2O)_6^{+3} + SCN^- \longrightarrow Cr(H_2O)_5SCN^{+2} + H_2O$	H_2O	$10^3A=6-24$; $10^3B=1-52$	$HClO_4$ + $LiClO_4$	0.1-0.001 $\mu=0.16$	kAB; $k=k_1+k_2[H^+]^{-1}+k_3[H^+]^{-2}$	14	$k_1=6.3$	-7				*	(2)
							14	$k_2=1.72$	-9					
							14	$k_3=1.3$	-13					
							25	$k_1=3.5$	-6					
							25	$k_2=1.41$	-8					
							25	$k_3=5.8$	-12					
							30	$k_1=6.7$	-6	26	2	13		
							30	$k_2=3.6$	-8	33	2	16		
							30	$k_3=1.8$	-11	54	2	28		
					$\mu=0$	k_oAB	14	2.0	-6					
							25	1.1	-5					
							30	2.2	-5	26	1	14		
			$10^2A\simeq2$; $10^2B\simeq2$	$NaClO_4$	1.0	kAB	25	6.2	-6					(3)
					0.0		50	5.0	-4					
					1.0		50	1.7	-4					
					0.0		75	5.5	-3	21	2	11		
					1.0		75	2.8	-3	25	2	13		
.2	$Cr^{+3} + H_2Y^{-2} \longrightarrow CrHY + H^+$ (H_2Y^{-2} is anion of disodium salt of ethylenediaminetetraacetic acid)	H_2O	$10^3A=1-2$	H^+	pH=1.6-5.9	$k'A$; $k'=k([H^+]K^{-1}+1)^{-1}$ $K=1.2\times10^{-5}$	25	$k=1.00$	-3				*	(1)
							31	$k=2.25$	-3					
							37	$k=4.6$	-3					
							42	$k=7.6$	-3	21	5	12		

COMMENTS

Reaction: (.1) Rate law studied for first 1% of reaction only to avoid consecutive reactions with more SCN^-. (2) find dependence of rate constants upon ionic strength given by the expression $\log k = \log k_o + \frac{0.358\,\Delta Z^2\sqrt{\mu}}{1 + A\sqrt{\mu}}$ for k_1 at 25° $\Delta Z^2 = -6$, $A = 1.7$ and for k_2 at 25° $\Delta Z^2 = -8$ and $A = 1.59$, k_o obtained by extrapolation. (3) report negligible dependence upon hydrogen ion concentration in the range 0.1–0.02. (.2) Pseudo first order rate constants k' vary from 1.2×10^{-6} at pH=1.65 to 2.0×10^{-3} at pH 5.86 and 31°C.

LITERATURE

(1) R.E. Hamm, *ACS* 1953, **75**, 5670. (2) C. Postmus, E.L. King, *J.P.C.* 1955, **59**, 1216.
(3) K.G. Poulsen, J. Bjerrum, I. Poulsen, *Acta. Chem. Scand.* 1954, **8**, 921.

COORDINATIVE EXCHANGE
$H_2O(H_3O^+)$ replacing C-compound on VI th group complex

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Cr(C_2O_4)_3^{-3} + 2H_3O^+ \longrightarrow$ *cis*-$Cr(C_2O_4)_2(H_2O)_2^- + H_2C_2O_4$	H_2O	$10^3A=5$; $10B=5$	$NaClO_4$	$\mu=1$	$-dA/dt=kA$	40	6.8	-5				*	(1)
			9.7				40	2.0	-4					
			2–25; 9.7				50	6.5	-4					
			5 0.1				50	3	-6					
			0.2				50	4	-6					
			0.5				50	1.1	-5					
			1.0				50	2.2	-5					
			2.0				50	5.7	-5					
			5.0				50	1.83	-4					
			8.0				50	4.4	-4					
			9.7				50	6.5	-4					
			5				60	6.5	-4					
			9.7				60	1.85	-3					
			5				75	2.7	-3	22.1	2	11		
			9.7				75	6.3	-3	22.1	5	11		
			2–25; 0.1–9.7			$-dA/dt=k_1AB+k_2AB^2$	50	k_1 1.7	-4					
							50	k_2 5.0	-4					
.2	$Cr(C_2O_4)_3^{-3} + 2D_3O^+ \longrightarrow$ *cis*-$Cr(C_2O_4)_2(D_2O)_2^- + D_2C_2O_4$	D_2O	$10^3A=5$; $10B=9.7$	$NaClO_4$	$\mu=1$	$-dA/dt=kA$	50	1.78	-3				*	(1)

COMMENTS

Reaction: (.1) Variation of ionic strength from 1.0 to 2.0 caused no appreciable change in rate constant. Addition of .005 M/l of $H_2C_2O_4$ had no effect on rate. (.2) Value listed for D_2O is extrapolated value from measured rate constants at D/(H+D) ratios from 0 to 0.91.

LITERATURE

(1) K.V. Krishnamurty, G.M. Harris, *JPC* 1960, **64**, 346.

COORDINATIVE EXCHANGE
$H_2O(H_3O^+)(OH^-)$ replacing N-compound on VIth group complex

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Cr(NH_3)_6^{+3} + H_2O \longrightarrow Cr(NH_3)_5(H_2O)^{+3} + NH_3$	H_2O	$10^2A \simeq 1$	HNO_2	1.0	kA	25	2.0	-7				*	(3)
			3		1.0		40	1.4	-6					
			5		0.4		40	1.42	-6					(4)
			13		1.0		64	3.1	-5	26	2	12		(3)
.2	$Cr(NH_3)_6^{+3} + OH^- \longrightarrow Cr(NH_3)_5(OH)^{+2} + NH_3$	H_2O	$10^2A=5.3; B=0.1$	KNO_3	0.3	kA	40	2.8	-6				*	(4)
.3	$Cr(NH_3)_5(H_2O)^{+3} + H_2O \longrightarrow Cr(NH_3)_4(H_2O)_2^{+3} + NH_3$ (*cis and trans*)	H_2O	$10^2A=5.7$	HNO_3	0.4	kA	40	2.36	-5					(4)
			6.0	$\left\{\begin{matrix} HNO_3 + \\ KNO_3 \end{matrix}\right.$	$\left.\begin{matrix} 0.2 \\ 0.2 \end{matrix}\right\}$		40	2.44	-5					
.4	$Cr(NH_3)_5(OH)^{+2} + OH^- \longrightarrow Cr(NH_3)_4(OH)_2^{+1} + NH_3$	H_2O	$10^2A=5.3; B=0.1$	KNO_3	0.3	kA	40	9.7	-6					(4)
.5	*cis*-$Cr(NH_3)_4(H_2O)_2^{+3} + H_2O \longrightarrow$ $Cr(NH_3)_3(H_2O)_3^{+3} + NH_3$ (*cis and trans*)	H_2O	not stated	HNO_3	0.4	kA	40	3.1	-5					(4)
.6	*cis*-$Cr(NH_3)_4(OH)_2^{+} + OH^- \longrightarrow$ $Cr(NH_3)_3(OH)_3 + NH_3$ (*cis and trans*)	H_2O	$10^2A=3.1; B=0.1$	KNO_3	0.3	kA	40	8	-4				*	(4)
.7	$Cr(NH_3)_5F^{+2} + 5H_3O^+ \longrightarrow Cr(H_2O)_5F^{+2} + 5NH_4^+$	H_2O	$10^3A=6.2; B=1.0$	Cr^{+2}	0.038	$kA[Cr^{+2}]=-dA/dt$	27	3.0	-4				*	(5)
			4.7				34	5.3	-4					
			4.7				41	8.7	-4	13	2	6		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.8	$Cr(NH_3)_5Cl^{+2}+5H_3O^+ \longrightarrow Cr(H_2O)_5Cl^{+2}+5NH_4^+$	H_2O	$10^3A=6$; B=1.0	Cr^{+2}	0.016	$-dA/dt=kA[Cr^{+2}]$	10	1.88	-2				*	(5)
			5		.015		14	2.45	-2					
			7-25		0.005-.01		26	5.5	-2					
			12 0.2		0.0092		26	5.4	-2					
			5 1.0	Cr^{+2} + added salts	0.0097 μ= 1.15		26	5.9	-2					
			7-11 1.0	Cr^{+2}	0.004		39	1.2	-1	11.1	7	6		
		86.4% D_2O	11 1.0		0.005		26	4.2	-2					
.9	$Cr(NH_3)_5Br^{+2} + 5H_3O^+ \longrightarrow Cr(H_2O)_5Br^{+2}+5NH_4^+$	H_2O	$10^3A=5$; B=1.0	Cr^{+2}	0.0035	$-dA/dt=kA[Cr^{+2}]$	12	1.66	-1				*	(5)
			4 0.9		0.0023		24	3.4	-1					
			5-10 1.0		0.0022		28	3.9	-1					
			10		0.0012		39	6.4	-1	8.5	6	5		
.10	$Cr(NH_3)_5I^{+2}+5H_3O^+ \longrightarrow Cr(H_2O)_5I^{+2} + 5NH_4^+$	H_2O	$10^3A=5$; B=1.0	Cr^{+2}	0.00023	$-dA/dt=kA[Cr^{+2}]$	26	6	0				*	(5)
.11	$Cr(SCN)_6^{-3} + H_2O \longrightarrow Cr(SCN)_5(H_2O)^{-2} + SCN^-$	H_2O	$10^2A=2$	$HClO_4$ + $NaClO_4$	0.02	kA							*	(6)
					0		15	5.2	-6					
					1.0		15	5.0	-6					
					0.0		25	2.32	-5	26	2	14		
					1.0		25	2.18	-5	25	1	14		
.12	$Cr(H_2O)_5SCN^{+2} + H_2O \longrightarrow Cr(H_2O)_6^{+3} + SCN^-$	H_2O	$10^2A \simeq 1.4$	$HClO_4$	0.25-1.0	kA	14	1.46	-9				*	(7)
					0.05-0.15		25	9.1	-9					
			$10^2L \simeq 2$; $10^2M \simeq 2$	$HClO_4$ + $NaClO_4$	0.02		25	8.4	-8					(6)
					1.0		50	2.75	-6					
							75	5.3	-5	26.5	6	12		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.13	$Cr(NH_3)_2(NCS)_4^- + H_2O \longrightarrow Cr(NH_3)_2(NCS)_3(H_2O) + NCS^-$	H_2O	$10^2A=1-2$	KI or NaN_3	0-.03	$dM/dt=kA$	50	6.7	-5				*	(^{1})
							60	2.4	-4	27	1	14		
.14	$Cr(NH_3)_2(NCS)_4^- + D_2O \longrightarrow Cr(NH_3)_2(NCS)_3(D_2O) + NCS^-$	D_2O	$10^2A\sim1$; B=99% D_2O			$dM/dt=kA$	60	1.25	-4				*	(^{1})
.15	$Cr(NH_3)_2(NCS)_4^- + CH_3OH \longrightarrow Cr(NH_3)_2(NCS)_3(CH_3OH) + NCS^-$	CH_3OH	$10^2A\sim1$			$dM/dt=kA$	50	6.6	-5				*	(^{1})
				KCN	0.01-.08		50	1.07	-4					
					0		60	2.6	-4	28	1	15		
		M 50 N*	$10^2A\sim1$			$dM/dt=kA$	60	1.03	-4	31				
				CH_3COONa	0.1		60	1.67	-4					
		M 10 N*	$10^2A\sim1$			$dM/dt=kA$	60	2.2	-5					
				KCN or KOH	0.1		60	6.7	-5					
		M 50 D*	$10^2A\sim1$			$dM/dt=kA$	60	2.2	-5					
.16	$Cr(NH_3)_2(NCS)_4^- + C_2H_5OH \longrightarrow Cr(NH_3)_2(NCS)_3(C_2H_5OH) + NCS^-$	C_2H_5OH	$10^2A\sim1$			$dM/dt=kA$	60	1.72	-4				*	(^{1})
.17	$Cr(NH_3)_5(NCS)^{+2} + H_2O \longrightarrow Cr(NH_3)_5(H_2O)^{+3} + NCS^-$	H_2O	$10^2A=2$	$HClO_4$	pH=2.5	kA	25	9.3	-8	25				(^{2})

CODED SOLVENTS

M 50 N* = CH_3OH 50% by volume + CH_3NO_2
M 10 N* = CH_3OH 10% by volume + CH_3NO_2
M 50 D* = CH_3OH 50% by volume + dioxane

COMMENTS

Reaction: (.1) Reaction followed by rate of production of NH_4^+. Reaction involves several consecutive steps with rate constants for each step calculated by (4) (see (.3)(.5). Temperature dependence of overall apparent rate observed by (3). (.2) Reaction involves several consecutive steps. See (.4) and (.6). (.6) Rate constant not accurate. Listed to give order of magnitude only. (.7) Exchange of F^- takes place simultaneously. The F^- exchange is not catalyzed by Cr^{+2}. See 382.670. (.8) Simultaneous exchange of Cl^- with H_2O is not catalyzed by Cr^{+2}. See 382.670. (.9) Simultaneous exchange of Br^- is not catalyzed by Cr^{+2}. See 382.670. (.10) Simultaneous exchange of I^- is not catalyzed by Cr^{+2}. See 382.670. NH_3 exchange was too rapid for accurate measurement. (.11) Only 20% reaction followed to avoid complications of consecutive exchanges. Reaction carried out in the dark. (.12) Calculated by (6) from rate of reverse reaction and equilibrium constant. Reverse reaction is independent of $[H^+]$ in range 0.02-0.10 see 382.605. (.13) Rate constant is based upon fraction NCS^- reacted per one NCS^- per Cr. For first 50% reaction the ratio of M produced to A reacted was 2.25 with a limiting value of 3.2. Reacted in dark.

(.14) Rate constant calculated on basis of fraction NCS^- produced per one NCS^- per Cr. Rate determining initial reaction followed by rapid equilibrium leading to between 2 and 3 NCS^- per Cr. Reacted in dark. (.15) Rate constant calculated on basis of fraction NCS^- produced per one NCS^- per Cr. Rate determining initial reaction probably followed by rapid equilibrium leading to 2.75 NCS^- per Cr. Reaction carried out in dark as it is light catalyzed. (.16) Rate constant calculated on basis of fraction of NCS^- produced per one NCS^- per Cr. Probably followed by rapid equilibrium leading to between 2 and 3 NCS^- per Cr reacted. Reaction carried out in dark as it is light catalyzed.

LITERATURE

(1) A.W. Adamson, *ACS* 1958, **80**, 3183. (2) A.W. Adamson, R.G. Wilkins, *ACS* 1954, **76**, 3379. (3) J. Bjerrum, C.G. Lamm, *Acta. Chem. Scand.* 1955, **9**, 216. (4) E. Jorgensen, J. Bjerrum, *Acta. Chem. Scand.* 1958, **12**, 1047. (5) A.E. Ogard, H. Taube, *ACS* 1958, **80**, 1084. (6) K.J. Poulsen, J. Bjerrum, I. Poulsen, *Acta. Chem. Scand.* 1954, **8**, 921. (7) C. Postmus, E.L. King, *J.P.C.* 1955, **59**, 1216.

COORDINATIVE EXCHANGE
Halogen replaced by $H_2O(H_3O^+)(OH^-)$ on VIth group complex
(H_2O not always shown in complex)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$CrCl^{+2} \longrightarrow Cr^{+3} + Cl^-$	H_2O	$10^2A=2.5–7.5$ $\mu = 1.5$	$\begin{cases} Mn^{+3} \\ H^+ \end{cases}$	.001–.008 0.5–1.0	$kA[Mn^{+3}] \times [H^+]$	25	7.6	-3				*	(4)
.2	$Cr(H_2O)_4Cl_2^+ + Ag^+ + H_2O \longrightarrow Cr(H_2O)_5Cl^{+2} + AgCl$	H_2O	$10^2A=2–7$; $10^2B=2–7$	$HClO_4$	6	kAB	25	3.5	-2				*	(2)
.3	$Cr(H_2O)_5Cl^{+2} + Ag^+ + H_2O \longrightarrow Cr(H_2O)_6^{+3} + AgCl$	H_2O	$10^3A=5–28$; $10^3B=8–97$	$HClO_4$	6	kAB	25	1.13	-4					(2)
			8 118		4		25	1.9	-4					
			16 94		4		25	2.2	-4					
			36 48		3		25	3.2	-4					
			27 35		3		30	6.3	-4	25	1	14		
.4	$Cr(NH_3)_5F^{+2} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{+3} + F^-$	H_2O	$10^2A=3.8$	$HClO_4$	1.0	kA	27	2	-7				*	(5)
							34	5	-7					
							41	1.6	-6	28	5	13		
.5	$Cr(NH_3)_5Cl^{+2} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{+3} + Cl^-$	H_2O				kA	25	$\underline{9}$	-6				*	(1) (3)
			$10^2A=1$	$HClO_4$	1.0		25	7.3	-6					(5)
							33	1.6	-5					
							41	5.7	-5	24	3	12		
.6	$Cr(NH_3)_5Br^{+2} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{+3} + Br^-$	H_2O		HCl	0.1	kA	0	1.7	-6					(3)
							25	5	-5					(1) (3)
			$10^2A \simeq 1$	$HClO_4$	1.0		25	6.8	-5					(5)
							25	1.0	-4					
							34	2.4	-4					
							39	4.4	-4	24	3	13		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.7	$Cr(NH_3)_5I^{+2} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{+3} + I^-$	H_2O		HCl	0.1	kA	0	~2	-4				*	(3)
							26	8	-4					(5)
.8	*cis*-$Cr(NH_2CH_2CH_2NH_2)_2Cl_2{}^+ + H_2O \longrightarrow$ *cis*-$Cr(NH_2CH_2CH_2NH_2)_2Cl(H_2O)^{+2} + Cl^-$	H_2O	$10^3A=5$	HNO_3	0.1	kA	20	1.60	-4				*	(7)
			5		0.1		25	3.30	-4					
			2		0.1		25	3.5	-4					(6)
			6	$HClO_4$	0.1		25	3.22	-4					(7)
			4		0.1		25	3.47	-4					
			2.5		0.1		25	3.58	-4					
			5	$HClO_4$ +	0.1									
				Na_2SO_4	0.01		25	3.30	-4					
					0.05		25	3.57	-4					
					0.10		25	4.03	-4					
			5	HNO_3	0.1		30	5.9	-4	21	1.0	12		
.9	*cis*-$Cr(NH_2CH_2CH_2NH_2)_2Cl_2{}^+ + OH^- \longrightarrow Cr(NH_2CH_2CH_2NH_2)_2Cl(OH)^+ + Cl^-$	H_2O	$10^3A=2$; B=0.1			kAB	25	2.7	-2					(6)
.10	*trans*-$Cr(NH_2CH_2CH_2NH_2)_2Cl_2{}^+ + H_2O \longrightarrow Cr(NH_2CH_2CH_2NH_2)_2Cl(H_2O)^{+2} + Cl^-$	H_2O	$10^3A=2$	HNO_3	0.1	kA	25	3.9	-5					(6)
				CH_3COOH CH_3COONa	pH=4.2-4.6 0.1		25	3.9	-5					
.11	*trans*-$Cr(NH_2CH_2CH_2NH_2)_2Cl_2{}^+ + OH^- \longrightarrow Cr(NH_2CH_2CH_2NH_2)_2Cl(OH)^+ + Cl^-$	H_2O	$10^3A=2$; B=0.1			kAB	25	3.7	-2					(6)
.12	*cis*-$Cr(NH_2CH_2CH_2NH_2)_2Cl(H_2O)^{+2} + H_2O \longrightarrow$ *cis*-$Cr(NH_2CH_2CH_2NH_2)_2(H_2O)_2{}^{+3} + Cl^-$	H_2O	$10^3A=5$	HNO_3	0.1	kA	20	1.0	-5				*	(7)
							25	2.8	-5					

COMMENTS

Reaction: **(.1)** Mn^{+3} generated in situ by oxidation of Mn^{+2} with Co^{+3} or Ce(IV). Units converted to sec from minutes although authors label data in minutes in one place and seconds in another. Value is for initial rate. **(.2)** Rate constant erratic with variation from 2×10^{-2} to 6×10^{-2}. Reaction followed from 10 to 50% completion. **(.4) (.5) (.6)** Simultaneous exchange of NH_3 catalyzed by Cr^{+2} see 382.650. **(.7)** Rate constant estimated as reaction is fast and iodosalt dissolved relatively slowly. **(.8)** Selected data of (7). Rate constant calculated for first 40% as consecutive reaction becomes important in later stages. See (.12). **(.12)** Rate constant calculated from equation for consecutive first order reactions with reaction (.8) the initial reaction.

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COORDINATIVE EXCHANGE
H_2O or OH^- replacing carboxylate in VIIIth group complex

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	$k = k^o \times 10^n$		Comments
								k^o	n	
.1	$Co(NH_3)_5(CH_3COO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + CH_3COO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	8.2	-6	*
.2	$Co(NH_3)_5(CH_3COO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + CH_3COO^-$	H_2O	$10^3A=4$; $10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	7.0	-4	*
.3	$Co(NH_3)_5(C_2H_5COO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + C_2H_5COO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	3.2	-6	*
.4	$Co(NH_3)_5(C_2H_5COO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + C_2H_5COO^-$	H_2O	$10^3A=4$; $10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	4.5	-4	*
.5	$Co(NH_3)_5((CH_3)_2CHCOO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + (CH_3)_2CHCOO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	2.7	-6	*
.6	$Co(NH_3)_5((CH_3)_2CHCOO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + (CH_3)_2CHCOO^-$	H_2O	$10^3A=4$; $10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	5.7	-4	*
.7	$Co(NH_3)_5((CH_3)_3CCOO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + (CH_3)_3CCOO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	4.3	-6	*
.8	$Co(NH_3)_5((CH_3)_3CCOO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + (CH_3)_3CCOO^-$	H_2O	$10^3A=4$; $10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	3.0	-4	*
.9	$Co(NH_3)_5(CH_2OHCOO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + CH_2OHCOO^-$	H_2O	$10^3A=4$; $10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	1.2	-3	*
.10	$Co(NH_3)_5(CF_3COO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + CF_3COO^-$	H_2O	$10^3A=4-8$	NO_3^-	2A	kA	70	5.5	-5	*
.11	$Co(NH_3)_5(CF_3COO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + CF_3COO^-$	H_2O	$10^3A=4$; $10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	7.3	-2	*
.12	$Co(NH_3)_5(CH_2ClCOO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + CH_2ClCOO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	5.8	-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
.13	$Co(NH_3)_5(CH_2ClCOO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + CH_2ClCOO^-$	H_2O	$10^3A=4;\ 10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	4.2	-3	*
.14	$Co(NH_3)_5(CHCl_2COO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + CHCl_2COO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	1.6	-5	*
.15	$Co(NH_3)_5(CHCl_2COO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + CHCl_2COO^-$	H_2O	$10^3A=4;\ 10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	2.7	-2	*
.16	$Co(NH_3)_5(CCl_3COO)^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + CCl_3COO^-$	H_2O	$10^3A=4$	NO_3^-	2A	kA	70	5.3	-5	*
.17	$Co(NH_3)_5(CCl_3COO)^{++} + OH^- \longrightarrow Co(NH_3)_5(OH)^{++} + CCl_3COO^-$	H_2O	$10^3A=4;\ 10^3B=4$	Na^+, NO_3^-	B, 2A	kAB	25	7.2	-2	*

COMMENTS

All reactions except (.10) and (.11) followed only to about 10% completion because of evolution of NH_3 which occurs autocatalytically on standing. This interference is not appreciable for (.10) and (.11) until after 60% completion. Rate constants converted to seconds from original minutes. (.2) (.4) (.6) (.8) (.9) (.11) (.13) (.15) (.17) Rate law with respect to each reactant not confirmed as initial concentrations of both reactants were equal.

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COORDINATIVE EXCHANGE

N compound replacing H_2O in VIIIth group complex
(H_2O not always shown in formula of complex)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Fe^{++} + 3\,dipy \longrightarrow Fe(dipy)_3^{++}$	H_2O	$10^5A \simeq 1$; $10^4B = 3-20$	buffers	pH=1.85-4.06 }	kAB^3	0	1.42	+13				*	(3)
	dipy = 2,2'-dipyridyl			$\mu = 0.025$			17	1.40	+13					
				$SO_4^=$	= A		35	1.48	+13	0	1.4	+13		
.2	$Fe^{++} + 3\,phen \longrightarrow Fe(phen)_3^{++}$	H_2O	$10^3A = 2-5$; $10^9B = 2-5$	H_2SO_4; $SO_4^=$	0.5; = A	kAB^3	25	2.2	+17				*	(6)
	phen = 1,10-phenanthroline		not stated	H_2SO_4; $SO_4^=$	0.5; = A		25	1.3	17					(5)
.3	$Fe^{++} + 3\,pphen \longrightarrow Fe(pphen)_3^{++}$	H_2O	not stated	H_2SO_4; $SO_4^=$	0.5; = A	kAB^3	25	1.3	+17				*	(5)
	pphen = 5-phenyl-1,10-phenanthroline													
.4	$Fe^{++} + 3\,nphen \longrightarrow Fe(nphen)^{++}$	H_2O	not stated	H_2SO_4; $SO_4^=$	0.5; = A	kAB^3	25	8.4	+14				*	(5)
	nphen = 5-nitro-1,10-phenanthroline													
.5	$Fe^{++} + 3\,cphen \longrightarrow Fe(cphen)^{++}$	H_2O	not stated	H_2SO_4; $SO_4^=$	0.5; = A	kAB^3	25	1.1	+16				*	(5)
	cphen = 5-chloro-1,10-phenanthroline													
.6	$Co(NH_3)_5H_2O^{+++} + NO_2^- \longrightarrow$	H_2O	$10^3A = 5$; $10^2B = 100$	HNO_2 }	= B/8 }	$kA = dL/dt$	25	7.7	-5				*	(8)
	$Co(NH_3)_5NO_2^{++} + H_2O$		60	$NaClO_4$ }	= B/8 }		25	5.7	-5					
			20		$\mu = 1.125$; pH $\simeq$ 4.1		25	4.5	-5					
			5				25	3.3	-5					
			2.5				25	1.6	-5					
			$10^3A = 5$; B=1.1	NaOH	0.005; $\mu = 1.125$		25	4.5	-7					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$Co(NH_3)_5H_2O^{+++} + NO_2^- \longrightarrow$ *(cont.)*	H_2O	$10^3A=5; 10^2B=5$	$HNO_2; NaClO_4$	$10^3HNO_2=6.3; \mu=1.125$	$kA=-dA/dt$	25	2.7	-4				*	(8)
			10		12.5		25	1.0	-3					
			20		25		25	4.2	-3					
			20		12.5		25	2.3	-3					
			20		6.3		25	9.8	-4					
			(Intermediate reaction see Supplementary Tables)											
.7	*cis*-$Co(en)_2(NO_2)H_2O^{++} + NO_2^- \longrightarrow$ *cis*-$Co(en)_2(NO_2)_2^+ + H_2O$ en = ethylenediamine	H_2O	$10^3A=5; 10B=4$	$\left.\begin{matrix}HNO_2\\NaClO_4\end{matrix}\right\}$	$10^3HNO_2=4$	$kA=-dA/dt$	25	8.5	-4				*	(8)
			6		6		25	1.6	-3					
			8		4		25	1.1	-3					
			8		8		25	2.3	-3					
			8		14		25	3.9	-3					
			10		10		25	3.5	-3					
			1		1		35	1.3	-4					
			10		10		35	5.6	-3					
			$10^3A=3; 10B=1$	$HClO_4$	pH=5.4	$kA=-dA/dt$	35	1.3	-4					(2)
			4				35	6.2	-4					
			10				35	8.4	-4					
			20				35	8.6	-4					
			(Intermediate reaction see Supplementary Tables)											
.8	*trans*-$Co(en)_2(NO_2)H_2O^{++} + NO_2^- \longrightarrow$ *trans*-$Co(en)_2(NO_2)_2^+ + H_2O$ en = ethylenediamine	H_2O	$10^3A=3; 10B=1$	$HClO_4$	pH=5.4	kA	35	7.0	-4				*	(2)
			4				35	3.4	-3					
			10				35	6.0	-3					
			20				35	9.2	-3					
.9	*cis*-$Co(en)_2(NO_2)H_2O^{++} + SCN^- \longrightarrow$ *cis*-$Co(en)_2(NO_2)SCN^+ + H_2O$ en = ethylenediamine	H_2O	$10^3A=3; 10B=1$	$HClO_4$	pH=5.4	kA	35	2.5	-5				*	(2)
			2.5				35	8.7	-5					
			10				35	1.5	-4					
			20				35	2.9	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.10	*cis*-$Co(en)_2(NO_2)H_2O^{++} + N_3^- \longrightarrow$ *cis*-$Co(en)_2(NO_2)N_3^+ + H_2O$ en = ethylenediamine	H_2O	$10^3A=3$; $10B=4$	$HClO_4$	pH=5.4	kA	35	1.25	-4				*	(2)
			8				35	2.4	-4					
			24				35	5.2	-4					
			32				35	7.0	-4					
.11	$HCo(edta)H_2O \longrightarrow Co(edta)^- + H^+ + H_2O$ edta = ethylenediaminetetraacetate ion	H_2O	$10^3A=2-4$	HCl KCl	pH=1; $\mu=0.1$	kA	8	1.6	-5				*	(9)
							15	5.7	-5					
					1.0		15	6.7	-5					
					0.1		25	2.2	-4	25	4	14		
.12	$Co(edta)H_2O^- \longrightarrow Co(edta)^- + H_2O$ edta = ethylenediaminetetraacetate ion	H_2O	$10^3A=2-4$	CH_3COOH	pH=5-6; $\mu=0.1$	kA	0	3.7	-5				*	(9)
				CH_3COO^-			8	1.2	-4					
				or $H_2PO_4^-$			15	4.1	-4	25	1.1	16		
				$HPO_4^=$	$\mu=1.0$		15	7.7	-4					
				KCl										
.13	$Co(edta)OH^= \longrightarrow Co(edta)^- + OH^-$ edta = ethylenediaminetetraacetate ion	H_2O	$10^3A=2-4$	$HClO_3^-$ CO_3^{-2} KCl	pH=10-10.5; $\mu=0.1$	kA	15	1.4	-5				*	(9)
							25	4.3	-5					
.14	$Ni^{++} + phen \longrightarrow Ni(phen)^{++}$ phen = 1,10-phenanthroline	H_2O	$10^6A=5-130$; $10^5B=6-300$	$HClO_4$	0.75-0.38	kAB	25	3.0	-4				*	(7)
				$HClO_4$, $NaClO_4$	0.38; 0.50		25	2.5	-4					
					0.11; 0		25	2.0	-4					
					0.07; 0.50		25	1.6	-4					
					0.021; 0		25	8.6	-5					
					0.0064; 0		25	2.1	-5					
.15	$Ni^{++} + 2dtc^- \longrightarrow Ni(dtc)_2$ dtc = N,N-di-*n*-propyldithiocarbamate ion	$CH_3OCH_2CH_2OH$	$10^5A=1-10$; $10^5B=1-10$	$NaClO_4$ K^+	0.1M = B	kAB^2	22	2	6				*	(4)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Literature
								k^o	n	
.16	*cis*-$Pt(NH_3)_2H_2OCl^+ + 2C_5H_5N \longrightarrow$ *cis*-$Pt(NH_3)_2(C_5H_5N)_2^{++} + H_2O + Cl^-$	H_2O	$10^4A=5; 10^2B=1-2$			kA	25	2.5	-5	(1)
.17	*cis*-$Pt(NH_3)_2H_2OCl^+ + 2NO_2^- \longrightarrow$ *cis*-$Pt(NH_3)_2(NO_2)_2 + H_2O + Cl^-$	H_2O	$10^4A=5; 10^3B=3.2$	K^+	=B	kA	25	6.5	-5	(1)
			5	K^+	=B		25	9.7	-5	

COMMENTS

Comments by Literature Reference: (1) (2) (3) (4) (5) (6) (8) (9) Units converted to seconds from original minutes.

Comments by Reaction: **(.1)** For reverse reaction see 382.850.2. **(.2)** Under reaction conditions reaction is pseudo zero order due to control of concentrations by a rapid equilibrium. Rate is proportional to AB^3 and fourth order specific rate constant calculated. **(.3) (.4) (.5)** Under reaction conditions reaction is pseudo zero order due to control of concentrations by a rapid equilibrium. Concentration of B calculated using acid dissociation constant of substituted phenanthrolium ion. Specific reaction rate constant for fourth order reaction kAB^3 was calculated. Temperature not specified by (5) and assumed to be 25°C. For reverse reactions see 382.850 (.5) (.6) and (.7) respectively. **(.6)** Reaction proceeds through formation of intermediate nitrito compound with subsequent rearrangement to L. Rearrangement also shows first order behavior with rates given in Supplementary Tables. Initial reaction for formation of nitrito complex can be written in terms of either of following (kinetically indistinguishable) rate expressions: $-dA/dt=k[\text{aquo complex}][HNO_2][NO_2^-]$ or $-dA/dt=[\text{hydroxocomplex}][HNO_2]^2$. Latter equation similar to that found for nitrosation of ammonia and amines (see A. T. Austin, E. D. Hughes, J. H. Ridd, C. K. Ingold, *ACS* 1952, **74**, 555). **(.7) (.8)** Zero order dependence upon B at high B concentration due to initial reaction forming nitritonitro complex,, $Co(en)_2(NO_2)ONO^+$, which then rearranges at limiting rate to dinitro complex. At pH=0.85 rate about 1/10 rate at pH=5.4. Rate constants are pseudo first order with B in large excess. **(.9)** Rate followed spectrophotometrically at 490 and 290 mμ. Absorbtion at $t = \infty$ is dependent on initial SCN^- concentration. Rate constants corrected for reverse reaction which is also assumed to be pseudo first order. Estimated value of equilibrium constant=1.7.

(.10) Reaction pseudo first order with B present in excess. **(.11) (.12) (.13)** All three reactions occur simultaneously. Rate of increase of L measured spectrophotometrically and is equal to $k_{.8}[HCo(edta)H_2O] + k_{.9}[Co(edta)H_2O^-]$

COMMENTS *(continued)*

$+k_{.10}[\mathrm{Co(edta)OH^{=}}]$. Assuming pK for $\mathrm{HCo(edta)H_2O}$ and $\mathrm{Co(edta)H_2O^{-}}$=3.1 and 8.1, respectively:

$$k_{obs} = \frac{[k_{.8}[\mathrm{H^+}]^2 + k_{.9}(10^{-3.1})[\mathrm{H^+}] + k_{.10}(10^{-11.2})]}{[(\mathrm{H^+})^2 + 10^{-3.1}(\mathrm{H^+}) + 10^{-11.2}]}$$

at pH=1, $k_{obs} \simeq k_{.8}$; pH=5-6, $k_{obs}=k_{.9}$; pH=10-10.5, $k_{obs}=k_{.10}$. **(.14)** For reverse reaction see 382.850(.23). Rate constant dependence upon concentration of $\mathrm{H^+}$ given by:

$$k = \frac{(\mathrm{H^+}) + 4.3 \times 10^{-3}}{2.62\times10^{-5}(\mathrm{H^+}) + 2.58\times10^{-6}}$$

(.15) For reverse reaction see 382.850(.32).

SUPPLEMENTARY TABLES

Intermediate Reactions					
(.6) $\mathrm{Co(NH_3)_5ONO^{++} \longrightarrow Co(NH_3)_5NO_2^{++}}$					
Solvent = $\mathrm{H_2O}$; 10^3A=5; μ = 1.125 with $\mathrm{NaClO_4}$; pH=4.1; kA=−dA/dt T=25					
$10^2[\mathrm{NO_2^-}]$	0	5	20	40	100
10^5k	3.2	4.2	4.2	4.8	7.7
(.7) $cis\text{-}\mathrm{Co(en)_2(NO_2)ONO^+} \longrightarrow cis\text{-}\mathrm{Co(en)_2(NO_2)_2^+}$					
Solvent= $\mathrm{H_2O}$; 10^3A=5; T = 35					
$10^2[\mathrm{NO_2^-}]$	0	100			
$10^2[\mathrm{HNO_2}]$	0	1			
10^4k	7.6	7.8			

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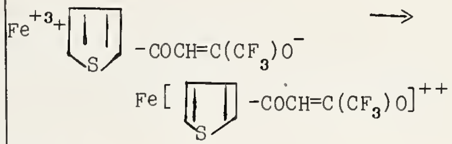
COORDINATIVE EXCHANGE
S compound replacing H_2O in VIIIth group complex
(H_2O not always shown)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Fe^{+++} + SCN^- \longrightarrow Fe(SCN)^{++}$	H_2O	$10^3A=5-8$; $10^3B=1-1.5$	$\begin{cases} H^+ \\ NaClO_4 \end{cases}$	0.0308, $\mu=0.4$	kAB	16	2.64	+2					(1)
							25	7.3	+2					
							30	1.40	+3					
			$10^3A=6-9$; $10^3B=1-1.5$		0.224, $\mu=0.4$		14	7.1	+1					
							23	1.88	+2					
							32	3.92	+2					
						$k=k_1+k_2[H^+]^{-1}$	25	$k_1=1.27$	+2	13	4	11		
							25	$k_2=2.02$	+1	20	1	16		
.2		H_2O	$10^4A=4$; $10^3HB=6$	HNO_3	0.1	kAB	16	2.9	+3				*	(2)
			3-13		0.1-0.2		25	1.33	+4					
			6		0.1		35	3.7	+4	21	3	19		
.3	$Co(NH_3)_5H_2O^{+++} + SO_4^{=} \longrightarrow Co(NH_3)_5SO_4^{+} + H_2O$	H_2O	A<8B; $10^3A=1-15$; $10^2B=1.4$	H^+, Na^+	0.01, =2B	kA	31	2.0	-6				*	(3)
			2.1				31	2.5	-6					
			5.2				31	3.2	-6					
			16		0.015		31	3.7	-6					
				H^+, K^+			31	3.3	-6					
				H^+, Mg^{++}	= B		31	4.0	-6					
			60	H^+, Na^+	0.050, = 2B		31	5.2	-6					
			300		0.3		31	7.8	-6					
			16		0.01, = 2B, $NaClO_4$=0.54		31	3.2	-6					
			5.4		2.0		31	9.2	-7					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.3	$Co(NH_3)_5H_2O^{+++} + SO_4^{=} \longrightarrow$ *(cont.)*	H_2O	$A<8B$; $10^3A=1-15$; $10^2B=1.4$	Na_2SO_4, $NaHSO_4$, $NaClO_4$	0.054, 0.1, 0.6	kA	31	2.5	-6				*	(3)
					0.54, 0.1, 1.4		31	4.2	-6					
					0.54, 1.5		31	6.0	-6					
				H_2SO_4	3		31	7.0	-6					
				$NaHSO_4$	3		31	6.5	-6					
				H_2SO_4	6		31	1.40	-5					
				H_2SO_4, $NaHSO_4$	1, 5		31	1.15	-5					
				H_2SO_4	9		31	2.5	-5					
			5	H^+, Na^+	0.01, =2B		44	1.5	-5	24	3	11		

COMMENTS

Reaction: **(.1)** Selected data. **(.2)** Units converted from original minutes. B added in form of keto compound which establishes rapid equilibrium with enolate ion and H^+. Rate determining step assumed to be reaction as written. Rate constants calculated from rate at which latter reaction approached equilibrium and equilibrium constants for the enolization of 1.49, 2.55 and 2.83 at 16, 25 and 35°C, respectively. **(.3)** Units converted from original minutes. Selected data. Forward and reverse reaction occur at nearly same rate and reaction studied as rate of approach to equilibrium. Rate constants for forward reaction calculated from pseudo first order rate constant of approach to equilibrium and equilibrium constant. For reverse reaction, see 382.860(.1).

LITERATURE

(1) J. F. Below, R. C. Connick, C. P. Coppel, *ACS* 1958, **80**, 2961. (2) R. W. Taft, E. H. Cook, *ACS* 1959, **81**, 46. (3) H. Taube, F. A. Posey, *ACS* 1953, **75**, 1463.

COORDINATIVE EXCHANGE

Halogen replacing H_2O in VIIIth group complex
(H_2O not always shown in formula of complex)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Fe^{+++} + Cl^- \longrightarrow FeCl^{++}$	H_2O	$10^3A=8$; $10^3B=5$	$HClO_4$; $NaClO_4$	0.90;μ=1	kAB	16	9.5	0				*	(^{1})
			8 5		0.311		17	2.3	+1					
			8 5		0.311		21	4.0	+1					
			5-9 4		0.90		25	3.0	+1					
			2-8 5		0.156		25	1.14	+2					
			3 15		0.0622		27	2.3	+2					
			8 5		0.90		32	6.9	+1	21	8	16		
			7 5		0.311		32	1.61	+2	22	9	17		
			2-9 5		0.06-0.9	$k=k_1+k_2/[H^+]$	25	k_1 9.4	0	17	1	13		
							25	k_2 1.80	+1	23	2	18		
.2	$Co(NH_3)_5H_2O^{+++} + Cl^- \longrightarrow Co(NH_3)_5Cl^{++} + H_2O$	H_2O	$10^3A=8.6$; B=3A		μ=0.051	kAB	25	6.7	-6				*	(^{3})
			20		0.121		25	5.0	-6					
				KNO_3	0.2;μ=0.32		25	3.0	-6					
				HNO_3			25	3.0	-6					
			$10^2A=1$	none	μ=0.06		30	1.35	-5					
			1.4		0.085		30	1.10	-5					
.3	$Pt(NH_3)Cl(H_2O)_2^+ + Cl^- \longrightarrow Pt(NH_3)Cl_2(H_2O) + H_2O$	H_2O				kAB	24	2	-1				*	(^{2})
.4	$Pt(NH_3)Cl_2(H_2O) + Cl^- \longrightarrow Pt(NH_3)Cl_3^- + H_2O$	H_2O	$10^2L=1.7$	Na_2SO_4	μ=0.318	kAB	0	1.9	-4				*	(^{2})
							6	3.0	-4					
							15	9.8	-4					
							20	1.65	-3					
							25	2.5	-3					
							30	3.7	-3	17	8	9		

COMMENTS

Reaction: **(.1)** Selected data. **(.2)** Values of *k* subject to experimental error of about 10%. **(.3)** Rate constant based on measurement of initial rate and is a rough estimate. **(.4)** Rate constants calculated from measurements of rate of approach to equilibrium and measured equilibrium constants for reaction. See 382.870 for reverse reaction. Rate of formation of $Pt(NH_3)Cl(H_2O)_2^+$ assumed to be negligible.

LITERATURE

(1) R.E. Connick, C.P. Coppel, *ACS* 1959, **81**, 6389. (2) T.S. Elleman, J.W. Reishus, D.S. Martin, *ACS* 1958, **80**, 536. (3) F.J. Garrick, *TFS* 1937, **33**, 486.

COORDINATIVE EXCHANGE

H_2O replacing $(CN^-)(SCN^-)(CO_3^=)$ on VIIIth group complex

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

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.1	$Fe(CN)_5H_2O^{-3} \longrightarrow$ No products specified	H_2O	$10^3A=1$	Buffers	pH=3.55	$-dA/dt=kA$	25	8.3	-5				*	(2)
							30	1.28	-4					
							35	2.55	-4					
							37	4.7	-4					
							40	9.2	-4					
							45	1.58	-3	28.2	4	16		
.2	$Fe(CN)_5H_2O^{-3} \longrightarrow$ Fe^{++} + no other products specified	H_2O	$10^3A=1$	Buffers	pH=4.0	$dL/dt=kA$	40	9.2	-6				*	(2)
.3	$Co(NH_3)_5(SCN)^{++} + H_2O \longrightarrow$ $Co(NH_3)_5(H_2O)^{+++} + SCN^-$	H_2O	$10^2A \approx 2$	$HClO_4$	pH $\approx$ 2.5	kA; $k=k_1+k_2[SCN^-]$	25	2.8	-9				*	(1)
							90	$k_1=3.2$	-6	27	1	11		
								$k_2=4.8$	-6					
.4	$Co(NH_3)_4CO_3^+ + 2H^+ + H_2O \longrightarrow$ $Co(NH_3)_4(H_2O)_2^{+++} + CO_2$	H_2O	$10^2A=1$; Buffers with $h_\infty=[HB]/[B^-]$ at $t=\infty$	acetate; h_∞	0.9-2	kA $k=k_o+k_1h_\infty$	25	k_o 1.06	-4				*	(3)
				total salt	0.98		25	k_1 7.3	-5					
				glycolate; h_∞	0.26-1.5		25	k_o 1.02	-4					
				total salt	0.11		25	k_1 2.7	-4					
				h_∞	0.4-1.4		25	k_o 1.05	-4					
				total salt	0.21		25	k_1 3.4	-4					

COMMENTS

Reaction: (.1) Reaction in the absence of light in phosphate-citric acid buffer. Rate constants based on 40% reaction after which pseudo first order constants decreased with time. (.2) Excess 2,2'-dipyridyl present in order to form ferrous ion complex by which reaction was followed spectrophotometrically. Reaction allowed to occur in absence of light in presence of phosphate-citric acid buffer. (.3) Value at 25° extrapolated from measured values of rate constants between 80 and 90°C. Units converted from minutes. $HClO_4$ added during reaction in order to maintain $pH<5$. (.4) Units converted from minutes. Logarithms to base 10 converted to logarithms to base e. Selected data. Ionization constant of acid present used in rate constant calculations since $[H^+]$ of solutions changed during reaction. Calculations based on assumption that $k=k_1+k_2[H^+]$. Rate of reaction measured by increase in pressure of system due to liberated CO_2 with time.

LITERATURE

(1) A.W. Adamson, R.G. Wilkins, *ACS* 1954, **76**, 3379. (2) S. Asperger, I. Murati, D. Pavlovic, *CSL* **1960**, 730. (3) K.J. Pederson, *ACS* 1931, **53**, 18.

COORDINATIVE EXCHANGE
N or P-compound replacing a C-compound in VIIIth group complex

Liquid phase
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
.1	$Ni(P(n\text{-}C_4H_9)_3)(CO)_3 + P(n\text{-}C_4H_9)_3 \longrightarrow Ni(P(n\text{-}C_4H_9)_3)_2(CO)_2 + CO$	*cyclo*-C_6H_{12}	$10^3A=5; 10B=5$	kA	25	6.0	-4
.2	$Ni(P(C_6H_5)_3)(CO)_3 + P(n\text{-}C_4H_9)_3 \longrightarrow Ni(P(C_6H_5)_3(P(n\text{-}C_4H_9)_3)(CO)_2 + CO$	*cyclo*-C_6H_{12}	$10^3A=6; 10B=5$	kA	25	8.2	-4
.3	$Ni(P(C_6H_5)_3)(CO)_3 + P(C_6H_5)_3 \longrightarrow Ni(P(C_6H_5)_3)_2(CO)_2 + CO$	CH_3CN *cyclo*-C_6H_{12}	$10^3A=7; 10B=5$	kA	25 25	1.34 5.7	-3 -4
.4	$Ni(P(C_6H_5)_3)(CO)_3 + P(CH_2CH_2CN)_3 \longrightarrow Ni(P(C_6H_5)_3)(P(CH_2CH_2CN)_3) + CO$	CH_3CN	$10^3A=6; 10B=5$	kA	25	1.37	-3
.5	$Ni(P(OC_2H_5)_3(CO)_3 + P(n\text{-}C_4H_9)_3 \longrightarrow Ni(P(OC_2H_5)_3)(P(n\text{-}C_4H_9)_3)(CO)_2 + CO$	*cyclo*-C_6H_{12}	$10^3A=13; 10B=5$	kA	25	2.8	-4

LITERATURE

L.S. Meriwether, M.L. Fiene, *ACS* 1959, **81**, 4200.

COORDINATIVE EXCHANGE
$H_2O(OH^-)$ replacing N compound in VIIIth group complex
(H_2O not always shown in formula of complex)

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

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$Fe(dipy)_3^{++} \longrightarrow Fe(dipy)_2^{++} + dipy$	H_2O	$10^4A=1$	Cu^{++}	0.001	kA	24	1.05	-4				*	(8)
	dipy = 2, 2'-dipyridyl		$10^5A \simeq 7$	Phthalate	0.025; pH=2.2–2.8		25	1.22	-4					(5)
				buffer			35	6.0	-4					
							45	2.0	-3	26	3	17		
				HCl; NaCl	0.2; 1.8		35	1.8	-4					
				H_2SO_4; Na_2SO_4	0.1; 1.9		35	6.3	-5					
		not stated		HCl	0.25		26	4.6	-4					(4)
					0.5–2.0		26	7.1	-4					
					1.5		18	2.5	-4					
							24	7.2	-4					
							32	2.4	-3	27	5	16		
.2	$Fe(dipy)_3^{++} \longrightarrow Fe^{++} + 3\ dipy$	H_2O	$10^5A \simeq 5$	HCl	1.0	kA	25	8.4	-4				*	(20)
	dipy = 2, 2'-dipyridyl				1.0		30	1.85	-3					
		M 20*			0.2		25	3.1	-4					
					1.0		25	5.8	-4					
					1.0		30	1.27	-4					
		M 40*			0.2		25	3.3	-4					
					1.0		25	6.5	-4					
					1.0		30	1.43	-3					
		M 60*			0.6		25	7.6	-4					
					1.0		25	8.9	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2	$Fe(dipy)_3^{++} \longrightarrow$ *(continued)*	M 60*	$10^5A \simeq 5$	HCl	1.0	kA	30	1.93	-3				*	(20)
	dipy = 2,2'-dipyridyl	M 80*			1.0		30	3.2	-3					
		M 84*			0.6		25	1.44	-3					
					1.0		25	1.70	-3					
		M 90*			1.0		30	4.1	-3					
		CH_3OH			1.0		25	2.5	-3					
					1.0		30	5.3	-3					
					2.0		25	2.8	-3					
					3.0		25	3.0	-3					
				$NiCl_2$	0.0005		25	2.2	-4					
					0.01		25	7.5	-4					
				$NiBr_2$	0.01		25	1.22	-4					
				$Ni(NO_3)_2$	0.01		25	8.3	-5					
				$Ni(ClO_4)_2$	0.005-0.05		25	4.2	-5					
				$NiCl_2$; LiCl	0.01; 1.0		25	2.5	-3					
				$NiBr_2$; LiCl	0.01; 1.0		25	2.7	-4					
				$Ni(NO_3)_2$; $LiNO_3$	0.01; 1.0		25	1.28	-4					
				HCl; LiCl	0.01; 0.5		25	2.1	-3					
				HCl; LiCl	0.01; 2.0		25	3.4	-3					
				HCl; LiCl	0.5; 1.0		25	2.9	-3					
				HBr	0.05		25	1.93	-4					
				HBr	1.0		25	3.9	-4					
				HCl; HBr	1.0; 0.25		25	1.92	-3					
				HCl; HBr	1.0; 1.0		25	1.28	-3					
				H_2SO_4	0.5		25	6.5	-5					
				H_2SO_4	1.0		25	1.32	-4					
				p-$CH_3C_6H_4SO_3H$	1.0-1.5		25	3.6	-4					
.3	$Fe(phen)_3^{++} \longrightarrow Fe(phen)_2^{++} + phen$	H_2O	not stated	HCl	1.0	kA	18	1.70	-5				*	(4)
	phen = 1,10-phenanthroline						25	7.4	-5					
							35	3.7	-4	32	2	19		

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
.4	$Fe(phen)_3^{++} \longrightarrow Fe^{++} + 3$ phen phen = 1,10-phenanthroline	H_2O	$10^5 A \simeq 3$	HCl	0.02-0.05	k A	25	7.5	-5	*	(11) (13)
					1.0		25	7.1	-5		(11) (20)
					1.9		25	6.1	-5		(11)
				HCl; KCl	0.10; 1.8		25	7.2	-5		
				HCl; LiCl	0.02; 2.4		25	6.3	-5		
				H_2SO_4	0.005-0.5		25	7.4	-5		(7) (16)
					1.64		25	5.4	-5		(11)
				H_2SO_4; $KHSO_4$	0.08; 2.18		25	6.0	-5		
				H_2SO_4; $LiHSO_4$	0.08; 1.45		25	5.8	-5		
				HNO_3	1.79		25	6.1	-5		
				HNO_3; KNO_3	0.010; 2.18		25	7.8	-5		
				HNO_3; $LiNO_3$	0.010; 2.18		25	6.2	-5		
				brucine·HCl	0.02; 0.013		25	8.0	-5		(13)
					0.02; 0.10		25	9.6	-5		
				quinine·HCl	0.02; 0.025		25	7.8	-5		
					0.02; 0.30		25	1.17	-4		
				strychnine·HCl	0.02; 0.025		25	7.9	-5		
					0.02; 0.050		25	8.2	-5		
	X=d,l-10-camphorsulfonic acid			HCl; X	0.02; 0.0005-0.01		25	7.6	-5		
					0.02; 0.40		25	4.5	-5		
				HCl; NaX	0.02; 0.60		25	3.7	-5		
				HCl; Y	0.02; 0.01%		25	1.70	-5		
	Y=sodium polystyrenesulphonate				0.20; 2.0%		25	1.21	-5		
				HCl; Z	0.20; 0.01%		25	7.8	-5		
	Z=polymethacrylic acid				0.02; 2.0%		25	1.47	-5		
				HCl; Q	0.02; 0.000125%		25	8.1	-5		
	Q=sodium laurylsulphate				0.02; 0.0010%		25	1.30	-4		
			$10^5 A \simeq 5$	NaOH; KCl	0.00047; μ=0.15		25	8.7	-5		(17)
					0.0103		25	2.1	-4		
					0.0374		25	5.2	-4		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.4	$Fe(phen)_3^{++} \longrightarrow Fe^{++} + 3$ phen *(continued)*	H_2O	$10^5A \simeq 5$	NaOH; KCl	0.0982	kA	25	1.58	-3	*	([17])
					0.000421; μ=0.55		25	8.0	-5		
					0.0453		25	4.1	-4		
					0.137		25	1.24	-3		
					0.496		25	5.2	-3		
					0.0079; μ= 1.05		25	1.39	-4		
					0.137		25	9.5	-4		
					0.495		25	3.8	-3		
					0.997		25	9.3	-3		
					0.0635; μ= 2.0		25	4.0	-4		
					0.752		25	4.3	-3		
					1.90		25	1.65	-2		
					1.79; μ= 4.5		25	7.1	-3		
					2.87		25	1.39	-2		
					4.46		25	3.5	-2		
		M 20*	$10^5A \simeq 3$	$Ni(ClO_4)_2$	0.005		25	9.3	-5		([20])
		M 80*			0.005		25	2.1	-4		
		CH_3OH			0.005		25	4.2	-5		
		M 37*		HCl	1.0		25	2.1	-4		
		M 68*			1.0		25	9.0	-4		
		M 87*			1.0		25	2.1	-3		
		M 80*		HCl; LiCl	0.1; 0.4		25	1.1	-3		
					0.5; 0.5		25	1.3	-3		
.5	$Fe(pphen)_3^{++} \longrightarrow Fe^{++} + 3$ pphen pphen = 5-phenyl-1, 10-phenanthroline	H_2O	not stated	H_2SO_4	0.5	kA	25	7.3	-5	*	([7])

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$			$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$Fe(nphen)_3^{++} \longrightarrow Fe^{++} + 3$ nphen nphen = 5-nitro-1,10-phenanthroline	H_2O	not stated	H_2SO_4	0.5	kA	25	6.3	-4				*	(7)
.7	$Fe(cphen)^{++} \longrightarrow Fe^{++} + 3$ cphen cphen = 5-chloro-1,10-phenanthroline	H_2O	not stated	H_2SO_4	0.5	kA	25	2.0	-4				*	(7)
.8	$Fe(phen)_3^{+++} \longrightarrow Fe^{+++} + 3$ phen phen = 1,10-phenanthroline	H_2O	$10^4A=1.5$	H_2SO_4	0.03	kA	25	9.8	-5				*	(11)
					0.30		25	4.3	-5					
					2.1		25	1.8	-5					
				H_2SO_4; $KHSO_4$	0.082; 0.50		25	5.5	-5					
				H_2SO_4; $LiHSO_4$	0.082; 0.25		25	6.4	-5					
					0.082; 1.6		25	2.4	-5					
				HNO_3	0.020		25	5.1	-5					
					0.098		25	2.6	-5					
					0.99		25	6.8	-6					
				HNO_3; KNO_3	0.044; 0.50		25	2.4	-5					
					0.044; 2.0		25	1.3	-5					
				HNO_3; $LiNO_3$	0.044; 0.50		25	2.0	-5					
					0.044; 2.0		25	7.3	-6					
			$10^3A=2.5$	H_2SO_4; $Fe(phen)_3^{++}$	0.05; 0.0025		25	2.3	-4				*	(16)
					0.50; 0.0025		25	7.8	-5					
					1.0; 0.0025		25	5.2	-5					
					2.0; 0.0025		25	<3	-5					
.9	$Co(NH_3)_5NO_3^{++} + H_2O \longrightarrow Co(NH_3)_5(H_2O)^{+++} + NO_3^-$	H_2O	$10^3A=5$	HNO_3; $Co(NH_3)_6(NO_3)_3$	0.0001; 0.01	kA	15	6.0	-6				*	(9)
			$10^3A=5-10$	HNO_3	0.001-0.005		20	1.3	-5	26	3	14		
			$10^3A=3-8$	NO_3^-	= 2A		25	3.0	-5					(15)
				NO_3^-; HNO_3	= 2A; 0.002		25	2.2	-5					
				NO_3^-; CH_3COONa	= 2A; 0.015		25	2.5	-5					
.10	$Co(NH_3)_5NO_3^{++} + OH^- \longrightarrow Co(NH_3)_5OH^{++} + NO_3^-$	H_2O	not stated	Na^+; KNO_3	= B; $\mu=0.001$	kAB	15	5.8	0				*	(10)
					$\mu=0.0018$		15	5.0	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.11	$Co(NH_3)_4(H_2O)NO_3^{++} + H_2O \longrightarrow$ $Co(NH_3)_4(H_2O)_2^{+++} + NO_3^-$	H_2O	$10^3A=5$	HNO_3; $Co(NH_3)_6(NO_3)_3$	0.0005-0.01; 0.01	$k_1A + k_2A[H^+]^{-1}$	15	k_1 1.27	-5				*	(9)
								k_2 1.78	-7					
					0.00025-0.001;.01; μ=0.07-0.09		20	k_1 2.7	-5					
								k_2 5.3	-7					
.12	$Co(NH_3)_5SCN^{++} + H_2O \longrightarrow$ $Co(NH_3)_5H_2O^{+++} + SCN^-$	H_2O	$10^2A=2$	$HClO_4$	pH$\simeq$2.5	kA	25	2.8	-9				*	(2)
							90	5.3	-6	27	2	11		
.13	$Co(en)_3^{+++} + 2\ OH^- \longrightarrow$ $Co(en)_2(OH)_2^+ + en$ en = ethylenediamine	H_2O	$10^3A=3$; $10B=5$	Na^+; Cl^-	=B; =3 A	kA	70	3.3	-5				*	(12)
							75	8.5	-5					
							80	2.0	-4					
							91	8.5	-4	38	7	19		
			$10^2B=5$				80	1.3	-4	32				
			B=1				80	2.7	-4					
			10B=1	Na^+; Cl^-, $NaNO_3$	=B; =3 A; 0.4		80	5.6	-5					
			10B=5		0.3		80	1.7	-4					
.14	dl-*cis*-$Co(en)_2(NH_3)NO_3^{++} + H_2O \longrightarrow$ $Co(en)_2(NH_3)H_2O^{+++} + NO_3^-$ en = ethylene diamine	H_2O	$10^3A=3-5$	NO_3^-	=2 A	kA	45	1.12	-4					(19a)
			3				63	8.5	-4	24	4	12		
.15	*trans*-$Co(en)_2(NH_3)NO_3^{++} + H_2O \longrightarrow$ *trans*-$Co(en)_2(NH_3)H_2O^{+++} + NO_3^-$ en = ethylene diamine	H_2O	$10^3A=1-2$	$HClO_4$	0.1	kA	30	1.41	-5					(22)
			$10^4A=4-14$				45	1.05	-4					
			$10^4A=3-12$				60	6.6	-4	26.5	3	13		
.16	*cis*-$Co(en)_2(N_3)_2^+ + OH^- \longrightarrow$ *cis*-$Co(en)_2(OH)N_3^+$, *trans*-$Co(en)_2(OH)N_3^+ + N_3^-$ en = ethylene diamine	H_2O	$10^4A=6-25$; $10^2B=5-10$	Na^+	= B	kAB	25	6.6	-3				*	(22)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.17	*cis*-$Co(en)_2(OH)N_3 + OH^- \longrightarrow$ *cis*-$Co(en)_2(OH)_2^+$, *trans*-$Co(en)_2(OH)_2^+ + N_3^-$ en = ethylene diamine	H_2O	$10^3A \simeq 1$; $10^2B = 5$	Na^+	= B	kAB	25	2.8	-3				*	(21)
.18	*trans*-$Co(en)_2(N_3)_2^+ + OH^- \longrightarrow$ *cis*-$Co(en)_2(OH)N_3^+$, *trans*-$Co(en)_2(OH)N_3^+ + N_3^-$ en = ethylene diamine	H_2O	$10^4A = 5-13$; $10^2B = 2-3$	Na^+	= B	kAB	25	1.13	-2				*	(21)
.19	*trans*-$Co(en)_2(OH)N_3^+ + OH^- \longrightarrow$ *cis*-$Co(en)_2(OH)_2^+$, *trans*-$Co(en)_2(OH)_2^+ + N_3^-$ en = ethylene diamine	H_2O	$10^4A = 8-12$; $10^2B = 5$	Na^+	= B	kAB	25	1.21	-3				*	(21)
.20	$Ni(en)(H_2O)_4^{++} \longrightarrow Ni^{++} + en + 4H_2O$ en = ethylene diamine	H_2O	$10^2A = 8$	Ni^{++}; NO_3^-	0.04; 0.24; pH=7.3	kA	0	6.9	-4				*	(1)
			8-4		6.8		0	1.42	-3					
			7		0.06; 0.26; 6.2		0	1.88	-3					
			6		0.09; 0.29; 5.7		0	4.0	-3					
			8		0.12; 0.40; 4.9		0	9.0	-3					
			10		0.10; 0.10; 1-3		0	1.12	-2					
			$10^4A = 8$	Ni^{++}; $HClO_4$ +	0.0012; $\mu = 0.0084$; pH=5.5		0	6.4	-3					
			30	$NaClO_4$	0.0013; $\mu = 2$; pH=3.5		0	6.6	-3					
					0.0014; $\mu = 2$; pH=4.0		2	8.6	-3					
							4	1.12	-2					
							6	1.41	-2	21	2	14		
.21	$Ni(dipy)_3^{++} \longrightarrow Ni(dipy)_2^{++} + dipy$ dipy = 2,2'-dipyridyl	H_2O	$10^2A = 3$	Ni^{++}; $HClO_4$	0.013; 3.15; $\mu > 2$		1	1.7	-2					
			$10^4A = 1-40$	HCl; LiCl	1; 1	kA	1	4.2	-4				*	(3)
					1; 1		11	1.52	-3					
				HCl	2		11	1.90	-3					
					0.5		13	1.65	-3					
					5		13	4.0	-3					
				HCl; LiCl	1; 1		16	3.1	-3	22	1.4	14		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.22	$Ni(phen)_3^{++} \longrightarrow Ni(phen)_2^{++} + phen$	H_2O	$10^2A \simeq 1.5$	HCl	2	kA	15	2.5	-6				*	(3)
	phen = 1,10-phenanthroline				5		15	1.60	-6					
					3		25	9.0	-6					
					5		25	7.8	-6					
					2		35	3.7	-5					
					5		35	2.5	-5	25	1.5	15		
			$10^3A=3$	Buffers	$\mu=0.36$; pH=7.0		35	4.5	-5					(24)
					5.7		45	1.5	-4				(24)	(25)
			$10^3A=1-6$		7.0		45	1.56	-4					(24)
			$10^3A=3$		9.6		45	1.4	-4					
					13.3		45	3.5	-4					
				NaOH	0.01		45	1.88	-4					
					0.13		45	2.1	-4					
		1		Buffers	$\mu=0.36$; pH=7		55	5.0	-4	25	3	13		
		M30*	$10^3A=6$				45	1.7	-4					
		Et30*					45	1.4	-4					
		C_2H_5OH					45	4.6	-5					
		$C_6H_5NO_2$	$10^3A=5-7$				45	2.3	-6					
.23	$Ni(phen)_2^{++} \longrightarrow Ni(phen)^{++} + phen$	H_2O	not stated			kA	25	1.78	-5				*	(25)
	phen = 1,10-phenanthroline						45	2.1	-4	23	1	14		
.24	$Ni(phen)^{++} \longrightarrow Ni^{++} + phen$	H_2O	$10^4A=1$	$HClO_4$	0.02	kA	25	1.52	-5					(18)
	phen = 1,10-phenanthroline			HNO_3	0.1		25	2.8	-5					(25)
				$HClO_4$	0.2		25	4.0	-5					(18)
					1		25	9.8	-5					
					4.5		25	9.2	-5					
			$10^3A=3$	Ni^{++}; NO_3^-	0.017; 0.04; pH=5.5	kA	25	7.9	-6				*	(25)
			$10^2A=2-5$		0.15-0.21; 0.41-0.46; pH=?		35	3.7	-5					
			$10^3A=5-50$		0.01-0.18; 0.021-0.41; pH=?		45	1.42	-4	26	1	16		
			$10^3A=5$	acetate buffer	0.3; pH=5.7		45	2.3	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.25	$Ni(m\text{-}bn)_2^{++} \longrightarrow Ni(m\text{-}bn)^{++} + m\text{-}bn$ m-bn= meso-2,3-diaminobutane	H_2O	$10^2A=1$	HCl	0.1	kA	0	1.7	0				*	(23)
.26	$Ni(m\text{-}bn)^{++} \longrightarrow Ni^{++} + m\text{-}bn$ m-bn = meso-2,3-diaminobutane	H_2O	$10^2A=1$	HCl	0.1	kA	0	1	-3				*	(23)
.27	$Ni(i\text{-}bn)_2^{++} \longrightarrow Ni(i\text{-}bn)^{++} + i\text{-}bn$ i-bn = 1,2-diamino-2-methylpropane	H_2O	$10^2A=1$	HCl	0.1	kA	0	1.7	0				*	(23)
.28	$Ni(i\text{-}bn)^{++} \longrightarrow Ni^{++} + i\text{-}bn$ i-bn = 1,2-diamino-2-methylpropane	H_2O	$10^2A=1$	HCl	0.1	kA	0	2	-3				*	(23)
.29	$Ni(t\text{-}mn)_2^{++} \longrightarrow Ni(t\text{-}mn)^{++} + t\text{-}mn$ t-mn = 2,3-diamino-2,3-dimethylbutane	H_2O	$10^2A=1.4$	HCl	0.14	kA	18	1.3	-3				*	(23)
							24	2.5	-3	18	3	10		
				neutral solution						21	2	11		
.30	$Ni(mbo)_2^{++} \longrightarrow Ni^{++} + 2mbo$ mbo = 2-methyl-2-amino-3-butanone oxime	H_2O	not stated	H^+; NaCl	0.3-1.0; $\mu = 1.0$	$kA(H^+)$	0	1.77	-3				*	(19)
.31	$Ni(pbo)_2^{++} \longrightarrow Ni^{++} + 2pbo$ pbo = 2-n-pentylamino-2-methyl-3-butanone oxime	H_2O	not stated	H^+; NaCl	0.3-1.0; $\mu = 1.0$	$kA(H^+)$	0	4.2	-3				*	(19)
.32	$Ni(ebdo)_2^{++} \longrightarrow Ni^{++} + 2ebdo$ ebdo = 2,2'-ethylenediamino-bis-(2-methyl-3-butanone)dioxime	H_2O	not stated	H^+; NaCl	0.3-1.0; $\mu = 1.0$	$kA(H^+)$	0	1.1	-4				*	(19)
.33	$Ni(dtc)_2 \longrightarrow Ni^{++} + 2dtc^-$ dtc = N,N-di-n-propyldithiocarbamate ion	$CH_3OCH_2CH_2OH$	not stated	$NaClO_4$	0.1	kA	22	≤ 2	-8				*	(6)
.34	$Ir(NH_3)_5NO_3^{++} + H_2O \longrightarrow Ir(NH_3)_5H_2O^{+++} + NO_3^-$	H_2O	$10^3A=4$	NO_3^-	$=2A$	kA	95	4.3	-4				*	(14)

COMMENTS

Comments by Literature References: (1) (2) (3) (4) (5) (6) (7) (9) (10) (11) (13) (14) (15) (16) (17) (19) (20) (23) (24) (25) Units converted to seconds from original minutes.

Comments by Reaction: **(.1)** Rate constant from (8) independent of Cu^{++} concentration. Cu^{++} added to remove free M from solution. **(.2)** Selected data. Results show specific anion catalysis. For reverse reaction see 382.805(.1). **(.4)** Temperature in (7) not stated and assumed to be 25°C. In (13) first order kinetics in presence of 0.0010% Q observed up to initial 25% of reaction. Molecular weight of Y $\simeq$ 10,000. Molecular weight Z = 560,000. Presence of a number of large ions and molecules other than those listed has no appreciable effect on reaction rate. Rate constants in (17) may be expressed as a function of OH^- concentration according to following equation: $k = k_d + k_1[OH^-] + k_2[OH^-]^2 + k_3[OH^-]^3$ where k_d=value of k in neutral solution. k_d, k_1, k_2 and k_3 vary considerably with μ and given values of k_3 are estimates. Reaction takes place in presence of small amounts of EDTA to prevent precipitation of iron hydroxide and to prevent reverse reaction. For reverse reaction see 382.805(.2). **(.5) (.6) (.7)** Temperature not stated and assumed to be 25°C. For reverse reactions see 382.805(.3), (.4), and (.5) respectively.

(.8) (11) used 0.001M $Ce(SO_4)_2$ to prevent reduction of ferric complex to ferrous complex. Rate in (16) followed potentiometrically by measurements of electrode potential of $Fe(phen)_3^{++}$-$Fe(phen)_3^{+++}$ half cell in which initial concentrations of both complexes=0.0025M. **(.9)** At 20°C, same rate constant observed by (9) in presence of 0.03M $HClO_4$, 0.01M $HClO_4$ +0.2M $NaClO_4$ and in absence of addends as in presence of 0.001-0.005M HNO_3. Presence of 0.002M HNO_3 found to retard rate by as much as 25% by (14). Rate constants from (15) converted to base e from base 10 logarithms. **(.11)** At $[H^+]<0.001$ reaction deviates from first order law and corresponding rate constants based on measurement of initial rates. Rate law valid in presence of HNO_3 or $HClO_4$ as acid as well as KNO_3 and $NaClO_4$ salts. **(.12)** SCN^- catalyzes the reaction. Effect at 90°C given by $k=5.3\times10^{-6}+8.1\times10^{-6}(SCN^-)$. Rate constant at 25°C calculated assuming $A=2\times10^{11}sec^{-1}$.

(.13) Pseudo first order rate constant proportional to B when B>.1M. Observed first order constant smaller than this proportionality when B<0.1M. **(.16) (.17) (.18) (.19)** Second order constants calculated from pseudo first order under conditions of large excess of B. Proportions of *cis* and *trans* products not determined. Rate constants for (.16) (.18) based on initial rate data because rates of (.17) and (.19) of same order of magnitude. **(.20)** Rate followed in pH range 5.7-7.3 by measurement of rate of $^{63}Ni^{++}$ exchange; in pH range 2.1-5.0 by continuous titration of free amine formed in the reaction; at pH=1 spectrophotometrically. **(.21) (.22)** Rate constants of (3) based on assumption that consecutive reactions displacing remaining ligands (dipy and phen) are very fast compared to rate of reaction in which first ligand is displaced. No initial concentration cited by (25). Result based on one experiment. **(.24)** Rate constants from (18) based on measurements of initial rates. Variation of k with $[H^+]$ may be expressed by: $k=\dfrac{[H^+]+1.5\times10^{-2}}{8.4\times10^{3}[H^+]+3.6\times10^{3}}$. For reverse reaction see 382.805(.14).

COMMENTS *(continued)*

(.25) (.26) (.27) (.28) Rate constants semiquantitative because of rapidity of reactions. **(.30) (.31) (.32)** Products as written assumed since (19) does not specify them. Source of H^+ not stated. **(.33)** Rate constant calculated from observed rate constant of reverse reaction and equilibrium constant of dissociation reaction. For reverse reaction see 382.805(.15). **(.34)** The rate constant for this reaction is cited in a table in (10) as the value for 25°C. Constant at 25°C calculated in (14) using temperature coefficient of bromide complex to indicate only an order of magnitude.

CODED SOLVENTS

M20*, (40), -(90)	CH_3OH mol % designated + H_2O
Et30*	30 mol % C_2H_5OH + H_2O + H_2O

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COORDINATIVE EXCHANGE
N or P-compound replacing N or P-compound in VIIIth group complex

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

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.1	$Ni(CO)_2[P(CH_2CH_2CN)_3]_2 + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)_2[P(CH_2CH_2CN)_3][P(n\text{-}C_4H_9)_3] + P(CH_2CH_2CN)_3$	CH_3CN	$10^3A=5$; $10B=5$	kA	25	1.16	-3				*	(3)
			10 1		25	4.7	-4					
			1 1		25	3.5	-4					
					36	1.79	-3					
					45	5.0	-3	26	4	15		
.2	$Ni(CO)_2[P(CH_2CH_2CN)_3]_2 + P(OC_6H_5)_3 \longrightarrow$ $Ni(CO)_2[P(CH_2CH_2CN)_3][P(OC_6H_5)_3] + P(CH_2CH_2CN)_3$	CH_3CN	$10^3A=6$; $10B=5$	kA	25	1.42	-3				*	(3)
.3	$Ni(CO)_2[P(CH_2CH_2CN)_3]_2 + PCl_3 \longrightarrow$ $Ni(CO)_2[P(CH_2CH_2CN)_3](PCl_3) + P(CH_2CH_2CN)_3$	CH_3CN	$10^3A=9$; $B=1.2$	kA	25	1.75	-4				*	(3)
.4	$Ni(CO)_2[P(CH_2CH_2CN)_3][P(n\text{-}C_4H_9)_3] + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2 + P(CH_2CH_2CN)_3$	CH_3CN	$10^3A=5$; $10B=5$	kA	25	2.9	-4				*	(3)
			1 1		36	6.4	-4					
			1 1		45	2.2	-3	~19	~4	10		
.5	$Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2 + P(CH_2CH_2CN)_3 \longrightarrow$ $Ni(CO)_2[P(CH_2CH_2CN)_3][P(n\text{-}C_4H_9)_3] + P(n\text{-}C_4H_9)_3$	CH_3CN	$10^3A=5$; $10B=5$	kA	25	1.24	-4				*	(3)
.6	$Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2 + P(C_6H_5)_3 \longrightarrow$ $Ni(CO)_2[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3] + P(n\text{-}C_4H_9)_3$	*cyclo*-C_6H_{12}	$10^3A=6$; $10B=5$	kA	25	3.9	-5				*	(3)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.7	$Ni(CO)_2[P\text{-}(n\text{-}C_4H_9)_3]_2 + P(OC_6H_5)_3 \longrightarrow$ $Ni(CO)_2[P(n\text{-}C_4H_9)_3][P(OC_6H_5)_3] + P(n\text{-}C_4H_9)_3$	*cyclo*-C_6H_{12}	10^3A=7; 10B=5	kA	25	3.2	-5				*	(3)
.8	$Ni(CO)_2[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3] + P(C_6H_5)_3 \longrightarrow$ $Ni(CO)_2[P(C_6H_5)_3]_2 + P(n\text{-}C_4H_9)_3$	*cyclo*-C_6H_{12}	10^3A=6; 10B=5	kA	25	<1	-6				*	(3)
.9	$Ni(CO)_2[P(n\text{-}C_4H_9)_3][P(C_6H_5)_3] + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2 + P(C_6H_5)_3$	*cyclo*-C_6H_{12}	10^3A=5-6; 10B=5	kA	25	4.3	-4				*	(3)
.10	$Ni(CO)_2[P(C_6H_5)_3]_2 + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)_2[P(C_6H_5)_3][P(n\text{-}C_4H_9)_3] + P(C_6H_5)_3$	*cyclo*-C_6H_{12}	10^3A=5; 10B=5	kA	25	5.3	-4				*	(3)
.11	$Ni(CO)_2[P(C_6H_5)_3]_2 + P(OC_6H_5)_3 \longrightarrow$ $Ni(CO)_2[P(C_6H_5)_3][P(OC_6H_5)_3] + P(C_6H_5)_3$	*cyclo*-C_6H_{12}	10^3A=5; 10B=5	kA	25	5.6	-4				*	(3)
.12	$Ni(CO)_2[P(OC_2H_5)_3]_2 + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)_2[P(OC_2H_5)_3][P(n\text{-}C_4H_9)_3] + P(OC_2H_5)_3$	*cyclo*-C_6H_{12}	10^3A=8; 10B=5	kA	25	<1	-7				*	(3)
.13	$Ni(CO)[P(OC_2H_5)_3]_3 + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)[P(OC_2H_5)_3]_2[P(n\text{-}C_4H_9)_3] + P(OC_2H_5)_3$	*cyclo*-C_6H_{12}	10^2A=1; 10B=5	kA	25	<1	-7				*	(3)
.14	$Ni(CO)_2[P(OC_6H_5)_3]_2 + P(n\text{-}C_4H_9)_3 \longrightarrow$ $Ni(CO)_2[P(OC_6H_5)_3][P(n\text{-}C_4H_9)_3] + P(OC_6H_5)_3$	*cyclo*-C_6H_{12}	10^3A=6; 10B=5	kA	25	<1	-7				*	(3)

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		
.15	$\mathrm{Ni(CO)_3PCl_3 + P(\mathit{n}\text{-}C_4H_9)_3 \longrightarrow Ni(CO)_3[P(\mathit{n}\text{-}C_4H_9)_3] + PCl_3}$	*cyclo*-C_6H_{12}	10^3A=5; 10B=5	kA	25	>1	-2				*	(3)
.16	$\mathrm{Ni(CO)_2(PCl_3)_2 + P(\mathit{n}\text{-}C_4H_9)_3 \longrightarrow Ni(CO)_2(PCl_3)[P(\mathit{n}\text{-}C_4H_9)_3] + PCl_3}$	*cyclo*-C_6H_{12}	10^3A=5; 10B=5	kA	25	>1	-2				*	(3)
.17	$\mathrm{Ni(CO)_2[P(\mathit{n}\text{-}C_4H_9)_3](PCl_3) + P(\mathit{n}\text{-}C_4H_9)_3 \longrightarrow}$ $\mathrm{Ni(CO)_2[P(\mathit{n}\text{-}C_4H_9)_3]_2 + PCl_3}$	*cyclo*-C_6H_{12}	10^3A=5; 10B=5	kA	25	>1	-2				*	(3)
.18	$\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(NO_2)_2 + H_2NCH_2COOH \longrightarrow}$ $\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(H_2NCH_2COOH)NO_2^+ + NO_2^-}$	H_2O	10^4A=10^4B=5	kA	36	7.8	-4				*	(1)
.19	$\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(NO_2)_2 + C_6H_5NH_2 \longrightarrow \mathit{cis}\text{-}Pd(NH_3)_2(C_6H_5NH_2)\ NO_2^+ + NO_2^-}$	H_2O	10^4A=10^4B=5	kAB	36	4.7	-3				*	(1)
.20	$\mathit{trans}\text{-}\mathrm{Pd(NH_3)_2(NO_2)_2 + C_6H_5NH_2 \longrightarrow}$ $\mathit{trans}\text{-}\mathrm{Pd(NH_3)_2(C_6H_5NH_2)NO_2^+ + NO_2^-}$	H_2O	10^4A=10^4B=5	kAB	36	1.22	-2				*	(1)
.21	$\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(H_2NCH_2COOH)NO_2^+ + H_2NCH_2COOH \longrightarrow}$ $\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(H_2NCH_2COOH)_2^{++} + NO_2^-}$	H_2O	10^4A=10^4B=5	kAB	36	1.67	-2				*	(1)
.22	$\mathit{trans}\text{-}\mathrm{Pd(NH_3)_2(H_2NCH_2COOH)NO_2^+ + H_2NCH_2COOH \longrightarrow}$ $\mathit{trans}\text{-}\mathrm{Pd(NH_3)_2(H_2NCH_2COOH)_2^{++} + NO_2^-}$	H_2O	10^4A=10^4B=5	kAB	36	1.93	-2				*	(1)
.23	$\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(C_6H_5NH_2)NO_2^+ + C_6H_5NH_2 \longrightarrow}$ $\mathit{cis}\text{-}\mathrm{Pd(NH_3)_2(C_6H_5NH_2)_2^{++} + NO_2^-}$	H_2O	10^4A=5; 10^4B=5-400	kA	36	1.07	-3				*	(1)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
						k^o	n		A^o	n		
.24	*trans*-$Pd(NH_3)_2(C_6H_5NH_2)NO_2^+ + C_6H_5NH_2 \longrightarrow$ *trans*-$Pd(NH_3)_2(C_6H_5NH_2)_2^{++} + NO_2^-$	H_2O	$10^4A=5; 10^4B=5-400$	k A	36	6.3	-4				*	(1)
.25	*cis*-$Pd(NH_3)_2(py)NO_2^+ + py \longrightarrow$ *cis*-$Pd(NH_3)_2(py)_2^{++} + NO_2^-$ py = pyridine	H_2O	$10^4A=10^4B=5$	k AB	36	4.7	-3				*	(1)
.26	*trans*-$Pd(NH_3)_2(py)NO_2^+ + py \longrightarrow$ *trans*-$Pd(NH_3)_2(py)_2^{++} + NO_2^-$ py = pyridine	H_2O	$10^4A=10^4B=5$	k AB	36	8.3	-3				*	(1)
.27	$Pd(dien)NO_2^+ + py \longrightarrow Pd(dien)(py)^{++} + NO_2^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$; py = pyridine	H_2O	$10^4A=4-10; 10^4B=12$	k A	0	3.3	-3				*	(2)
			25		0	3.7	-3					
			120		0	5.4	-3					
			12		25	3.3	-2	15	4	9		
.28	$Pd(tripy)NO_2^+ + py \longrightarrow Pd(tripy)(py)^{++} + NO_2^-$ tripy = 2,2',2"-tripyridyl; py = pyridine	H_2O	$10^4A=4-10; 10^3B=1$		0	very fast					*	(2)
.29	$Pt(dien)CN^+ + py \longrightarrow Pt(dien)(py)^{++} + CN^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$; py = pyridine	H_2O	$10^4A=4-10; 10^3B=6$	k A	25	1.7	-8				*	(2)
.30	$Pt(dien)NO_2^+ + py \longrightarrow Pt(dien)(py)^{++} + NO_2^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$; py = pyridine	H_2O	$10^4A=4-10; 10^3B=6$	k A	25	5.0	-8				*	(2)
			60		25	2.5	-7					
.31	$Pt(dien)N_3^+ + py \longrightarrow Pt(dien)(py)^{++} + N_3^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$; py = pyridine	H_2O	$10^4A=4-10; 10^4B=9$	k A	25	2.0	-7				*	(2)
			60		25	8.3	-7					
.32	$Pt(tripy)NO_2^+ + py \longrightarrow Pt(tripy)(py)^{++} + NO_2^-$ tripy = 2,2',2"-tripyridyl; py = pyridine	H_2O	$10^4A=4-10; 10^4B=9$	k A	25	5.1	-5				*	(2)
			60		25	8.8	-5					

COMMENTS

References: (1) Units converted from original minutes. (2) Units converted from original minutes. Reactions pseudo first order at each pyridine concentration but calculated first order constants vary with pyridine concentration as $k_{obs.} = k_1 + k_2 B$.

Reactions: (.15) (.16) Concentration of A based on assumed 50-50 mixture of dicarbonyl and tricarbonyl complex. (.28) Reaction complete in 10 seconds.

LITERATURE

(1) D. Banerjea, K.K. Tripathi, *J. Inorg, Nucl. Chem.* 1958, **7**, 78. (2) F. Basolo, H.B. Gray, R.G. Pearson, *ACS* 1960, **82**, 4200. (3) L.S. Meriwether, M.L. Fiene, *ACS* 1959, **81**, 4200.

COORDINATIVE EXCHANGE

S-compound replacing N-compound in VIIIth group complex.

Liquid phase
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
.1	*trans*-$Pd(NH_3)_2(SC(NH_2)_2)NO_2^+ + SC(NH_2)_2 \longrightarrow$ *trans*-$Pd(NH_3)_2(SC(NH_2)_2)_2^{++} + NO_2^-$	H_2O	$10^4A=10^4B=5$	k AB	36	2.6	-2

COMMENTS

Units converted from original minutes.

LITERATURE

D. Banerjea, K.K. Tripathi, *J. Inorg. Nuclear Chem.* 1958, 7, 78.

COORDINATIVE EXCHANGE
H_2O replacing S-compound in VIIIth group complex

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$	
								k^o	n		A^o	n
.1	$Co(NH_3)_5SO_4^+ + H_2O \longrightarrow Co(NH_3)_5H_2O^{+++} + SO_4^=$	H_2O	$A<8[SO_4^=]$; $10^3A=1-15$	H^+, Na_2SO_4	0.01, 0.014	kA	31	2.8	-6			
					0.015, 0.156		31	4.3	-6			
				K_2SO_4	0.015, 0.156		31	3.8	-6			
				$MgSO_4$	0.015, 0.156		31	4.7	-6			
				Na_2SO_4	0.050, 0.57		31	6.2	-6			
					0.30, 2.90		31	1.1	-5			
				$H^+, Na_2SO_4, NaClO_4$	0.01, 0.156, 0.54		31	4.1	-6			
					0.054, 2.0		31	2.5	-6			
				$Na_2SO_4, NaHSO_4, NaClO_4$	0.054, 0.1, 0.6		31	3.5	-6			
					0.54, 0.1, 1.4		31	4.5	-6			
				$Na_2SO_4, NaHSO_4$	0.54, 1.5		31	9.0	-6			
				H_2SO_4	3		31	1.98	-5			
				$NaHSO_4$	3		31	1.05	-5			
				H_2SO_4	6		31	3.2	-5			
				H_2SO_4	9		31	3.5	-5			
				H^+, Na_2SO_4	0.01, 0.05		44	1.52	-5	19	2	8

COMMENTS

Units converted from minutes. Selected data. For reverse reaction see 382.806(.3). Forward and reverse reactions occur at nearly same rate. Rate constant calculated from constant for rate of approach to equilibrium and the equilibrium constant.

LITERATURE

H. Taube, F.A. Posey, *ACS* 1953, 75, 1463.

COORDINATIVE EXCHANGE
N-compound replacing S-compound in VIIIth group complex

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
							k^o	n		A^o	n		
.1	$Pd(dien)(SCN)^+ + py \longrightarrow Pd(dien)(py)^{++} + SCN^-$	H_2O	$10^4A=4-10;\ 10^3B=1.2$	NO_3^-	=A	kA	0	6.6	-3				*
	dien = $H_2N-CH_2CH_2NHCH_2CH_2-NH_2$; py = pyridine		2.5				0	8.2	-3				
			12				0	2.6	-2				
			1.2				25	4.3	-2				
							33	7.4	-2	12	4	7	
.2	$Pd(tripy)(SCN)^+ + py \longrightarrow Pd(tripy)(py)^{++} + SCN^-$	H_2O	$10^4A=4-10;\ 10^3B=1$				0	very fast					*
	tripy = 2,2',2"-tripyridyl; py = pyridine												
.3	$Pt(dien)(SCN)^+ + py \longrightarrow Pt(dien)(py)^{++} + SCN^-$	H_2O	$10^4A=4-10;\ 10^4B=9$	NO_3^-	=A	kA	25	6.2	-8				*
	dien = $H_2N-CH_2CH_2NHCH_2CH_2-NH_2$; py = pyridine		59				25	3.0	-7				
			9				33	1.70	-7				
			9				50	8.9	-7	21	2	8	
			59				50	6.2	-6	23	2	10	
.4	$Pt(tripy)(SCN)^+ + py \longrightarrow Pt(tripy)(py)^{++} + SCN^-$	H_2O	$10^4A=4-10;\ 10^3B=1.2$	SCN^-	=A	kA	25	1.02	-4				*
	tripy = 2,2',2"-tripyridyl; py = pyridine		12				25	4.8	-4				

COMMENTS

General: Units converted from original minutes. Reactions pseudo first order at each pyridine concentration but calculated constants vary with concentration of pyridine, $k_{obs} = k_1 + k_2B$.

Reaction: (.2) Complete in 10 seconds.

LITERATURE

F. Basolo, H.B. Gray, R.G. Pearson, *ACS* 1960, **82**, 4200.

COORDINATIVE EXCHANGE
H_2O, OH^- or OR^- replacing halogen in VIIIth group complex
(H_2O not always shown in complex)

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.3	*trans*-$Co(en)_2F_2^+ + H_2O \longrightarrow Co(en)_2(H_2O)F^{+2} + F^-$ en = $H_2NCH_2CH_2NH_2$	H_2O			pH=3	kA	25	1	-6				*	(23)
.4	*trans*-$Co(en)_2F_2^+ + OH^- \longrightarrow Co(en)_2(OH)F^+ + F^-$ en = $H_2NCH_2CH_2NH_2$	H_2O				kAB	25	6.4	+1				*	(33)
.5	*trans*-$Co(pn)_2F_2^+ + OH^- \longrightarrow Co(pn)_2(OH)F^+ + F^-$ pn = $H_2NCH_2CH(CH_3)NH_2$	H_2O				kAB	25	4.3	+1				*	(33)
.6	*d-cis*-$Co(en)_2F_2^+ + H_2O \longrightarrow Co(en)_2(H_2O)F^{+2} + F^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=3-4$	HNO_3	0	kA	25	3.0	-6				*	(7a)
					0.001		25	6.0	-6					
					0.1		25	~5	-5					
					0.1		35	~ 2	-4					
.7	*trans*-$Co(en)_2F_2^+ + H_2O \longrightarrow Co(en)_2(H_2O)F^{+2} + F^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=3-4$	HNO_3	0-0.001	kA	25	1.0	-6				*	(7a)
					0.01		25	1.7	-6					
					0.1		25	9	-6					
					1.0		25	1.1	-4					
					2.0		25	3.5	-4					
					4.0		25	8.3	-4					
				buffers	pH=1.0		59	1.4	-3	29	2	16		
					2.0		59	1.8	-4					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.7		*trans*-$Co(en)_2F_2^+ + H_2O \longrightarrow$ *(continued)*	H_2O	$10^3A=3-4$	buffers	pH=3.0	kA	59	1.2	-4				*	(7a)
						4.0		59	1.1	-4					
						5.0		59	1.3	-4					
						6.0		59	2.2	-4					
						6.9		59	6.0	-4					
						7.7		59	1.7	-3					
.8		*trans*-$Co(en)_2F_2^+ + D_2O \longrightarrow Co(en)_2(D_2O)F^{+2} + F^-$ en = $H_2NCH_2CH_2NH_2$	D_2O	$10^3A=3-4$	p-$CH_3C_6H_4SO_3H$	0.1	kA	25	1.8	-5				*	(7a)
.9		*trans*-$Co(en)_2F_2^+ + OH^- \longrightarrow Co(en)_2(OH)F^+ + F^-$	H_2O	$10^3A=3-4$			kAB	25	1.1	0				*	(7a)
.10	.1	$Co(NH_3)_5Cl^{+2} + H_2O \longrightarrow Co(NH_3)_5H_2O^{+3} + Cl^-$	H_2O	$10^3A=8-13$	NO_3^-	2A	kA	20	8.5	-7				*	(16)
				7-13				25	1.76	-6		(2) (12) (16) (22) (31)			
				9-14				30	3.25	-6	24	2	13		(16)
				5	HNO_3	0.1		35	6.7	-6					(30)
								49	3.2	-5					(35)
								52	4.2	-5	22.9	1.0	11		(1)
				10	KNO_3	0.05		25	1.72	-6					(16)
						0.1		25	1.78	-6					
						0.2		25	1.80	-6					
					$KClO_3$	0.1		25	1.70	-6					
						0.2		25	1.75	-6					
					$HClO_4$	0.08		25	1.55	-6					
						.20		25	1.48	-6					
					NaOOCH	0.2		25	2.0	-6					
					$NaOOCCH_3$	0.3		25	2.5	-6					
					K_2SO_4	0.1		25	3.4	-6					
						0.2		25	3.9	-6					

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.10	.1	$Co(NH_3)_5Cl^{+2} + H_2O \longrightarrow$ *(continued)*	H_2O	$10^2A=10$	$KHSO_4$	0.1	kA	25	3.2	-6				*	(^{16})
						0.2		25	3.6	-6					
					H_2SO_4	0.1		25	2.4	-6					
					$SO_4^=, NO_3^-$		$kA;$	25	$k_1=1.67$	-6					(^{17})
							$k=k_1+k_2[NO_3^-]$	25	$\log k_2=-5.47-2.02\mu^{1/2}+1.1\mu (\mu=0-1)$						
							$+k_3[SO_4^=]$	25	$\log k_3=-3.46-4.04\mu^{1/2}+3.87\mu-1.45\mu^{3/2}$						
.10.1	.2	$Co(NH_3)_5H_2O^{+3} + Cl^- \longrightarrow Co(NH_3)_5Cl^{+2} + H_2O$	H_2O	$10^3A=8-20; B=3A$			kAB	25	5.9	-6				*	(^{16})
				$10^2A=1-1.5$				30	1.2	-5	25	1	13		
		(see 382.807)		$10^2A=2$	HNO_3	0.2		25	3.0	-6					
					KNO_3	0.2		25	3.0	-6					
.11		$Co(NH_3)_5Cl^{+2} + H_2O + SO_4^= \longrightarrow$ $Co(NH_3)_5H_2O^{+3}, Co(NH_3)_5SO_4^- + Cl^-$	H_2O	$10^3A=1;$	$Hg(ClO_4)_2$	0.005	$-dA/dt=kA$	25	$k_1=5.7$	-2				*	(^{36})
				$10^3C=0-46$		$\mu=0.30$	$k=(k_1+k_2C$		$k_2=8.0$	0					
							$+k_3C^2)[Hg^{++}]$		$k_3=1.85$	+2					
.12		$Co(NH_3)_5Cl^{+2} + OH^- \longrightarrow Co(NH_3)_5OH^{+2} + Cl^-$	H_2O	$10^3A=5-14;$	Na^+, Cl^-	$B, =2A$	kAB	2	1.52	-2				*	(^{1})
				$10^3B=6-50$				11	7.5	-2					
								18	2.53	-1					
								25	8.6	-1	28.7	1	21		
								25	1.30	0					(^{12})
.13		$Co(NH_3)_5Cl^{+2} + D_2O \longrightarrow Co(NH_3)_5D_2O^{+2} + Cl^-$	D_2O		HNO_3	0.1	kA	49	2.23	-5				*	(^{35})
			D_2O 85-90*	$10^2A=1-2$				52	2.75	-5					(^{1})
.14		$Co(ND_3)_5Cl^{+2} + H_2O \longrightarrow Co(ND_3)_5H_2O^{+2} + Cl^-$	H_2O		HNO_3	0.1	kA	49	2.42	-5				*	(^{35})
			D_2O 85-90*	$10^2A=1-2$				52	3.02	-5					(^{1})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.15	$Co(ND_3)_5Cl^{+2}+D_2O \longrightarrow Co(ND_3)_5D_2O^{+3}+Cl^-$	D_2O D_2O 85-90*	$10^2A=1-2$	HNO_3	0.1	kA	49 52	1.92 3.2	-5 -5				*	(35) (1)
.16	$Co(ND_3)_5Cl^{+2}+OH^- \longrightarrow Co(ND_3)_5OH^{+2} + Cl^-$	H_2O	$10^3A=5-14$; $10^3B=6-50$	Na^+, Cl^-	B, = 2A	kAB	2 18	9.5 1.4	-3 -1	27	3	19	*	(1)
.17	$Co(NH_3)_4(H_2O)Cl^{+2}+H_2O \longrightarrow Co(NH_3)_4(H_2O)_2^{+3} + Cl^-$	H_2O			$kA+k_HA/[H^+]$		20	k=2.2 k_H=2.7	-6 -8				*	(9)
.18	*cis*-$Co(NH_3)_4Cl_2^+ + H_2O \longrightarrow$	H_2O				(very fast)							*	(30)
.19	*trans*-$Co(NH_3)_4Cl_2^+ + H_2O \longrightarrow Co(NH_3)_4(H_2O)Cl^{+2}+Cl^-$	H_2O	$10^3A=5$	HNO_3	0.1	kA	25	1.8	-3				*	(30)
.20	*trans*-$Co(NH_3)_4Cl_2^+ + OH^- \longrightarrow$ *trans*-$Co(NH_3)_4(OH)Cl^+ + Cl^-$	H_2O		$Na_2B_4O_7$	0.05, pH=9.2	kAB	25	1.8	+3				*	(33)
.21	*cis*-$Co(en)(NH_3)_2Cl_2^+ + H_2O \longrightarrow$ $Co(en)(NH_3)_2(H_2O)Cl^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	25	2.3	-4				*	(30)
.22	*trans*-$Co(en)(NH_3)_2Cl_2^+ + H_2O \longrightarrow$ $Co(en)(NH_3)_2(H_2O)Cl^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	25	2.2	-4				*	(30)
.23	*cis*-$Co(en)_2(NH_3)Cl^{+2} + H_2O \longrightarrow$ $Co(en)_2(NH_3)H_2O^{+3} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=5$ $10^3A=4-11$	HNO_3 Br^-	0.1 2A	kA	35 63	1.4 4.0	-6 -5				*	(30) (26)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.24	*cis*-$\mathrm{Co(en)_2(NH_3)Cl^{+2} + OH^- \longrightarrow}$	H_2O	10^3A=1-10; 10^3B=4-14		μ= .01-.04	k AB	0	5.0	-1				*	(26)
	cis-$\mathrm{Co(en)_2(NH_3)OH^{+2} + Cl^-}$						25	5.4	+1					(33)
	en = $\mathrm{H_2NCH_2CH_2NH_2}$													
.25	*trans*-$\mathrm{Co(en)_2(NH_3)Cl^{+2} + H_2O \longrightarrow}$	H_2O	10^3A=2-4	$HClO_4$	0.1-0.17	k A	63	<u>2.92</u>	-5				*	(26) (38)
	trans-$\mathrm{Co(en)_2(NH_3)H_2O^{+3} + Cl^-}$		2.5				73	8.1	-5					(38)
	en = $\mathrm{H_2NCH_2CH_2NH_2}$		3.8				90	4.2	-4	23.6	8	10		
.26	*trans*-$\mathrm{Co(en)_2(NH_3)Cl^{+2} + OH^- \longrightarrow}$	H_2O	10^3A=1.5; 10^4B=5.5		$10^3\mu$= 5.1	k AB	0	1.43	0				*	(26)
	$\mathrm{Co(en)_2(NH_3)OH^{+2} + Cl^-}$		1.6 8		13		0	1.20	0					
	en = $\mathrm{H_2NCH_2CH_2NH_2}$		2.8 12		21		0	1.10	0					
			8.4 12		37		0	9.4	-1					
			2.8 12	$NaClO_4$	0.04, $10^3\mu$= 61		0	7.3	-1					
.27	*cis*-$\mathrm{Co(en)_2(NO_2)Cl^{+} + H_2O \longrightarrow}$	H_2O	10^4A=4-67	$HClO_4$	pH=2.1	k A	0	3.32	-6				*	(3)
	cis-$\mathrm{Co(en)_2(NO_2)H_2O^{+2} + Cl^-}$				5.1		0	3.65	-6					
					~5		20	6.1	-5					
	en = $\mathrm{H_2NCH_2CH_2NH_2}$		10^3A=5	HNO_3, $NaNO_2$	0.05, 0.2		25	1.03	-4					(8)
				HNO_3, NaN_3	0.05, 0.5		25	1.13	-4					
			10^4A=4-67	$HClO_4$	pH~5		30	2.05	-4					(3)
.28	*cis*-$\mathrm{Co(en)_2(NO_2)Cl^{+} + OH^- \longrightarrow}$	H_2O	10^4A=4-67; 10^3B=5-120			k AB	0	3.2	-2				*	(3)
	$\mathrm{Co(en)_2(NO_2)OH^{+} + Cl^-}$													
	en = $\mathrm{H_2NCH_2CH_2NH_2}$													

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.29	*trans*-$Co(en)_2(NO_2)Cl^+ + H_2O \longrightarrow$ *trans*-$Co(en)_2(NO_2)H_2O^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=4-67$	$HClO_4$	pH=1.5-5	kA	0	3.64	-5					(3)
					pH~5		14	2.82	-4					
							20	5.3	-4					
			$10^3A=5$	HNO_3, $NaNO_2$	0.05, 1.0		25	1.12	-3				*	(8)
			$10^4A=4-67$	$HClO_4$	pH~5		30	1.49	-3	21.5	6	12		(3)
.30	*trans*-$Co(en)_2(NO_2)Cl^+ + OH^- \longrightarrow Co(en)_2(NO_2)OH^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=4-67$; B=5-120			kAB	0	8.0	-2				*	(3)
.31	*cis*-$Co(en)_2(NCS)Cl^+ + H_2O \longrightarrow$ *cis*-$Co(en)_2(NCS)H_2O^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=2-10$			kA	25	1.14	-5				*	(16)
							45	1.07	-4					
							55	3.08	-4					
							65	6.9	-4					
							75	1.71	-3	20.8	2	10		
.32	*cis*-$Co(en)_2(NCS)Cl^+ + OH^- \longrightarrow Co(en)_2(NCS)OH^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=2-5$; $10^3B=4-8$			kAB	0	1.40	0				*	(20)
.33	*trans*-$Co(en)_2(NCS)Cl^+ + H_2O \longrightarrow Co(en)_2(NCS)H_2O^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=2-5$	$HClO_4$	0.007, pH=2.2	kA	45	1.13	-6				*	(20)
							71	4.1	-5					
							90	4.3	-4	30.4	9	14		
.34	*trans*-$Co(en)_2(NCS)Cl^+ + OH^- \longrightarrow Co(en)_2(NCS)OH^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=1-6$; $10^3B=2-22$			kAB	0	3.4	-1				*	(20)
							10	1.47	0					
							20	6.4	0	23	7	13		
		M82*	$10^3A=2-4$; $10^3B=3-11$				0	1.16	-1					
		M87*					0	9.8	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.35	$cis\text{-}Co(en)_2N_3Cl^+ + H_2O \longrightarrow cis\text{-}Co(en)_2N_3(H_2O)^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=4-20$	$HClO_4$	pH=2	k A	10	3.5	-5				*	(37)
			5-20				25	2.4	-4					
			10-23				35	8.0	-4	22	2	12		
.36	$cis\text{-}Co(en)_2N_3Cl^+ + OH^- \longrightarrow Co(en)_2N_3(OH)^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A \simeq 1$; $10^3B=3-5$			k AB	0	1.7	-1				*	(37)
.37	$trans\text{-}Co(en)_2N_3Cl^+ + H_2O \longrightarrow Co(en)_2N_3(H_2O)^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=2-9.6$	$HClO_4$	pH=2	k A	10	3.2	-5				*	(37)
			1-10				25	2.2	-4					
			1-3				35	8.7	-4	23	2	13		
.38	$trans\text{-}Co(en)_2N_3Cl^+ + OH^- \longrightarrow Co(en)_2N_3(OH)^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=1-2$; $10^3B=5-8$			k AB	0	4.1	-1				*	(37)
.39	$cis\text{-}Co(en)_2(H_2O)Cl^{+2} + H_2O \longrightarrow cis\text{-}Co(en)_2(H_2O)_2^{+3} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O		Buffers	pH=3.7	k A	30	1.54	-5				*	(24)
					4.7		30	7.3	-5					
					5.1		30	1.7	-4					
					5.56		30	3.4	-4					
				HNO_3	2.26		40	8.1	-6					
.40	$cis\text{-}Co(en)_2(OH)Cl^+ + H_2O \longrightarrow Co(en)_2(OH)H_2O^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A \simeq 2$			k A	25	1.30	-2					(34)
.41	$trans\text{-}Co(en)_2(OH)Cl^+ + H_2O \longrightarrow Co(en)_2(OH)(H_2O)^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A \simeq 2$			k A	25	1.4	-3					(34)
.42	$trans\text{-}Co(en)_2(OH)Cl^+ + OH^- \longrightarrow Co(en)_2(OH)_2^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O				k AB	25	2.0	+2					(33)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.43	*cis*-$Co(en)_2Cl_2^+ + H_2O \longrightarrow$ *cis*-$Co(en)_2(H_2O)Cl^{+2} + Cl^-$	H_2O	$10^3A \sim 2$			kA	25	3.1	-4				*	(34)
	en = $H_2NCH_2CH_2NH_2$		$10^3A=5$	HNO_3	0.1		25	2.5	-4					(30)
			$10^2A=1$		0.12		30	5.5	-4					
				Buffers	pH=3.95		30	7.5	-4					(24)
					5.5		30	8.5	-4					
				NaOH	0.01		30	1.76	-3					
							40	1.5	-3					
			$10^3A=5-20$	HNO_3	0.012-0.06		40	1.6	-3					
.44	*cis*-$Co(en)_2Cl_2^+ + OH^- \longrightarrow Co(en)_2(OH)Cl^+ + Cl^-$	H_2O				kAB	25	1	+3				*	(33)
	en = $H_2NCH_2CH_2NH_2$													
.45	*cis*-$Co(en)_2Cl_2^+ + OCH_3^- \longrightarrow$ *cis*-$Co(en)_2(OCH_3)Cl^+ + Cl^-$	CH_3OH	$10^3A=10^3B=1$			kAB	0	1.8	0				*	(11)
	en = $H_2NCH_2CH_2NH_2$													
.46	*trans*-$Co(en)_2Cl_2^+ + H_2O \longrightarrow Co(en)_2(H_2O)Cl^{+2} + Cl^-$	H_2O	$10^3A=5$	HNO_3	0.1	kA	15	7.7	-6				*	(29)
	en = $H_2NCH_2CH_2NH_2$				0.0		25	1.1	-4					(34)
					0.1		25	3.0	-5				(29)	(30)
					0.1		35	1.6	-4	28	1	16		(29)
		M 50*					25	1.3	-5					
.47	*trans*-$Co(en)_2Cl_2^+ + OH^- \longrightarrow Co(en)_2(OH)Cl^+ + Cl^-$	H_2O				kAB	25	3.0	+3				*	(33)
	en = $H_2NCH_2CH_2NH_2$													
.48	*trans*-$Co(pn)_2(OH)Cl^+ + H_2O \longrightarrow Co(pn)_2(OH)H_2O^{+2} + Cl^-$	H_2O	$10^3A \simeq 2$			kA	25	1.3	-3					(34)
	pn = $H_2NCH_2CH(CH_3)NH_2$													

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.49	*trans*-$Co(pn)_2(OH)Cl^+ + OH^- \longrightarrow Co(pn)_2(OH)_2^+ + Cl^-$ pn = $H_2NCH_2CH(CH_3)NH_2$	H_2O				kAB	25	2.1	+2				*	(33)
.50	*trans*-$Co(pn)_2Cl_2^+ + H_2O \longrightarrow Co(pn)_2(H_2O)Cl^{+2} + Cl^-$ pn = $H_2NCH_2CH(CH_3)NH_2$	H_2O	$10^3A \simeq 5$	HNO_3	0.1	kA	15	1.4	-5				*	(29)
			$\simeq 2$		0.0		25	2.2	-4					(34)
					0.1		25	6.1	-5					(29)
					0.1		35	3.0	-4	28	2	16		
.51	*trans*-$Co(pn)_2Cl_2^+ + OH^- \longrightarrow Co(pn)_2(OH)Cl^+ + Cl^-$ pn = $H_2NCH_2CH(CH_3)NH_2$	H_2O				kAB	25	2.3	+3					(33)
.52	*trans*-$Co(en)(tn)Cl_2^+ + H_2O \longrightarrow Co(en)(tn)(H_2O)Cl^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$; tn = $H_2NCH_2CH_2CH_2NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	15	9.8	-5				*	(29)
							25	4.3	-4					
							35	1.50	-3	26	5	15		
.53	*trans*-$Co(tn)_2Cl_2^+ + H_2O \longrightarrow Co(tn)_2(H_2O)Cl^{+2} + Cl^-$ tn = $H_2NCH_2CH_2CH_2NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	10	1.0	-2				*	(29)
.54	*trans*-$Co(Me\text{-}en)_2(OH)Cl^+ + OH^- \longrightarrow Co(Me\text{-}en)_2(OH)_2^+ + Cl^-$ Me-en = $H_2NCH_2CH_2NH(CH_3)$	H_2O				kAB	25	3.3	+3					(33)
.55	*trans*-$Co(Me\text{-}en)_2Cl_2^+ + H_2O \longrightarrow Co(Me\text{-}en)_2(H_2O)Cl^{+2} + Cl^-$ Me-en = $H_2NCH_2CH_2NH(CH_3)$	H_2O	$10^3A=5$	HNO_3	0.1	kA	15	4.0	-6				*	(29)
							25	1.6	-5					
							35	7.3	-5	27	1	15		
.56	*trans*-$Co(Me\text{-}en)_2Cl_2^+ + OH^- \longrightarrow Co(Me\text{-}en)_2(OH)Cl^+ + Cl^-$ Me-en = $H_2NCH_2CH_2NH(CH_3)$	H_2O				kAB	25	1.1	+4					(33)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
.57	*trans*-$Co(Et\text{-}en)_2Cl_2^{+} + H_2O \longrightarrow Co(Et\text{-}en)_2(H_2O)Cl^{+2} + Cl^{-}$ Et-en = $H_2NCH_2CH_2NH(C_2H_5)$	H_2O	$10^3A=5$	HNO_3	0.1	kA	15 25 35	2.0 9.8 4.7	-5 -5 -4	 28	 4	 16	*	(29)
.58	*trans*-$Co(Pr\text{-}en)_2(OH)Cl^{+} + OH^{-} \longrightarrow Co(Pr\text{-}en)_2(OH)_2^{+} + Cl^{-}$ Pr-en = $H_2NCH_2CH_2NH(n\text{-}C_3H_7)$	H_2O				kAB	25	3.0	+3					(33)
.59	*trans*-$Co(Pr\text{-}en)_2Cl_2^{+} + H_2O \longrightarrow Co(Pr\text{-}en)_2(H_2O)Cl^{+2} + Cl^{-}$ Pr-en = $H_2NCH_2CH_2NH(n\text{-}C_3H_7)$	H_2O	$10^3A=5$	HNO_3	0.1	kA	15 25 35	2.7 1.18 5.3	-5 -4 -4	 27	 8	 15	*	(29)
.60	*trans*-$Co(Pr\text{-}en)_2Cl_2^{+} + OH^{-} \longrightarrow Co(Pr\text{-}en)_2(OH)Cl^{+} + Cl^{-}$ Pr-en = $H_2NCH_2CH_2NH(n\text{-}C_3H_7)$	H_2O				kAB	25	2.1	+4					(33)
.61	*trans*-$Co(dl\text{-}bn)_2(OH)Cl^{+} + OH^{-} \longrightarrow Co(dl\text{-}bn)_2(OH)_2^{+} + Cl^{-}$ dl-bn = d, l-$H_2NCH(CH_3)CH(CH_3)NH_2$	H_2O				kAB	25	2.2	+2					(33)
.62	*trans*-$Co(dl\text{-}bn)_2Cl_2^{+} + H_2O \longrightarrow Co(dl\text{-}bn)_2(H_2O)Cl^{+2} + Cl^{-}$ dl-bn = d, l-$H_2NCH(CH_3)CH(CH_3)NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	15 25 35	3.5 1.46 6.2	-5 -4 -4	 26	 2	 15	*	(29)
.63	*trans*-$Co(dl\text{-}bn)_2Cl_2^{+} + OH^{-} \longrightarrow Co(dl\text{-}bn)_2(OH)Cl^{+} + Cl^{-}$ dl-bn = d, l-$H_2NCH(CH_3)CH(CH_3)NH_2$	H_2O				kAB	25	2.1	+3					(33)
.64	*trans*-$Co(m\text{-}bn)_2Cl_2^{+} + H_2O \longrightarrow Co(m\text{-}bn)_2(H_2O)Cl^{+2} + Cl^{-}$ m-bn = meso-$H_2NCH(CH_3)CH(CH_3)NH_2$	H_2O	$10^3A=5$	HNO_3	0.1 PH=2.6	kA	10 15 25	5.3 1.37 ~4.2	-4 -3 -3	 24	 2	 15	*	(29)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.65	*trans*-$Co(m\text{-}bn)_2Cl_2^+ + OH^- \longrightarrow Co(m\text{-}bn)_2(OH)Cl^+ + Cl^-$ m-bn = meso-$H_2NCH(CH_3)CH(CH_3)NH_2$	H_2O		$Na_2B_4O_7$	0.05; pH=9.2	k AB	25	9.8	+3					$(^{33})$
.66	*trans*-$Co(i\text{-}bn)_2Cl_2^+ + H_2O \longrightarrow Co(i\text{-}bn)_2(H_2O)Cl^{+2} + Cl^-$ i-bn = $H_2NCH_2C(CH_3)_2NH_2$	H_2O	10^3A=5	HNO_3	0.1	k A	10 15 25	2.1 5.0 ~2.2	-4 -4 -3	26	3	16	*	$(^{29})$
.67	*trans*-$Co(i\text{-}bn)_2Cl_2^+ + OH^- \longrightarrow Co(i\text{-}bn)_2(OH)Cl^+ + Cl^-$ i-bn = $H_2NCH_2C(CH_3)_2NH_2$	H_2O				k AB	25	9.8	+3					$(^{33})$
.68	*trans*-$Co(dan)_2Cl_2^+ + H_2O \longrightarrow Co(dan)_2(H_2O)Cl^{+2} + Cl^-$ dan = $H_2NCH_2C(CH_3)_2CH_2NH_2$	H_2O	10^3A=5	HNO_3	0.1	k A	10 15 25	3.8 1.13 ~3.0	-4 -3 -3	24	2	15	*	$(^{29})$
.69	*trans*-$Co(dan)_2Cl_2^+ + OH^- \longrightarrow Co(dan)_2(OH)Cl^+ + Cl^-$ dan = $H_2NCH_2C(CH_3)_2CH_2NH_2$	H_2O		$Na_2B_4O_7$	0.05; pH=9.2	k AB	25	1.7	+4					$(^{33})$
.70	*trans*-$Co(tet\text{-}me)_2Cl_2^+ + H_2O \longrightarrow Co(tet\text{-}me)_2(H_2O)Cl^{+2} + Cl^-$ tet-me = $H_2NC(CH_3)_2C(CH_3)_2NH_2$	H_2O	10^3A=5	HNO_3	0.1	instantaneous								$(^{29})$
.71	$Co(en)(dien)Cl^{+2} + H_2O \longrightarrow Co(en)(dien)(H_2O)^{+3} + Cl^-$ en = $H_2NCH_2CH_2NH_2$; dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$	H_2O	10^3A=5	HNO_3	0.1	k A	35	5.1	-7				*	$(^{30})$
.72	*cis*-$Co(trien)(NH_3)Cl^{+2} + H_2O \longrightarrow Co(trien)(NH_3)H_2O^{+3} + Cl^-$ trien = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	H_2O	10^3A=5	HNO_3	0.1	k A	35	6.7	-7				*	$(^{30})$

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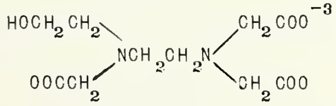
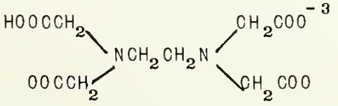
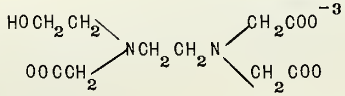
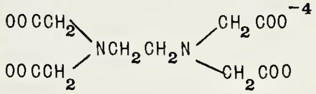
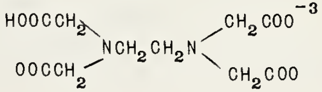
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.73	*cis*-$Co(trien)(NH_3)Cl^{+2} + OH^- \longrightarrow Co(trien)(NH_3)OH^{+2} + Cl^-$ trien = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	H_2O				kAB	25	1.6	+2					(^{33})
.74	*cis*-$Co(trien)Cl_2^+ + H_2O \longrightarrow Co(trien)(H_2O)Cl^{+2} + Cl^-$ trien = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	25	1.5	-4				*	(^{30})
.75	*cis*-$Co(trien)Cl_2^+ + OH^- \longrightarrow Co(trien)(OH)Cl^+ + Cl^-$ trien = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	H_2O				kAB	25	2	+5				*	(^{33})
.76	$Co(tetraen)Cl^{+2} + H_2O \longrightarrow Co(tetraen)H_2O^{+3} + Cl^-$ tetraen = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	H_2O	$10^3A=5$	HNO_3	0.1	kA	35	2.5	-7				*	(^{30})
.77	$Co(YOH)Cl^- + H_2O \longrightarrow Co(YOH)H_2O + Cl^-$ YOH = 	H_2O	$10^3A\simeq2$	$NaNO_3$	0.1	kA	30	3.2	-6				*	(^{25})
							40	1.11	-5					
							50	3.1	-5	21	7	9		
.78	$Co(HY)Cl^- \longrightarrow CoY^- + H^+ + Cl^-$ HY = 	H_2O	$10^3A\simeq2$	$NaNO_3$	0.1	kA	30	3.2	-6				*	(^{25})
				buffers	μ= 1; pH=4.3		35	9.7	-6					(^{14})
					1 4.3		40	1.86	-5					
				$NaNO_3$	0.1		40	7.4	-6					(^{25})
				buffers	μ= 1; pH=0.2		45	3.0	-5					(^{14})
					1 2-6		45	3.2	-5					
					1 4.3		50	6.0	-5					
				$NaNO_3$	0.1		50	2.7	-5	24	4	11		(^{25})
				buffers	μ= 1; pH=4.3		55	1.00	-4	23.4	4	11		(^{14})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^{o} \times 10^{n}$		E	$A = A^{o} \times 10^{n}$		Comments	Literature
								k^{o}	n		A^{o}	n		
.79	*trans*-$Co(l\text{-}ph\text{-}en)_2Cl_2^{+} + H_2O \longrightarrow Co(l\text{-}ph\text{-}en)_2(H_2O)Cl^{+2} + Cl^{-}$ l-ph-en = l-$H_2NCH(C_6H_5)CH(C_6H_5)NH_2$	M 50*	$10^3A=5$	HNO_3	0.1	kA	25	5	-6				*	(29)
.80	*trans*-$Co(m\ ph\text{-}en)_2Cl_2^{+} + H_2O \longrightarrow Co(m\ ph\text{-}en)_2(H_2O)Cl^{+2} + Cl^{-}$ m ph-en = meso-$H_2NCH(C_6H_5)CH(C_6H_5)NH_2$	M 50*	$10^3A=5$	HNO_3	0.1	kA	25	2.8	-4				*	(29)
.81	$Co(en)_2(py)Cl^{+2} + H_2O \longrightarrow Co(en)_2(py)H_2O^{+3} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; py = pyridine, C_5H_5N	H_2O	$10^3A=2.5$	$HClO_4$	0.0025	kA	50	1.1	-5				*	(7)
.82	$Co(en)_2(py)Cl^{+2} + OH^{-} \longrightarrow Co(en)_2(py)OH^{+2} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; py = pyridine, C_5H_5N	H_2O	$10^3A=2.5$			kAB	25	1.6	+3				*	(7)
.83	$Co(en)_2(\beta\text{-}CH_3\text{-}py)Cl^{+2} + H_2O \longrightarrow Co(en)_2(\beta\text{-}CH_3\text{-}py)H_2O^{+3} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; β-CH_3-py = beta-picoline, $CH_3C_5H_4N$	H_2O	$10^3A=2.5$	$HClO_4$	0.0025	kA	50	1.3	-5				*	(7)
.84	$Co(en)_2(\beta\text{-}CH_3\text{-}py)Cl^{+2} + OH^{-} \longrightarrow Co(en)_2(\beta\text{-}CH_3\text{-}py)OH^{+2} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; β-CH_3-py = beta-picoline, $CH_3C_5H_4N$	H_2O	$10^3A=2.5$			kAB	25	1.3	+3				*	(7)
.85	$Co(en)_2(\gamma\text{-}CH_3\text{-}py)Cl^{+2} + H_2O \longrightarrow Co(en)_2(\gamma\text{-}CH_3\text{-}py)H_2O^{+3} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; γ-CH_3-py = gamma-picoline, $CH_3C_5H_4N$	H_2O	$10^3A=2.5$	$HClO_4$	0.0025	kA	50	1.4	-5				*	(7)
.86	$Co(en)_2(\gamma\text{-}CH_3\text{-}py)Cl^{+2} + OH^{-} \longrightarrow Co(en)_2(\gamma\text{-}CH_3\text{-}py)OH^{+2} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; γ-CH_3-py = gamma-picoline, $CH_3C_5H_4N$	H_2O	$10^3A=2.5$			kAB	25	1.3	+3				*	(7)
.87	$Co(en)_2(\gamma\text{-}CH_3O\text{-}py)Cl^{+2} + H_2O \longrightarrow Co(en)_2(\gamma\text{-}CH_3O\text{-}py)H_2O^{+3} + Cl^{-}$ en = $H_2NCH_2CH_2NH_2$; γ-CH_3O-py = gamma methoxypyridine, $CH_3OC_5H_4N$	H_2O	$10^3A=2.5$	$HClO_4$	0.0025	kA	50	1.5	-5				*	(7)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.88	$Co(en)_2(\gamma\text{-}CH_3O\text{-}py)Cl^{+2} + OH^- \rightarrow Co(en)_2(\gamma\text{-}CH_3O\text{-}py)OH^{+2} + Cl^-$		$10^3A=2.5$			kAB	25	1.2	+3				*	(7)
	en = $H_2NCH_2CH_2NH_2$; γ-CH_3O-py = gamma methoxypyridine, $CH_3OC_5H_4N$													
.89	*trans*-$Co(py)_4Cl_2^+ + H_2O \longrightarrow Co(py)_4(H_2O)Cl^{+2} + Cl^-$	H_2O	$10^3A=2.5$	HNO_3	pH=1-2	kA	25	8.3	-6				*	(7) (32)
	py = pyridine, C_5H_5N			$Na_2B_4O_7$	pH=9.2									
.90	2*trans*-$Co(py)_4Cl_2^+ + Hg^{+2} + 2H_2O \rightarrow 2Co(py)_4(H_2O)Cl^{+2} + HgCl_2$	H_2O	$10^3A=10^3B=1$	NO_3^-	0.003	kAB	25	1.8	-1				*	(32)
	py = pyridine, C_5H_5N													
.91	*trans*-$Co(\beta\text{-}CH_3\text{-}py)_4Cl_2^+ + H_2O \rightarrow Co(\beta\text{-}CH_3\text{-}py)_4(H_2O)Cl^{+2} + Cl^-$	H_2O	$10^3A=2.5$	HNO_3	pH=1-2	kA	25	2.5	-5				*	(7) (32)
	β-CH_3-py = beta-picoline, $CH_3C_5H_4N$			$Na_2B_4O_7$	pH=9.2									
				HNO_3	0.1		49	7.0	-4					(35)
.92	$Co(\beta\text{-}CH_3\text{-}py)_4Cl_2^+ + D_2O \rightarrow Co(\beta\text{-}CH_3\text{-}py)_4(D_2O)Cl^{+2} + Cl^-$	D_2O		HNO_3	0.1	kA	49	5.5	-4				*	(35)
	β-CH_3-py = beta-picoline, β-$CH_3C_5H_4N$													
.93	$Co(\gamma\text{-}CH_3\text{-}py)_4Cl_2^+ + H_2O \longrightarrow Co(\gamma\text{-}CH_3\text{-}py)_4(H_2O)Cl^{+2} + Cl^-$	H_2O	$10^3A=2.5$	HNO_3	pH=1-2	kA	25	1.52	-5				*	(7) (32)
	γ-CH_3-py = γ-picoline, γ-CH_3-C_5H_4N			$Na_2B_4O_7$	pH=8.5									
.94	$Co(NH_3)_5Br^{+2} + H_2O \longrightarrow Co(NH_3)_5H_2O^{+3} + Br^-$	H_2O	$10^3A=1-10$			kA	15	2.02	-6				*	(10) (12)
			1	$HClO_4$	5×10^{-6}		15	1.57	-6					(10)
					1×10^{-5}		15	1.92	-6					
							25	6.5	-6					(12) (22)
			12 - 20	HNO_3	0.1		48	1.28	-4					(1)
.95	$Co(NH_3)_5Br^{+2} + D_2O \longrightarrow Co(NH_3)_5D_2O^{+3} + Br^-$	D_2O	$10^2A=1-2$	HNO_3	0.1		48	9.3	-5				*	(1)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.96	$2Co(NH_3)_5Br^{+2} + Hg^{+2} + 2H_2O \longrightarrow 2Co(NH_3)_5H_2O^{+3} + HgBr_2$	H_2O	$10^4A=2-6;$		$\mu=0.0014$	k AB	15	1.37	0				*	(10)
			$10^4B=2-11$		0.0048		15	2.1	0					
				$Ba(NO_3)_2$	0.010		15	2.5	0					
				KNO_3	0.010		15	3.1	0					
				HNO_3	0.022		15	4.4	0					
				HNO_3	0.032		15	5.5	0					
					0.0020		25	3.3	0	6.4				
.97	$Co(NH_3)_5Br^{+2} + OH^- \longrightarrow Co(NH_3)_5OH^{+2} + Br^-$	H_2O	$10^3A=6-14;$			k AB	5	1.97	-1				*	(1)
			$10^3B=6-50$				15	$\underline{1.48}$	0					(1) (27)
			$10^6A=5;$	NaBr	0.05		15	8.0	-1					
			$10^3B=3.5$		0.26		15	4.3	-1					
				Na_2SO_4	0.003		15	9.4	-1					
					0.03		15	5.1	-1					
			$10^4A=5-10;$		$\mu=0.008$		15	1.1	0					(10)
			$10^4B=6-11$		0.032		15	9.5	-1					
					0.0025		25	5.9	0	27	8	20		(1) (10)
			$10^5A=8-10;$	p = 10,000 psi			30	4.0	0					(13)
			$10^4B=1$	p = 15,000 psi			30	3.6	0					
				p = 18,000 psi			30	3.4	0					
.98	*cis*-$Co(en)_2(NH_3)Br^{+2} + H_2O \longrightarrow Co(en)_2(NH_3)H_2O^{+3} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=2-10$			k A	45	1.68	-5				*	(26)
							63	1.24	-4	23	1	11		
.99	d-*cis*-$Co(en)_2(NH_3)Br^{+2} + OH^- \longrightarrow Co(en)_2(NH_3)OH^{+2} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=7-16;$ $10^3B=1-10$			k AB	0	3.3	0				*	(26)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o			A^o	n		
.100	*l-cis*-$Co(en)_2(NH_3)Br^{+2} + OH^- \longrightarrow Co(en)_2(NH_3)OH^{+2} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A = 7-16$; $10^3B = 1-10$			$k AB$	0	3.4	0				*	(4)
.101	*trans*-$Co(en)_2(NH_3)Br^{+2} + H_2O \longrightarrow$ *trans*-$Co(en)_2(NH_3)H_2O^{+3} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A = 1-5$	$HClO_4$	0.1	$k A$	45	1.61	-5				*	(38)
			1-27				60	9.4	-5					
			1-30				73	3.8	-4	25	1	12		
.102	*cis*-$Co(en)_2(NCS)Br^+ + H_2O \longrightarrow$ *cis*-$Co(en)_2(NCS)H_2O^{+2} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A = 5-30$	$HClO_4$	0.004	$k A$	30	4.6	-5				*	(4)
							43	2.36	-4					
							60	1.36	-3	23	2	12		
.103	*trans*-$Co(en)_2(NCS)Br^+ + H_2O \longrightarrow Co(en)_2(NCS)H_2O^{+2} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A = 2-5$	$HClO_4$	0.007, pH=2.2	$k A$	63	5.8	-5				*	(20)
							71	1.65	-4					
							90	1.61	-3	30	2	15		
.104	*trans*-$Co(en)_2(NCS)Br^+ + OH^- \longrightarrow Co(en)_2(NCS)OH^+ + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A = 7-25$;	$10^3B = 2-6$		$k AB$	0	1.95	0				*	(20)
.105	*trans*-$Co(en)_2Br_2^+ + H_2O \longrightarrow Co(en)_2(H_2O)Br^{+2} + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O				$k A$	25	1.4	-4				*	(23)
.106	*trans*-$Co(en)_2Br_2^+ + OH^- \longrightarrow Co(en)_2(OH)Br^+ + Br^-$ en = $H_2NCH_2CH_2NH_2$	H_2O				$k AB$	25	1.2	+4					(33)
.107	$Co(YOH)Br^- + H_2O \longrightarrow Co(YOH)H_2O + Cl^-$ YOH =  $(HOCH_2CH_2)(^-OOCCH_2)NCH_2CH_2N(CH_2COO^-)_2$ $^{-3}$	H_2O	$10^3A = 1-3$	$NaNO_3$	0.1	$k A$	30	1.35	-5				*	(25)
							40	4.1	-5					
							50	1.20	-4	21	2	10		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.108	$Co(Y)Br^{-2} \longrightarrow Co(Y)^- + Br^-$ Y = 	H_2O	$10^4A=5-20$	$Pb(ClO_4)_2$; buffers	0.005-0.08 $\mu=1$; pH=0.4-5.5	$kA[Pb^{++}]$	25	5.6	-1				*	(19)
.109	$Co(HY)Br^- \longrightarrow CoY^- + H^+ + Br^-$ HY = 	H_2O	$10^4A=5-20$	$Pb(ClO_4)_2$; buffers	0.005-0.08 $\mu=1$; pH=0.4-5.5	$kA[Pb^{++}]$	25	2.5	-3				*	(19)
			$10^3A=2$			kA	30	6.3	-6					(25)
			1	$NaNO_3$	0.1		30	7.1	-6					
			2	$NaClO_4$	0.1		30	6.8	-6					
				$HClO_4$	1		30	8.3	-6					
				$Sr(NO_3)_2$	0.1		30	8.2	-6					
				$NaNO_3$	0.1		40	2.11	-5					
					0.1		50	5.4	-5	20	2	9		
.110	$Co(NH_3)_5I^{+2} + H_2O \longrightarrow Co(NH_3)_5H_2O^{+3} + I^-$	H_2O	$10^5A=1$	$HClO_4$	0.001	kA	45	6.0	-5				*	(39)
			$10^5A=1-250$	NaI	0.001-0.1	$-dA/dt=k_1A + k_2A[I^-]$	45	$k_1=6.7$	-5					
							45	$k_2=1.95$	-1					
.111	*trans*-$Pd(NH_3)_2H_2OCl^+ + H_2O \longrightarrow$ *trans*-$Pd(NH_3)_2(H_2O)_2^{+2} + Cl^-$	H_2O	$10^4A=5$			kA	36	1.22	-4				*	(6)
.112	*trans*-$Pd(NH_3)_2Cl_2 + H_2O \longrightarrow$ *trans*-$Pd(NH_3)_2H_2OCl^+ + Cl^-$	H_2O	$10^4A=5$			kA	36	3.8	-4				*	(6)
.113	$Ir(NH_3)_5Cl^{+2} + H_2O \longrightarrow Ir(NH_3)_5H_2O^{+3} + Cl^-$	H_2O				kA	95	6.4	-7				*	(21)
.114	$Ir(NH_3)_5Br^{+2} + H_2O \longrightarrow Ir(NH_3)_5H_2O^{+3} + Br^-$	H_2O				kA	80	7.8	-7				*	(21)
							95	2.3	-6	18	1	5		
.115	*cis*-$Pt(NH_3)_2(OH)Cl + OH^- \longrightarrow Pt(NH_3)_2(OH)_2 + Cl^-$	H_2O	$10^4A=5$; $10^3B=16-32$			kA	25	2.2	-5				*	(5)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	n	E	$A = A^o \times 10^n$ A^o	n	Comments	Literature
.116	*trans*-$Pt(NH_3)_2(OH)Cl + OH^- \rightarrow Pt(NH_3)_2(OH)_2 + Cl^-$	H_2O	$10^4A=5; 10^3B=8-16$			kA	25	3.8	-5				*	(^{5})
.117	*cis*-$Pt(NH_3)_2Cl_2 + H_2O \rightarrow Pt(NH_3)_2(H_2O)Cl^+ + Cl^-$	H_2O	$10^4A=5$	HNO_3	0.01	kA	25	3.8	-5				*	(^{5})
.118	*cis*-$Pt(NH_3)_2Cl_2 + OH^- \rightarrow Pt(NH_3)_2(OH)Cl + Cl^-$	H_2O	$10^4A=5; 10^3B=8-16$			kA	25	3.8	-5				*	(^{5})
.119	*trans*-$Pt(NH_3)_2Cl_2 + OH^- \rightarrow Pt(NH_3)_2(OH)Cl + Cl^-$	H_2O	$10^4A=5; 10^3B=1-16$			kA	25	1.02	-4				*	(^{5})
.120	$Pt(NH_3)(H_2O)Cl_2 + H_2O \rightarrow Pt(NH_3)(H_2O)_2Cl^+ + Cl^-$	H_2O		Na_2SO_4	$\mu=0.318$	kA	24	1	-5				*	(^{15})
.121	$Pt(NH_3)Cl_3^- + H_2O \rightarrow Pt(NH_3)(H_2O)(Cl_2) + Cl^-$	H_2O	$10^2A=1.7$	Na_2SO_4	$\mu=0.318$	kA	0	2.1	-6				*	(^{15})
							6	3.7	-6					
							15	1.31	-5					
							20	2.35	-5					
							25	3.6	-5					
							30	5.8	-5	19	3	9		
.122	$Pt(en)(OH)Cl + OH^- \rightarrow Pt(en)(OH)_2 + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=5; 10^3B=8-16$			kA	25	2.5	-5				*	(^{5})
.123	$Pt(en)Cl_2 + H_2O \rightarrow Pt(en)(H_2O)Cl^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=5$	HNO_3	0.01	kA	25	5.3	-5				*	(^{5})
.124	$Pt(en)Cl_2 + OH^- \rightarrow Pt(en)(OH)Cl + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=5; 10^3B=8-16$			kA	25	5.3	-5				*	(^{5})
.125	*trans*-$Pt(en)_2Cl_2^{+2} + OH^- \rightarrow Pt(en)_2(OH)Cl^{+2} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^3A=5; 10^2B=5$			kA	25	3.8	-5				*	(^{28})
			5-20	$NaClO_4$	0.15		25	5.2	-5					
			20		0.20		25	6.8	-5					
.126	$PtCl_4^{-2} + H_2O \rightarrow Pt(H_2O)Cl_3^- + Cl^-$	H_2O	$10^2A=1.7$		$\mu=0.3$	$-dA/dt=k_1A-k_2LM$	25	k_1=3.9 k_2=2.1	-5 -3					(^{18})

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^{\circ} \times 10^{n}$		Comments	Literature
						k°	n		
.127	$PtCl_4^{-2} + OH^- \longrightarrow Pt(OH)Cl_3^{-2} + Cl^-$	H_2O	$10^3A=2; 10^3B=2$	kA	25	3.2	-5	*	(5)

CODED SOLVENTS

D_2O 85-90*	D_2O-H_2O mixture containing 85-90% D
M 50 (82) (87)*	CH_3OH vol % designated + H_2O

COMMENTS

Classification: Reactions are grouped first according to central metal forming complex, then according to complexing groups or ions and then according to exchanging reactant. Order of the complexing groups is: NH_3, NO_2, NCS, $H_2NCH_2CH_2NH_2$, $H_2NCH_2CH(CH_3)NH_2$, $H_2NCH_2CH_2CH_2NH_2$, $H_2NCH_2CH_2NHCH_3$, $H_2NCH_2CH_2NHC_2H_5$, $H_2NCH_2CH_2NH(n\text{-}C_3H_7)$, $H_2NCH(CH_3)CH(CH_3)NH_2$, $H_2NCH_2C(CH_3)_2NH_2$, $H_2NCH_2CH_2NHCH_2CH_2NH_2$, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, $(HOCH_2CH_2)(OOCCH_2)NCH_2CH_2N(CH_2COO)_2^{-3}$, $(HOOCCH_2)(OOCCH_2)NCH_2CH_2N(CH_2COO)_2^{-3}$, $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{-4}$, $H_2NCH(C_6H_5)CH(C_6H_5)NH_2$, C_5H_5N, α-$CH_3C_5H_4N$, β-$CH_3C_5H_4N$, α-$CH_3OC_5H_4N$, β-$CH_3OC_5H_4N$.
Mono-halogen precede di-halogen complexes and the halogens are listed in the order F, Cl, Br, I.

Reactions **(.3)-(.9)** fluoride ion exchange on Co complexes
(.10)-(.93) chloride ion exchange on Co complexes
(.94)-(.109) bromide ion exchange on Co complexes
(.110) iodide ion exchange on Co complexes
(.111)-(.112) chloride ion exchange on Pd complexes
(.113)-(.114) halogen ion exchange on Ir complex
(.115)-(.127) chloride ion exchange on Pt complexes.

Comments by Literature Reference: (1) (2) (5) (6) (7a) (8) (9) (10) (14) (16) (17) (19) (21) (22) (24) (27) (28) (29) (30) (31) (32) (35) (36) (39) Units converted to seconds from original minutes. (16) (23) Units converted to seconds from original hours. (24) Constants converted to base e from original base 10 logarithms.

COMMENTS *(continued)*

Comments by Reaction: **(.3)** Reaction catalyzed by acid and value of rate constant listed is minimum at pH=3. **(.10)** Reaction followed to about 60% completion by (2)(12)(22)(31)(35) and to about 65% completion by (1). Expression for k_3 in (17) valid in presence of univalent sulphates for μ=0 to μ=1 and for bivalent sulphates for μ=0 to μ=0.5. NO_3^- and $SO_4^=$ added in form of $NaNO_3$, KNO_3, HNO_3, $Ca(NO_3)_2$, $Ba(NO_3)_2$, Na_2SO_4, K_2SO_4, $MgSO_4$, $CuSO_4$ and $ZnSO_4$. Rate constants in (16) identical for chloride, nitrate and perchlorate. **(.10.1)** Rate constants subject to experimental error of about 10%. **(.11)** C added in form of mixture of Na_2SO_4+$NaHSO_4$. μ adjusted to 0.3 by addition of $NaClO_4$. **(.12)** **(.13)** **(.14)** **(.15)** **(.16)** Reactions followed to at least 65% completion by (1). **(.18)** Rate too fast to be measured. **(.20)** Rate constant calculated from k=0.693/($t_{\frac{1}{2}}$[OH^-]). **(.21)** **(.22)** Reactions followed to about 60% completion. **(.23)** Equilibrium reached after 83 to 99% A has reacted. dl and d isomers of A used as reactants by (26). **(.24)** Slight decrease in k with increase in μ observed by (26). Steric analysis of products by (26) shows 60% d-*cis*, 24% l-*cis* and 16% *trans* isomers when d-*cis* isomer used as starting material. **(.25)** Rate constants calculated from initial rates. Reaction reversible and no *cis* isomer product detected up to 25% reaction.

(.26) Final product 76% *cis* and 24% *trans* isomers. Decrease in rate with increase in μ attributed to salt effect. **(.28)** Final product 66% *cis* and 34% *trans* isomers. **(.30)** Final product 6% *cis* and 94% *trans* isomers. **(.31)** Shiny Pt electrodes used in conductimetric measurements since Pt black catalyzes reaction. Polarimetric measurements indicate that aquation proceeds with practically complete retention of configuration. **(.32)** Final product 82% *cis* and 18% *trans* isomers. **(.33)** Rate of isomerization of product much faster that rate of aquotization of A. Reaction followed to 80% completion. **(.34)** In aqueous solution final product 74% *cis* and 26% *trans* isomers. **(.35)** Product 100% *cis*-isomer. **(.36)** Product 51% *cis* and 49% *trans*-isomer. **(.37)** Product 20% *cis* and 80% *trans*-isomer. **(.38)** Product 13% *cis* and 87% *trans*-isomer. **(.39)** Reverse reaction assumed to be second order although experimental results do not distinguish first or second order.

(.43) Final products by (34) 79% *cis* and 21% *trans*-isomers. Reaction followed to 60% completion by (30). Rate constants of (34) based on measurements of initial rates since (.39) becomes appreciable after (.43) has proceeded to a material extent. **(.44)** Rate constant accurate to only 1 significant figure because of simultaneous rapid aquation reaction. **(.45)** Value of rate constant approximate. **(.46)** HNO_3 present in (29) and (30) prevents replacement of Cl in L. **(.50)** **(.52)** **(.53)** **(.55)** **(.57)** **(.59)**-**(.62)** **(.64)** **(.66)** **(.70)** HNO_3 present prevents replacement of Cl. **(.69)** Rate constant calculated from k=0.693/($t_{\frac{1}{2}}$[OH^-]). **(.71)** **(.72)** Reactions followed to about 60% completion. **(.75)** Rate constant accurate to one significant figure because of rapidity of reaction. **(.76)** Rate constant tentative because A was contaminated with an isomeric tertiary pentamine. **(.77)** **(.78)** After one half life rate constant increased for (25) because of presence of isomeric forms of A. **(.79)** **(.80)** First order rate constant corrected for second order reverse reaction. **(.81)**-**(.89)** Reactions followed to more than 50% completion.

COMMENTS *(continued)*

(.91) (.92) Rate constant by (35) same at pH=1-2 as at pH=9.2. **(.93)** Decomposition of A occurs above pH=8.5. **(.94) (.96)** Pt black used in conductimetric measurements by (10) caused discrepancies. Authors demonstrate that:- $-dA/dt = kAB\left(\frac{f_A f_B}{f_X}\right)$ where f_X=activity coefficient of complex formed by A and B. **(.97)** Selected data. Change of rate constant interpreted by (7) in terms of an ion association constant and specific rate constants of associated and non-associated reactants. Change of rate constant with pressure leads to value of ΔV^*=8.5 ml/mole by (13). **(.98)** Reaction reaches equilibrium with 83-99% aquo product present. Rate constants are mean values for dl and l isomers of A. **(.99)** Final product 59% d-*cis*, 26% l-*cis* and 15% *trans*-isomer. **(.100)** Final product 27% d-*cis*, 58% l-*cis* and 15% *trans*-isomer. **(.101)** *Cis*-isomer of product detected only after 50% A has reacted. Reverse reaction important after 75% A reacts. **(.103)** Reaction followed to 80% completion. **(.105)** Reaction catalyzed by acid and given rate constant is its minimum value at pH=3.

(.104) Final product 81% *cis* and 19% *trans*-isomers. **(.107) (.108) (.109)** Second order rate constant calculated by (19) by dividing observed first order constant by $[Pb^{++}]$. $HClO_4$ used as buffer in pH range 0.4-3; pyridine-pyridinium perchlorate in range 3-5.5. Reaction pseudo first order to 75% completion. In (25) reaction first order to one half-life after which more active isomeric forms of A increase rate. **(.110)** Replacement of I in complex accompanied by parallel second order reaction of A with I^- leading to reduction of Co(III) and formation of I_2. Rate constant for this reaction given by k_2. See 732.780. Reaction pseudo first order only at $A < 10^{-5}$ or $A \gg M$. **(.113) (.114)** Reactions proceed to equilibrium and measured rate constants in agreement with values predicted from measured equilibrium constants. **(.120)** Rate constant calculated from approximate value of rate constant for reverse reaction (see 382.807.3)and measured equilibrium constant. **(.121)** For reverse reaction, see 382.807.4. **(.125)** Some reduction to Pt(II) occurred during each run.

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COORDINATIVE EXCHANGE
N-compound replacing halogen in VIIIth group complex

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	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$\mathrm{Co(NH_3)_5Cl^{++} + NO_2^- \longrightarrow Co(NH_3)_5NO_2^{++} + Cl^-}$	H_2O	B=1			kA	25	2.0	-6				*	(7)
.2	*cis*-$\mathrm{Co(en)_2(NO_2)Cl^+ + N_3^- \longrightarrow}$ *cis*-$\mathrm{Co(en)_2(NO_2)N_3^+ + Cl^-}$ en = $\mathrm{H_2NCH_2CH_2NH_2}$	H_2O	10^3A=5; 10B=0-5	HNO_3	0.05	dM/dt=kA	25	1.14	-4				*	(4)
.3	*cis*-$\mathrm{Co(en)_2(NO_2)Cl^+ + NO_2^- \longrightarrow}$ *cis*-$\mathrm{Co(en)_2(NO_2)_2 + Cl^-}$ en = $\mathrm{H_2NCH_2CH_2NH_2}$	H_2O	10^3A=5; 10B=0-2	HNO_3	0.05	dM/dt=kA	25	1.04	-4				*	(4)
.4	*trans*-$\mathrm{Co(en)_2(NO_2)Cl^+ + NO_2^- \longrightarrow}$ *trans*-$\mathrm{Co(en)_2(NO_2)_2^+ + Cl^-}$ en = $\mathrm{H_2NCH_2CH_2NH_2}$	H_2O	10^3A=5; B=0-1	HNO_3	0.05	dM/dt=kA	25	1.12	-3				*	(4)
.5	*cis*-$\mathrm{Co(en)_2Cl_2^+ + N_3^- \longrightarrow}$ *cis*-$\mathrm{Co(en)_2ClN_3^+ + Cl^-}$	CH_3OH	10^4A=6; 10^3B=1.2			kA	25	1.08	-4				*	(6)
	en = $\mathrm{H_2NCH_2CH_2NH_2}$			HN_3	0.0006		25	5.7	-5					
			4.8		0.0024		25	8.0	-5					
			19		0.0096		25	9.2	-5					
				HN_3, Cl^-	0.0096, 0.0192		25	3.7	-5					
			10^4A=8-9; 10^3B=1-2	Cl^-, Na^+	=A, =B	$k_1A + k_2AB$	26	k_2 1.0	-1					(5)
							36	k_1 1.0	-4					
							36	k_2 2.6	-1	18	1	12		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.6	*cis*-$Co(en)_2Cl_2^+ + NO^- \longrightarrow$ *cis*-$Co(en)_2(NO_2)Cl^+ + Cl^-$	CH_3OH	$10^4A=6;\ 10^2B=2.4$	HNO_2	0.0048	kA	25	9.7	-5				*	(^{6})
	en = $H_2NCH_2CH_2NH_2$				0.0016		25	9.3	-5					
			$10^4A=5.8;\ 10B=1.7$	NO_3^-, Na^+	=A, =B	k_1A+	36	$k_1=1.7$	-4					(^{5})
						k_2AB	36	$k_2=2.6$	-3					
.7	*cis*-$Co(en)_2Cl_2^+ + NO_3^- \longrightarrow$ *cis*-$Co(en)_2(NO_3)Cl^+ + Cl^-$	CH_3OH	$10^4A=7.3;\ 10B=1$	Li^+	B-A	kA	36	1.15	-4				*	(^{5})
	en = $H_2NCH_2CH_2NH_2$		A=7.5 4.4				36	1.37	-4					
			14.6 3.1				36	1.68	-4					
			7.4 3.7	Li^+, Cl^-	0.72, 0.35		36	1.91	-4					
.8	*cis*-$Co(trien)Cl_2^+ + N_3^- \longrightarrow Co(trien)(N_3)Cl^+ + Cl^-$	CH_3OH	$10^3B=4.8$	HN_3	0.0024	kA	25	8.8	-3				*	(^{6})
	trien = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$				0.0048		25	8.0	-3					
.9	*trans*-$Pd(NH_3)_2(H_2NCH_2COOH)Cl^+ + H_2NCH_2COOH \longrightarrow$ *trans*-$Pd(NH_3)_2(H_2NCH_2COOH)_2^{++} + Cl^-$	H_2O	$10^4A=10^4B=5$			kAB	36	3.2	-2				*	(^{2})
.10	*trans*-$Pd(NH_3)_2(C_5H_5N)Cl^+ + C_5H_5N \longrightarrow$ *trans*-$Pd(NH_3)_2(C_5H_5N)_2^{++} + Cl^-$	H_2O	$10^4A=10^4B=5$			kAB	36	1.21	-1				*	(^{2})
.11	*trans*-$Pd(NH_3)_2(C_6H_5NH_2)Cl^+ + C_6H_5NH_2 \longrightarrow$ *trans*-$Pd(NH_3)_2(C_6H_5NH_2)_2^{++} + Cl^-$	H_2O	$10^4A=10^4B=5$			kAB	36	5.8	-3				*	(^{2})
.12	$Pd(en)(H_2NCH_2COOH)Cl^+ + H_2NCH_2COOH \longrightarrow Pd(en)(H_2NCH_2COOH)_2^{++} + Cl^-$ en = $H_2NCH_2CH_2NH_2$	H_2O	$10^4A=10^4B=5$			kAB	36	6.5	-3				*	(^{2})

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
								k°	n		A°	n		
.13	$Pd(dien)Cl^+ + C_5H_5N \longrightarrow Pd(dien)(C_5H_5N)^{++} + Cl^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$	H_2O	$10^4A=4-10; 10^3B=1.2$				0	very fast					*	(3)
.14	$Pd(dien)Br^+ + C_5H_5N \longrightarrow Pd(dien)(C_5H_5N)^{++} + Br^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$	H_2O	$10^4A=4-10; 10^3B=1.2$				0	very fast					*	(3)
.15	$Pd(dien)I^+ + C_5H_5N \longrightarrow Pd(dien)(C_5H_5N)^{++} + I^-$ dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$	H_2O	$10^4A=4-10; 10^4B=6.2$			kA	0	2.6	-2				*	(3)
			12.4				0	3.3	-2					
			24.8				0	5.6	-2					
.16	$Pd(tripy)Cl^+ + C_5H_5N \longrightarrow Pd(tripy)(C_5H_5N)^{++} + Cl^-$ tripy = 2,2',2"-tripyridyl	H_2O	$10^4A=4-10; 10^3B=1.2$				0	very fast					*	(3)
.17	$Pd(tripy)Br^+ + C_5H_5N \longrightarrow Pd(tripy)(C_5H_5N)^{++} + Br^-$ tripy = 2,2',2"-tripyridyl	H_2O	$10^4A=4-10; 10^3B=1.2$				0	very fast					*	(3)
.18	$Pd(tripy)I^+ + C_5H_5N \longrightarrow Pd(tripy)(C_5H_5N)^{++} + I^-$ tripy = 2,2',2"-tripyridyl	H_2O	$10^4A=4-10; 10^3B=1.2$				0	very fast					*	(3)
.19	$Pt(NH_3)_3Cl^+ + NH_3 \longrightarrow Pt(NH_3)_4^{++} + Cl^-$	H_2O	$10^4A=5; 10^3B=9$	NH_4NO_3	0.2	kA	25	3.2	-5				*	(1)
			9	NH_4NO_3, KNO_3	0.10, 0.10		25	2.8	-5					
			36		0.05, 0.15		25	2.5	-5					
			36	NH_4NO_3	0.19		25	4.5	-5					
.20	$Pt(NH_3)_3Cl^+ + NO_2^- \longrightarrow Pt(NH_3)_3NO_2^+ + Cl^-$	H_2O	$10^4A=5; 10^3B=5$			kA	25	5.3	-5				*	(1)
			10				25	9.7	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.21	$Pt(NH_3)_3Cl^+ + C_5H_5N \longrightarrow Pt(NH_3)_3(C_5H_5N)^{++} + Cl^-$	H_2O	$10^4A=5;\ 10^2B=1-2$			kA	18	8.3	-6				*	(1)
							25	2.2	-5					
							35	6.5	-5	21	5	10		
			1	KNO_3	0.2		25	1.67	-5					
.22	$Pt(NH_3)_3Cl^+ + SC(NH_2)_2 \longrightarrow Pt(NH_3)_3[SC(NH_2)_2]^{++} + Cl^-$	H_2O	$10^4A=5;\ 10^3B=5$			kA	18	1.92	-4				*	(1)
							25	4.2	-4					
							35	8.5	-4	15	4	7		
			10				25	7.8	-4					
			15				25	1.40	-3					
.23	*trans*-$Pt(NH_3)_2Cl_2 + NH_3 \longrightarrow Pt(NH_3)_3Cl^+ + Cl^-$	H_2O	$10^4A=5;\ 10^3B=9$	NH_4NO_3	0.1	kA	25	1.83	-4				*	(1)
			18		0.1		25	3.5	-4					
.24	*trans*-$Pt(NH_3)_2Cl_2 + NO_2^- \longrightarrow Pt(NH_3)_2(NO_2)Cl + Cl^-$	H_2O	$10^4A=5$				25	very fast					*	(1)
.25	*trans*-$Pt(NH_3)_2Cl_2 + H_2NCH_2COOH \longrightarrow$ $Pt(NH_3)_2(H_2NCH_2COOH)Cl^+ + Cl^-$	H_2O	$10^4A=5;\ 10^2B=1-2$			kA	25	7.7	-5				*	(1)
.26	*trans*-$Pt(NH_3)_2Cl_2 + SC(NH_2)_2 \longrightarrow Pt(NH_3)_2[SC(NH_2)_2]Cl^+ + Cl^-$	H_2O	$10^4A=5$				25	very fast					*	(1)
.27	*trans*-$Pt(NH_3)_2Cl_2 + C_5H_5N \longrightarrow Pt(NH_3)_2(C_5H_5N)Cl^+ + Cl^-$	H_2O	$10^4A=5;\ 10^3B=10$			kA	25	8.3	-5				*	(1)
			5-10	KNO_3	0.2		25	1.08	-4					
.28	*trans*-$Pt(NH_3)_2Cl_2 + C_6H_5NH_2 \longrightarrow Pt(NH_3)_2(C_6H_5NH_2)Cl^+ + Cl^-$	H_2O	$10^4A=5;\ 10^2B=1-2$			kA	25	9.5	-5				*	(1)
.29	$Pt(dien)Cl^+ + C_5H_5N \longrightarrow Pt(dien)(C_5H_5N)^{++} + Cl^-$	H_2O	$10^4A=4-10;\ 10^4B=9$			kA	25	7.1	-6				*	(3)
	dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$		59				25	3.5	-5					
			96				25	5.3	-5					
			9				33	1.52	-5					
			9				50	5.6	-5	16	4	6		

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		
.30	$Pt(dien)Br^+ + C_5H_5N \longrightarrow Pt(dien)(C_5H_5N)^{++} + Br^-$	H_2O	$10^4A=4-10$; $10^4B=9$	kA	25	5.1	-6				*	(^{3})
	dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$		37.2		25	1.72	-5					
			124		25	4.3	-5					
			620		25	2.15	-4					
			9		33	1.03	-5					
			9		50	4.0	-5	16	3	6		
.31	$Pt(dien)I^+ + C_5H_5N \longrightarrow Pt(dien)(C_5H_5N)^{++} + I^-$	H_2O	$10^4A=4-10$; $10^4B=9$	kA	25	2.5	-6				*	(^{3})
	dien = $H_2NCH_2CH_2NHCH_2CH_2NH_2$		59		25	1.03	-5					
			96		25	1.55	-5					
.32	$Pt(tripy)Cl^+ + C_5H_5N \longrightarrow Pt(tripy)(C_5H_5N)^{++} + Cl^-$	H_2O	$10^4A=4-10$; $10^2B=1.24$	kA	0	1.15	-2				*	(^{3})
	tripy = 2,2',2"-tripyridyl				25	6.7	-2	11	8	6		
.33	$Pt(tripy)Br^+ + C_5H_5N \longrightarrow Pt(tripy)(C_5H_5N)^{++} + Br^-$	H_2O	$10^4A=4-10$; $10^4B=12$		25	very fast					*	(^{3})
	tripy = 2,2',2"-tripyridyl											
.34	$Pt(tripy)I^+ + C_5H_5N \longrightarrow Pt(tripy)(C_5H_5N)^{++} + I^-$	H_2O	$10^4A=4-10$; $10^3B=1.24$	kA	0	9.2	-3				*	(^{3})
	tripy = 2,2',2"-tripyridyl		2.58		0	2.3	-2					
			12.4		0	very fast						
			1.24		25	6.5	-2	13	2	8		

COMMENTS

Literature: (1) (2) (3) (4) (6) (7) Units converted from original minutes.

Reaction: **(.1)** Reaction assumed to proceed through formation of aquo complex since rate constant in absence of B is 1.5×10^{-5} see 382.870). **(.2) (.3) (.4)** Pseudo first order rate constants independent of [B] considered to indicate that rate determining step involves replacement of halogen by water followed by the rapid displacement of H_2O by B. **(.5)** Selected data from (6). After one half-life rate of exchange of second Cl^- ion caused positive deviations from first order law. *k* of (5) is calculated second order constant based upon initial rate and corrected for simultaneous unimolecular reaction occurring at one third to one sixth the rate of the second order process. **(.6)** Rate observed to be composite of first and second order reactions by (5) as in reaction (.5). Values of first and second order constants estimated by increasing B to a 300 fold excess and calculating by difference. **(.7)** Selected data. 0.5% H_2O added to solvent to increase solubility of nitrates. **(.13)** Reaction complete in 10 seconds. **(.14)** Reaction complete in 15 seconds. **(.16) (.17) (.18)** Reactions complete in 10 seconds. **(.19)-(.28)** Rate constants are first order or pseudo first order. **(.27) (.28)** Rate of replacement of second Cl^- ion appreciable and rate constants based on measurements of initial rates. Value of rate constant listed is one half observed constant for Cl^- formation. **(.30)** Selected data. **(.33)** Reaction complete in 10 seconds.

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(1) D. Banerjea, F. Basolo, R.G. Pearson, *ACS* 1957, **79**, 4055. (2) D. Banerjea, K.K. Tripathi, *J. Inorg, Nucl. Chem.* 1958, **7**, 78. (3) F. Basolo, H.B. Gray, R.G. Pearson, *ACS* 1960, **82**, 4200. (4) F. Basolo, B.D. Stone, J.G. Bergmann, R.G. Pearson, *ACS* 1954, **76**, 3079. (5) D.D. Brown, C.K. Ingold, *CSL* **1953**, 2680. (6) R.G. Pearson, P.M. Henry, F. Basolo, *ACS* 1957, **79**, 5382. (7) R.G. Pearson, P.M. Henry, J.G. Bergmann, F. Basolo, *ACS* 1954, **76**, 5920.

COORDINATIVE EXCHANGE
ROH, RCOO⁻, $CO_3^=$ or S compound replacing halogen in VIIIth group complex

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	Comments	Literature
.1	*cis*-$Co(en)_2Cl_2^+ + CH_3COO^- \longrightarrow$ *cis*-$Co(en)_2Cl(CH_3COO)^+ + Cl^-$	CH_3OH	$10^2B=1.9$			kA	25	7.6	-3	*	(^{3})
	en = $H_2NCH_2CH_2NH_2$			CH_3COOH	0.0022		25	2.2	-3		
					0.005-0.01		25	1.94	-3		
.2	*cis*-$Co(en)_2Cl_2^+ + 2CH_3COO^- \longrightarrow$ *cis*-$Co(en)_2(CH_3COO)_2^+ + 2Cl^-$	CH_3OH	$10^4A=6$; $10^4B=192$	CH_3COOH	$=\frac{1}{2}B$	kA	25	7.8	-5	*	(^{3})
	en = $H_2NCH_2CH_2NH_2$		196				25	7.0	-5		
			24				25	5.5	-5		
			6				25	3.8	-5		
			144	CH_3COOH; $LiClO_4$	$=\frac{1}{2}B$; 0.0048		25	6.7	-5		
			6		0.0186		25	3.0	-5		
.3	*cis*-$Co(en)_2Cl_2^+ + NCS^- \longrightarrow$ *cis*-$Co(en)_2Cl(NCS)^+ + Cl^-$	CH_3OH	$10^4A=7$; $10^3B=14$	Cl^-, Li^+	=A, =B	kA	36	7.8	-5	*	(^{2})
	en = $H_2NCH_2CH_2NH_2$		50				36	1.30	-4		
.4	$Pt(NH_3)_2Cl_2 + CH_2{=}CHCH_2OH \longrightarrow Pt(NH_3)_2(CH_2{=}CHCH_2OH)Cl^+ + Cl^-$	H_2O	$10^4A=5$; $10^3B=5$			kA	25	6.3	-5	*	(^{1})
			10				25	1.25	-4		
			15				25	1.80	-4		
.5	$Pt(NH_3)_2Cl_2 + C_2O_4^= \longrightarrow Pt(NH_3)_2(C_2O_4)Cl^- + Cl^-$	H_2O	$10^4A=5$; $10^2B=1$	Na^+	= 2B	kA	25	8.0	-5	*	(^{1})
			2				25	1.50	-4		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.6	$PtCl_4^= + CH_2{=}CHCH_2OH \longrightarrow PtCl_3(CH_2{=}CHCH_2OH)^- + Cl^-$	H_2O	$10^3A=2;\ 10^2B=6$	K^+	= 2A	kA	25	2.7	-5	*	(¹)
			12				25	5.0	-5		
			30				25	1.42	-4		

COMMENTS

Reaction: (.1) Units converted from original minutes. Rate constants are pseudo first order. Limiting rate reached on increasing $[CH_3COOH]$ believed to be due to suppression of $[CH_3O^-]$ which reacts with A at a very high rate. See 382.870 .45. (.2) Units converted from original minutes. Selected data. Reaction first order over entire range if rate constants calculated assuming that two Cl^- removed in rate determining step. (.3) Selected data. Rate constants determined on basis of measurements of initial stages of reaction because of a slow substitution of second Cl^- by NCS^-. Rate constants based on spectrophotometric measurements which measured rate of exchange by B alone. Rate constants measured polarimetrically were observed to be slightly greater as they included exchange with Cl^-. (.4) (.5) (.6) Units converted from original minutes.

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(¹) D. Banerjea, F. Basolo, R. G. Pearson, *ACS* 1957, **79,** 4055. (²) D. D. Brown, C.K. Ingold, *CSL* **1953,** 2680. (³) R. Pearson, P.M. Henry, F. Basolo, *ACS* 1957, **79,** 5382.

COORDINATIVE EXCHANGE
Halogen replacing halogen in VIIIth group complex

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
.1	*cis*-$Co(en)_2Cl_2^+ + Br^- \longrightarrow$ *cis*-$Co(en)_2ClBr^+ + Cl^-$ en = $H_2NCH_2CH_2NH_2$	CH_3OH	$10^3A=1.8; 10^3B=2.8$	Li^+, NO_3^-	=B, =A	kA	36	1.08	-4
			10				36	1.20	-4
			57				36	1.52	-4

COMMENTS

Reaction rate measured polarimetrically. Rate is first order in A and zero order in B, with rate essentially the same as with $B=NO_3^-$ or NCS^- see 382.875 and 382.876.3. This is in contrast to more rapid rate with NO_2^-, N_3^- and CH_3O^- which give first order dependence in B as well as A. See 382.875.

LITERATURE

D. D. Brown, C.K. Ingold, *CSL* **1953**, 2680.

PROTON ELIMINATION
Proton elimination from OH-bond
(Carboxylic acids and phenols, ionization and recombination)

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	Comments	Literature
.1	$HCOOH + H_2O \longrightarrow HCOO^- + H_3O^+$	50 vol % $C_2H_5OH-H_2O$	$10^4A=4-25$		$\mu=1$	kA	25	5.5	+4	*	(2)
.2	$H_3O^+ + HCOO^- \longrightarrow H_2O + HCOOH$	50 vol % $C_2H_5OH-H_2O$	$10^4M=4-25$; $10^2B=1-5$	KCl	$\mu=1$	kAB	25	1	+9	*	(2)
.3	$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$	H_2O 50 vol % $C_2H_5OH-H_2O$	$10^4A=1-3$; $10^4A=4-25$; $10^2L=1-5$	 KCl	 $\mu=1$	kA kA	~25 25	9 2.9	+5 +5	*	(4) (2)
.4	$H_3O^+ + CH_3COO^- \longrightarrow H_2O + CH_3COOH$	H_2O 50 vol % $C_2H_5OH-H_2O$	$10^4M=1-3$ $4-25$; $10^2B=1-5$	 KCl	 $\mu=1$	kAB kAB	~25 25	4.5 9	+10 +10	*	(4) (2)
.5	$ClCH_2COOH + H_2O \longrightarrow ClCH_2COO^- + H_3O^+$	50 vol % $C_2H_5OH-H_2O$	$L=0.25-1$	$NaNO_3$	$\mu=1$	kA	25	1.8	+6	*	(1)
.6	$H_3O^+ + ClCH_2COO^- \longrightarrow H_2O + ClCH_2COOH$	50 vol % $C_2H_5OH-H_2O$	$B=0.25-1$	$NaNO_3$	$\mu=1$	kAB	25	1.3	+10	*	(1)
.7	$C_6H_5COCOOH + H_2O \longrightarrow C_6H_5COCOO^- + H_3O^+$	H_2O	$10^2A=1-2$	H_3BO_3 + $Na_2B_4O_7$	$\mu=0.2$	kA	25	3	+8	*	(5)
.8	$C_6H_5COCOOH + OH^- \longrightarrow C_6H_5COCOO^- + H_2O$	H_2O	$10^2A=1-2$	H_3BO_3 + $Na_2B_4O_7$	$\mu=0.2$	kAB	25	1	+13	*	(5)
.9	$C_6H_5COCOOH + H_3BO_3 \longrightarrow C_6H_5COCOO^- + H_2BO_3^-$	H_2O	$10^2A=1-2$; $10^2B=5-20$	NaCl	$\mu=0.2$	kAB	25	2	+8	*	(5)
.10	$H_3O^+ + C_6H_5COCOO^- \longrightarrow H_2O + C_6H_5COCOOH$	H_2O	$10^2M=1-2$	H_3BO_3 + $Na_2B_4O_7$	$\mu=0.2$	kAB	25	5.7	+10	*	(5)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.11	$H_2O + C_6H_5COCOO^- \longrightarrow OH^- + C_6H_5COCOOH$	H_2O	$10^2M=1-2$	$H_3BO_3 +$ $Na_2B_4O_7$	$\mu=0.2$	kB	25	2	+1	*	(^{5})
.12	$H_3BO_3 + C_6H_5COCOO^- \longrightarrow H_2BO_3^- + C_6H_5COCOOH$	H_2O	$10^2M=1-2$; $10^2B=5-20$	NaCl	$\mu=0.2$	kAB	25	6	+2	*	(^{5})
.13	$m\text{-}NO_2C_6H_4OH + H_2O \longrightarrow m\text{-}NO_2C_6H_4O^- + H_3O^+$	H_2O	not stated			kA	25	1.9	+2	*	(^{3})
.14	$H_3O^+ + m\text{-}NO_2C_6H_4O^- \longrightarrow H_2O + m\text{-}NO_2C_6H_4OH$	H_2O	not stated			kAB	25	4.2	+10	*	(^{3})
.15	$p\text{-}NO_2C_6H_4OH + H_2O \longrightarrow p\text{-}NO_2C_6H_4O^- + H_3O^+$	H_2O	not stated			kA	25	2.6	+3	*	(^{3})
.16	$H_3O^+ + p\text{-}NO_2C_6H_4O^- \longrightarrow H_2O + p\text{-}NO_2C_6H_4OH$	H_2O	not stated			kAB	25	3.6	+10	*	(^{3})

COMMENTS

Reaction: **(.1)** Rate constant calculated from measured rate constant for reverse reaction (.2) and equilibrium constant. **(.2)** Rate constant determined by polarographic method involving reduction of azobenzene. **(.3)** Rate constant calculated from measured reverse reaction (.4) and the equilibrium constant. **(.4)** Rate constant determined by (^{1}) by polarographic method involving reduction of azobenzene, and by (^{4}) by change in conductivity with periodic impulses of very high electric fields. **(.5)** Rate constant calculated from measured rate of reverse reaction (.6) and equilibrium constant. **(.6)** Rate constant determined by polarographic method involving reduction of azobenzene. **(.7) (.8) (.9)** Rate constant calculated from rate constant of reverse reaction (.10)(.11)(.12) respectively and equilibrium constants. Probably give order of magnitude only. **(.10) (.11) (.12)** Simultaneous reactions for the transfer of a proton to $C_6H_5COCOO^-$. Rate constants calculated by analysis of polarographic data under varying conditions of pH and borate buffer concentration. (.11)(.12) can at best give order of magnitude only. **(.13) (.14) (.15) (.16)** Rate constants determined by perturbation of chemical equilibrium by rapidly changing electric field and relaxation time to return to equilibrium related to reaction rate constants.

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(1) P. Delahay, S. Oka, *ACS* 1960, **82**, 329. (2) P. Delahay, W. Vielstich, *ACS* 1955, **77**, 4955. (3) M. Eigen, K. Kustin, *ACS* 1960, **82**, 5952. (4) M. Eigen, J. Schoen, *Zeit. Elektrochem.* 1955, **59**, 483. (5) K. Wiesner, M. Wheatley, J.M. Los, *ACS* 1954, **76**, 4858.

BOND-UNSATURATION ELIMINATION
Hg(II) from ethylenic addition compound.

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

Reaction type: $ROCR_1R_2CR_3R_4HgX + HX \longrightarrow ROH + R_1R_2C{:}CR_3R_4 + HgX_2$

or

$ROCR_1R_2CR_3R_4HgX + H^+ \longrightarrow ROH + R_1R_2C{:}CR_3R_4 + HgX^+$

followed by rapid $ROCR_1R_2CR_3R_4HgX + HgX^+ \longrightarrow ROCR_1R_2CR_3R_4Hg^+ + HgX_2$

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	$HOCH_2CH_2HgCl + HCl \longrightarrow CH_2{:}CH_2 + H_2O + HgCl$	Et75*	$10^2A=2.4$; $10^2B=16$			$kA[H^+][Cl^-]$	0	1.33	-2				*	(2)
			16.				25	2.20	-1	18	6	12		
			9.8				25	2.27	-1					
			5.0				25	2.48	-1					
			2.4				25	2.78	-1					
			1.2				25	3.28	-1					
.2	$CH_3OCH_2CH_2HgCl + HCl \longrightarrow CH_2{:}CH_2 + CH_3OH + HgCl_2$	Et75*	$10^2A=5$; $10^2B=16$			$kA[H^+][Cl^-]$	0	1.63	-3				*	(2)
			5-20	NaCl	0-0.05		25	3.50	-2	20	2	13		
			2.6				25	3.9	-2					
.3	$CH_3OCH_2CH_2HgCl + H^+ \longrightarrow CH_2{:}CH_2 + CH_3OH + HgCl^+$	H_2O	not given	ClO_4^-	= B	kAB	25	3.32	-2				*	(4)(5)
.4	$CH_3OCD_2CD_2HgCl + H^+ \longrightarrow CD_2{:}CD_2 + CH_3OH + HgCl^+$	H_2O	not given	ClO_4^-	= B	kAB	25	3.14	-2				*	(4)
.5	$CH_3CH(OH)CH_2HgI + H^+ \longrightarrow CH_3CH{:}CH_2 + H_2O + HgI^+$	H_2O	$10^5A=5-19$; $10^4B=2-13$	ClO_4^-	= B	kAB	25	2.09	0				*	(3)
				$NaClO_4$	0-.17		25	2.11	0					
				CH_3COOH CH_3COONa	.019-1.9 .0016-0.16		25	2.13	0					
		M96*	$10^4B=2-20$				25	1.31	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.6	$CH_3CH(OH)CH_2HgI + D^+ \longrightarrow CH_3CH{:}CH_2 + HOD + HgI^+$	99% D_2O	$10^4A \simeq 1$; $B > A$	ClO_4^-	$=B$	kAB	25	4.4	0				*	(3)
.7	$C_2H_5OCH_2CH_2HgCl + HCl \longrightarrow CH_2{:}CH_2 + C_2H_5OH + HgCl_2$	Et75*	$10^2A=5$; $10^2B=16$			$kA[H^+][Cl^-]$	0	1.76	-2				*	(2)
			5-16	NaCl	C-0.05		25	3.90	-2	20	3	13		
			2.6				25	4.3	-2					
			2.6	$HgCl_2$	0.030		25	3.4	-2					
		Et 60*	5 9.8				25	3.0	-2					
		Et 67*	5 9.8				25	3.3	-2					
		Et 80*	5 9.8				25	5.0	-2					
		Et 88*	5 9.8				25	7.2	-2					
		Et 94*	5 9.8				25	1.87	-1					
.8	$CH_3CH(OCH_3)CH_2HgI + H^+ \longrightarrow CH_3CH{:}CH_2 + CH_3OH + HgI^+$	H_2O	$10^4A \simeq 1$; $10^4B=7-44$	ClO_4^-	$=B$	kAB	25	6.6	-1				*	(3) (5)
			85-1210				25	3.3	-2					
.9	$CH_3CH(OCH_3)CH_2HgI + D^+ \longrightarrow CH_3CH{:}CH_2 + CH_3OD + HgI^+$	99% D_2O	$10^4A \simeq 1$; $B > A$	ClO_4^-	$=B$	kAB	25	1.8	0				*	(3) (5)
			$10^3B=8-120$				25	1.12	-1					
.10	$CH_3COOCH_2CH_2HgCl + HCl \longrightarrow CH_2{:}CH_2 + CH_3COOH + HgCl_2$	Et75*	$10^2A=5$; $10^2B=16$			$kA[H^+][Cl^-]$	0	7.9	-4				*	(2)
			20				25	1.34	-2					
			16				25	1.39	-2	19	8	11		
			10	NaCl	0-0.05		25	1.49	-2					
			5				25	2.14	-2					
			2.6				25	3.4	-2					
			2.6	$HgCl_2$	0.03		25	1.92	-2					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.11	$(CH_3)_2CHOCH_2CH_2HgCl + HCl \longrightarrow$ $CH_2{:}CH_2 + (CH_3)_2CHOH + HgCl_2$	Et75*	$10^2A=5$; $10^2B=16$			$kA[H^+][Cl^-]$	0	2.90	-3				*	(2)
			16				25	5.6	-2					
			10	NaCl	0-0.05		25	5.6	-2					
			5				25	5.9	-2					
			2.6				25	6.5	-2					
			2.6	$HgCl_2$	0.03		25	4.2	-2					
			1.3				25	8.5	-2					
.12	α-*cyclo*-2-$CH_3OC_6H_{10}HgCl + HCl \longrightarrow$ *cyclo*-$C_6H_{10} + CH_3OH + HgCl_2$	CH_3OH	$10^3A=1$; $10^4B=5$-20				25	3.53	0					(1)
				H_2O	4 vol.%		25	6.5	-1					
		C_6H_6	$10^4A=2$; $10^4B=2$				25	5.6	0					
				H_2O	0.005 vol.%		25	1.9	0					
.13	α-*cyclo*-2-$CH_3OC_6H_{10}HgBr + HBr \longrightarrow$ *cyclo*-$C_6H_{10} + CH_3OH + HgBr_2$	M96*	$10^3A=1$; $10^4B=5$-20			kAB	25	7.5	-1				*	(1)
.14	α-*cyclo*-2-$CH_3OC_6H_{10}HgI + HI \longrightarrow$ *cyclo*-$C_6H_{10} + CH_3OH + HgI_2$	M96*	$10^3A=1$; $10^4B=5$-20			kAB	25	7.1	-1				*	(1)
.15	α-*cyclo*-2-$CH_3OC_6H_{10}HgI + H^+ \longrightarrow$ *cyclo*-$C_6H_{10} + CH_3OH + HgI^+$	H_2O	$10^4A=1$; $10^4B=3.6$	ClO_4^-	=B	$kA[H^+]$	25	5.8	0				*	(6)
				CH_3COOH CH_3COONa	0.1-0.5 0.02-0.1		25	6.1	0	17.2	2	13		
		M96*	$10^4B=4$-22				25	1.68	0					
.16	α-*cyclo*-2-$CH_3OC_6H_{10}HgI + D^+ \longrightarrow$ *cyclo*-$C_6H_{10} + CH_3OD + HgI^+$	98% D_2O	$10^4B=3.6$	ClO_4^-	=B	$kA[D^+]$	25	1.94	+1					(6)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.17	β-*cyclo*-2-$CH_3OC_6H_{10}HgCl + HCl \longrightarrow$	CH_3OH	10^3A=1-4; 10^3B=1-4			kAB	25	~2	-3					(1)
	cyclo-$C_6H_{10} + CH_3OH + HgCl_2$	M99*					25	~2	-4					
.18	β-*cyclo*-2-$CH_3OC_6H_{10}HgI + H^+ \longrightarrow$	H_2O	10^4A~1; H_2SO_4 =1.87			kA	25	3.2	-5				*	(6)
	cyclo-$C_6H_{10} + CH_3OH + HgI^+$		10^2B=3-12	ClO_4^-	=B	kAB	60	4.2	-4					
			25.7				60	4.75	-4					
			47.4				60	6.29	-4	25.6	4	13		
.19	β-*cyclo*-2-$CH_3OC_6H_{10}HgI + D^+ \longrightarrow$	90% D_2O	10^4A~1; H_2SO_4=1.87			kA	25	8.4	-5					(6)
	cyclo-$C_6H_{10} + CH_3OD + HgI^+$													
.20	α-$C_6H_5CH(OCH_3)CH(C_6H_5)HgCl + HCl \longrightarrow$	CH_3OH	10^3A=1-4; 10^3B=1-4			kAB	25	~5	-2				*	(1)
	$C_6H_5CH{:}CHC_6H_5 + CH_3OH + HgCl_2$	M96*					25	~1	-2					
.21	β-$C_6H_5CH(OCH_3)CH(C_6H_5)HgCl + HCl \longrightarrow$	CH_3OH	10^3A=1-4; 10^3B=1-4			kAB	25	2.1	0				*	(1)
	$C_6H_5CH{:}CHC_6H_5 + CH_3OH + HgCl_2$	M96*					25	~1	0					

CODED SOLVENTS

Et75*(60,67,80,88,94)	C_2H_5OH vol % indicated + H_2O
M96*(99)	CH_3OH vol % indicated + H_2O

COMMENTS

Reaction: **(.1) (.2)** Rate constants calculated for first 50% reaction. Slight increase in calculated constants by 73% reaction. Increase in rate constant with decrease in HCl concentration probably due to increase of activity coefficient with dilution. **(.3) (.4) (.5) (.6)** Stoichiometry indicates second molecule of A reacts rapidly with $HgCl^+$ forming $CH_3OCH_2CH_2Hg^+ + HgCl_2$. Second order constant calculated by dividing pseudo first order constant by $[H^+]$. **(.7)** Rate constants calculated for first 50% reaction. Slight increase in calculated constants by 73% reaction. Increase in rate constant with decrease in HCl concentration may be due to increase of activity coefficient with dilution. **(.8) (.9)** Stoichiometry indicates second molecule of A reacts rapidly with $HgCl^+$ forming $CH_3CH(OCH_3)CH_2Hg^+ + HgCl_2$. Second order constant calculated by dividing pseudo first order constant by $[H^+]$. **(.10) (.11)** Rate constants calculated for first 50% reaction. Slight increase in calculated rate constant as reaction proceeds. Increase in rate constant with decrease in [HCl] may be due to increase of activity coefficient with dilution. Selected data.

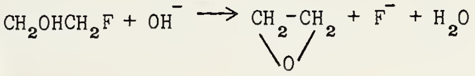
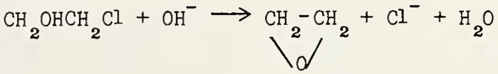
(.13) (.14) Rate law valid for initial stage of reaction only, in contrast to (.12) where it is valid over extended range. Rate drops off with course of reaction which may indicate rate law such as $k\,A[H^+][X^-]$ as observed for (.1) (.2) (.7) (.10) and (.11). **(.15)** Temperature dependence was studied at six temperatures from 0 to 60° but no data given. Authors list $\Delta H^{\ddagger}=17.7\pm0.2$ and $\Delta S^{\ddagger}=4.6\pm0.6$ for enthalpy and entropy of activation at 25°C. **(.18)** Temperature dependence was studied at six temperatures from 15 to 75°C. but no data given. Authors list $\Delta H^{\ddagger}=26.2\pm0.7$ and $\Delta S^{\ddagger}=4\pm2$ for enthalpy and entropy of activation at 25°C and 0.474 M perchloric acid. Plot of log of pseudo first order rate constants versus $-H_o$, the Hammett acidity function, was linear from 0.5 to 6M perchloric and sulfuric acids, with slope of 1.17 at 25°C. **(.20)** α-diastereomer derived from *cis*-stilbene. **(.21)** β-diastereomer derived from *trans*-stilbene.

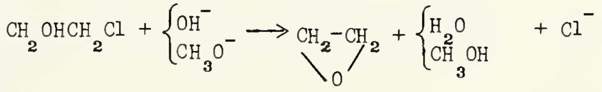
LITERATURE

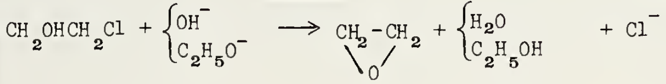
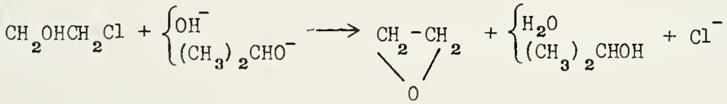
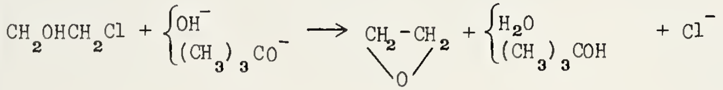
(1) O.W. Berg, W.P. Lay, A. Rodgman, G.F. Wright, *CJC* 1958, **36**, 358. (2) K. Ichikawa, H. Ouchi, S. Araki, *ACS* 1960 **82**, 3880. (3) M.M. Kreevoy, *ACS* 1959, **81**, 1099. (4) M.M. Kreevoy, L.T. Ditsch, *ACS* 1960, **82**, 6127. (5) M.M. Kreevoy, L.T. Ditsch, *JOC* 1960, **25**, 134. (6) M.M. Kreevoy, F.R. Kowitt, *ACS* 1960, **82**, 739.

ELIMINATION
of hydrogen halide from halohydrins with ring closure

Liquid phase
Amounts are in M/l.
Rate constants are in M/l and sec.
For coded solvents see at end of table.

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.8	.1	 $CH_2OHCH_2F + OH^- \longrightarrow CH_2-CH_2(O) + F^- + H_2O$	H_2O	not stated			kAB	30	2.5	-5				*	(9)
								40	8.5	-5					
								60	6.3	-4	21.5	8	10		
			Dl 55.0*				kAB	60	7.0	-4					
			Me 55.0*				kAB	60	3.8	-4					
.9	.2	 $CH_2OHCH_2Cl + OH^- \longrightarrow CH_2-CH_2(O) + Cl^- + H_2O$	H_2O	A=B~0.1	Na^+	= B	kAB	0	<u>3.0</u>	-4				*	(9) (10)
								10	1.31	-3					(10)
								20	4.94	-3					
								30	1.81	-2	22.6	3.2	14		
								35	3.6	-2	23	1	15		(9)
				0.03				20	5.45	-3					(10)
				0.06				"	5.10	-3					
				0.2				"	4.31	-3					
				1.0				"	3.72	-3					
				A=B=0.1	NaCl	0.500		"	4.87	-3					
					"	1.000		"	4.72	-3					
			H_2O	A=B=0.025	Na^+	= B		25	1.04	-2				(2)	(12) (13) (14)
				0.1				"	9.3	-3					
				0.2				"	8.8	-3					
				0.5				"	7.8	-3					

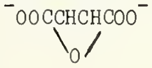
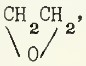
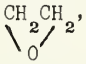
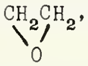
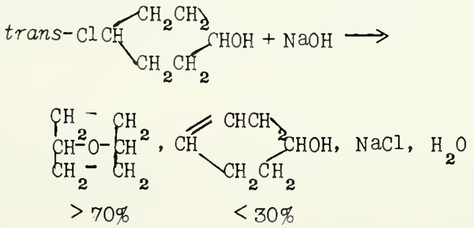
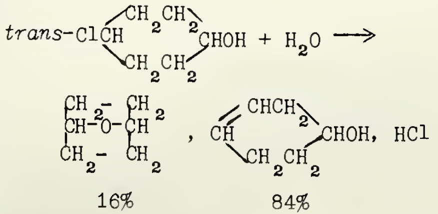
No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		*E*	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.9	.2	$CH_2OHCH_2Cl + OH^- \longrightarrow$ *(continued)*	H_2O	A=B=0.02-0.05	Ba^{++}	=B/2	*k* AB	25	9.8	-3				*	(13)
				0.01-0.02	Ca^{++}	=B/2		"	1.02	-2					
				0.02-0.4	$(CH_3)_4N^+$	=B		"	1.04	-2					(3)
				0.4	$NaNO_3$	0.4		"	9.6	-3					
			D_2O	A≃0.08; B≃0.03	Na^+	= B		"	1.54	-2					(3) (12)
			DiW12.3*	A=B	Na^+	= B		0	4.95	-4					(11)
			DiW34.3*					0	1.29	-3					
			DiW6.2*					15	3.4	-3					
			DiW29.7*					15	7.84	-3					
			DiW34.3*					15	9.64	-3					
			DiW7.6*					30	2.50	-2					
			DiW34.6*					"	5.79	-2					
			DiW71.4*					"	1.41	-1					
.10		 $CH_2OHCH_2Cl + \left\{\begin{matrix} OH^- \\ CH_3O^- \end{matrix}\right. \longrightarrow CH_2{-}CH_2\,(O) + \left\{\begin{matrix} H_2O \\ CH_3OH \end{matrix}\right. + Cl^-$	Mt0.0*	A=B	Na^+	= B	*k* AB	0	3.10	-4				*	(11)
			Mt22.8*					0	1.44	-4					
			Mt64.6*					0	3.30	-5					
			Mt0.0*					15	2.82	-3					
			Mt12.0*					15	2.05	-3					
			Mt54.9*					15	5.72	-4					
			Mt0.0*					30	1.89	-2					
			Mt37.9*					30	9.1	-3					
			Mt61.5*					30	4.02	-3					
			Mt84.7*					30	1.17	-3					
			Mt100*					30	3.75	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		Comments	Literature
								k^o	n		
.11		Et0.0*	A=B	Na^+	= B	kAB	0	3.10	-4	*	(^{11})
		Et 18.6*					0	5.12	-4		
		Et 36.6*					0	7.50	-4		
		Et 68.6*					0	4.84	-4		
		Et0.0*					15	2.77	-3		
		Et9.6*					15	1.19	-2		
		Et 20.6*					15	4.74	-3		
		Et 61.7*					15	5.04	-3		
		Et0.0*					30	1.89	-2		
		Et 30.0*					30	3.72	-2		
		Et 37.6*					30	3.88	-2		
		Et75.0*					30	3.02	-2		
		Et 100*					30	1.59	-2		
.12		*i*-Pr5.0*	A=B	Na^+	= B	kAB	30	2.58	-2	*	(^{11})
		i-Pr37.4*					30	5.39	-2		
		i-Pr70.3*					30	7.80	-2		
.13		*t*-Bu 10.4*	A=B	Na^+	= B	kAB	30	3.42	-2	*	(^{11})
		t-Bu 18.8*					30	4.44	-2		
		t-Bu 39.8*					30	5.14	-2		
		t-Bu 63.2*					30	5.79	-2		

Supplement 1960

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
.14	.3	$CH_2OHCH_2Br + OH^- \longrightarrow \underset{\diagdown O \diagup}{CH_2{-}CH_2} + Br^- + H_2O$	H_2O	not stated			kAB	0	1.64	-3				*	(9)
								5	3.38	-2					
								10	6.59	-2	22	5	15		
			Di 64.2*				kAB	0	7.6	-2					
			Me 66.3*				kAB	0	7.4	-3					
.15	.4	$CH_2OHCH_2I + OH^- \longrightarrow \underset{\diagdown O \diagup}{CH_2{-}CH_2} + I^- + H_2O$	H_2O	not stated			kAB	0	1.50	-2				*	(9)
								5	3.05	-2					
								10	6.40	-2	22	8	15		
			Di 64.2*				kAB	0	9.9	-2					
			Me 66.3*				kAB	0	1.0	-2					
.16		$CH_3CHOHCH_2Cl + OH^- \longrightarrow CH_3\underset{\mid\ O \diagup}{CHCH_2} + H_2O + Cl^-$	H_2O	A=B≃0.01	Ba^{++}	=B/2	kAB	18	1.09	-1					(14)
.17		$CH_3CHClCH_2OH + OH^- \longrightarrow CH_3\underset{\mid\ O \diagup}{CHCH_2} + H_2O + Cl^-$	H_2O	A=B≃0.01	Na^+	=B	kAB	25	7.26	-2				*	(2)
			D_2O 49.7*					25	8.60	-2					
			D_2O 99.5*					25	1.15	-1					
.18		$CH_2OHCHOHCH_2Cl + OH^- \longrightarrow CH_2OH\underset{\diagdown O \diagup}{CH{-}CH_2} + H_2O + Cl^-$	H_2O	A=0.03-0.04	NH_3	0.1	kAB	20	9.5	-2				*	(15)
					$+NH_4NO_3$	0.02		20	9.5	-2					(4)
					$C_6H_5CH(CH_3)NH_2$	0.1		20	9.3	-2					(15)
					CH_3NH_2	0.06		20	1.05	-1					
					$+CH_3NH_3NO_3$	0.05		20	1.04	-1					
					$(CH_3)_2NH$	0.06		20	1.02	-1					
					$+(CH_3)_2NH_2NO_3$	0.02		20	9.9	-2					
				10^3A=8; 10^3B=8-11	Na^+	=B	kA^2B	20	2.2	+1					(13)
				24 24	Ba^{++}	=B/2		20	6.8	0					
				22 13	"	"		20	7.3	0					
				14 14	"	"		20	1.3	+1					
				6 6	" $+BaCl_2$	" 0.01		20	2.8	+1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.19	$CH_2ClCHOHCH_2Cl + OH^- \longrightarrow CH_2Cl\underset{\backslash O /}{CHCH_2} + H_2O + Cl^-$	H_2O	A=B=0.008	Na^+	=B	kAB	25	1.17	0					(13)
			A=B=0.007	+NaCl	0.02		25	1.21	0					
			A=B=0.008	Ba^{++}	=B/2		25	1.15	0					
			A=B=0.007	$+BaCl_2$	0.03		25	1.10	0					
.20	$CH_2ClCHClCH_2OH + OH^- \longrightarrow CH_2Cl\underset{\backslash O /}{CHCH_2} + H_2O + Cl^-$	H_2O	A=B=0.04	Na^+	=B	kAB	25	5.3	-3					(3)
.21	$CH_2OHCH_2CH_2CH_2Cl + OH^- \rightarrow \overline{CH_2CH_2CH_2CH_2O} + H_2O + Cl^-$	H_2O	$10^2A \sim 4$; $10B \sim 1$	Na^+	=B	kAB	20	9.32	-4					(7)
			4 1-9				30	2.83	-3	20	7	11		
.22	$CH_2OHCH_2CH_2CH_2Cl \longrightarrow \underbrace{CH_2CH_2CH_2CH_2}_{O} + HCl$	H_2O	0.05-0.10			kA	50	3.63	-5					(6)
							60	9.87	-5					
							70	2.87	-4	21.9	2	10		
.23	$CH_2ClC(CH_3)ClCH_2OH + OH^- \longrightarrow CH_2Cl\underset{\backslash O /}{C(CH_3)CH_2} + H_2O + Cl^-$	H_2O	$A \simeq 0.02$; $B \simeq 0.07$	Na^+	=B	kAB	25	3.98	-2					(1)
			A=B=0.05	Na^+	=B		25	4.65	-2					
.24	$^-OOCCHOHCH_2Cl + OH^- \longrightarrow {}^-OOC\underset{\backslash O /}{CHCH} + H_2O + Cl^-$	H_2O	A=B=0.007-.07	Na^+	=2B	$k\,AB[Na^+]^{1/7}$	25	1.23	-2					(13)
			.007-0.1	K^+	=2B	$k\,AB[K^+]^{1/7}$	25	1.23	-2					
			.005-.02	Ca^{++}	=B	$k\,AB[Ca^{++}]^{1/4}$	25	6.33	-2					
			.008-.03	Ba^{++}	=B	$k\,AB[Ba^{++}]^{1/4}$	25	3.0	-2					
.25	$^-OOCCHClCH(C_6H_5)OH + OH^- \longrightarrow {}^-OOC\underset{\backslash O /}{CHCH}C_6H_5 + H_2O + Cl^-$	H_2O	A=B=0.004	Na^+	=2B	kAB	25	1.87	0					(13)
			.004	K^+	=2B		25	1.70	0					
			.010	K^+	=2B		25	1.58	0					
			.005	Ca^{++}	= B		25	2.25	0					
			.010	Ca^{++}	= B		25	2.45	0					
			.004	Ba^{++}	= B		25	2.33	0					
			.009	Ba^{++}	= B		25	2.50	0					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.26	$^-OOCCHClCH(COO^-)OH + OH^- \longrightarrow$  $\underset{O}{^-OOCCHCHCOO^-}$ $+ H_2O + Cl^-$	H_2O	A=B=0.005-0.02	Na^+	=3B	$kAB[Na^+]^{1/4}$	25	1.77	-1					(^{13})
			10^3A=1-2; 10^3B=1-25	K^+	.03-0.1	$kAB[K^+]^{1/4}$	25	1.90	-1					
			A=B=0.004	Ca^{++}	=3 B/2	kAB	25	6.17	-1					
			.007	"	"		25	6.12	-1					
			.010	"	"		25	6.65	-1					
			.005-.016	Ba^{++}	=3 B/2	$kAB[Ba^{++}]^{1/3}$	25	7.15	-1					
.27	$FCH_2CH_2Br + NaOH \longrightarrow$  $\underset{O}{CH_2CH_2}$, $HOCH_2CH_2OH$, NaF, NaBr	DW 50*	A=0.018; B=0.025	$(C_6H_5)_2NH$	0.01	kAB	50	4.95	-5					(^{8})
							70	3.52	-4	21.1	1.0	10		
.28	$ClCH_2CH_2Br + NaOH \longrightarrow$  $\underset{O}{CH_2CH_2}$, $HOCH_2CH_2OH$, NaCl, NaBr	DW 50*	A=0.018; B=0.025	$(C_6H_5)_2NH$	0.01	kAB	30	~6	-6				*	(^{8})
							70	~4	-4	~21	~2	10		
.29	$BrCH_2CH_2Br + NaOH \longrightarrow$  $\underset{O}{CH_2CH_2}$, $HOCH_2CH_2OH$, NaBr	DW 50*	A=0.018; B=0.025	$(C_6H_5)_2NH$	0.01	kAB	30	~2	-5				*	(^{8})
							70	~1	-3	~22	~3	10		
.30		H_2O	A=0.02; B=0.09-0.2			kAB	70	3.19	-4				*	(^{5})
							80	8.99	-4	24	1.0	12		
.31		H_2O	A=0.02			kA	70	8.43	-6					(^{5})
							80	2.75	-5	28	1	13		

SOLVENTS

Di 55.0(64.2)	H_2O + 1,4-dioxane, dielectric constant=(55.0)(64.2)
Me 55.0(66.3)	H_2O + CH_3OH, dielectric constant=(55.0)(66.3)
DiW 6.2*(12.3, 34.3 etc.)	H_2O + 1,4-dioxane(wt % as indicated)
DW 50*	H_2O + 1,4-dioxane 50 vol %
Mt 0.0*(12.0, 22.8 etc.)	H_2O + CH_3OH(wt % as indicated)
Et 0.0*(9.6, 18.6 etc.)	H_2O + C_2H_5OH(wt % as indicated)
i-Pr 5.0*(37.4, 70.3)	H_2O + $(CH_3)_2CHOH$(wt % as indicated)
t-Bu 10.4*(18.8, 39.8, 63.2)	H_2O + $(CH_3)_3COH$(wt % as indicated)
D_2O 49.7*(99.5)	H_2O + D_2O(wt % as indicated)

COMMENTS

Comments by Literature Reference: (1)(3)(4)(6)(7)(9)(11)(13)(14) Units converted to seconds from original minutes. In some instances authors listed units of second order constants as reciprocal minutes omitting 1/M designation.

Reaction: **(.8)** Rate constant is for second order rate law instead of first order as listed in 1951 Tables. Initial concentrations not stated but probably about 0.05. **(.9)** Rate constants of (2) are for about first 35% reaction. Reaction must be carried out in absence of CO_2 and using CO_2 free base for reliable results. Loss of volatile chlorhydrin and reaction of CO_2 with base caused calculated rate constants to decrease with time for most investigators prior to (13). **(.10) (.11) (.12) (.13)** Initial concentration of reactants not specified. Data tabulated or selected from large number of values in mixed solvents of different dielectric constants. **(.14) (.15)** Rate constant is for second order rate law instead of first order as listed in 1951 Tables. Initial concentrations not stated but probably about 0.05 as in other work of authors. **(.17)** Rate constant listed is for initial stage of reaction. **(.18)** Rate constants of (4) and (14) calculated using dissociation constants of NH_3 and amines. Epoxide produced reacts further with added amine producing $CH_2OHCHOHCH_2NR_2$. Third order rate constants calculated by (12) increase gradually with progress of reaction.

(.28) (.29) Rate constant listed gives order of magnitude only as reaction represents only 8% and 3% respectively of concurrent elimination with double bond formation see 422.471. **(.30)** Rate constant corrected for simultaneous reaction (.31). Product ratio determined under conditions such that solvolysis reaction contributed, and caused bias in favor of olefinic product.

LITERATURE

(1) P. Ballinger, P.B.D. de la Mare, *CSL* **1957,** 1481. (2) P. Ballinger, F.A. Long, *ACS* 1959, **81,** 2347. (3) P.B.D. de la Mare, J.G. Pritchard, *CSL* **1954,** 3910. (4) H. Grimsson, L. Smith, *Acta. Chem. Scand.* 1950, **4,** 719. (5) H.W. Heine, *ACS* 1957, **79,** 6268. (6) H.W. Heine, A.D. Miller, W.H. Barton, R.W. Grenier, *ACS* 1953, **75,** 4778. (7) H.W. Heine, W. Siegfried, *ACS* 1954, **76,** 489. (8) J. Hine, P.B. Langford, *ACS* 1956, **78,** 5002. (9) C.L. McCabe, J.C. Warner, *ACS* 1948, **70,** 4031. (10) D. Poret, *HCA* 1941, **24,** 80E.

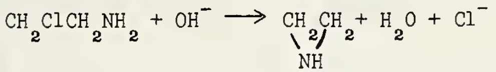
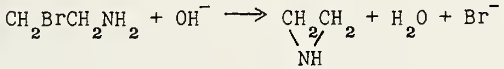
(11) J.E. Stevens, C.L. McCabe, J.C. Warner, *ACS* 1948, **70,** 2449. (12) C.G. Swain, A.D. Ketley, R.F.W. Bader, *ACS* 1959, **81,** 2353. (13) L. Smith, *ZPC* 1912, **81,** 339. (14) L. Smith, *ZPC* 1931, **A152,** 153. (15) L. Smith, T. Nilsson, *J. prakt. Chem.* 1943, **162,** 63.

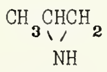
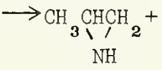
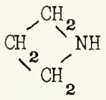
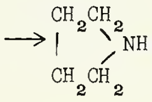
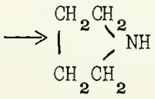
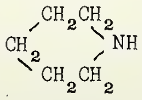
ELIMINATION

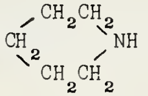
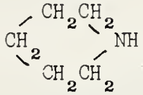
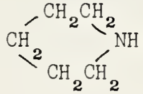
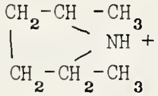
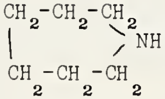
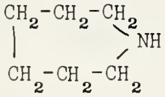
Elimination of hydrogen halide, or halide ion to form N-containing ring

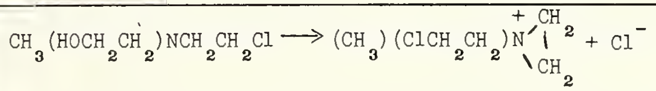
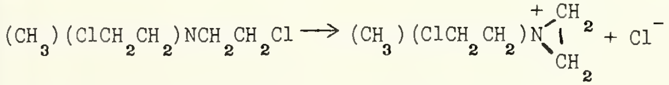
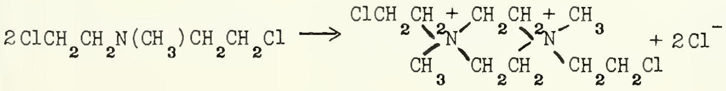
Liquid phase

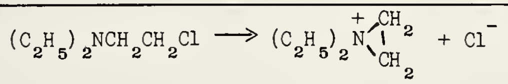
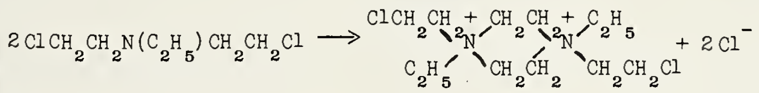
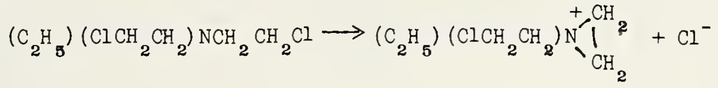
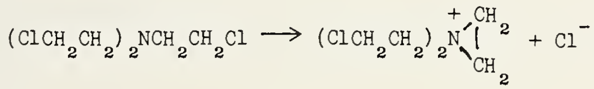
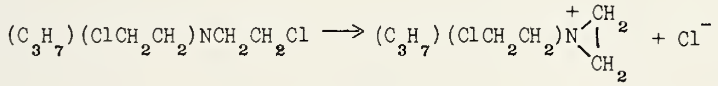
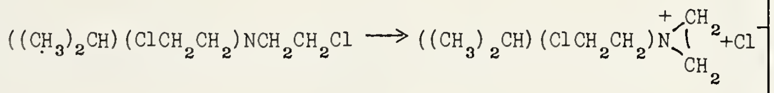
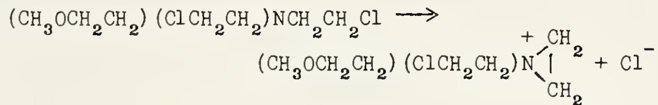
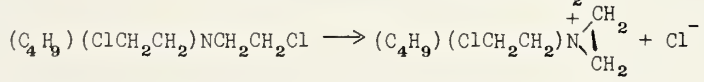
Amounts are in M/l. Rate constants are in M/l and sec. For coded solvents, see at end of table.

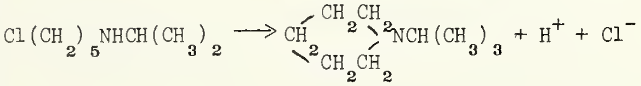
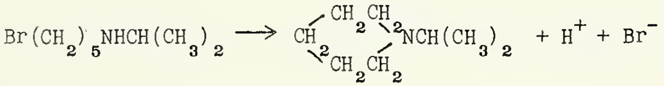
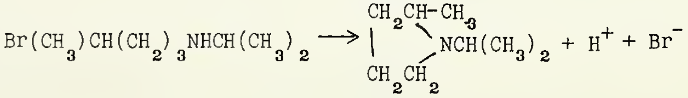
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.1	 $CH_2ClCH_2NH_2 + OH^- \longrightarrow \underset{NH}{CH_2CH_2} + H_2O + Cl^-$	H_2O		Na^+	=B	kA	0	2	-7				*	(^{11})
.2	 $CH_2BrCH_2NH_2 + OH^- \longrightarrow \underset{NH}{CH_2CH_2} + H_2O + Br^-$	H_2O	$10^2A=2-3$; $10^2B=10-20$	Na^+, Br^-	=B, =A	kA	0	1.3	-5				*	(^{8}) (^{9})
							10	6.0	-5					(^{8})
							16	1.5	-4					(^{9})
							25	6.0	-4					(^{8})
							26	4.8	-4					(^{9})
							30	1.1	-3	24	2	14		(^{8})
		Mt 11.4*	A=0.025; B=5A	Na^+, Br^-	=B, =A	kA	0	1.0	-5					(^{8})
							11	7.8	-5					
							25	5.0	-4					
							30	9.5	-4	24	2	14		
		Mt 25*					0	8.7	-6					
							12	6.7	-5					
							25.	4.2	-4					
							30.	7.2	-4	24	2	14		
		Mt 50*					0	7	-6					
							10	2.8	-5					
							25	2.2	-4					
							30	3.8	-4	22	3	12		
		Mt 75*					0	3.5	-6					
							16.	4.3	-5					

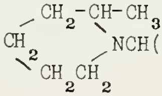
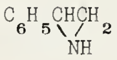
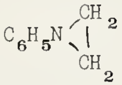
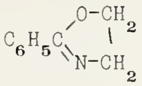
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.2	$CH_2BrCH_2NH_2 + OH^- \longrightarrow$ (*cont.*)	Mt75*	A=0.025; B=5A	Na^+, Br^-	=B, =A	kA	25.	1.2	-4				*	(8)
							30	2.2	-4	23	1	13		
		CH_3OH		K^+, Br^-	=B, =A		0	3	-6					
							25.	1.2	-4					
							30.	2	-4	23	9	12		
.3	$CH_3CHClCH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	A=0.01; B=0.03	Ba^{++}, picrate$^-$	=B/2, =A	kAB	25	1.13	-3				*	(19)
.4	$CH_2ClCH(CH_3)NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	A=0.01; B=0.03	Ba^{++}, picrate$^-$	=B/2, =A	kAB	25	8.2	-3				*	(19)
.5	$CH_2BrCH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Br^-$	H_2O	not stated	Na^+	=B	kA	25	9.0	-6					(8)
							31	1.7	-5					
							36	3.2	-5	21	2	10		
.6	$CH_2ClCH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	A=0.03; B=0.06	Na^+, Cl^-	0.09, 0.04	kA	0	3.5	-4				*	(7)
			.05 .03		0.04, 0.05		25	7.5	-3	20	4	12		
.7	$CH_2BrCH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Br^-$	H_2O	not stated			kA	25	5	-3				*	(8)
.8	$CH_2ClCH_2CH_2CH_2CH_2NH_2 \longrightarrow$  $+ H^+ + Cl^-$	H_2O	A not stated	NaOH	0.20	kA	25	1.2	-4					(10)
		$C_2H_2Cl_4$	0.04	H_2O	sat.		0	3.2	-6					
			0.04	"	"		26	3.2	-5					
			0.03	"	"		37	7.5	-5					
		$C_6H_5NO_2$	0.04	"	"		25	2.1	-5					
		C_6H_6	0.04	"	"		25	8.2	-7					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.9	$CH_2ClCH_2CH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	A=0.04; B=0.3	Na^+, Cl^-	0.3, 0.04	kA	0	4.8	-6				*	(7)
					0.09, 0.04		25	1.08	-4					
					0.3, 0.04		25	1.20	-4					
					0.5, 0.04		25	1.42	-4					
					2.1, 0.04		25	1.63	-4					
					0.3, 0.2		25	1.17	-4					
				Na^+, K^+, Cl^-	0.09, 2.3, 2.3		25	1.75	-4					
				Na^+, Cl^-	0.3, 0.04		37.	4.98	-4	21				
		Et 59.7*			0.3, 0.04		25	4.67	-5					
		Et 91.2*			0.3, 0.04		25	1.67	-5					
.10	$CH_2BrCH_2CH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Br^-$	H_2O	not stated	Na^+	=B	kA	0	3	-4				*	(6)
							25	8.3	-3	22	1	14		(8)
.11	$CH_2ICH_2CH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + I^-$	H_2O	not stated	Na^+	=B	kA	0	3	-2				*	(6)
.12	$CH_3CHClCH_2CH_2CH(CH_3)NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	A=0.03; B=0.3	Na^+	=B	kA	0	2.0	-5				*	(10)
							25	6.8	-4	23	5	13		
.13	$ClCH_2CH_2CH_2CH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	not stated	Na^+	=B	kA	25	1.5	-6				*	(8)
.14	$BrCH_2CH_2CH_2CH_2CH_2CH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Br^-$	H_2O	not stated	Na^+	=B	kA	25	1.7	-5				*	(8)
							~35	1	-4	~32	~6	18		

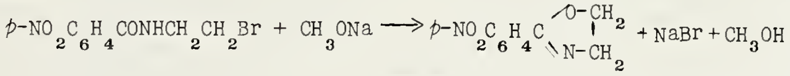
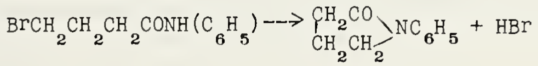
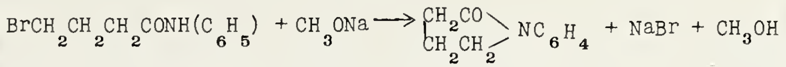
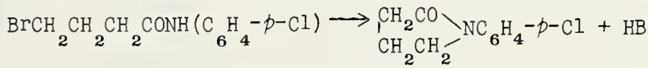
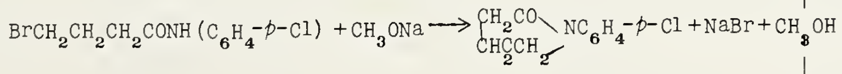
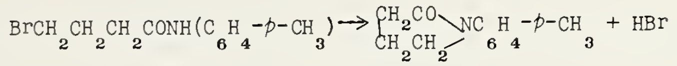
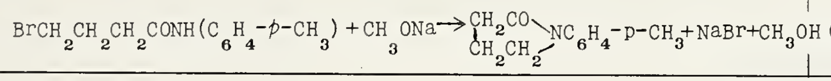
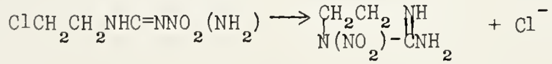
No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.15		H_2O	$10^3A=2.5$	NaOH	pH=7.9	k A	0	4.50	-5				*	(4)
							15	3.84	-4	22	1.6	13		
.16		H_2O	$10^3A=2.5$	NaOH	pH=8.0	k A	0	3.84	-5				*	(4)
			63				10	1.87	-4					(13)
			2.5				15	4.00	-4					(4)
			63				25	1.61	-3	24	8	14		(13)
			2.5				30	3.25	-3					(4)
.17		CH_3OH	10A=6-12			k A	0	2	-6				*	(14)
							25	6.1	-5					
							41	3.1	-4	19.6	1.1	10		
		WA 4*	$10^2A=10$			k A	25	1.7	-6					(20)
							41	5.8	-6					
							72	1.7	-5					
							100	4.8	-4	10	3	1		
		WA 8*					25	1.55	-5					
							38	4.8	-5					
							59	1.55	-4					
							72	2.76	-4	12	1.1	4		
		WA 16*					0	2.67	-5					
							9	6.83	-5					
							25	3.25	-4	17.4	1.9	9		
		WA 27*					0	4.67	-5					
							9	1.47	-4					
							25	8.0	-4	17.9	9	9		
		A 2 W*	$10^2A=4-10$			k A	25	3	-4					(1)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.18		H_2O	10^3A=2.5	NaOH	pH~8	kA	0	2.64	-4				*	(4)
							15	2.42	-3	23	8	14		
		A2W*	20-150				25	1.42	-3					(2)
.19		A2W*	10^2A=2-15	$-dA/dt = k_1A + k_2AL'$			25	k_1=1.42	-3				*	(2)
								k_2=1.4	-3					
		A 1/3 W*		$-dA/dt = k_1A + k_2AL'$			25	k_1=4.0	-3					
								k_2=4	-5					
.20		H_2O	10^3A=2.5	NaOH	pH=9.1	kA	0	1.95	-4				*	(4)
							15	2.14	-3	25	2	16		
				(no base added)			25	1.37	-5					(13)
.21		H_2O	10^3A=2.5	NaOH	pH~8	kA	0	1.15	-4				*	(4)
							15	1.22	-3	25	7	15		
.22		H_2O	10^3A=2.5	NaOH	pH~8	kA	0	3.37	-4				*	(4)
							15	3.62	-3	25	2	16		
				(no base added)			25	1.81	-5					(13)
.23		H_2O	10^3A=2.5	NaOH	pH=7.4	kA	0	9.20	-4				*	(4)
							15	8.16	-3	23	2	15		
				(no base added)			25	2.61	-5					(13)
.24		H_2O	10^3A=2.5	NaOH	pH~8	kA	0	8.16	-5				*	(4)
							15	8.67	-4	25	4	15		
.25		H_2O	10^3A=2.5	NaOH	pH~8	kA	0	2.57	-4				*	(4)
							15	2.57	-3	24	4	15		

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.26		H_2O	10^2A=7-13	buffers	pH=2.61	kA	70	9.11	-6				*	(^{5})
				μ= 1.9	3.75		70	1.26	-5					
					4.64		70	1.52	-5					
					5.40		70	1.67	-5					
					2.56		79	1.48	-5					
					3.70		79	2.15	-5					
					4.54		79	2.53	-5					
					5.33		79	3.01	-5					
					2.51		92	3.28	-5					
					3.65		92	4.80	-5					
					4.45		92	5.57	-5					
					5.24		92	6.61	-5	16.4	4	5		
.27		H_2O	10^2A=7-13	buffers	pH=3.85	kA	51	3.81	-5				*	(^{5})
				μ= 1.909	3.80		59	7.21	-5					
					2.60		70	1.06	-4					
					3.75		70	1.53	-4					
					4.65		70	1.79	-4					
					5.40		70	2.09	-4	14.6	3	5		
.28		H_2O	10^2A=7-13	buffers	pH=2.70	kA	51	4.68	-5				*	(^{5})
				μ= 1.909	3.85		51	6.51	-5					
					4.82		51	8.72	-5					
					5.56		51	1.03	-4					
					2.65		59	1.23	-4					
					3.80		59	1.89	-4					
					4.73		59	2.42	-4					
					5.48		59	3.16	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$ k^o	 n	E	$A = A^o \times 10^n$ A^o	 n	Comments	Literature
.28	$Br(CH_3)CH(CH_2)_3NHCH(CH_3)_2 \longrightarrow$ *(continued)*	H_2O	$10^2A=7-13$	buffers	pH=2.61	kA	70	2.57	-4				*	(5)
				μ= 1.909	3.75		70	4.34	-4					
					4.64		70	5.60	-4					
					5.40		70	6.92	-4	20.2	3	9		
.29	$Br(CH_3)CH(CH_2)_4NHCH(CH_3)_2 \longrightarrow$  $+H^+ + Br^-$	H_2O	$10^2A=7-13$	buffers	pH=3.85	kA	51	4.92	-5				*	(5)
				μ= 1.909	3.80		59	9.15	-5					
					2.60		70	1.41	-4					
					3.75		70	1.95	-4					
					4.65		70	2.90	-4					
					5.40		70	4.24	-4	13.8	1.2	5		
.30	$Cl(C_6H_5)CHCH_2NH_2 + OH^- \longrightarrow$  $+ H_2O + Cl^-$	H_2O	$10^2A=2-10;$ $10^2B=5-50$	Na^+, Cl^-	$Na^+ =B$ $Cl^- =A+B$	kA	0	3.0	-4				*	(12)
							11	1.4	-3					
							20	3.5	-3					
							25	7.0	-3					
							37	2.0	-2	19.1	6	11		
.31	$BrCH_2CH_2NHC_6H_5 + OH^- \longrightarrow$  $+ H_2O + Br^-$	Et 70*	A=B=0.03	Na^+, Br^-	$Na^+=A+B$	kA	30	1.67	-4				*	(16)
			A=0.03; B=0.12		$Br^- =A$		30	1.98	-4					
			0.03; 0.31				30	2.60	-4					
			0.05; 0.10				30	1.88	-4					
			0.05; 0.20				30	2.23	-4					
			A=B=0.05	$NaNO_3$	0.20		30	1.77	-4					
			A=0.03; B=0.31	Na^+, Br^-	0.4,0.06		30	2.55	-4					
.32	$C_6H_5CONHCH_2CH_2Br \longrightarrow$  $+ Br^-$	Et 30*	$10^2A=5$			kA	25	1.13	-4				*	(18)
		Et 50*					25	8.0	-5					
		Et 80*					25	4.7	-5					
		C_2H_5OH					25	2.4	-5					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^o \times 10^n$		E	$A = A^o \times 10^n$		Comments	Literature
								k^o	n		A^o	n		
.32	$C_6H_5CONHCH_2CH_2Br \longrightarrow$ *(continued)*	C_2H_5OH	$10^2A=5$	$(C_2H_5)_4NClO_4$	0.10	kA	25	2.58	-5				*	(^{18})
				$(C_2H_5)_4NBF_4$			25	2.56	-5					
				$(C_2H_5)_4NNO_3$			25	2.56	-5					
				$(C_2H_5)_4NCl$			25	2.54	-5					
				$(C_2H_5)_4NBr$			25	2.60	-5					
				$(C_2H_5)_4NI$			25	2.57	-5					
				$(C_2H_5)_4NNO_2$			25	2.58	-5					
				$(C_2H_5)_4NN_3$			25	2.53	-5					
		CH_3NO_2	$10^2A=2$			kA	25	6.65	-5					
				$(C_2H_5)_4NClO_4$	0.05		25	6.97	-5					
				$(C_2H_5)_4NBF_4$			25	6.98	-5					
				$(C_2H_5)_4NNO_3$			25	7.02	-5					
				$(C_2H_5)_4NBr$			25	7.0	-5					
				$(C_2H_5)_4NI$			25	6.94	-5					
		$C_6H_5CH_2OH$				kA	25	8.06	-5					
		CH_3CN				kA	25	5.36	-5					
		$C_6H_5NO_2$				kA	25	5.32	-5					
		C_6H_5CN				kA	25	4.91	-5					
		$(CH_3)_2CO$				kA	25	3.84	-5					
		CH_3OH				kA	25	3.22	-5					
		$(CH_3)_2CHOH$				kA	25	1.86	-5					
		$CHCl_3$				kA	25	1.74	-5					
		EtCN*				kA	25	6.44	-5					
.33	$C_6H_5CONHCH_2CH_2Br + CH_3ONa \longrightarrow C_6H_5C\begin{matrix}O-CH_2\\ \backslash\\ N-CH_2\end{matrix} + NaBr + CH_3OH$	CH_3OH	$10^2A=3-4$; $10^2B=4$			kAB	23	2.20	-3				*	(^{15})
.34	$p\text{-}ClC_6H_4CONHCH_2CH_2Br + CH_3ONa \longrightarrow p\text{-}ClC_6H_4C\begin{matrix}O-CH_2\\ \backslash\\ N-CH_2\end{matrix} + NaBr + CH_3OH$	CH_3OH	$10^2A=4$; $10^2B=4-9$			kAB	23	4.53	-3				*	(^{15})

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k = k^\circ \times 10^n$		E	$A = A^\circ \times 10^n$		Comments	Literature
						k°	n		A°	n		
.35	 $p\text{-}NO_2C_6H_4CONHCH_2CH_2Br + CH_3ONa \longrightarrow p\text{-}NO_2C_6H_4C\begin{matrix}/O-CH_2\\ \backslash\backslash N-CH_2\end{matrix} + NaBr + CH_3OH$	CH_3OH	10^2A=2-4; 10^2B=4-5	kAB	23	1.71	-2				*	(^{15})
	N-Alkyl(Aryl) amide halides											
.36	 $BrCH_2CH_2CH_2CONH(C_6H_5) \dashrightarrow \begin{matrix}CH_2CO\\CH_2CH_2\end{matrix}>NC_6H_5 + HBr$	CH_3OH	10^2A=4-5	kA	23	1.30	-5				*	(^{17})
.37	 $BrCH_2CH_2CH_2CONH(C_6H_5) + CH_3ONa \longrightarrow \begin{matrix}CH_2CO\\CH_2CH_2\end{matrix}>NC_6H_4 + NaBr + CH_3OH$	CH_3OH	10^2A=4-5; 10^2B=10-15	kAB	23	3.0	-3				*	(^{17})
.38	 $BrCH_2CH_2CH_2CONH(C_6H_4\text{-}p\text{-}Cl) \longrightarrow \begin{matrix}CH_2CO\\CH_2CH_2\end{matrix}>NC_6H_4\text{-}p\text{-}Cl + HBr$	CH_3OH	10^2A=4-5	kA	23	8.3	-6				*	(^{17})
.39	 $BrCH_2CH_2CH_2CONH(C_6H_4\text{-}p\text{-}Cl) + CH_3ONa \longrightarrow \begin{matrix}CH_2CO\\CHCCH_2\end{matrix}>NC_6H_4\text{-}p\text{-}Cl + NaBr + CH_3OH$	CH_3OH	10^2A=4-5; 10^2B=4-9	kAB	23	9.4	-3				*	(^{17})
.40	 $BrCH_2CH_2CH_2CONH(C_6H_4\text{-}p\text{-}CH_3) \longrightarrow \begin{matrix}CH_2CO\\CH_2CH_2\end{matrix}>NC_6H_4\text{-}p\text{-}CH_3 + HBr$	CH_3OH	10^2A=4-5	kA	23	1.48	-5				*	(^{17})
.41	 $BrCH_2CH_2CH_2CONH(C_6H_4\text{-}p\text{-}CH_3) + CH_3ONa \longrightarrow \begin{matrix}CH_2CO\\CH_2CH_2\end{matrix}>NC_6H_4\text{-}p\text{-}CH_3 + NaBr + CH_3OH$	CH_3OH	10^2A=4-5; 10^2B=20	kAB	23	1.72	-3				*	(^{17})
	Alkyl amine-imine halides											
.42	 $ClCH_2CH_2NHC{=}NNO_2(NH_2) \longrightarrow \begin{matrix}CH_2CH_2\ NH\\N(NO_2)\text{-}CNH_2\end{matrix} + Cl^-$	H_2O	10^4A=5-14	kA	30 40 50	4.75 1.77 6.16	-6 -5 -5	25.1	6	12	*	(^{3})

CODED SOLVENTS

Mt 11.4*(25) (50) (75) = CH_3OH Mol % indicated + H_2O
Et 59.7*(30) (50 (70) (80) (91.2) = C_2H_5OH volume % indicated + H_2O
WA 4*(8) (16) (27) = $(CH_3)_2CO$ + H_2O of molarity stated
A 2 W*(1/3) = $(CH_3)_2CO$ volumes stated + 1 volume H_2O
EtCN* = C_2H_5OH + CH_3CN equal volumes

COMMENTS

Comments by Literature References. (1) (2) (4) (6) (7) (8) (9) (10) (11) (12) (16)(17) (19) (20) Units converted to seconds from original minutes. (14) Units converted to seconds from original hours.

Comments by Reactions: **(.1)** Details not stated. Units converted to seconds from assumed minutes. **(.2)** Amine in (8) initially present as hydrobromide of melting point 172.5-173°C. Previous work with hydrobromide of melting point 155-160°C yielded same results for rate constants. Rate constants for reverse reaction determined in (9). Ratio of rate constants for forward and reverse reactions = 0.10 while experimentally determined equilibrium constant = $[A]^{-1}[L][N]=3.6$ at 25°C. **(.3) (.4)** Rate constants increase gradually with progress of reaction. **(.6)** Rate constants approximate because of rapidity of reaction. **(.7)** Rate constant listed gives order of magnitude only. **(.9)** Effect of changing B is no larger than effect of neutral salts which indicates that only free amine is involved in rate determining step. **(.10 (.11)** Values of rate constants taken from (6) are approximate. 86% of amine in (.11) transformed in 1 minute. **(.12)** Original amine slightly more than 50% pure as determined by Cl^- present when reaction was complete. Rate constants considered to be semiquantitative. **(.15) (.16)** Rate constant corrected for fraction of amine in form of quaternary ion using ionization constant.

(.17) Reaction followed to 85% completion in CH_3OH by (14) and 80% completion in $(CH_3)_2CO$ with H_2O by (20) with first order behavior. (1) gives initial rate only and states that order is complex as reaction involves (.16) as initial step. **(.18)** Rate constant in acetone-water solvent determined by (2) as first step of consecutive reaction see (19). Rate constants of (4) corrected for fraction of amine in form of quaternary ion using acid ionization constant of quaternary ion. **(.19)** Rate constant calculated on basis of consecutive reactions with (.18) as first step k_1A followed by dimerization with rate k_2AL. Simultaneous hydrolysis and substitution also possible. **(.20) (.21) (.22) (.23) (.24) (.25)** Rates constants of (4) corrected for fractions of amine in form of quaternary ion using acid ionization constant of quaternary ion. **(.26) (.27) (.28) (.29)** Reactions occur as side reactions during alkylation of 6-methoxy-8-aminoquinoline (see 232.457). First order reactions indicate cyclization rather than polymerization. Rate increases linearly with pH over range studied and is unaffected by presence of substituted quinoline. This is in contrast to the alkylation reaction where the rate is a maximum at pH=4.5.

COMMENTS *(continued)*

(.31) Reactions followed to 60% completion. Rate constants varied linearly with [B] in accordance with equation: $k=1.57\times10^{-4}+3.3\times10^{-4}B$. **(.32)** Rate constants based on measurements of initial rates of reaction. Rates determined by measurement of amount of cyclic product as well as amount of Br^- formed. **(.33) (.34) (.35)** Reactions followed beyond 50% completion at lower concentrations and accompanied by simultaneous solvolysis reactions with first order constants=2.36×10^{-5}, 1.52×10^{-5} and 0 respectively. **(.37) (.39) (.41)** After 70% reaction rate constants show a slight downward drift. **(.42)** Concurrent hydrolysis of M corrected for in calculations of rate constants. Reactions followed to about 70% completion.

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(11) H. Freundlich, G. Salomon, *BDC* 1933, **66B**, 355. (12) H. Freundlich, G. Salomon, *ZPC* 1933, **166**, 161. (13) W.E. Handy, G.S. Hartley, E.O. Powell, H.N. Rydon, *CSL* **1947**, 519. (14) A.W. Hay, A.L. Thompson, C.A. Winkler, *CJC* 1948, **26B**, 175. (15) H.W. Heine, *ACS* 1956, **78**, 3708. (16) H.W. Heine, B.L. Kapur, *ACS* 1955, **77**, 4892. (17) H.W. Heine, P. Love, J.L. Bove, *ACS* 1955, **77**, 5420. (18) Y. Pocker, *CSL* **1959**, 2319. (19) L. Smith, B. Platon, **BDC** 1922, **55**, 3143. (20) A.L. Thompson, T.J. Hardwick, C.A. Winkler, *CJC* 1948, **26B**, 181.

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