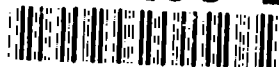


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Homogeneous Reactions
(Supplementary Tables)

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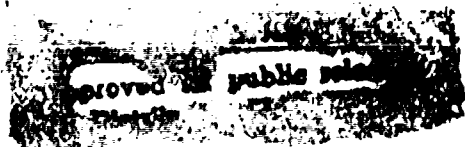


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Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

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Tables of Chemical Kinetics

Homogeneous Reactions

(Supplementary Tables)

National Bureau of Standards

A. V. Astin, Director

National Research Council, Division of Chemistry
Committee on Kinetics of Chemical Reactions

M. L. Kilpatrick, Chairman

J. Bigeleisen
R. Noyes
C. Satterfield

H. Taube
K. Wiberg

Project Office: Hepburn Hall, St. Lawrence University, Canton, New York

C. H. Stauffer, Project Director

A. R. Amell
E. Bunce
T. W. Davis
J. O. Edwards
H. B. Feldman
C. L. Gage
H. S. Johnston

D. M. Kern
H. G. Kuivila
P. E. Merritt
M. Szwarc
H. Taube
M. H. J. Wijnen



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National Bureau of Standards Monograph 34

To Accompany National Bureau of Standards C510, Supplements 1 and 2

Issued September 15, 1961

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(Supplementary Tables)

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SUPPLEMENT 3 TO TABLES OF CHEMICAL KINETICS HOMOGENEOUS REACTIONS

PREFACE

A description of these Tables and definition of the terms and abbreviations used may be found in the introduction to the 1951 publication. A brief description of the method used in compiling these tables and the limitation of coverage is given in the preface to Supplement 1. A description of the numbering system used in classifying reactions for the tables is given in Supplement 2. The present supplement contains information pertaining to Substitution, Exchange and Elimination reaction types. It is not complete as still more material falling in these groups is being prepared. The amount of kinetic data to be studied made it seem advisable to present all the material completed to date without further delay. The date on each section gives the year and month to which the literature had been surveyed. Significant omissions or errors should be reported to Dr. Charles H. Stauffer, Head, Department of Chemistry, St. Lawrence University, Canton, New York.

The Director and his associates gratefully acknowledge the financial assistance provided by the Office of Ordnance Research, Department of the Army which made this work possible. The Director of the Project gratefully acknowledges the able assistance of his associates and collaborators, the help of the National Bureau of Standards, the National Academy of Sciences and the members of the Committee on Chemical Kinetics of N.R.C. Division of Chemistry.

C.H. Stauffer

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450	ELIMINATION FROM Vth GROUP ELEMENT (continued)	Title of Table (number of pages)	Table number
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460	ELIMINATION FROM FUNCTIONAL GROUP		
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Homogeneous Reactions
301.401

ISOTOPIc EXCHANGE
Hydrogen exchange on aliphatic C

Con: dtase
Amounts are in M/l.
Rate constants are
in M/l and sec.
Rates are in gram
atoms/l and sec.

P listed under mass action law indicates quantity listed under k is rate of reaction not mass constant.

No.	Reaction	Amount of reactant	Defined mass-action law	$k \times 10^4$ k^0 k^1	$k \times 10^4$ k^0 k^1	$A = A^0 \times 10^4$ A^0 A^1	$k \times 10^4$ k^0 k^1
1	$C_2H_4 + C_2 \rightarrow C_2H_3, C_2H_2, C_2H, C_2H_4, C_2H_3, C_2H_2, C_2H, C_2H_4, C_2H_3, C_2H_2, C_2H, C_2H_4$ (A) (B) (C) (D) (E) (F) (G) (H) (I) (J) (K) (L) (M) (N) (O) (P) (Q)	$A = B = 1.8 \times 10^{-3}$	$dA/dt = P$ $dQ/dt = P$ $dQ/dt = P$ $-dA/dt = P$	569 509 416 443 402 569 416 443 402 569 509 416 443 402	2.4 5.9 1.00 4.7 2.4 1.0 7.3 4.7 4.7 4.7 1.0 5.4 1.0 2.4 4.1 1.7 2.0 4.7 9.3	-7 -7 -6 -5 -6 -7 -7 -7 -7 -7 -6 -6 -6 -6 -7 -6 -6 -6 -6	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5
2	$C_2H_6 + D_2 \rightarrow C_2H_5D + HD$	$10^3 A = 1-24$ $10^3 B = 1-12$	kAB	152 106	7.0 1.7	-10 -6	40

COMMENTS

Reaction: (1) Selected data. Complex chain reaction involves both exchange and addition. Authors list 14 reactions as contributing to mechanism. Determined rates of formation of all six products listed and both reactants. Units converted from molecules $\text{cc}^{-1} \text{min}^{-1}$. (2) Data erratic and results give only order of magnitude. Reaction partially heterogeneous. air and Br_2 accelerate exchange and Hg inhibits exchange.

LITERATURE

- (1) J.E. Perl, E. Daniels, *ACS* 1950, 72, 424. (2) R.E. Vamagin, J.S. Dooling, *ACS* 1952, 78, 1113.

ISOTOPE EXCHANGE

Oxides of carbon

Gas phase

Amounts are in M/l unless stated otherwise.

Rate constants are in M/l and sec.

SUPPLEMENT 1955

No.	Reaction	Amount of reactant	Isotopic tracer	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		Comments	Literature
								k^0	n		
.1	$C^{18}O_2 + CO \longrightarrow CO_2 + C^{18}O$	$10^3 A = 1-12$ $10^3 B = 1-8$	C^{14} C^{13} C^{14} C^{13}	Argon N_2	0-0.008 0.0005 0.0003	$k A^{0.85} B^{0.73}$	799 850 867 898 900 917 850 850 900	1.2	-4	*	(2) (1) (2) (1) (2)
								5.6	-4		
								5.0	-4		
								8.3	-4		
								2.6	-3		
								1.3	-3		
								5.6	-4		
								1.2	-3		
								4.6	-3		

COMMENTS

Reference. (1) Used mass-spectrometric method with enriched C^{13} or O^{18} to follow exchange. Results of (1) recalculated by (2) to fit empirical rate law of (2). Definite heterogeneous catalysis observed by (1) with quartz or gold surface, also catalysis by H_2O or H_2 with concentration ~ 0.0002 increasing rate by a factor of five. (2) Increased S/V ratio

COMMENTS *(continued)*

by factor of 6 using packed quartz vessel with almost negligible effect, but still concluded reaction to be predominantly heterogeneous because of the erratic nature of results. Both observed normal first order exchange rate (McKay rate law) and chemical kinetic rate law obtained from variation of exchange rate with concentrations of reactants.

LITERATURE

- (¹) J. D. Brandner, H. C. Urey, *J.C.P.* 1945, 13, 351.
- (²) T. H. Norris, S. Ruben, *J.C.F.* 1950, 18, 1585.

Homogeneous Reactions
301.471ISOTOPIC EXCHANGE
Halogen on aliphatic-C

Gas phase

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

k_F in mass action law column indicates quantity listed under k is pseudo first order rate constant for isotopic equilibration.
 R in mass action law column indicates quantity listed under k is rate of isotope exchange in gram atoms per liter sec (^{4}).

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		B	$A = A^0 \times 10^n$		Comments	Literature
							k^0	n		A^0	n		
.1	$\text{C}^{14}\text{O} + \text{COCl}_2 \longrightarrow \text{CO} + \text{C}^{14}\text{OCl}_2$	$10^4\text{A}=1-6$; $10^4\text{B}=2-20$	Cl_2	0.003 ± 0.016	$k_A^{\frac{1}{2}}\text{B}^{\frac{1}{2}}[\text{Cl}_2]$	375 400 420 450	2.0 5.7 1.5 4.8	-3 -3 -2 -2				*	(⁷)
.2	$\text{CH}_3\text{Cl} + \text{HCl}^* \longrightarrow \text{CH}_3\text{Cl}^* + \text{HCl}$	$10^3\text{A}=1.3-6$; $10^3\text{B}=1.3-6$	pyrex glass	$S/V=7.4 \text{ cm}^{-1}$	k_A	375 390 405 420 435 450 465	2.2 4.8 1.1 2.4 4.4 8.2 1.67	-6 -6 -5 -5 -5 -5 -4	30.3	4	10	*	(¹)
.3	$\text{CH}_3\text{I} + \text{I}_2^* \longrightarrow \text{CH}_3\text{I}^* + \text{I}_2^*$	$10^2\text{A} \sim 2$; $10^4\text{B} \sim 3$			$k_{AB}^{\frac{1}{2}}$	185 250 375	3 4 6	-4 -3 -1	43.6	1.4	9	*	(²)
.4	$\text{CH}_2\text{FCl} + \text{HCl}^* \longrightarrow \text{CH}_2\text{FCl}^* + \text{HCl}$	$10^3\text{A}=1-6$; $10^3\text{B}=1-6$	pyrex glass	$S/V=7.4 \text{ cm}^{-1}$	k_A	420 450 480 510	1.55 8.2 2.6 8.9	-6 -6 -5 -5	>32 47.1			*	(¹)

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k = k^0 \times 10^n$		g	$A = A^0 \times 10^n$		Comments	Literature
							k^0	n		A^0	n		
.5	$\text{CHF}_2\text{Cl} + \text{HCl}^* \longrightarrow \text{CHF}_2\text{Cl}^* + \text{HCl}$	$10^3\text{A}=1.3-6; 10^3\text{B}=1.3-6$	Pyrex Glass	$\text{S/V}=4-1800 \text{ cm}^{-1}$	$k_A^{\ddagger}\text{B}^{\ddagger}$	360 375 405 420 465	2.8 5.3 1.47 2.5 8.7	-6 -6 -5 -5 -5				*	(1)
.6	$\text{CF}_3\text{Cl} + \text{HCl}^* \longrightarrow \text{CF}_3\text{Cl}^* + \text{HCl}$	$\text{A} \sim 10^{-3}; \text{B} \sim 10^{-3}$			k_{F_X}	405 510	<2 7	-7 -7				*	(1)
.7	$\text{Cl}_3\text{CBr} + \text{Br}_2^* \longrightarrow \text{Cl}_3\text{CBr}^* + \text{BrBr}^*$	$10^2\text{A}=1-4; 10^3\text{B}=3-17$			$k_{\text{AB}}^{\ddagger}$	146 159 172 183	2.97 9.63 3.03 7.26	-5 -5 -4 -4				*	(3)
		$10^3\text{A}=4-20; 10^4\text{B}=3-5$			$k_{\text{AB}}^{\ddagger}$	150 170 200 220	7.2 3.1 2.9 9.5	-5 -4 -3 -3	33.1	5.6	12		(6)
.8	$\text{Cl}_3\text{CBr} + \text{Br}_2^* \longrightarrow \text{Cl}_3\text{CBr}^* + \text{Br}$	$10^2\text{A}=1-4; 10^3[\text{Br}_2]=3-17$	$\text{O}_2, \text{H}_2\text{O}, \text{Cl}_2$	$\left. \begin{matrix} 0.00006 \\ 0.00016 \end{matrix} \right\}$	(see comments)	145-183						*	(3)
.9	$\text{C}_2\text{H}_5\text{Br} + \text{HBr}^* \longrightarrow \text{C}_2\text{H}_5\text{Br}^* + \text{HBr}$	$10^3\text{A}=2-16; 10^6\text{B}=3-2000$	$\text{S/V} =$ air $\text{S/V} =$	$\left. \begin{matrix} 1 \text{ cm}^2/\text{cm}^3 \\ 2 \\ 150 \text{ mm.} \\ 1 \text{ cm}^2/\text{cm}^3 \end{matrix} \right\}$	k_A	200 200 200 243	4.0 5.8 7.0 3.0	-7 -6 -7 -6	10.3	7.9	10	*	(8)
.10	$\text{C}_2\text{H}_5\text{Br} + \text{DBr}^* \longrightarrow \text{C}_2\text{H}_5\text{Br}^* + \text{DBr}$	$10^3\text{A}=8; 10^3\text{B} \sim 3$ $10^3\text{A}=2; 10^3\text{B}=1-4$				254 258 306	1.3 6 2	-5 -6 -4	32			*	(6)
.11	$(\text{CH}_3)_3\text{CCl}^* + \text{SnCl}_4$	not stated			k_{AB}	25	2	-1	>3			*	(3)

COMMENTS

General. Exchange follows general first order rate law (McKay). Chemical kinetic order of exchange reactions determined from variation of exchange rate with concentrations of reactants (*).

Reaction: (.1) Rate law calculated by editor from half times and concentrations of reactants. Listed because of excellent agreement of sixteen out of seventeen separate values at 400°C. (.2) Reaction predominantly heterogeneous as rate constant found to be linear with respect to surface to volume ratio, S/V , from 3 to 14 cm^{-1} with straight line going through origin. Activity of surface increased with use but reproducibility obtained by baking and evacuating. (.3) Reaction predominantly heterogeneous even at highest temperature in pyrex bulb of 1 l. capacity. Packed reaction vessel gave straight line plot of $\log k$ vs. T^{-1} . Activation energy 17 kcal. for heterogeneous reaction and >32 kcal. for homogeneous reaction estimated from slope of $\log k$ vs. T^{-1} plot at highest T in unpacked flask. (.4) Reaction predominantly heterogeneous as rate constant found to be linear with respect to surface to volume ratio, S/V , from 3 to 14 cm^{-1} with straight line going through origin. Activity of surface increased with use, but reproducibility obtained by baking and evacuating. (.5) Reaction homogeneous as cal-

culated rate constants independent of surface to volume ratio, $S/V=4-1800 \text{ cm}^{-1}$. (.6) Pseudo first order rate constant for isotopic equilibration gives order of magnitude only. (.7) Reaction homogeneous as proved by increasing S/V ratio by factor of 12. Quartz and Pyrex vessels gave identical results. Addition of O_2 , H_2O , and Cl_2 in amounts indicated had no effect. Both (*) and (9) consider reaction to involve rapid equilibrium $\text{Br}_2 \rightleftharpoons 2\text{Br}$ followed by rate determining step (.8). (.8) Calculated from (.7) and equilibrium constant for reaction forming bromine atoms. Addition of HBr at $[\text{HBr}] = 0.038$ results in parallel formation of Cl_3CH to extent of about 20% at half time of exchange. (.9)(.10) Reaction heterogeneous as increase of S/V ratio by factor of 6 increased rate of exchange 200 times. Coating surface with "Dri-film" had no effect. Coating walls with black decomposition product decreased rate and gave reproducible results, but did not change activation energy. (.10) Parallel H-D exchange about four orders of ten slower. See 301.401. (.11) Reaction partially heterogeneous as glass packing increased exchange rate several fold. Authors also observed less than 1% exchange in 6 hrs. at 200°C for SnCl_4 with CH_3Cl , $\text{C}_2\text{H}_6(\text{CH}_3)\text{CHCl}$, CH_3CCl_3 and CCl_4 .

LITERATURE

- (¹) J.E. Boggs, L.O. Brockway, *ACS* 1955, 77, 3444. (²) D. Clark, H.O. Pritchard, A.F. Trotman-Dickenson, *CSL* 1954, 2633.
(³) N. Davidson, J.H. Sullivan, *J.C.P.* 1949, 17, 176. (⁴) G.M. Harris, *FPS* 1951, 47, 716. (⁵) R.A. Howard, J.E. Willard, *ACS* 1955, 77, 2046. (⁶) J.B. Peri, F. Daniels, *ACS* 1950, 72, 424. (⁷) D.R. Stranks, *FPS* 1955, 51, 524.
(⁸) J. Willard, A. Miller, *JCP* 1949, 17, 168.

Homogeneous Reactions
301.474ISOTOPIC EXCHANGE
Halogen in IVth group halideGas phase
Amounts are in M/l.
Rate constants are
in M/l and sec.

No.	Reaction	Amount of reactant	Defined law	Temperature	$k =$ $k^0 \times 10^n$		B	$A =$ $A^0 \times 10^n$		$\Delta S^\ddagger$
					k^0	n		A^0	n	
..	$\text{SiCl}_4 + \text{HCl}^{36} \longrightarrow \text{SiCl}_3^{36} + \text{HCl}$	$10^2 A = 1-5; 10^2 B = 1-2$	$k A^{2B}$	90	2.7	-2	22	1.1	9	-18
		2.5 1-6		100	6.1	-2				
		2.2 0.7		108	9	-2				

COMMENTS

Rate constant of exchange reaction calculated from half time of isotopic equilibration and concentration of $A+L$ and $B+M$. Order with respect to A found to be 1.9 ± 0.1 and B $0.95 \pm .05$. Authors found no effect upon rate of reaction by a threefold change in S/V or by strong illumination.

LITERATURE

R.H. Herber, *J.C.P.* 1957, 27, 653.

Homogeneous Reactions
301.565

ISOTOPIC EXCHANGE
Oxides of Nitrogen

Gas phase
Amounts are in M/i.
Rate constants are
in M/i and sec.

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	$A \times 10^n$ A^0 n	Comments	Literature
.1	$\text{NO} + \text{N}^{15}\text{O}_2 \rightleftharpoons \text{N}^{15}\text{O} + \text{NO}_2$	A+B = 0.0018				-35	>1 3		*	(²)
.2	$\text{N}^{15}\text{O}_2 + \text{N}_2\text{O} \rightarrow \text{NO}_2 + \text{N}^{15}\text{NO}$	$10^3 \text{A}=1.5-2; 10^4 \text{B}=7-10$ 2-3 15-20 1-2 30 3-4 30-50	CO_2 NO	0-.03 0.002 0	kB	-9 0 0 0 10	1.9 -3 5.2 -3 5.2 -3 1.6 -2 1.4 -2		*	(¹)

COMMENTS

Reaction: (.1) Rate law not verified value gives only lower limit. (.2) Change of surface volume ratio has no effect on rate in absence of NO.

LITERATURE

(¹) A. R. Ameil, F. Daniels, ACS 1952, 74, 6210. (²) E. Leifer, JCP 1940, 8, 301.

Homogeneous Reactions

301.701

ISOTOPIC EXCHANGE
Hydrogen-hydrogen halide

Gas Phase

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

No.	Reaction	Activation Energy, kcal/mole	Temperature	$k^o \times 10^n$		k	$A^o \times 10^n$	
				k^o	n		A^o	n
.1	$D_2 + HCl \longrightarrow HD + DCl$	k AB	492	2.0	-3			
			511	5.3	-3			
			533	1.34	-2			
			553	2.9	-2			
			570	9.4	-2	53	3	15

COMMENTS

Homogeneous reaction accompanied by small amount of heterogeneous reaction, correction for which has been made. Unit converted from M/cc and temperatures from °K. Authors assume Arrhenius constant A to have $T^{1/2}$ dependence and consequently give $E = 52.1$ and $A = 6.3 \times 10^{10} T^{1/2}$.

LITERATURE

P. Cross, H. Steiner, *JCP*, 1936, 4, 165.

ISOTOPIC EXCHANGE
Halogen-halogen halide

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

R listed under mass action law indicates quantity listed is rate of isotope exchange see (3).

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k \times 10^n$		R	$A \times 10^n$		Comments	Literature
					k^0	n		A^0	n		
.1	$\text{ClF}_3 + \text{F}_2^{18}$	$10^4 \text{A}=3-120; 10^3 \text{B}=8-36$	kA	174	1.57	-5				*	(1)
				274	5.0	-5					
				257	4.2	-4	29	4	8		
.2	$\text{Br}_2 + \text{F}_2^{18}$	$10^4 \text{A}=5.1; 10^3 \text{B}=6.32$	R	193	8.5	-7				*	(1)
		14.7		193	8.0	-7					
		29.6		193	6.7	-7					
		55.2		193	5.8	-7					
		55.1		193	1.15	-6					
		55.1		193	2.25	-6					
		4.0		224	3.0	-6					
		12.5		224	3.7	-6					
		44.9		224	2.25	-6					
		84.5		224	2.12	-6					
		44.8		224	7.2	-6					
		44.8		224	1.38	-5					
		5.0		256	1.20	-5					
		15.0		256	9.8	-6					
		35.0		256	9.0	-6					
		86		256	7.2	-6					
		34.9		256	7.3	-5					

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k = k^0 \times 10^n$	R	$A = A^0 \times 10^n$	Comments	Literature
13	$IF_7 + F_2$	$10^3 A = 5-11; 10^3 B = 1.4-3$ $1.4-20$ $4-17$		181 194 224	2.7 3.3 3.5	-5 -4 -3	1 15	*	(1)

COMMENTS

General: For general treatment of isotope exchange reactions see (2). In cases where the rate constant for the chemical process responsible for exchange has not been explicitly determined the quantity listed under k will be the rate of isotope exchange, R , in gram atoms per liter per second. This is indicated by listing R^* in the defined mass action law column:

$$R = - \frac{m \cdot n \cdot A \cdot B}{(m \cdot A + n \cdot B)} \ln(1-x)$$

where m and n are the number of exchangeable atoms of the labeled species in A and B respectively. A represents the sum of $[A] + [L]$ and B represents the sum of $[B] + [M]$. X is the fractional extent of isotopic equilibration having taken place at time t .

Reaction: (1) Authors consider exchange is simultaneously taking place by a heterogeneous and a homogeneous reaction and have separated the total rate of exchange into these two parts. Values listed are for the assumed homogeneous reaction. Rate of the heterogeneous reaction, is given by $R_{het} = k_{het} \cdot xByA / (1 + xB + yA)^2$, where x and y represent adsorption coefficients of B and A respectively at the nickel halide surface of the nickel reaction vessel.

Authors list $10^4 k_{het} \cdot x$ as 4.5, 18 and 85 at 194, 224 and 257°C respectively with $E_{het} = 24$. Addition of H_2F_2 had no effect on exchange rate. Preliminary experiments by (2) indicated reaction about 10 times faster in aluminum reaction vessel. (2) Exchange considered to be principally heterogeneous with rate law given by:

$$R = k_{het} \cdot xByA / (1 + xB + yA)^2$$

where x and y represent adsorption coefficients of B and A respectively at the nickel halide surface of the nickel reaction vessel. Authors list $10^4 k_{het} \cdot x = 5.5, 37$ and 125 at 193, 224 and 256°C respectively with $E_{het} = 23$. Preliminary studies by (2) showed no effect by NiF_2 . (3) Exchange considered to consist of simultaneous homogeneous and heterogeneous reaction at nickel halide surface of nickel reactor. Values listed are for the assumed homogeneous reaction. Rate of the heterogeneous reaction is expressed by $R_{het} = k_{het} \cdot xByA / (1 + xB + yA)^2$, where x and y represent adsorption coefficients of B and A respectively at the reaction vessel surface. Authors list $10^4 k_{het} \cdot x$ as 4.5, 6.2 and 25 at 181, 194 and 224°C. respectively with $E_{het} = 18.5$.

LITERATURE

- (¹) R.M. Adams, R.B. Bernstein, J.J. Katz, *J.C.P.* 1954, 22, 13. (²) R.B. Bernstein, J.J. Katz, *J.P.C.* 1952, 56, 885. (³) G.M. Harris, *PPS* 1951, 47, 718.

ISOTOPIC EXCHANGE
Ammonia(amine) complex on Group I element

Liquid phase
Amounts are in M/l.
Rate constants are
in M/l and sec.
Time of fractional
exchange in seconds.

No.	Reaction	Solvent	Amount of reactant	% exchange	Time	Defined fraction	Temperature	$k = k^0 \times 10^n$ k^0 n	Comments	Literature
1	$\text{Cu}(\text{N}^{15}\text{H}_3)_4^{++} + \text{NH}_3$	NH_3	$10^3 \text{ A} = 6$	100	180		-33			(2)
2	$\text{Ag}(\text{N}^{15}\text{H}_3)_2^+ + \text{NH}_3$	NH_3	$10^2 \text{ A} = 2$	99.6	30		-33			(2)
3	$\text{CuK}_2 + \text{Cu}^{++} \longrightarrow \text{CuK}_2 + \text{Cu}^{++}$ (copper II salicylaldehydestylenediamine)	pyridine	$10^3 \text{ A} = 10^3 \text{ B} = 1.5-15$			AB	25	2.6 -3	*	(1)

COMMENTS

(3) Rate law with respect to A and B individually not verified as A = B in all experiments.

LITERATURE

(1) R.B. Duffield, M. Calvin, *JCS* 1946, 68, 557. (2) H.U.D. Wiesenbarger, W.H. Jones, C.S. Garner, *JCP* 1957, 27, 668.

ISOTOPIC EXCHANGE
Halogen complex on group I element

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

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k \times 10^7$		k^0	n	$k^0 \times 10^7$		n	A^0	$A^0 \times 10^7$
								k^0	n			k^0	n			
.1	$\text{AuCl}_4^- + 4\text{Cl}^{*-} \rightarrow \text{AuCl}_4^{*-} + 4\text{Cl}^-$	H_2O	$10^3 \text{ A} = 3-12$ $10^3 \text{ B} = 8-72$	PCl NaCl	$0.003-0.12$ $\mu = 0.088$	$k_1 \text{ A} + k_2 \text{ AB}$	0	k^0_1	-7	k^0_1	-7	k^0_1	-7			
								k^0_2	-1	k^0_2	-1	k^0_2	-1			
								k^0_1	-7	k^0_1	-7	k^0_1	-7			
								k^0_2	-1	k^0_2	-1	k^0_2	-1			
								k^0_2	-1	k^0_2	-1	k^0_2	-1			

COMMENTS

(.1) Value of k_2 calculated at $\mu = 0.248$ on basis of assumed no change for k_1 with ionic strength.

LITERATURE

P.L. Pich, H. Taube, *JPC* 1954, 58, 1.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$		$k = k^0 \times 10^n$	
								k^0	n	k^0	n
.1	$Ag^{+2} + Ag^{+2} \longrightarrow Ag^+ + Ag^{+2}$	H_2O	$10^3(A+B)=5-16; A/B=5-17$	$HClO_4$	5.87	k_B^2	-15	3.0	+2		
			3-31 2-25		5.87		0	1.02	+3		
			5-8 5-20		4.9		0	1.8	+3		
			10 20		4.4		0	3.1	+3		
			8 20-30		7.94		0	4.9	+3		
			4-18 5-20		5.87		11	2.74	+3	12.5	1.1 13

COMMENTS

In the limited range studied reaction appears to follow inverse fourth order with respect to H^+ .
Mechanism of exchange probably involves a rapid equilibrium of the type $2Ag^{+2} \rightleftharpoons Ag^+ + Ag^{+3}$.

LITERATURE

B.M. Gordon, A.C. Wahl, *ACS* 1958, 80, 273.

ISOTOPIC EXCHANGE
Cyanide complex group II 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	$k \times 10^n$ k^0 n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
1	$Zn(CN)_4^{-2} + C^{14}N^-$	H ₂ O	A = B = 0.025	KOH	pH = 10.3		25	very fast			(1)
2	$HgCN^+ + Hg^{2+} \rightarrow Hg^+CN^+ + Hg^{2+}$	H ₂ O	$10^3 A = 2-16; 10^3 B = 6-49$ 7 2	HNO ₃	pH = 2.4-2.8 $\mu = 0.12$	k _{AB}	0 5 17 25 30	7 -3 1.6 -2 3.5 -2 6 -2 9 -2			(1) (2)
3	$HgCN^+ + Hg^{2+} \rightarrow Hg^+CN^+ + Hg^{2+}$	H ₂ O	$10^3 A = 6-34; 10^3 B = 6-200$	$\left. \begin{matrix} NaClO_4 \\ HClO_4 \end{matrix} \right\}$	pH = 1.5-2.8 $\mu = 0.02-0.12$	k _{AB} k* _{AB}	0 13 20 0 13 20	1.7 -2 4.9 -2 9.2 -2 1.3 -2 3.4 -2 6.0 -2	1 3 6 8 4 7	*	(2)

COMMENTS

Reaction: (1) Complete exchange within 120 seconds. (2) In absence of CN⁻ exchange is immeasurably fast. Rate constant calculated by (2) from rate data of (1). No effect on rate observable by authors of pH=0.85-2.7, ionic strength=0.1-2., C₂=0.1-760 mm of H₂ or colloidal Hg. (3) Rate constant listed as k is observed value calculated from pseudo first order exchange rate and concentrations of A and B. Rate constant listed as k* is value of constant corrected by activities for apparent exchange caused by the disproportionation reaction $2HgCN^+ \rightleftharpoons Hg^{2+} + Hg(CN)_2$.

LITERATURE

- (¹) A. C. MacDiarmid, N. F. Hall, *ACS* 1954, 76, 4222.
- (²) R. L. Wolfgang, R. W. Dodson, *JPC* 1952, 56, 872.
- (³) R. L. Wolfgang, R. W. Dodson, *ACS* 1954, 76, 2004.

ISOTOPIC EXCHANGE
Valence states Group III ions

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

Concentrations in gross concentration of all forms unless indicated otherwise.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k \times 10^n$		$A \times 10^n$		Comments	Literature	
								k^0	n	A^0	n			
.1	$Ce^{+3} + Ce^{+4} \longrightarrow Ce^{+3} + Ce^{+4}$	H_2O	$10^3 A = 2-18; 10^3 B = 2-17$ $\mu = 6.18$	HNO_3	6.00	k_{AB}	-14	1.28	-2	12	1	8	*	(15) (12) (12) (12) (11) (12) (15) (15) (5) (27) (27) (10)
					1.00		-10	6.9	-2					
					2.01		-10	3.0	-2					
					1.00		-6	1.16	-1					
					1.00		0	3.2	-1					
					2.01		0	9.8	-2					
					2.42		0	7.5	-2					
					3.68		0	4.2	-2					
					6.18		0	3.7	-2					
					6.18		25	2.9	-1					
					6.00		-14	1.11	-1					
					0.00013		-14	2.3	-1					
					0.00025		-14	4.2	-1					
					0.00047		-14	5.0	-1					
					0.00087		-14	6.7	-1					
0.00090	-14	1.02	0											
0.10020	0	4.2	-1											
0.4	10	1.16	-1											
6.0	0	5	-2											
		0	4' 5.7	0										
			$k_{AB} + k' AB^2$											

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k \times 10^n$ k^0 n	B	$A \times 10^n$ A^0 n	Comments	Temperature
.1	$Ce^{+3} + Ce^{+4} \longrightarrow (continued)$	H_2C	$10^3A = 0.8-8; 10^3B = 1-10$	$HClO_4$	5.85 5.04 3.97 3.00 2.04 6.18	$k_{AB} + k'_{AB^2}$	0 0 0 0 0 0 0 0 0 0 10 10	$k \times 10^n$ k^0 n 9.3 9.8 1.5 1.44 4.8 7.0 1.12 1.8 6.7 1.3 1.9			*	(10)
.2	$Eu^{+2} + Eu^{+3} \longrightarrow Eu^{+2} + Eu^{+3}$	H_2C	$10^3A = 2-20; 10^3B = 2-42$	$HClO_4$		$k_1A + k_2AB$	0 0 0 10 10	$k \times 10^n$ k^0 n 1.8 6.7 1.3 1.9		3 11 2 11	*	(12)
.3	$Tl^{+1} + Tl^{+3} \longrightarrow Tl^{+1} + Tl^{+3}$	H_2C	$10^2A = 3-7; 10^2B = 3-12$ $10^4A = 8-85; 10^4B = 8-34$	H^+ Cl^- $NaClO_4$	0.1-1.6 0.1-2 $\mu = 2.0$	$k_{AB}[Cl^-]$	32 39 50	$k \times 10^n$ k^0 n 8.2 1.80 5.3		6 11	*	(21) (20) (21) (21)
			$10^2A = 10^2B = 2.44$	HNO_3	1.0 1.5	k_{AB}	25 25	$k \times 10^n$ k^0 n 1.6 2.3			*	(23)
			$10^4A = 8-85; 10^4B = 8-34$	H_2SO_4	1.6 1.6 2.2 1.6		0 25 25 44	$k \times 10^n$ k^0 n 2.25 1.98 1.3 7.7				(6) (3) (6) (3)
			$10^2A = 10^2B = 1.0$ $\mu = 3.68$	$H_2SO_4 = 1.60; Na_2SO_4 = 0.39$ 1.28 0.57 0.85 0.85			25 25 25 25	$k \times 10^n$ k^0 n 1.60 1.80 2.33 2.92		8		(30)
			$10^2A = 10^2B = 1.0$	$H_2SO_4 = 0.0$ 0.006 0.015 0.030	$HClO_4 = 3.12$ 3.11 3.10 3.09		24 24 24 24	$k \times 10^n$ k^0 n 6.4 1.0 1.6 2.6				

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature		$k^o \times 10^7$		g	$A^o \times 10^n$		Comments	Literature
									k^o	n		A^o	n		
3	$\text{Tl}^{+1} + \text{Tl}^{+3} \longrightarrow$ (continued)	H_2O	$10^2\text{A} = 10^2\text{B} = 1.0$	$\text{H}_2\text{SO}_4 = 0.047; \text{HClO}_4 = 3.07$	k_{AB}	k_{AB}	24		3.5	-4				*	(30)
							24		7.4	-4					
							24		1.1	-3					
							37		1.8	-4					
							37		4.4	-4					
							37		7.0	-4					
							37		9.7	-4					
							37		1.7	-3					
							37		2.9	-3					
							37		1.05	-2					
							50		5.0	-4	15	1	7		
							50		2.7	-3	15	4	7		
							50		4.8	-3	14	1	7		
							50		5.3	-3	12	4	5		
							25		1.18	-2					
							25		1.03	-2					
							25		6.8	-3					
							25		3.7	-3					
							25		2.2	-3					
							25		8.2	-4					
							25		2.3	-4					
							25		3.6	-5					
							25		6.7	-5					
							25		6.8	-5					
							25		9.8	-5					
							25		1.07	-4					
							25		1.55	-4					
							25		5.7	-4					
		H_2O	$10^2\text{A} = 10^2\text{B} = 1.0$	$\text{H}_2\text{SO}_4 = 0; \text{NaClO}_4 = 3.12$	k_{AB}	k_{AB}	50		5.0	-4	15	1	7	(3)	
							50		2.7	-3	15	4	7		
							50		4.8	-3	14	1	7		
							50		5.3	-3	12	4	5		
							25		1.18	-2					
							25		1.03	-2					
							25		6.8	-3					
							25		3.7	-3					
							25		2.2	-3					
							25		8.2	-4					
							25		2.3	-4					
							25		3.6	-5					
							25		6.7	-5					
		H_2O	$10^2\text{A} \sim 1.0; 10^2\text{B} = 1.08$	$\text{H}_2\text{SO}_4 = 2.19; \text{HCl} = 0.0010$			25		1.18	-2					
							25		1.03	-2					
							25		6.8	-3					
							25		3.7	-3					
							25		2.2	-3					
							25		8.2	-4					
		H_2O	$10^2\text{A} \sim 1.0; 10^2\text{B} = 1.08$	$\text{H}_2\text{SO}_4 = 2.19; \text{HCl} = 0.0010$			25		2.3	-4					
							25		3.6	-5					
							25		6.7	-5					
							25		6.8	-5					
							25		9.8	-5					
							25		1.07	-4					
		H_2O	$10^2\text{A} \sim 1.0; 10^2\text{B} = 1.08$	$\text{H}_2\text{SO}_4 = 2.19; \text{HCl} = 0.0010$			25		1.55	-4					
							25		5.7	-4					
							25		1.07	-4					
							25		1.55	-4					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k \times 10^n$	B	$A \times 10^n$	Comments	Literature		
								k^0 n		A^0 n				
.3	$\text{Tl}^{*+1} + \text{Tl}^{+3} \longrightarrow$ (continued)	H_2O	$10^2 \text{A} \geq 2.5; 10^2 \text{B} \leq 2.5$	HClO_4 NaNO_3	$\left. \begin{array}{l} 0.8-3.5 \\ 0-0.4 \\ \mu=3.68 \end{array} \right\}$	$k_{AB};$ $k=k_1+k_2[\text{H}^+]^{-1}+$ $k_3[\text{NO}_3^-]$	10	$k_1 8.9$	-6			*	(24)	
							10	$k_2 6.4$	-6					
							10	$k_3 1.05$	-4					
							25	$k_1 4.3$	-5					
							25	$k_2 1.9$	-5					
							25	$k_3 4.4$	-4					
							37	$k_1 1.41$	-4					
							37	$k_2 4.2$	-5					
							37	$k_3 1.30$	-3					
							50	$k_1 4.5$	-4	18	4			8
							50	$k_2 6.7$	-5	10	9			2
							50	$k_3 3.6$	-3	16	2			6
			$10^4 \text{A} = 1-250; 10^4 \text{B} = 1-170$	$\text{HClO}_4 =$ $+ \text{NaClO}_4$ $\mu = 6.0$	k_{AB}	25	2.12	-5				(14)		
						25	1.94	-5						
						25	1.83	-5						
						25	1.19	-5						
						25	8.7	-6						
						32	3.86	-5						
						32	3.64	-5						
						32	3.25	-5						
						32	2.67	-5						
						32	1.93	-5						
						42	8.8	-5						
						42	8.4	-5						
42	7.8	-5												
42	6.0	-5												
42	5.1	-5												

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature, °C	$k \times 10^n$		B	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.3	$\text{Ti}^{*+1} + \text{Ti}^{+3} \longrightarrow (\text{continued})$	H_2O	$10^5 \text{A} = 3; 10^3 \text{B} = 4$	$\text{HClO}_4 =$ $+ \text{NaClO}_4$ $\mu = 6.0$	0.5	k_{AB}	50	2.08	-4				*	(9)
					1.0		50	1.83	-4					
					2.0		50	1.58	-4					
					4.0		50	1.19	-4					
					6.0		50	1.05	-4					
					0.5		50	5.54	-4					
					1.0		50	4.34	-4					
					2.0		50	4.08	-4					
					4.0		50	3.92	-4					
					0.5		50	6.7	-4					
					1.0		50	8.1	-4					
					2.0		50	8.1	-4					
					0.5		50	7.4	-4					
					1.0		50	8.7	-4					
					0.5		50	7.4	-4					
			$10^4 \text{A} = 1-250; 10^4 \text{B} = 1-170$	$\mu = 0.5$ HClO_4 $+ \text{NaCl} =$	6.0		32	1.93	-5					(9) (13)
					0.01		32	< 6	-9					
					0.02		32	1.7	-8					
					0.06		32	3	-6					
					0.12		32	3.0	-5					
					0.30		32	9.7	-5					
					0.40		32	7.6	-4					
					1.00		32	6.4	-3					
					1.50		32	9.6	-3					
					0.40		42	3.6	-3					
					1.50		42	3.1	-2					
			$10^3 \text{A} = 5-50; 10^3 \text{B} = 5-50$	HClO_4 $+ \text{CH}_3\text{COOH} =$	3.50		25	3.6	-5					(2)
					0.005		25	3.5	-5					
					0.010		25	3.2	-5					
					0.020		25	2.6	-5					
					0.050		25							

302.330

$$U^+ + U^+ \rightarrow U^+ + U^+$$

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass-action law	$k \times 10^n$		E	$A^\circ \times 10^n$		Comments	Literature
							k°	n		A°	n		
.4	$U^{+6} + U^{+6} \rightarrow (continued)$	Et_2O	$10^3 A = 1.7; 10^3 B = 2.1$	HCl	0.186	k_A^3	2.5	0				*	(19)
			0.6-2.4 1-2.8		0.252		1.88	0					
			1.7 2.1		0.314		1.4	0					
			C_2H_5OH 0.67 0.69		0.0078		2.3	+1					
			1.3 1.4		0.039		7.0	0					
.5	$Np^{+4} + Np^{+6} \rightarrow Np^{+4} + Np^{+6}$	H_2O	1-2 1.4-2.8	$\begin{cases} HClO_4 \\ NaClO_4 \end{cases}$	0.077	$k_A^2/2B^2 [H^+]^{-2}$	2.1	0				*	(28)
			1.3 1.4		0.116		1.6	0					
			$10^3 A = 4-100; 10^3 B = 5-50$		$[H^+] = 0.4-0.3$		6.4	-8					
			4-30 13-50		$\mu = 0.8-1.7$		5.0	-8		6	19		
					$[H^+] = 0.5-1$		1.1	-5		1	8		
.6	$Np^{+6} + Np^{+6} \rightarrow Np^{+6} + Np^{+6}$	H_2O	$10^3 A = 10^6 B = 1.5$ $10^3 A = 3-10; 10^3 B = 2-9$	HClO ₄	$\mu = 1.2$	$k_B^2 [H^+]$	9.8	-6				*	(6)
					1.7		1.6	-4					
					2.1		2.1	-4					
					3.0		3.3	-4					
					0.106		2.1	+1					
					$0.3-1.0$		3.0	+1					
					$\mu = 1$		3.1	+1					
					0.99		8.9	+1					
					3.00								
					0.99		3.6	+1					
					$\mu = 1.6$		4.6	+1					
					2.3		7.0	+1					
					2.9		1.21	+2					
					4.2		k_1^5	+1		2	11		
					$[H^+] = 0.1-3$		k_2^1	+1		1	13		
					$\mu = 3.0$		$k_1^7.4$	+1					
							$k_2^1.5$	+1					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mechanism law	Temperature		$k \times 10^3$		E	$A \times 10^3$		Comments	Literature
							k^0	n	k^0	n		A^0	n		
.6	$\text{Np}^{+5} + \text{Nd}^{+3} \longrightarrow (\text{continued})$	H_2O	$10^3\text{A}=3-10; 10^3\text{B}=2-9$ $10^3\text{A}=10^3\text{B}=2$	$\left. \begin{array}{l} \text{HClO}_4 \\ \text{NaClO}_4 \\ [\text{H}^+] = 3 \\ \text{Cl}^- = \end{array} \right\}$	$\left. \begin{array}{l} [\text{H}^+] = 0.3-1 \\ \mu = 1.0 \\ \mu = 3 \\ 0.10 \\ 0.23 \\ 0.55 \\ 1.37 \\ 1.5-2.7 \\ 0.21 \\ 0.55 \\ 1.37 \end{array} \right\}$	k_{AB}	10		5.1	+1	8	1	8	*	(¹)
							0		1.07	+2					(²)
							0		1.19	+2					
							0		1.32	+2					
							0		1.52	+2					
							0		1.6	+2					
							5		1.75	+2					
							5		1.92	+2					
							5		2.4	+2					
							10		2.4	+2					
.7	$\text{Pu}^{+3} + \text{Pu}^{+4} \longrightarrow \text{Pu}^{+3} + \text{Pu}^{+4}$	D_2O	$10^3\text{A}=10^3\text{B}=2$	$\left. \begin{array}{l} \text{NaClO}_4 \\ \text{DClO}_4 = \end{array} \right\}$	$\left. \begin{array}{l} \mu = 3.0 \\ 0.1 \\ 1.0 \\ 3.0 \end{array} \right\}$	k_{AB}	5		5.4	+1					
							5		6.6	+1					
							5		9.8	+1					
							0		k_1	+2				* (¹⁶) (¹⁷)	
							0		k_2	+4					
							12		k_1	+2					(¹⁸)
							12		k_2	+4					
							25		k_1	+1	8	3	8		
							25		k_2	+4	3	2	6		
									k_1						

CODED SOLVENTS

Et 30* (60) (90) C₂H₅OH vol. % indicated + H₂O

COMMENTS

Reaction: (1) Rate constants calculated on basis of first order dependence with respect to each reactant although log plot indicated order with respect to B to be $0.9 \pm .05$. Rate constants calculated from data of (19) in half times. (12) observe that plot of rate constant vs. $[H^+]^{-2}$ is linear. (19) observe that plot of rate versus $[KF]$ is linear. (19) concludes that data conforms to rate law $R = k_1 [Ce^{+3}] [Ce(OH)_3] + k_2 (Ce^{+3})(HOOCeO^{+}Ce^{+})$. Values of k_1 and k_2 are not given. In range $B = 0.0009$ to 0.010 (19) finds plot of $RA^{-1}B^{-1}$ linear with respect to B and concludes reaction is best expressed by the combined second and third order rate law given. In range $B = 0.002-0.04$ (12) finds plot of RA^{-1} linear with respect to B but straight line does not go through the origin. (12) therefore concludes reaction is best expressed by the combined first and second order rate law given. (2) Variation of $[H^+]$ from 0.1 to 1.56 caused change in calculated k of only 1.60×10^{-3} to 1.82×10^{-3} at $39^\circ C$. (3) Data of (23) calculated for rate law determined by later investigators. (9) observed slight catalysis of ex-

change by platinum foil, and also studied x-ray induced exchange. Selected data of (3). Dependence of calculated second order constant upon $[H^+]$ not completely determined. (12) (23) express $k = k_0 + k_1 [H^+]^{-1}$ based upon parallel exchange occurring with Tl^{+3} and $Tl(OH)^{+2}$ ions as exchanging species with Tl^{+1} . In contrast (9) uses $k^{-1} = k_0 + k_1 [H^+]$ based upon the assumption $Tl(OH)^{+2}$ is the only exchanging species. Plots of k vs. $[H^+]^{-1}$ and also k^{-1} vs. $[H^+]$ show some curvature for all data collected. Tables are therefore composed principally of the of the second order rate constants based upon total concentrations of the reacting species, as determined by the various investigators, with concentrations of acids and added salts given. Selected data for reasons of conservation of space. Ions such as Cl^- and CN^- both reduce exchange rate at low concentration and increase rate at higher concentrations. (4) Exchange observed by (1) to be about 20 times faster when illuminated by 300 watt lamp 4cm. from reaction flask than in dark. Value listed is for reaction in dark. Activation energy of light reaction

COMMENTS

(continued)

8 kcal. (²⁰) observed no effect of light in presence of HCl and a negligible salt effect. Exchange rate proportional to $[H^+]^{-3}$ in the pH range 0.85 to 1.6 in H_2O as solvent. In mixed ethanol-water solvent (¹⁹) observed wide variation of order with solvent composition. Log-log plots gave best fit for the order 0.93 for A, 1.11 for B and -1.74 for HCl in 30 vol. % C_2H_5OH ; 0.87 for A, 1.08 for B and -0.97 for HCl in 60 vol. % C_2H_5OH ; 2.89 for A, 0.10 for B and -1.06 for HCl in 90 vol. % C_2H_5OH ; and 0.0 for A, 2.70 for B and -1.26 for HCl in pure C_2H_5OH . (¹⁹) proposes rate expression is $k'[UOH^{+3}]^2[UO_2OH^+]$ and calculate k' from the expression:

$$R = k' \frac{A^{2B}}{\left(\frac{[H^+]}{3.4 \times 10^{-5}} + 1 \right)^2 \left(\frac{[H^+]}{1.3 \times 10^{-6}} + 1 \right)}$$

derived from the hydrolysis constants, $3.4 \times 10^{-6} = [UOH^{+3}][H^+]/[U^{+4}]$ and $1.3 \times 10^{-6} = [UO_2OH^+][H^+]/[UO_2^{+3}]$. No definite trends in the calculated k' in any one solvent system although values vary by as much as a factor of two in both the 30 and the 60 vol. % ethanol. Agreement between values of calculated k' is better in the other solvents. (.5) At $[H^+]$ less than, 0.3 exchange reaction appears to be independent of ionic strength or glass or platinum surfaces. At $[H^+]$

greater than 0.5 exchange reaction shows positive dependence upon ionic strength and some catalysis by platinum foil, gold foil and pyrex helices. At both the higher and lower acidities the exchange reaction is faster than the oxidation-reduction disproportionation reaction. (.6)

Reaction found to be essentially independent of dielectric constant of solvent in range from 68 to 88.3 using ethylene glycol or sucrose with H_2O . At constant ionic strength exchange appears independent of $[H^+]$ up to $HNO_3=2.0$. This is possibly due to slight retarding effect observed for nitrate ion (⁹) balancing slight positive H^+ effect (²⁰). Below $\mu=3.0$ exchange rate is observed to be independent of positive ion Na^+ , Mg^{++} or La^{+++} . At $\mu>3$, (²⁰) shows that effect of $Na^+ > Mg^{++} > La^{+++}$. (⁹) study catalysis by Cl^- at constant $[H^+]$ and ionic strength. They suggest two reaction schemes:

$R = k_0(NpO_2^+)(NpO_2^{++}) + k_1(NpO_2^+)(NpO_2Cl^+)$ or
 $R = k_0'(NpO_2^+)(NpO_2^{++}) + k_1'(NpO_2^+)(NpO_2Cl^+) + k_2(NpO_2^+)(NpO_2Cl_2^-)$ and calculate the values of k_0 , k_1 and k_2 according to each scheme. Data does not appreciably differentiate between these two rate expressions. (.7) Slight positive dependence upon ionic strength in range 0.7 to 2. Values probably give little more than order of magnitude because of difficulties of measuring such a rapid exchange.

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ISOTOPE EXCHANGE
H-D,(T) exchange on aliphatic C

Liquid phase

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

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

No.	Suppl. No. 1951	Reaction	Solvent (Medium)	Amount of reactant	Amount added	Defined action mass	Temperature	$k \times 10^n$ k^0 η	k_F	$A = A^0 \times 10^n$ A^0 η	Comments	Order of reaction
.11		$(CH_3)_2CHCH_2CH_2CH_3 + D_2SO_4$	A	A sat. with B		k_F	44	1.1 -5			*	(10)
.12		$d-C_2H_5CH(CH_3)CH_2CH_2CH_3 + D_2SO_4$	A	A sat. with B		k_F	80	1.0 -5			*	(10)
.13		$n-C_8H_{18} + D_2SO_4$	A	A sat. with B		k_F	80	2.7 -8			*	(10)
.14		$d-C_2H_5CH(CH_3)CH_2CH_2CH_2CH_3 + C_2H_5SO_3D$	A	A sat. with B		k_F	104	4 -7			*	(10)
.15		$C_2H_5CH(CH_3)CH_2CH_2CH_2CH_3 + ClSO_3D$	A	A sat. with B		k_F	-78 -50	2 -6 6 -6				(10)
.16		$(CH_3)_3CCH_2CH_2CH_2CH_3 + D_2SO_4$	A	A sat. with B		k_F	60	5 -9			*	(10)
.17		$d-C_2H_5CH(CH_3)(CH_2)_7CH_3 + D_2SO_4$	A	A sat. with B		k_F	60	4 -6				(10)
Unsaturated Hydrocarbons												
.18		$HClCH + D_2O$	B	B sat. with A	pH=8.6 phosphate buffer	k_A	25 25	2.6 -3 6.0 -3			*	(1)
.19		$C_6H_5C:CD + H_2O$	B	B sat. with A	HCl acetate buffer=.04 phosphate buffer=.02	k_A	25 25 25 25	0 -6 2 -5 7.1 -5 5.1 -4			*	(1)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass- action law	Temperature	$k \times 10^n$ k^0 π	δ	$A \times 10^n$ A^0 π	Comments	Literature
.15		$C_6H_5C(=O)Cl + H_2O \rightarrow C_6H_5C(=O)OH + HCl$ (continued)	B	B sat. with A	phosphate buffer = .02	pH = 8.6	kA	25	1.3 -3			*	(1)
					borate buffer = .014	8.6		25	1.5 -3				
						9.0		25	4.6 -3				
						.012		25	1.2 -2				
						7-9.5	$k_A[OH^-]$	25	4.6 +2				
.20		$C_6H_5C(=O)CH_3 + OH^- \rightarrow C_6H_5C(=O)CH_2^- + H_2O$	C_6H_5N	A=0.4-1.4; $10^4 B = 1-100$ M=5	$(CH_3)_4N^+$	= B	kAB	25	3.4 +3			*	(8)
Ketones													
.21	.3	$CH_3COCH_2CH_3 + DOH \rightarrow CH_3COCH_2CH_2OH + H_2O$	A+M	2 vol. (A+L); 1 vol. (S+H)	K_2CO_3	.001 .003 .01 .03 .01	kAB	35 35 35 35 40	3.1 7.8 9.0 1.09 1.47	-5 -5 -5 -4 -4		*	(11)
.22		$CH_3COCH_2CH_3 + H_2O \rightarrow CH_3COCH_2CH_2OH + DOH$	B+L	2 vol. (A+L); 1 vol. (B+H)	K_2CO_3	.001 .003 .01 .03 .01	kAB	35 35 35 35 40	1.25 3.1 3.6 4.3 5.8	-5 -5 -5 -5 -5		*	(11)
.23		$d,l-C_6H_5C(=O)C(=O)C(=O)CH_2CH_2CH_3 + H_2O$	B.4 DI*	A=0.1; $[CH_3COOH] = [CH_3COO^-]$		0.030 0.050 0.070 0.100	kA	98 98 98 98	5.7 9.8 1.40 2.05	-8 -8 -7 -7		*	(21)

Heterogeneous Reaction Kinetics
302.401

No.	Supplementing No. 1961	Reaction	Solvent (Medium)	Amount of Reactant	Addend	Amount of addend	Reaction Condition	Temperature, °C	$k \times 10^n$ k^0 n	$A^0 \times 10^n$ A^0 n	Comments	Literature
22		$4\text{-C}_6\text{H}_5\text{COOEt}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}(\text{CH}_3)_2 + \text{H}_2\text{O}$	S. 4 DI*	A=0.1; $\mu=0.1$	HCl	0.020 0.040 0.060 0.50 0.75 1.00	k_A	98 98 98 98 98 98	5.2 1.05 1.61 3.9 5.3 7.8	-7 -6 -6 -9 -9 -9		(21)
					CH_3COOH							
					CH_3COONa	0.01 0.02 0.06 0.02 0.10 0.0050 0.0075 0.010		98 98 98 98 98 98 98 98	1.12 2.01 6.1 8.1 1.03 2.57 4.3 6.4	-8 -8 -8 -8 -7 -5 -5 -5		
					NaOH							
					HCl	0.02-.06	$k_A[\text{H}^+]$	98	2.72	-5		
					CH_3COOH	0.5-1	$k_A[\text{CH}_3\text{COOH}]$	98	7.7	-9		
					CH_3COONa	.01-0.1	$k_A[\text{CH}_3\text{COO}^-]$	98	1.05	-6		
					NaOH	.005-.01	$k_A[\text{OH}^-]$	98	7.7	-3		
Carboxylic acid, (salt), (ester)												
25		$\text{HCOONa} + \text{D}_2\text{O}$	B				k_{FE}	160 183 214	3.3 1.42 1.29	-7 -6 -5	30 4 9	(3)
26		$\text{DCCONa} + \text{H}_2\text{O}$	B				k_{FE}	179 195 208	1.91 7.1 1.72	-6 -6 -5	34 3 10	(3)
27	5	$\text{CH}_3\text{COOL} + \text{D}_2\text{O} \longrightarrow \text{CH}_3\text{COOD} + \text{DOH}$	B				k_{FE}	~130 160	3 ~2	-7 -6	*	(2) (4)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined reaction	Temperature	$k \times 10^n$ k° n	$A = A^\circ \times 10^n$ A° n	Comments	Literature
.28		$\text{CH}_3\text{COO}^- + \text{D}_2\text{O} \longrightarrow \text{CH}_3\text{DCOO}^- + \text{DOH}$	B		Na^+ Ca^{++} Ba^{++} K^+	$= A$ $= A/2$ $= A/2$ $= A$	k_{F_2}	150 150 150 160	1.1 ~1 ~1 ~4	-6 -6 -6 -6	*	(18)
.29		$(\text{CH}_3\text{COO})_2\text{Co} + \text{D}_2\text{O}$	B	A sat.			k_{F_2}	150	1.0	-6	*	(18)
.30		$(\text{CH}_3\text{COO})_2\text{Cd} + \text{D}_2\text{O}$	B	A sat.			k_{F_2}	150	3.2	-6	*	(18)
.31		$(\text{CH}_3\text{COO})_2\text{Hg} + \text{D}_2\text{O}$	B	A sat.			k_{F_2}	150	6	-6	*	(18)
.32		$(\text{CH}_3\text{COO})_2\text{Pb} + \text{D}_2\text{O}$	B				k_{F_2}	150	3	-5	*	(18)
.33		$\text{CH}_3\text{CH}_2\text{COOD} + \text{D}_2\text{O} \longrightarrow \text{CH}_3\text{CHDCOOD} + \text{DOH}$	B	A = 7-12; B = 15-25			k_{F_2}	~130	6	-8	*	(2)
.34		$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 6	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	4.7	-6	*	(7)
.35		$\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 5	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	9	-7	*	(7)
.36		$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 5	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	3.8	-7	*	(7)
.37		$(\text{CH}_3)_2\text{CHCOOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 5	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	1.1	-7	*	(7)
.38		$(\text{CH}_3)_2\text{CHCH}_2\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 5	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	1.3	-7	*	(7)
.39		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 5	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	3.2	-7	*	(7)
.40		$\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	A ~ 5	$\text{C}_2\text{H}_5\text{ONa}$	~0.2	k_{F_2}	25	3.8	-7	*	(7)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of added solvent	Temperature	$k^0 \times 10^7$	k^0	$k^0 \times 10^7$	k^0	Comments	Literature
Hydroxy, (alkoxy)-substituted carboxylic acid, (salt), (ester)												
.41	$\text{CH}_3(\text{CH}_2)_{15}\text{COCC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 5$	$\text{C}_2\text{H}_5\text{ONa}$	~ 0.2	25	3.1	-7			*	(7)
.42	$\text{C}_6\text{H}_5\text{CH}_2\text{COCC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 1$	$\text{C}_2\text{H}_5\text{ONa}$	~ 0.2	0	5.4	-3			*	(7)
.43	$\text{C}_6\text{H}_5(\text{CH}_2)_3\text{CHCOCC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 2$	$\text{C}_2\text{H}_5\text{ONa}$	~ 0.2	0	1.2	-3			*	(7)
.44	$(\text{C}_6\text{H}_5)_2\text{CHCOCC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 1$	$\text{C}_2\text{H}_5\text{ONa}$	~ 0.2	0	2.3	-3			*	(7)
NR ₂ -substituted carboxylic acid												
.45	$\text{DOCH}_2\text{COOD} + \text{D}_2\text{O}$	B	$A \sim 2.5$			160	5.8	-7			*	(6)
.46	$\text{HOCD}_2\text{COOH} + \text{H}_2\text{O}$	B	$A \sim 2.5$			160	4.1	-7			*	(6)
.47	$\text{CH}_3\text{O}(\text{CH}_2)_3\text{CHCOCC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 5$	$\text{C}_2\text{H}_5\text{ONa}$	~ 0.2	25	2.1	-7			*	(7)
.48	$\text{CH}_3\text{O}(\text{C}_6\text{H}_5)_2\text{CHCOCC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 1$	$\text{C}_2\text{H}_5\text{ONa}$	~ 0.2	0	1.6	-3			*	(7)
Di-carboxylic acid ester												
.49	$\text{ND}_2\text{CH}_2\text{COOD} + \text{D}_2\text{O}$	B				140	4.9	-5				(6)
.50	$\text{NH}_2\text{CD}_2\text{COOH} + \text{H}_2\text{O}$	B				150	8.3	-5				(6)
						160	1.4	-4	18	2	5	
.51	$(\text{C}_6\text{H}_5\text{OCC})_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 2$	$\text{o-HOC}_6\text{H}_4\text{COONa}$	~ 0.003	140	2.2	-5				(7)
						150	3.8	-5				
						160	6.5	-5	19	4	5	
.52	$(\text{C}_6\text{H}_5\text{OCC})_2\text{CHCH}_3 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 2$	$\text{o-HOC}_6\text{H}_4\text{COONa}$	~ 0.003	25	1.1	-5			*	(7)
.53	$(\text{C}_6\text{H}_5\text{OCC})_2\text{CHC}_6\text{H}_5 + \text{C}_2\text{H}_5\text{OD}$	B	$A \sim 2$	$\text{o-HOC}_6\text{H}_4\text{COONa}$	~ 0.003	25	1.6	-6			*	(7)
		B	$A \sim 2$	$\text{o-HOC}_6\text{H}_4\text{COONa}$	~ 0.003	25	2.1	-6			*	(7)

No.	Reaction	Solvent (medium)	Amount of reactant	Addend	Amount added	Defined mass	Temperature	$k^\circ \times 10^n$	k°	$A^\circ \times 10^n$	Comments	Temperature
Tetra-alkyl ion of Vth group element												
.54	$(\text{CH}_3)_4\text{N}^+ + \text{OD}^-$	D_2O	$A=0.3; B \sim 0.3$	Na^+, I^-	$=B, A$	k_{AB}	84 100	3.1 2.3	-9 -8	6 11	*	(22)
.55	$(\text{CH}_3)_4\text{P}^+ + \text{OD}^-$	D_2O	$A=0.3; B=0.28-0.4$	Na^+, I^-	$=B, A$	k_{AB}	27 56	9.8 4.7	-6 -4	1 14	*	(22)
.56	$(\text{CH}_3)_4\text{As}^+ + \text{OD}^-$	D_2O	$A=0.3; B \sim 0.3$	Na^+, I^-	$=B, A$	k_{FE}	62	7.2	-8		*	(22)
.57	$(\text{CH}_3)_4\text{Sb}^+ + \text{OD}^-$	D_2O	$A=0.3; B \sim 0.3$	Na^+, I^-	$=B, A$	k_{FE}	62	7	-7		*	(22)
Tri-alkyl ion of VIth group element												
.58	$(\text{CH}_3)_3\text{Se}^+ + \text{OD}^-$	D_2O	$A=0.3; B \sim 0.3$	Na^+, I^-	$=B, A$	k_{AB}	0 27	2.9 1.16	-6 -4	2 12	*	(22)
.59	$(\text{CH}_3)_3\text{Se}^+ + \text{OD}^-$	D_2O	$A=0.3; B \sim 0.3$	Na^+, I^-	$=B, A$	k_{FE}	62	1.3	-5		*	(22)
.60	$(\text{CH}_3)_3\text{Te}^+ + \text{OD}^-$	D_2O	$A=0.15; B \sim 0.3$	Na^+, I^-	$=B, A$	k_{FE}	62	4	-6		*	(22)
.61	$\begin{array}{c} \text{CH}_2 \text{ CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} - \text{CH}_2 - \text{S}^+ + \text{OD}^- \\ \diagdown \quad \diagup \\ \text{CH}_2 \text{ CH}_2 \end{array}$ (bicyclo[2.2.1]heptane-1-sulfonium ion)	D_2O	$A=1; B=0.31$	Na^+, I^-	$=B, A$	k_{FE}	56	3	-7		*	(22)
Alkyl sulfinyl, (sulfonyl)												
.62	$(n\text{-C}_4\text{H}_9)_2\text{SO} + \text{OH}^-$	D_2O	$A \sim 1; B=2.2$	Na^+, I^-	$=B, A$	k_{FE}	56	1.0	-8		*	(22)

No.	Reaction	Solvent (medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	k ^o × 10 ⁿ	B	A ^o × 10 ⁿ	Comments	Literature
								k ^o	n	A ^o		
.63	$\text{CH}_2(\text{OH})_2 + \text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_2 - b + \text{OH}^- \xrightarrow{\text{DMSO}}$	DMSO*	10 ² A ~ 5; B ~ 0.4			k _{AB}	50 60 71	1.67 5.2 1.67	-5 -5 -4	5 11 24.4	*	(23)
.64	$\text{CF}_2(\text{CH}_2)_4\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_2 - b + \text{OH}^- \xrightarrow{\text{DMSO}}$	DMSO*	10 ² A ~ 5; B ~ 0.4			k _{AB}	40 50 70 79	2.18 1.11 8.4 2.2	-6 -5 -5 -4	1 12 25	*	(23)
Alkyl halides												
.65	$\text{CHCl}_2\text{F} + \text{OH}^- \longrightarrow \text{CCl}_2\text{F}^- + \text{H}_2\text{O}$	H ₂ O	10 ² A = 3; 10 ² B = 3	Na ⁺	= B	k _{AB}	0 20	1.57 3.9	-4 -3	2 25	*	(13)
.66	$\text{CDCl}_2\text{F} + \text{OH}^- \longrightarrow \text{CCl}_2\text{F}^- + \text{DOH}$	H ₂ O	10 ² A = 3; 10 ² B = 3	Na ⁺	= B	k _{AB}	0 20	8.9 2.55	-5 -3	1 28	*	(13)
.67	$\text{CEBr}_2\text{ClF} + \text{OH}^-$	H ₂ O	10 ² A ~ 1; 10 ² B = 1.7	Na ⁺	= B	k _{AB}	0 15	2.10 2.27	-3 -2	1 25	*	(14)
.68	$\text{CDBr}_2\text{F} + \text{OH}^-$	H ₂ O	10 ² A ~ 2	$\left\{ \begin{array}{l} \text{CH}_3\text{NH}_2 \\ \text{CH}_3\text{NH}_3\text{ClO}_4 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.04 \\ 0.05 \end{array} \right\}$	k _{AB} + k ₁ A[CH ₃ NH ₂]	0 0 25	k 2.07 k' 1.3 k 7.3	-2 -5 -1	5 16 23	*	(15)
.69	$\text{CCI}_2\text{F} + \text{OH}^-$	H ₂ O	10 ³ A ~ 3	$\left\{ \begin{array}{l} \text{CH}_3\text{NH}_2 \\ \text{CH}_3\text{NH}_3\text{ClO}_4 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.112 \\ 0.096 \end{array} \right\}$	k _{AB} + k'A[CH ₃ NH ₂]	0 0 20 20	k 5.07 k' 2.7 k 8.2 k' 6.7	-2 -5 -1 -4	2 16 22 26	*	(15)
.70	$\text{CHCl}_3 + \text{OD}^-$	D ₂ O	10 ² A = 1.3; 10 ³ B = 3.1	Na ⁺	= E	k _{AB}	20	2.07	-1		*	(15)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass-action law	Temperature	$k \times 10^n$ k^0 n	E	$A^0 \times 10^n$ A^0 n	Comments	Literature
.71	$\text{CDCl}_3 + \text{OH}^-$	H_2O	$10^2 A = 1.3; 10^3 B = 3.1$ 41 3.1 3.1 3.1 buffer	Na^+ NaClO_4 $\left\{ \begin{array}{l} \text{CH}_3\text{NH}_2 \\ \text{CH}_3\text{NH}_3\text{Cl} \end{array} \right.$ buffer	$= B$.038 .016 .0012	k_{AB} $k_{AB} + k'A[\text{CH}_3\text{NH}_2]$	0 0 0 20 35 35	4.7 5.0 4.8 1.02 7.4 k'3	-3 -3 -3 -1 -1 -4	8 16	*	(16)
.72	$\text{CDBr}_2\text{Cl} + \text{OH}^-$	H_2O	$10^2 A \sim 1$; buffer	NH_3 NH_4ClO_4	.1-.2 .15-.4	$k_{AB} + k'A[\text{NH}_3]$	0 0 35 35	k 1.44 k'8 k 1.38 k'1.9	-1 -7 +1 -4	4 16	*	(14)
.73	$\text{CDICl}_2 + \text{OH}^-$	H_2O	$10^2 A \sim 1$; buffer	NH_3 NH_4ClO_4	.1-.2 .15-.4	$k_{AB} + k'A[\text{NH}_3]$	0 0 35 35	k 2.75 k'4 k 3.14 k'6.5	-2 -7 0 -5	3 16	*	(14)
.74	$\text{CDBr}_3 + \text{OH}^-$	H_2O	$10^2 A \sim 1$; buffer	NH_3 NH_4ClO_4	.1-.2 .15-.4	$k_{AB} + k'A[\text{NH}_3]$	0 0 20 20 35 35	k 5.8 k'1.3 k 8.3 k'2.0 k 4.7 k'1.4	-1 -5 0 -4 +1 -3	3 16	*	(14)
.75	$\text{CDI}_3 + \text{OH}^-$	H_2O	$10^3 A \sim 5$; buffer	NH_3 NH_4ClO_4	.02-.05 .02-.05	k_{AB}	0 24	6.0 1.39	-1 +1	3 16	*	(14)

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mechanism law	Temperature	$k \times 10^2$ k^0	n	E	$A = A^0 \times 10^2$ A^0	Comments	Temperature
.76	<i>cis</i> -ClCH:CHCl + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	70	very fast				*	(19)
.77	<i>trans</i> -ClCH:CHCl + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	3	1.7	-7			*	(19)
.78	<i>cis</i> -BrCH:CHBr + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	25	1.8	-6			*	(19)
.79	<i>cis</i> -BrCD:CDBr + CH ₃ OH	B	A=0.25-.26	CH ₃ ONa	.006-.08	$k_A[CH_3ONa]$	26 31	3.3 1.0	-3 -2			*	(19)
.80	<i>trans</i> -BrCH:CHBr + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	26	1.2	-6			*	(19)
.81	<i>cis</i> -ICH:CHI + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	25	< 2	-7			*	(19)
.82	<i>trans</i> -ICH:CHI + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	55	very fast				*	(19)
.83	BrCH:CHBr + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	26	1.8	-5			*	(19)
.84	C ₆ H ₅ CH:CHBr + D ₂ O	B	saturated 2 phases	CH ₃ ONa	1-2	k_F	110	1.2	-7			*	(19)
.85	Cl ₂ C:CClH + OD ⁻	H ₂ O	A (sat.): B ⁻ 6	Na ⁺	= B	k_F	~82	4	-6			*	(17)
.86	Cl ₂ C:CClD + OH ⁻	D ₂ O	A (sat.): B ⁻ 6	Na ⁺	= B	k_F	~82	3	-6			*	(17)
.87	C ₁₀ H ₁₆ .HCl + DCl (camphene hydrochloride)	CHCl ₃	A=0.15-0.17; B=.05-.1			k_{AB}	0	1.6	-3			*	(20)
.88	β -C ₆ H ₄ Cl + C ₂ H ₅ OD	B	10 ³ A=1.8	C ₂ H ₅ O ⁻	0.07	$k_A[C_2H_5O^-]$	44	~1	-6			*	(8)

CODED SOLVENTS

8.4 DI* 8.4 M dioxane in H₂O
DI 50* 50 vol. dioxane with 50 vol. of H₂O

COMMENTS

General: For general treatment of isotope exchange reactions see (12). In all cases where defined mass action law is given as kF_p the pseudo first order isotopic equilibrium constant is given as the rate constant. This is calculated from the fractional exchange, X , at time, t , by using the equation $k = 1/t \ln(1-X)$. In cases where the reverse exchange is negligible due to a large excess of one isotopic species this might be equal to first order rate constant for the reaction but this is not verified unless exchange dependence on reactant concentration has been determined.

Reaction: (.11) Exchange rate constant calculated from only one fractional exchange time. (.12) Exchange rate constant an average of three fractional exchange times. (.13) Exchange rate constant calculated from only one fractional exchange time. (.14) Average of exchange rates at 102 and 104°C. (.16) Exchange rate constant calculated from only one fractional exchange time. (.18) Exchange rate corrected for amount of A in gas phase by multiplying observed exchange rate by ratio of total A to A in liquid phase. Exchange rate independent of rate of shaking under conditions used. Total buffer conc. = .02. (.19) Exchange rate corrected for amount of A in second liquid phase by multiplying observed exchange rate by ratio of total A to amount of A in aqueous phase. Exchange rate not dependent upon rate of shaking under conditions used.

(.20) Rate constant for exchange calculated from nuclear magnetic resonance measurements. Effective relaxation time is dependent upon rate constant of exchange reaction. (.21)(.22) Approximate values of rate constants for forward and reverse reaction of first step in isotope exchange calculated from analysis of rate of exchange and equilibrium isotope distribution. Rate law with respect to A and B not verified as ratio of (A+L) to (B+M) kept constant. (.23) Pseudo first order exchange rate law not verified as concentration of A kept constant. Under same conditions rate is about one fifth of observed rate of racemization for H-substituted compound interpreted to indicate an H/D isotope effect about equal to 5. (.24) Pseudo first order rate law with respect to A not confirmed as concentration of A kept constant. Ratio of catalytic constants to the catalytic constants for racemization of H-substituted compound averages about 11 interpreted to indicate an H/T isotope effect about 11 compared to H/D effect of 5, see (.23). (.25) Partial conversion of salt to HCOOD had no effect on exchange rate. Excess DCl however accelerated exchange. (.27) Calculated from a half time of about 100 hrs. (.28)(.29)(.30)(.31)(.32) Calculated from time for half exchange in hours. (.33) Calculated from percent exchange per day. (.34) through (.48) Approximate value of pseudo first order exchange rate constant calculated from percent exchange at one time only. Exchange probably occurs only

COMMENTS

(continued)

at α -hydrogen. (.51)(.52)(.53) Approximate values as pseudo first order exchange rate constant calculated from percent exchange at one time only. Exchange probably occurs only at α -hydrogen. (.54)(.55) Second order rate law not verified. Rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. (.56)(.57) Approximate value as pseudo first order exchange rate constant calculated from percent exchange at one time only. (.58) Rate law not verified. Second order rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. (.59)(.60)(.61)(.62) Approximate value as pseudo first order exchange rate constant calculated from percent exchange at one time only. (.63)(.64) Second order rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. Activation energy recalculated and corrected by reviewer. (.65)(.66) Rate constant listed is for first step in isotope exchange and hydrolysis reaction. Hydrolysis reaction yields as products, NaF, NaCl, HCOONa and CO. Constants are based upon an assumed mechanism and steady state approximation. (.67) Concurrent hydrolysis reaction also studied, see 212.471. Products of hydrolysis are NaBr, NaCl, NaF, HCOONa and CO. (.68) Simultaneous hydrolysis reaction causes change of OH⁻ concentration during exchange. Samples titrated prior to determining D content. For hydrolysis reaction see 212.471 listed by authors. (.69) Simultaneous hydrolysis reaction not as appreciable as in (.68) see 212.471. (.70)(.71)(.72) (.73)(.74)(.75) Simultaneous solvolysis reaction is slower

than exchange. Second order rate constant calculated by dividing pseudo first order exchange rate constant by concentration of B. Rate law with respect to A not verified. (.76) Complete in 20 hours. Authors estimate rate under similar conditions about that of (.78). (.77) (.78) Approximate value of exchange rate constant based on assumed identical extinction coefficients for C-D and C-H. (.79) Second order rate constant calculated by dividing pseudo first order equilibration constant by concentration of [CH₃ONa]. Approximate value as extinction coefficients for C-D and C-H assumed identical. Exchange rate falls off rapidly probably due to parallel elimination reaction. (.80)(.81) Approximate value of exchange rate constant based on assumed identical extinction coefficients for C-D and C-H. (.82) Complete in 20 hours. Authors estimate rate under similar conditions to be less than (.80). (.83)(.84) Approximate value of exchange rate constant based on assumed identical extinction coefficients for C-D and C-H. (.85) (.86) Simultaneous solvolysis reaction caused concentration of B to drop to half its initial value during exchange. Value of pseudo first order exchange rate constant calculated from time of half exchange in hours and should be interpreted as only giving a rough order of magnitude. (.87) Second order rate constant identical within experimental order to second order rate constant for exchange of radioactive chlorine isotope between A and B. (.88) Simultaneous elimination reaction about 150 times faster than isotope exchange see 422.471. Exchange constant listed for order of magnitude only.

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ISOTOPE EXCHANGE
H-D(T) exchange on aromatic C

Liquid phase

Amounts are in M/l unless
otherwise indicated.
Rate constants are in M/l
and sec.

The position of the substitution is indicated in parentheses after the arrow in those cases where it has been determined.

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

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined as action = k_F	Temperature	$k = k^0 \times 10^n$ k^0 n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.4	$C_6H_6D + H^+ \longrightarrow$	$H_2O-HClO_4$	B=10.43 11.01 11.71 $10^3 A = 8$; wt % H_2SO_4 66.5 68.7 73.5 75.8 79.2 83.2	ClO_4^-	10.43 11.01 11.71	$k_F A$	25 25 25	k^0 n 2.82 -6 1.75 -5 1.35 -4		*	(19)
.4.1	$C_6H_6T + H^+ \longrightarrow$	$H_2O-H_2SO_4$	A=sat.; wt % $H_2SO_4 = 79.2$			$k_F A$	25	2.68 -7 5.75 -7 3.52 -6 1.15 -5 4.53 -5 3.45 -4		*	(4)
.5	$C_6H_6D + NH_3 \longrightarrow$	NH_3	A=0.25-0.6; B=0.6	K^+	=B	k_A	~ -13	k^0 n ~ 1 -7		*	(7)
.5.1	$C_6H_6 + ND_2 \longrightarrow$	ND_3	B=0.06 0.03			$k_F A$	25 25	2 -4 1.7 -4		*	(23)

Homogeneous Reaction Kinetics

502.402

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Order of reaction	Temperature		$k \times 10^n$		δ	$A \times 10^n$		Comments	Literature
							k_0	π	k_0	π		A_0	n		
6	$O-CH_3C_6H_4I + H^+ \longrightarrow$	$H_2O-H_2SO_4$	A=sat.; wt. % $H_2SO_4 = 89.0$ 81.8			$k_F A$	25	-7	3.56	-7				*	(6) (17) (18)
		H_2O-CF_3COOH	Mole % A=24.6; $CF_3COOH = 82.9$; $H_2O = 12.5$			$k_F A$	25	-4	3.4	-4					(15)
6.1	$O-CH_3C_6H_4I + H^+ \longrightarrow$	$H_2O-H_2SO_4$	A=sat.; wt. % $H_2SO_4 = 81.8$			$k_F A$	25	-4	1.8	-4				*	(18)
7	$O-CH_3C_6H_4I + H^+ \longrightarrow$	NH_3	A=0.25-0.6; B=0.6	K^+	B		~33	(no measurable exchange in 10 hrs.)							(7)
8	$\pi-CH_3C_6H_4I + H^+$	$H_2O-H_2SO_4$	10 ³ A=2; wt. % $H_2SO_4 = 68.0$ A=sat. 81.8			$k_F A$	25	-7	8.2	-7				*	(6) (17) (18)
8.1	$\pi-CH_3C_6H_4I + H^+$	$H_2O-H_2SO_4$	A=sat.; wt. % $H_2SO_4 = 81.8$			$k_F A$	25	-6	6.0	-6				*	(18)
8.2	$\pi-CH_3C_6H_4I + H^+$	$H_2O-H_2SO_4$	10 ³ A=2; wt. % $H_2SO_4 = 53.0$ 58.5			$k_F A$	25	-7	1.38	-7				*	(6)
8.3	$\pi-CH_3C_6H_4I + H^+$	$H_2O-H_2SO_4$	62.9				25	-7	9.4	-7					
			68.9				25	-6	5.7	-6					
			73.4				25	-5	5.0	-5					
							25	-4	4.2	-4					
							70	-6	1.00	-6					(15) (16)
							70	-8	7.7	-8					(16)
9.1	$p-CH_3C_6H_4I + H^+$	$H_2O-H_2SO_4$	A=sat.; wt. % $H_2SO_4 = 81.8$			$k_F A$	25	-4	1.7	-4				*	(18)
10	$C_6H_5CH_3 + T^+ (o.m.; p=47; 1:4:1) A$		10 ² B=7	NO_2	.001-.002	$k_B [NO_2]$	25	-4	7	-4				*	(1) (17)
			2-7		.0002-.02		140	-2	1.9	-2	10	4	3		
			2-14	$SnCl_4$	.007-0.5	$k_B [SnCl_4]$	25	-4	2.2	-4					
			7		0.07		140	-3	4.4	-3	10	5	3		
11	$p-(CH_3)_3CC_6H_4D + H^+$	H_2O-CF_3COOH	Mole % A=1.8; $CF_3COOH = 81.9$; $H_2O = 16.3$			$k_F A$	70	-6	8.2	-6				*	(16)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature		$k \times 10^7$		R	$A \times 10^7$		Comments	Literature
							k°	n	k°	n		A°	n		
Phenols, phenolates and alkyl-phenyl ethers															
.12	$\text{C}_6\text{H}_5\text{OH} + \text{I}^+$	H_2O	$10^2 A = 2.10^3 B = 42$ 7.8 23.5 42 83 118 187 222	Cl^-	= B	k_{AB}	90 100 100 100 100 100 100 100	-7 -8 -7 -7 -7 -6 -6 -6	1.33 5.0 2.00 3.5 9.0 1.4 2.3 3.5						
.13	$\text{C}_6\text{H}_5\text{O}^- + \text{I}^+$	H_2O	7.8 42 7.8 42				110 110 120 120	-7 -8 -7 -6	1.5 1.11 3.67 2.56			5 4 8 9		*	(9)
.14	$2,6\text{-O}_2\text{-4-CH}_3\text{C}_6\text{H}_3\text{OH} + \text{H}^+$	$\text{H}_2\text{O}-\text{H}_2\text{SO}_4$	$10^2 A = 2.5 \text{ wt. \% H}_2\text{SO}_4 = 9.8$ 14.5 10.3 27.0 34.5 45.3	OH^-		k_{AB}	25 25 25 25 25 25	-8 -7 -7 -8 -6 -5	6.1 1.73 4.00 1.33 4.70 4.38					*	(5) (6)
		$\text{H}_2\text{O}-\text{HCl}$	$10^2 A = 2.5 \text{ wt. \% HCl} = 7.10$ 11.66 15.18 21.5			k_{F_A}	25 25 25 25	-7 -8 -6 -5	3.95 1.33 3.89 3.06						
.15	$\text{C}_6\text{H}_5\text{O}^- + \text{H}_2\text{O} + \text{H}^+$	$\text{H}_2\text{O}-\text{H}_2\text{SO}_4$	$10^3 A = 3.5$	H_2SO_4	5.16 5.90 6.82	k_{F_A}	25 25 25	-8 -8 -5	1.49 3.63 1.21					*	(12)

No.	Reaction	Solvent	Amount of reactants	Addend	Amount of added	Defined reaction law	Temperature	$k \times 10^n$		E	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.15	o-CH ₃ OC ₆ H ₄ + H ⁺ (continued)	H ₂ O-H ₂ SO ₄	10 ³ A=3.5	H ₂ SO ₄	7.34	kF _A	25	2.31	-5				*	(19)
		CH ₃ COOH	A ~ 0.1	H ₂ SO ₄	7.88		25	5.2	-5					
					0.550		25	1.40	-6					
					1.23		25	5.10	-6					
					2.64		25	4.50	-5					
.16	m-CH ₃ OC ₆ H ₄ + H ⁺		A ~ 3	H ₂ SO ₄	~0.3		80	2.9	-5					(14)
			(mole ratio CH ₃ COOH:A:H ₂ SO ₄ = 5:1:0.1)		~0.3		100	1.5	-4	22	1	9		
		H ₂ O-HClO ₄	10 ² A ~ 1.5	HClO ₄	10.04	kF _A	25	3.00	-7				*	(19)
.17	p-CH ₃ OC ₆ H ₄ + H ⁺				10.43		25	7.20	-7					
					11.01		25	7.24	-6					
					11.71		25	2.00	-5					
													*	(19)
		H ₂ O-H ₂ SO ₄	10 ³ A=3.5	H ₂ SO ₄	3.51	kF _A	25	2.11	-7					
					4.86		25	1.85	-8					
					5.95		25	8.8	-8					
					6.77		25	2.55	-5					
					7.59		25	8.4	-5					
		CH ₃ COOH	A ~ 0.1	F ₂ SO ₄	0.232		25	5.0	-7					
					0.632		25	3.00	-6					
					0.916		25	5.0	-6					
					1.72		25	2.30	-5					
					2.68		25	8.2	-5					
					3.52		25	2.10	-4					
					~0.3	kF _A	80	8.8	-5				*	(14)
					~0.3		100	3.0	-4	16	7	5		(20)
					1.90		25	3.10	-7					
					2.07		25	4.05	-7					
					2.68		25	8.2	-7					
					3.19		25	1.66	-6					

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Temperature	Defined rate	$k \times 10^n$		β	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.17	<i>p</i> -CH ₃ OC ₆ H ₄ S + H ⁺ (continued)	CH ₃ COOH	$10^2 A \approx 8$; [HCl]=0.05	ZnCl ₂	0.015	$k_F A$	25	3.24	-7				*	(20)
					0.040			5.8	-7					
					0.101			7.9	-7					
					0.220			7.2	-7					
					0.350			6.0	-7					
					0.650			3.71	-7					
					0.024			1.36	-6					
					0.048			2.19	-6					
					0.144			5.7	-9					
					0.290			1.05	-5					
					0.480			1.39	-5					
					1.12			1.77	-5					
					1.48			2.01	-5					
.18	<i>o</i> -CH ₃ OC ₆ H ₄ D + NH ₂ ⁻	NH ₃	$10^2 A \approx 8$	SnCl ₂	0.059		25	3.01	-7					(22)
					0.118			7.1	-7					
					0.22			1.95	-6					
					0.596			6.3	-6					
					0.879			2.11	-5					
					2.90			1.59	-3					
					0.015			3.05	-7					
					0.147			2.98	-6					
					0.732			2.25	-5					
					1.10			6.2	-5					
					B			1	-3					
					B			~1	-7					
					B			~1	-8					
.19	<i>p</i> -CH ₃ OC ₆ H ₄ D + NH ₂ ⁻	NH ₃	A=0.25-0.6; B=0.6	X ⁺	B	$k_F A$	~33							(7)
.20	<i>p</i> -CH ₃ OC ₆ H ₄ D + NH ₂ ⁻	NH ₃	A=0.25-0.6; B=0.6	X ⁺	B	$k_F A$	~33							(7)
		NH ₃	A=0.25-0.6; B=0.6	X ⁺	B	$k_F A$	~33							(7)

Homogeneous Reaction Kinetics
322.402

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rate law	Temperature, °C	$k^o \times 10^n$ k^o n	$A^o \times 10^n$ A^o n	Comments	Literature
.01	$p\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4\text{I} + \text{H}^+$	CH_3COOH	$A \sim 2.5$	H_2SO_4	~ 0.25	kF_A	100	4.0 -4			(14)
.02	$p\text{-CH}_3\text{CH}_2\text{CH}_2\text{OC}_6\text{H}_4 + \text{H}^+$	CH_3COOH	$A \sim 2.5$	H_2SO_4	~ 0.25	kF_A	100	4.0 -4			(14)
.03	$p\text{-(CH}_3)_2\text{CHOC}_6\text{H}_4 + \text{H}^+$	CH_3COOH	$A \sim 2.5$	H_2SO_4	~ 0.25	kF_A	100	7.4 -4			(14)
.04	$p\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4 + \text{H}^+$	CH_3COOH	not stated	H_2SO_4		kF_A	100	4. -4		*	(14)
.05	$2,3,4\text{-(CH}_3)_3\text{C}_6\text{H}_2 + \text{H}^+$	H_2O	$A < 0.04$	KHSO_4	0.50 1.00 2.00 2.50	kF_A	25 25 25 25	1.84 4.4 -7 1.05 -6 1.44 -6			(21)
				CHCl_2COOH	0.12 0.24 1.21 2.42 4.84 7.24 12.13		25 25 25 25 25 25 25	3.4 -9 4.8 -8 1.51 -7 2.40 -7 6.0 -7 1.10 -6 1.23 -4			
				CF_3COOH	0.99 2.16 4.04 6.73		25 25 25 25	4.8 -7 1.22 -6 5.0 -6 1.37 -5			
.06	$2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2 + \text{H}^+$	H_2O	$10^3 B = 1.3 [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COONa}]$ $\mu = 0.1$	CH_3COONa strong acid	0.01 0.025 0.05 0.1 0.05	kF_A	~ 25 ~ 25 ~ 25 ~ 25 ~ 25	2.3 -7 3.8 -7 4.5 -7 3.3 -7 4 -4		*	(13)

No.	Reaction	Solvent	Amount of reactant	Amount of added	Defined reaction law	Temperature	$k \times 10^n$ k^0 n	$A \times 10^n$ A^0 n	Comments	Literature
N-substituted benzene (NH ₂), (NR'R''), (NO ₂)										
.27	$C_6H_5NH_3^+ + H_2O$	H ₂ O	A = 0.017		kF_A	79 90 95 100	2.14 6.7 1.22 2.24	-7 -7 -6 -6	*	(12)
.28	$2-OH-5-NO_2C_6H_2-1,3-D_2 + H^+$	H ₂ O	$10^2 A = 1.9$; wt. % H ₂ SO ₄ = 64.3 70.3 71.1 78.8 81.3 82.9 87.2 92.2 97.6		kF_A	25 25 25 25 25 25 25 25 25	1.16 4.40 5.33 4.85 1.23 2.70 5.09 1.01 1.93	-7 -7 -7 -6 -5 -5 -5 -4 -4	*	(3)
.29	$\pi-C_6H_4(NO_2)_2 + ND_3$	ND ₃			kF_A	50	1.2	-6	*	(23)
.30	$p-C_6H_4(NO_2)_2 + ND_3$	ND ₃			kF_A	50	3.7	-7	*	(23)
Halogen-substituted Benzene										
.31	$2-FC_6H_4D + NH_2^-$	NH ₃	A=0.25-0.6; B=0.6	K^+	kF_A	~33	> 4	-1	*	(7)
.32	$3-FC_6H_4D + NH_2^-$	NH ₃	A=0.25-0.6; B=0.6	K^+	kF_A	~33	4	-4	*	(7)
.33	$4-FC_6H_4D + NH_2^-$	NH ₃	A=0.25-0.6; B=0.6	K^+	kF_A	~33	2	-5	*	(7)
.34	$2-F_3CC_6H_4D + NH_2^-$	NH ₃	A=0.25-0.6; B=0.6	K^+	kF_A	~33	6	-2	*	(7)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined reaction order	Temperature	$k \times 10^n$		$A \times 10^3$		Comments	Literature
								k^0	n	A^0	n		
.35	3-F ₃ CC ₆ H ₄ D + NH ₂ ⁻	NH ₃	A=0.25-0.6; B=0.6	K ⁺	= B	kF _A	~33	1	-3			*	(7)
.36	4-F ₃ CC ₆ H ₄ D + NH ₂ ⁻	NH ₃	A=0.25-0.6; B=0.6	K ⁺	= B	kF _A	~33	1	-3			*	(7)
.37	2-HO-5-ClC ₆ H ₂ -1,3-D ₂ + H ⁺	H ₂ O	10 ³ A=2.1; wt. % H ₂ SO ₄ = 40.5 47.0 53.0 59.0 63.5 wt. % H ₃ PO ₄ = 63.6 68.1 72.7 76.4			kF _A	25 25 25 25 25 25 25 25	1.57 4.73 1.59 5.32 1.59 1.17 2.67 5.6 1.48	-7 -7 -6 -6 -5 -7 -7 -7 -6			*	(3) (5)
Anthracene													
.38	9,10-D ₂ C ₁₀ H ₈ + H ⁺	H ₂ O	wt. % H ₂ SO ₄ = 84.0 85.0 85.9 87.8 90.0	CCl ₄	2x vol.	kF _A	25 25 25 25 25	5.2 1.0 1.7 4. 2.3	-4 -3 -3 -3 -2			*	(4)

COMMENTS

General: For general treatment of isotope exchange reactions see (6). In all cases where defined mass action law is given as kF_A the first order isotopic equilibration is given as the rate constant. This is calculated from the fractional exchange, X , at time, t , by the equation $k = -1/t \ln(1-X)$. The rate constant for this may in special cases be a pseudo first order rate constant for the actual exchange reaction. For example this occurs if the reverse reaction is negligible due to an unlimited supply of one isotope from the solvent. It should be noted however that such a rate law has not been confirmed as being pseudo first order so long as dependence of exchange rate upon concentration of reactant has not been determined.

Reaction: (.4) First order rate constant only for isotopic equilibration, fractional exchange. (.4.1) Calculated first order constant for rate of isotopic equilibration from relative value of (¹⁷) combined with deuterium exchange rate of (⁹). (.5) Pseudo first order rate constant for reaction as written since reverse reaction eliminated by rapid exchange between NHD^- and solvent. (.5.1) First order rate constant only for isotopic equilibration, fractional exchange. (.6) Rate constant for first order isotopic equilibration only, value in 81.8 wt. % H_2SO_4 calculated from relative rate of (¹⁷) and rate for tritium exchange (.6.1) of (¹⁹). (.6.1) Rate constant for first order isotopic equilibration only, calculated from time vs. relative activity data of authors. (.8) Rate constant for first order isotopic equilibration only. Value for 81.8 wt. % H_2SO_4 calculated from relative rate (¹⁷) with rate for tritium exchange (.8.1) of (¹⁹). (.8.1) Rate constant for first order isotopic equilibration calculated from time vs. relative activity data of authors. Simultaneous sulfonation to extent of about 5% of the exchange observed. (.9) Rate constant for first order isotopic equilibration only. (.9.1) Rate constant for first order isotopic equilibration calculated from time vs. relative activity data of authors. (.10) Isomer distribution determined by (¹⁷) and kinetic data by (¹). In absence of catalysts results erratic and first order rate constant estimated to be less than $10^{-6} \text{ sec.}^{-1}$ at 140°C . In presence of NO_2 as catalyst HCl was lost to extent of 1.5 to 2.3 times the amount of catalyst. No correction made for portion of reactants in vapor phase. The volume of vapor was from 5 to 10

times the volume of liquid. (.11) First order rate constant for isotopic equilibration. (.12) Rate law is for exchange of deuterium with ring hydrogen. Dependence of calculated rate constants upon hydrogen concentration of medium may be expressed at 100°C by:

$$\log k = 1.26 \log [\text{H}^+] - 4.68$$

or using an average activation energy of $E = 27.3$ the Arrhenius constant $A = 2.2 \times 10^{11} [\text{H}^+]^{1.26}$. (.14)

First order rate constant for isotopic equilibration. Log k observed to be linear function of Hammett's acidity function $-\text{H}_0$ with slope of 1.08 in H_2SO_4 solution and slope of 1.42 in HCl solution. (.15) First order rate constant for isotopic equilibration. (.16) First order rate constant for isotopic equilibration for less than 25% reaction due to side reactions producing precipitate and dark coloration. It was impossible to obtain isotopic exchange data in $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ medium. (.17) First order rate constant for isotopic equilibration. (.24) Concentra-

tions of reactants not stated but probably the same as (.21)(.22) and (.23). (.26) Temperature not stated but assumed to be room temperature. (.27) Rate data is only for exchange of ring hydrogen. (.28) Author's observe that $\log k$ is linear with Hammett's acidity function H_0 with a slope = 0.94 up to about 85% H_2SO_4 . Rate of sulfonation observed to be slow compared to exchange. (.29)(.30) Rate constants based on no more than one or two point determinations. (.31)(.32)(.33)(.34)(.35)(.36) Rate constant for isotope equilibration is pseudo first order rate constant for reaction as written since reverse reaction is negligible due to large excess of protons in

COMMENTS

solvent and rapid exchange between solvent and NH_4^+ .
(.37) Authors observe that $\log k$ is linear with Hammett's acidity function H_0 with slope = 0.90 in H_2SO_4 and 1.00 in the H_3PO_4 solution. (.38) Reaction carried out in two phase system of 2 volumes of CCl_4 to 1 volume of

acid solution. Concentration of A in CCl_4 layer = 0.1 M/l. Rate of stirring showed no appreciable effect. Initial rates are listed as rate of exchange increased with progress of reaction. Authors attribute this to increase in solubility of A in acid layer as parallel sulfonation proceeds.

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Homogeneous Reaction,
302.403

ISOTOPE EXCHANGE
H-D exchange on C in heterocyclic ring

Liquid phase

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

k_F under rate law indicates rate constant is for pseudo first order rate of isotope equilibration

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	pH	Defined rate law	Temperature	$t_{1/2}$	$k = k^0 \times 10^n$
1	$\text{CH}_3\text{N}^+-\text{CCH}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{N}^+-\text{CCH}_3 + \text{HOD}$  (3,4-dimethylthiazolium bromide)	H ₂ O	A = 1.1	Phosphate buffer, Br ⁻	0.02 = A	5.37	k_F	~25	1,400	5 -4
2	$\text{C}_6\text{H}_5\text{CH}_2\text{N}^+-\text{CCH}_3 + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{N}^+-\text{CCH}_3 + \text{HOD}$  (3-benzyl-4-methylthiazolium bromide)	H ₂ O	A = 1.1	Phosphate buffer, Br ⁻	0.02 = A	5.37	k_F	~25	450	1.5 -3

COMMENTS

Exchange followed spectrophotometrically in the infrared using O-D bond at 3.98 μ and Beer's law followed in the region 20-80% transmittance.

LITERATURE

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ISOTOPIC EXCHANGE

Oxygen exchange on carbon

Liquid phase

Amounts are in M/l.
Rates and rate constants are in gram atoms/l and sec.
Coded solvents at end of table.

k under rate law indicates that constant listed is the rate of the chemical process responsible for exchange ⁽¹⁶⁾.

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

No.	Supplementing 1957 No.	Reaction	Solvent (Medium)	Amount of reactant	Amount of addend	Determined by	Temperature	$k \times 10^n$ k^0 n	$k^0 \times 10^n$ k^0 n	Comments	Literature
.2		$\pi\text{-C}_4\text{H}_9\text{OH} + \text{H}_2\text{O}^{18}$	B	A=0.73	H_2SO_4	k_F	125	7 5.6 -7			(13)
.3		$\text{C}_2\text{H}_5(\text{CH}_2)_3\text{CHOH} + \text{H}_2\text{O}^{18}$	B	A=0.8-1.6	HClO_4	k_A	101 101 101 101 101 101 100 100 100 100	9.7 1.08 3.2 5.1 8.6 1.25 1.09 3.4 8.6 1.34 -5 -5 -5 -4		*	(8)
.4		$(\text{CH}_3)_3\text{COH} + \text{H}_2\text{O}^{18}$	B	A=1.04	H_2SO_4	k_F	55 55 75	1.33 1.54 1.97 -5 -4 -4			(13)
.5		$(\text{CH}_3)_3\text{CCH}_2\text{OH} + \text{H}_2\text{O}^{18}$	B	A=0.242	H_2SO_4	k_A	125	1.4 -8	30		(12)

No.	Supplementing No. 1951	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined rate law	Temperature	$k \times 10^n$ k° n	k	$A \times 10^n$ A° n	Comments	Literature
.6		$C_6H_5(CH_3)CHOH + H_2O^{18}$	B	not stated	HClO ₄	.07-.08	$kA[H^+]$	30 54	1.07 3.3 -4		3 15	*	(14)
.7		$(CH_3)_2C(OH)C(CH_3)_2OH + H_2O^{18}$	B	A~1	H ₂ SO ₄	0.05 1.6 2.1 5.35	kF_g	73 73 73 73	9 6 -5 7 -5 5 -4				(7)
.8		$4-CH_3OC_6H_4(C_6H_5)CHO^{18} + H_2O$	DI 60*	A~0.1; B~22	HClO ₄	0.101 0.265 0.394 0.936 0.35 0.63	kA	25 25 25 25 25 25	8 3.8 -4 7.5 -4 1.04 -3 1.2 -3 6.7 -3			*	(10)
Carbonyl oxygen													
.9		$CH_2OH(CHCH_3)_4CHO^{18} + H_2O$	B	A~1.1	buffers	pH=7.0 7.0 7.0 8.1 8.5 6.0 5.0 3.4 2.6 2.1 1.5	kF_g	40 50 61 61 61 61 61 61 61 61	1.0 2.8 -5 1.03 -4 2.3 -4 8.2 -5 4.4 -5 1.88 -5 1.92 -5 2.5 -5 1.05 -4 2.9 -4	23 2 11	*	(17)	

No.	Supplementing 1951 No.	Reaction	(S.D.P.) 1951 No.	Amount of reactant	Addend	Amount of addend	Defined rate law	Temperature	$k \times 10^n$	k^0	n	$A = 10^n$	Comments	Literature
.20		$C_6H_5CO^{18}OCH(CH_3)_2 + OH^-$	H ₂ O D: 33*	$10^{-3} A = 10^{-3} B = 1-7$	Na ⁺	= B	k _{AB}	25 62	2.3 4.9	-3 -3			*	(1)
.21		$C_6H_5CO^{18}OC(CH_3)_3 + OH^-$	D: 33*	$10^{-3} A = 10^{-3} B = 1-7$	Na ⁺	= B	k _{AB}	62	1.7	-4			*	(1)
.22		$C_6H_5CH_2CH_2CO^{18}OCH_3 + OH^-$	M: 20*	$10^{-3} A = 10^{-3} B \sim 5$	Na ⁺	= B	k _{AB}	25	1.46	-3			*	(4)
.23		$C_6H_5CH_2CH_2CO^{18}OC_2H_5 + OH^-$	M: 30*	$10^{-3} A = 10^{-3} B \sim 5$	Na ⁺	= B	k _{AB}	25	8.5	-4			*	(4)
.24		2, 4, 6-(CH ₃) ₃ C ₆ H ₂ COOCH ₃ + H ₂ O ¹⁸	D: 60*	$10^{-2} A = 2$	Cu ⁺⁺ buffer, pH=7.3	0.0774	k _A	128	1.5	-2			*	(2)
.25		$C_6H_5CH_2CHNH_2CO^{18}OC_2H_5 + H_2O$	B	$10^{-2} A = 1.5$			k _A	25	7	-4			*	(6)
.26		$C_6H_5CH_2CH(NHCOOC_6H_5)CO^{18}OC_2H_5 + OH^-$	M: 50*	$10^{-2} A = 10^{-3} B \sim 3$	Na ⁺	= B	k _{AB}	25	0.0	-2			*	(4)
Oxygen of amide														
.27		$C_6H_5CO^{18}NH_2 + OH^-$	H ₂ O	A=B=0.1	Na ⁺	= B	k _{AB}	41 80 109	7.6 1.87 1.28	-5 -3 -2			*	(3)
CODED SOLVENTS														
D: 33* (40), (60) Dioxane volume % indicated + H ₂ O														
M: 20* (30), (50) Methanol volume % indicated + H ₂ O														

COMMENTS

General. For general treatment of isotope exchange reactions see (19). In all cases where defined mass action law is given as kF_x the pseudo first order isotopic equilibrium constant is given as the rate constant. This is calculated from the fractional exchange, X , at time, t , using the equation $k = -1/t \ln(1-X)$. In cases where the reverse exchange is negligible due to a large excess of one isotopic species this might be equal to a first order rate constant for the reaction but this is not verified unless exchange dependence on reactant concentration has been determined. In most 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 R , where R is the rate of the chemical process responsible for exchange, see (19).

Reaction. (3) Selected values. (9) Labeled oxygen in either A or B, also observed that racemization reaction twice as fast as exchange. (9) plotted $\log k$ vs. $-\text{H}_0$, Hammett's acidity function and obtained a straight line with slope of 1, at $[\text{HClO}_4] > 0.6$. (6) Rate constant for exchange reaction about 20% smaller than rate constant for racemization reaction corrected for simultaneous elimination reaction. (8) Rate law with respect to A not verified as $[A]$ constant. Rate of exchange and rate of racemization essentially the same. (9) Buffers used were barbiturate, phosphate, acetate, phthalate, HCl-KCl , and oxalic acid. (10) Selected data. Second order rate

law not confirmed as concentrations of A and B not varied. Rate constant expressed by authors in terms of catalytic constants, $k = k_a [\text{acid}] + k_b [\text{base}] + k_g [\text{H}^+]$, where $k_a = 1.14 \times 10^{-3}$, $k_b = 2.5 \times 10^{-6}$, $k_g = 1.95$. Reaction found to be too sensitive to catalysis by both H^+ and OH^- to measure directly in absence of a buffer. (11) Rate law calculated from only three observed points is based on calculated concentrations of species indicated not on total stoichiometric concentrations. (12) Addition of 0.09 N KCl caused no significant change in rate. Either reactant labeled initially. (13)(14)(15)(16)(17) Rate law with respect to H^+ not confirmed experimentally but assumed by (9). (18) Rate constant calculated from pseudo first order rate constant of simultaneous hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally. (19)(20)(21)(22)(23) Rate constant calculated from second order rate constant of simultaneous alkaline hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally. Authors use data to calculate rate constants for intermediate steps in their proposed mechanism of hydrolysis and exchange. (24)(25) Rate constant calculated from pseudo first order rate constant of simultaneous hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally. (26)(27) Rate constant calculated from second order rate constant of simultaneous alkaline hydrolysis reaction and ratio of hydrolysis rate constant to exchange rate constant determined experimentally.

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ISOTOPIC EXCHANGE
Sulfur exchange between disulfide and thiol

Liquid phase

Amounts are in M/l.
Rate constants are
in gram atoms/l and
sec.
Coded so 'vents at
end of table.

R under rate law indicates that constant listed is the rate of the chemical process responsible for exchange (2)

No.	Reaction	Solvent (Mol %)	Amount of reactant	Adding	Amount of addend	Defined mass- action law	Temperature	$k \times 10^n$ k^0 n	g	$A \times 10^n$ A^0 n	Comments	Temperature
.1	$(n-C_4H_9S^*)_2 + n-C_4H_9SH$	BW6*	A = B = 0.01 $10^2 A = 1.5-6$ $10^2 B = 1-8$	NaOH	0.008 .005-.01	$k_A[OH^-]$	25 0 15 25 35	$t_1 = 2 \times 10^6$ 3.8 1.5 3.1 6.7	-2 -1 -1 -1	7 9	*	(1)
.2	$[(CH_3)_3CS^*]_2 + (CH_3)_3CSH$	MW12*	A = B = 0.0375	NaOH	0.0062	$k_A[OH^-]$	0 15 25 35	2.9 1.2 2.6 5.8	-2 -1 -1 -1	1 10	*	(1)
.3	$(n-C_6H_{13}S^*)_2 + n-C_6H_{13}SH$	MW12*	A = B = 0.061	NaOH	0.010	R $k_A[(CH_3)_3CS^-]$ $k_A[OH^-]$	85 95 100 105 25	2.0 4.5 6.7 9.3 1	-7 -7 -7 -7 -7	22	*	(1)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Definer mass-action law	Temperature	$k \times 10^2$	k^0	n	$A^0 \times 10^2$	A^0	n	Comments	Literature
4	$(C_2H_5S^*)_2 + C_2H_5SH$	MW 12*	A = B = 0.0375	NaOH	$kA[OH^-]$	0 15 25 35	4.6 2.0 4.9 1.3	-2 -1 -1 0						(1)

CODED SOLVENTS

BW6* $n-C_4H_9OH + H_2O$ (86)MW12* $CH_3OH + H_2O$ (128)

COMMENTS

General: For general treatment of isotopic exchange reactions see (2).

Reaction: (1) Rate law verified by variation of concentrations of A, B and NaOH. Rate constants calculated by dividing exchange rate, $R = -\frac{1}{t} \frac{A \times B}{A+B} \ln(1-X)$, by A and B represent concentrations of reactants and X is fractional extent of exchange at time t. Authors suggest mechanism involves direct reaction of thiol ion rather than catalysis by OH^- . Since $[OH^-] < B$ the $[OH^-] \approx [n-C_4H_9S^-]$. (2) Rate constant not calculated from R since $[OH^-] > B$ and authors do not give sufficient proof of rate law to validate such a calculation. Value of rate constant listed was extrapolated to 25° by authors and at best only gives order of magnitude.

LITERATURE

- (1) A. Fava, A. Illiceto, E. Camera, *ACS* 1957, 79, 833. (2) G.M. Harris, *TFS* 1951, 47, 718.

No.	Reaction	Solvent	Amount of reactant	Defining reaction	Temperature	$k \times 10^n$		$A \times 10^{12}$		$\Delta S^\ddagger$
						k^0	n	A^0	n	
1	$\text{SnCl}_2 + \text{Sn}^*\text{Cl}_4 \longrightarrow \text{Sn}^*\text{Cl}_2 + \text{SnCl}_4$	$\text{C}_2\text{H}_5\text{OH}$	$10^2 A = 2-10; 10^2 B = 2-20$	kAB	25 29 36 42	6.0 1.04 2.31 5.3	-5 -4 -4 -4	1	13	+16

COMMENTS

Reaction homogeneous as addition of glass wool and pyrex helices did not effect rate.

LITERATURE

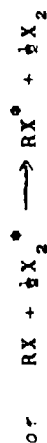
E.G. Meyer, M. Kahn, *ACS* 1951, 73, 4950.

ISOTOPE EXCHANGE

Halogen for halogen, in organic compounds

Liquid phase

Reaction types:



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

A = concentration of A + L and B = analytical concentration of B + M unless stated otherwise

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$k = 10^n$ k^0 n	$A = 10^n$ A^0 n	Comments	Literature
Saturated Alkyl Halide												
.19		$CH_3Cl + Cl^{\bullet-}$	$(CH_3)_2CO$	$A \sim 0.3; B \sim 0.03$	Li^+	= B	k AB	-3 25 45	1.09 3.88 3.18	-6 -5 -4	2 10 20.1	(2)
.20		$CH_3Br + Br^{\bullet-}$	$(CH_3)_2CO$	$A = 0.15-0.2$ $B = 0.024$	Li^+	= B	k AB	-31 -25 -18 -11	2.68 6.30 1.46 3.40	-4 -4 -3 -3		(3)
.21		$C_2H_5Cl + Cl^{\bullet-}$	$(CH_3)_2CO$	$A \sim 0.2; B \sim 0.03$	Li^+	= B	k AB	25 40 60	5.5 3.09 2.40	-7 -6 -5	5 10 21.5	(2)
.22		$C_2H_5Br + Br^{\bullet-}$	$(CH_3)_2CO$	$A \sim 0.2; B = 0.024$	Li^+	= B	k AB	-11 0 8	2.89 1.08 2.78	-5 -4 -4	3 9	(3)

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Optimum solvent	Temperature	k = k° × 10 ⁿ	log k°	A = A° × 10 ⁿ	Comments	Literature
.22		C ₂ H ₅ Br + Br ^{••} (continued)	(CH ₃) ₂ CO	A ≈ 0.2 B = 0.024	Li ⁺	= B	k _{AB}	16 25	6.62 1.70	17.5	1.3 10	*	(³)
.23	.1	C ₂ H ₅ I + I ^{••}	CH ₃ OH C ₂ H ₅ OH	A = 0.04; 10 ⁴ B = 2-70 A = 0.9; B = 0.14 0.9-4 0.017 0.030 0.075 0.15 0.8 1.5 0.9 0.14 0.14 A = 0.02 B = 0.017	Na ⁺	= B	k _{AB}	25	8.0			*	(⁷) (⁸)
.24		n-C ₃ H ₇ Cl + Cl ^{••}	(CH ₃) ₂ CO (CH ₃) ₂ CO + 20% CH ₃ NO ₂	A ≈ 0.3 B = 0.10 A ≈ 0.1; B ≈ 0.03	Li ⁺	= B	k _{AB}	60 44 44	2.07 1.23 4.80	21.3	7 11	*	(²⁰)
.25		(CH ₃) ₂ CHCl + Cl ^{••}	(CH ₃) ₂ CO	A = 0.2 B = 0.028	Li ⁺	= B	k _{AB}	60	4.55	17.4	3 11	*	(⁴)
.26	.5	n-C ₃ H ₇ Br + Br ^{••}	H ₂ O	A = B = 0.1	Na ⁺	= B	k _{AB}	35 41 79 100	2.13 2.13 8.4 3.6	18		*	(²²)

Homogeneous Reaction Kinetics

302.477

A = concentration of A + L and B = analytical concentration of B + M

No.	Applying equation	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	B	$A \times 10^n$ A^0 n	Comments	Literature
20	3	$n\text{-C}_3\text{H}_7\text{Br} + \text{Br}^{*-}$ (continued)	$(\text{CH}_3)_2\text{CO}$	$A = 0.16; B = 0.024$	Li^+	$= B$	k_{AB}	-7 15 25 31	3.30 4.10 1.08 1.91	-5 -4 -3 -3	6	*	(3) (5) (3)
21	4	$(\text{CH}_3)_2\text{CHBr} + \text{Br}^{*-}$	CH_3NO_2 $(\text{CH}_3)_2\text{CO}$	$B = 0.024$ $A = 0.2; B = 0.024$	$(\text{C}_2\text{H}_5)_4\text{N}^+$ Li^+	$= B$ $= B$	k_{AB} k_{AB}	25 35 42 50 58 58 58 55	2.4 5.07 1.05 2.48 5.30 4.87 3.6 9.74	-4 -5 -4 -4 -4 -4 -4 -4	9	*	(5) (3)
22	7	$n\text{-C}_3\text{H}_7\text{I} + \text{I}^{*-}$	$(\text{CH}_3)_2\text{CO}$	$A = 0.4; 10^3 B = 5-50$ (α = degree of dissociation of LiBr)			k/α_{AB}	20 40 60	4.86 4.43 2.95	-5 -4 -3	10	*	(16)
23	8	$(\text{CH}_3)_2\text{CHI} + \text{I}^{*-}$	$\text{C}_2\text{H}_5\text{OH}$	$A = 0.75; B = 0.14$ 0.02 0.017 0.75 0.14 0.02 0.017	Na^+	$= B$	k_{AB}	35 45 50 55 60 70	3.7 9.4 1.95 2.35 5.33 1.36	-4 -4 -3 -3 -3 -2	11	*	(21) (28) (21) (28)
24	9	$(\text{CH}_3)_2\text{CHI} + \text{I}^{*-}$	$\text{C}_2\text{H}_5\text{OH}$	$A = 0.02; B = 0.017$	Na^+	$= B$	k_{AB}	45 60 70	5.6 3.42 9.6	-5 -4 -4	12	*	(28)

A = concentration of A + L and B = analytical concentration of B + M

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined as	Temperature	$k = k^0 \times 10^n$	k^0	n	R	$A = A^0 \times 10^n$	Comments	Literature
.29	.9	$(\text{CH}_3)_2\text{CHI} + \text{I}^{*-}$ (continued)	$\text{C}_2\text{H}_5\text{OH}$	A = 1.62; B = 0.14	Na^+	= B	k AB	45 55 60 70 70 25	6.4 1.04 2.6 7.0 2.93 5.87	-5 -4 -4 -4 -5 -4		20.5 19.4	7 1 9 11	*	(21)
.30		$\text{C}_2\text{H}_5(\text{CH}_3)\text{CHCl} + \text{SnCl}_4^*$	$(\text{CH}_3)_2\text{CO}$	A = 0.12; B = 0.1	Na^+	= B								*	(4)
.31	.10	$\text{C}_2\text{H}_5(\text{CH}_3)\text{CHCl} + \text{SnCl}_4^*$	$n\text{-C}_7\text{H}_{16}$	A = 0.06-0.47; B = 0.008-0.065		k AB/(K + A)		160 200 160	3.8 ~1 K = 1.5	-6 -4 -1				*	(13)
.32		$n\text{-C}_4\text{H}_9\text{Br} + \text{Br}^{*-}$	$(\text{CH}_3)_2\text{CO}$	A = 0.04; $10^4\text{B} = 0.5$ 2.5 17.1 79 191	Li^+	= B	k AB	26 26 26 26 26	3.93 3.13 2.56 1.44 1.07	-3 -3 -3 -3 -3				*	(7)(8)
.33		$(\text{CH}_3)_2\text{CHCH}_2\text{Br} + \text{Br}^{*-}$	$(\text{CH}_3)_2\text{CO}$	A = 0.14-0.17; B = 0.024	Li^+	= B	k AB	25 33 42 50 56	5.82 1.40 3.43 7.04 1.44	-5 -4 -4 -4 -3		18.9	4 9	*	(3)
.35	.13	$(\text{CH}_3)_3\text{CBr} + \text{Br}^{*-}$	$(\text{CH}_3)_2\text{CO}$	A = 0.16; B = 0.024	Li^+	= B	k AB	25 40 49 60 71 79	5.28 3.03 8.48 2.58 7.35 1.48	-6 -5 -5 -4 -4 -3		21.8	5 10	*	(3)(5) (3)

HOMOGENEOUS Reaction Kinetics

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A = concentration of A + I, and B = analytical concentration of B + M

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No.	Supplementing 1951 No.	Reaction.	Solvent	Amount of reactant	Addend	Amount of addend	Defined bases	Temperature	$k^0 \times 10^n$	β	$A^0 \times 10^n$	Comments	Literature
33	13	$(CH_3)_3CBr + Br^{\cdot-}$ (continued)	H_2O	A = 0.07; B = 0.05	Li^+	= B	k_{AB}	25	4.06			*	(3)
								35	1.50				
								44	3.99				
								60	1.91				
				A = 0.1;			$k_1 A^+$ $k_2 AB$	20	$k_1 3.6$				(15)
				B = 0.005-0.1				20	$k_2 5.5$				
								40	$k_1 3.2$				
								40	$k_2 6.05$				
								80	$k_1 2.0$	19.7	1.6		
								80	$k_2 4.87$	21.8	1.0		
34		$n-C_4H_9I + I^{\cdot-}$	CH_3NO_2	A = 0.05; B = 0.023	$(C_2H_5)_4N^+$	= C	k_A	22	2.98			*	(5)
				0.012				41	2.62				
				0.024				41	2.53				
				0.048				41	2.88				
				0.022				50	6.54	20.6	6		
		$n-C_4H_9I + I^{\cdot-}$	C_2H_5OH	A = 0.6; B = 0.14	Na^+	= B	k_{AB}	30	1.65			*	(21)
								40	4.4				
								50	1.09				
								60	2.85	19			
								0	1.9				
								14	1.0				
								29	4.8				
								29	4.4				
								48	3.0	18.2			
								0	1.8				
		$n-C_4H_9I + I^{\cdot-}$	CH_3CN	A = 0.05; B = 0.01	Li^+	= B	k_{AB}					*	(11)
				0.05									
				0.05									
				0.025									
		$n-C_4H_9I + I^{\cdot-}$	CH_3CN	0.024	Na^+	= B	k_{AB}					*	(11)
				0.02-0.3									
				0.05									
				0.25									

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Homogeneous Reaction Kinetics

RD-477

λ = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass	Temperature	$k \times 10^n$		δ	$A = A^0 \times 10^n$		Comments	Literature	
								k^0	n		A^0	n			
.35	$n\text{-C}_4\text{H}_9\text{I} + \text{HJ}^*$ (continued)	$\text{C}_6\text{H}_5\text{OH}$	A = 0.1-0.6; B = 0.10			k AB	0	7.22	-8				*	(10)	
			0.10				25	1.56	-4						
			0.079				36	5.20	-4						
			0.17				36	5.17	-4						
			0.079				49	1.71	-3	19.4	1.0	14			
		$\text{C}_6\text{H}_{13}\text{OH}$	A = 0.2-0.8; B = 0.10			0	7.67	-6							
			0.025			25	1.01	-4							
			0.10			25	1.34	-4							
			0.34			25	1.50	-4							
			0.69			25	1.53	-4							
		$\text{C}_{12}\text{H}_{25}\text{OH}$	0.044			36	4.30	-4							
			0.12			36	4.58	-4							
CH_3COOH	A = 1.0; B = 0.012			49	1.29	-3	19.4	2	13						
	0.080			25	4.93	-5									
	0.125			25	6.90	-5									
	0.251			25	8.86	-5									
	0.318			25	9.70	-5									
	A = 1.0; B = 0.082			25	1.07	-4									
	"			0	1.19	-6									

A = concentration of A + I and B = analytical concentration of B + M

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature $k^0 \times 10^n$	$k = k^0 \times 10^n$	E	$A = A^0 \times 10^n$	Comments	Literature
.36	$n\text{-C}_4\text{H}_9\text{I} + \frac{1}{2}\text{I}_2^*$	CH_3CN	A = 0.09; B = 0.02 0.09 0.02 0.09 0.02 0.04-0.09 0.02-0.04			k_{AB}	70 5.70 81 1.25 100 5.14 122 1.94	-5 -4 -4 -3	17.5			(14)
.37	$(\text{CH}_3)_2\text{CHCH}_2\text{I} + \text{I}^*$	$\text{C}_2\text{H}_5\text{OH}$	A = 1.4; B = 0.14	NE^+	= B	k_{AB}	40 5.9 50 1.80 60 3.5 70 8.5	-5 -4 -4 -4	19		*	(21)
.38	$\text{C}_2\text{H}_5(\text{CH}_2)_3\text{CHI} + \text{I}^*$	$\text{C}_2\text{H}_5\text{OH}$	A = 1.4; B = 0.14	Na^+	= B	k_{AB}	45 7.0 50 1.22 60 3.2 70 8.8	-5 -4 -4 -4	20.5		*	(21)
.39	$(\text{CH}_3)_3\text{CI} + \text{I}^*$	$\text{C}_2\text{H}_5\text{OH}$ $(\text{CH}_3)_2\text{CO}$	A = 1.2; B = 0.37 0.2 0.10 0.1-0.5 0.10 0.1 0.10	Na^+ Na^+	= B = B	k_{AB}	40 9.4 0 6.30 25 1.82 45 1.58	-4 -6 -4 -3	21.5	1.0 12	*	(21) (4)
.40	$(\text{CH}_3)_2\text{CHOHBr} + \text{Br}^*$	$(\text{CH}_3)_2\text{CO}$	A = 0.2; B = 0.024	Li^+	= B	k_{AB}	69 1.88 105 7.10 116 1.61 124 2.80 135 5.69	-5 -5 -4 -4 -4	22.0	4 8	*	(2)
.41	$n\text{-C}_6\text{H}_{11}\text{I} + \text{I}^*$	$\text{C}_2\text{H}_5\text{OH}$	A = 0.6; B = 0.14	Na^+	= B	k_{AB}	40 5.3 50 1.32 60 3.56	-4 -3 -3	19			(21)

Homogeneous Reaction Kinetics

302.477

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Corrected rate	Temperature	$k \times 10^n$		R	$A = A^0 \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.42	$(CH_3)_2CHCH_2CH_2I + I^{*-}$	C_2H_5OH	A = 0.7; B = 0.14	Na^+	= B	k AB	50	5.7	-4					(21)
.43	$(CH_3)_3CCH_2I + I^{*-}$	$(CH_3)_2CO$	A = 0.2; B = 0.10	Na^+	= B	k AB	35 45 65	4.48 1.13 9.08	-6 -5 -5				*	(4)
.44	$CH_2CH_2CH_2CH_2CH_2CH_2Br + Br^{*-}$	$(CH_3CO)_2CH_2$	A = 0.05; B = 0.035	Li^+	= B	k AB	90 100 111 122	1.23 2.87 6.13 1.19	-4 -4 -4 -3	22.0	1.6	10	*	(34)
.45	$C_8H_{11}(CH_3)CHI + I^{*-}$	C_2H_5OH	$10^2 A = 4-5; 10^4 B = 2.61$	Li^+	= D	k AB	25	7.7	-6	21.8	8	10	*	(36)
.46	$C_8H_{13}(CH_3)CHBr + Br^{*-}$	$(CH_3)_2CO$	3.02 6.61 15.7 78.0 150 250 700 1400			k AB	66 66 66 66 66 66 66 66	7.21 7.05 4.94 4.15 2.34 1.53 1.32 8.3 7.7 1.10	-3 -3 -3 -3 -3 -3 -3 -4 -4 -2				*	(7)
			$10^4 B = 2-1400$			k'/α AB	66							(α = degree of dissociation of LiBr)
Cyclo-Alkyl halides														
.47	$cyclo-C_8H_9I + I^{*-}$	C_2H_5OH	A = 0.2-0.5; B = 0.1-0.4			k AB	25 37	(8.8) 3.2	-8 -5				*	(26)

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Refined mass	Temperature	$k \times 10^n$		δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
47	cyclo-C ₆ H ₉ I + I ⁻ (continued)	C ₂ H ₅ OH	A = 0.2-0.5; B = 0.1-0.4			k AB	47	9.0	-5				*	(36)
							58	2.49	-4					
							64	4.73	-4	21.0	2	10		
48	cyclo-C ₆ H ₁₁ I + I ⁻	C ₂ H ₅ OH	A = B = 0.30			k AB	69	2.3	-7					(36)
							80	6.2	-7					
							90	2.12	-6					
							100	5.12	-6	25.6	5	11		
49	cyclo-C ₇ H ₁₃ I + I ⁻	C ₂ H ₅ OH				k AB	25	(1.2)	-5	21.3	5	10	*	(36)
50	cyclo-C ₈ H ₁₅ I + I ⁻	C ₂ H ₅ OH				k AB	25	(2.8)	-6	22.0	4	10	*	(36)
51	bicyclo-C ₁₀ H ₁₇ Cl + HCl* (camphene hydrochloride)	CHCl ₃	A = 0.16; B = 0.1-0.16			k AB	0	1.5	-3				*	(23)
52	bicyclo-C ₁₀ H ₁₇ Cl + DCl* (camphene hydrochloride)	CHCl ₃	A = 0.16; B = 0.02-0.1			k AB	0	1.4	-3				*	(23)
53	cyclo-C ₁₅ H ₂₉ I + I ⁻	C ₂ H ₅ OH				k AB	25	(9.0)	-7	20.1	6	8	*	(36)
Carboxyl-substituted alkyl halides														
54	C ₂ H ₅ COOH + I ⁻	H ₂ O	10 ³ A = 2-9; 10 ³ B = 2-30	H ₂ O ₄	0.005-0.01	k AB	25	8.7	-3					(32)
							60	1.49	-1	16	5	9		
55	CH ₃ COOH + I ⁻	H ₂ O				k AB	25	5	-4					(32)
56	CH ₃ COOH + I ₃ ⁻	H ₂ O	10 ³ A = 9; 10 ³ B = 1.5-3	I ⁻	0.0046-B	k AB	25	< 8	-3					(32)

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1. Concentration of A, B, and E = analytical concentration of B + A

Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Conc. of bases	Temperature	$k \times 10^3$		$k^0 \times 10^3$		F	$A^0 \times 10^2$		Comments	Literature
							k^0	n	k^0	n		A^0	n		
1.1	H_2O	$10^2 A = 7-200$ $10^2 B = 6-400$	(dark)		k AB	0	7.7	-4						*	(24) (29)
1.2	H_2O	$10^2 A = 3-100$			k AB	25	5	+6						*	(30)
1.3	H_2O	$A \approx 0.1; B \approx 0.03$	Li^+	= B	k AB	44	1.49	-4						*	(37)
1.4	CH_3OH	$A \approx 0.1; B \approx 0.03$	Li^+	= B	k AB	44	1.82	-6						*	(37)
1.5	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	-33	3.49	-4						*	(6)
1.6	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	-27	7.13	-4						*	(6)
1.7	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	-19	1.98	-3			14.7	2	9	*	(37)
1.8	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	-6	3.44	-5						*	(6)
1.9	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	16	3.67	-4						*	(6)
1.10	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	25	8.66	-4						*	(6)
1.11	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	30	1.42	-3			16.5	1.1	9	*	(37)
1.12	CH_3OH	$A \approx 0.1; B \approx 0.04$	Li^+	= B	k AB	44	1.25	-3						*	(37)
Unsaturated alkynyl halides															
2.1	CH_3OH	$A \approx 0.1; B \approx 0.03$	Li^+	= B	k AB	44	8.57	-5						*	(37)
Unsaturated alkenyl di-halides															
3.1	CH_3OH	$A \approx 0.1; B \approx 0.01$			k AB	30	7.5	-6						*	(31)

Heterogeneous Reaction Kinetics

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A = concentration of A; B = analytical concentration of B + X

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No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$R = R^0 \times 10^n$	$A = A^0 \times 10^n$	Comments	Literature
101		cis-9- <i>trans</i> -E-CH:CH: + H ₂ ³ (continued)	CCl ₄	A = 0.17; B = 0.01			k AB ¹	36 45	1.50 4.4	1 11	*	(31)
102		cis-10-CH:CH: + I ₂ ⁴	decalin	10 ³ A = 5-70; 10 ³ B = 3-13	decalin		k AB ¹	78 100	1.2 1.25	4 9	*	(24a)
103	10	<i>trans</i> -10-CH:CH: + I ₂ ⁴	decalin	10 ³ A = 5-70; 10 ³ B = 3-13 A = 0.1; 10 ³ B = 3.5			k AB ¹	100	1.0	9	*	(24a)
104		<i>trans</i> -10-CH:CH: + I ₂ ⁴	C ₆ H ₁₄	10 ⁴ B = 3.3 10 ⁵ B = 3.5	H ₂ O	trace		25 25 25	9.3 1.6 4	-9 -8 -8	*	(40)
105		<i>trans</i> -10-CH:CH: + I ₂ ⁴	C ₆ H ₁₄	A = 0.02-0.2; 10 ⁶ [I ₂] = 3.5			k AB	25	2.8	4 9	*	(28)

Aryl-substituted alkyl halide

106		C ₆ H ₅ CH ₂ Br + Br ⁻	(CH ₃ COOCH ₂) ₂	A = 0.05; B = 0.03	Li ⁺	= B	k AB	6 17 25 35 45	1.21 3.38 7.89 1.68 3.64	-4 -4 -4 -3 -3		(34)
107		C ₆ H ₅ CH ₂ I + I ⁻	CH ₃ OH C ₂ H ₅ OH	10 ³ A = 1-10; 10 ³ B = 1-10 10 ³ A = 1-14; 10 ⁴ B = 8-170	K ⁺ K ⁺	= B = B	k AB	0 27 44 0 27 44	1.0 1.5 6.4 1.65 2.87 1.40	-3 -2 -2 -4 -3 -2	*	(32)

Heterogeneous Reaction Kinetics

700.47

A = concentration of A + B and B = analytical concentration of B + M

14

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$k \times 10^n$		β	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
100	$C_6H_5CH_2Br + Li^+$	$CH_3COOCH_2CH_3$	$10^4 A = 1-1500$ $10^6 B = 3-5000$			$k_{AB}^{\dagger}$	60	2.15	-5				*	(9)
							70	6.30	-5					
							80	2.00	-4					
							90	5.41	-4	28.1	3	12		
101	$C_6H_5CH_2CH_2CH_2Br + Br^-$	$(CH_3COOCH_2CH_3)_2$	$A = 0.05$; $B = 0.03$	Li^+	$= B$	k_{AB}	-5	3.14	-4				*	(34)
							5	8.33	-4					
							15	2.00	-3					
							25	4.52	-3	13.9	5	7		
102	$C_6H_5CH_2CH_2CH_2Br + Br^-$	$(CH_3COOCH_2CH_3)_2$	$A = 0.05$; $B = 0.03$	Li^+	$= B$	k_{AB}	-7	2.29	-4				*	(34)
							5	9.47	-4					
							15	2.71	-3					
							25	7.59	-3	18.6	1.0	10		
103	$C_6H_5CH_2CH_2CH_2Br + Br^-$	$CH_3COOCH_2CH_3$	$A = 0.05$; $10^4 B = 1.2$ 6.0 21 104 390 1.2 4.9 12 102 313	Li^+	$= B$	k_{AB}	0	8.98	-3				*	(1)
							0	8.18	-3					
							0	5.82	-3					
							0	4.33	-3					
							0	1.98	-3					
							30	2.23	-1					
							30	1.60	-1					
							30	1.34	-1					
							30	9.57	-2					
							30	7.5	-2					
							30	1.01	-2					
						$k = k/\alpha$	0	2.21	-1	18	1	11	*	(34)
			$(\alpha = \text{calculated degree of dissociation of } LiBr)$				30	4.57	-4					
			$10^4 A = 1-10$; $10^2 B = 1-10$	Li^+	$= B$	k_{AB}	-5	7.58	-4					
							0	2.45	-3					
							11	5.41	-3	15.4	1.0	9		

Heterogeneous Reaction Kinetics

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A = concentration of A + B and B = analytical concentration of B + M

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$k \times 10^n$		δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
181	$n\text{-C}_2\text{H}_5\text{MgI} + \text{I}^{\bullet-}$	CH_3OH	$10^4 A = 5-30; 10^4 B = 4-30$	I^+	$= B$	k_{AB}	0	2.2	-3				*	(27)
							20	1.5	-2					
		$\text{C}_2\text{H}_5\text{OH}$					31	4.0	-2	15.6	3	9		
							0	6.0	-3					
							20	5.0	-2					
							21	1.32	-1	16.5	9	10		
182	$\text{C}_6\text{H}_5\text{MgBr} + \text{Br}^{\bullet-}$	$(\text{CH}_3\text{COOCH}_2)_2$	$A = 0.05; B = 0.03$	Li^+	$= B$	k_{AB}	-27	3.10	-4				*	(34)
							-20	8.16	-4					
							-7	4.20	-3	16.4	1.2	11		
183	$(\text{C}_6\text{H}_5)_3\text{COI} + (\text{C}_6\text{H}_5)_2(\text{CH}_3)_2\text{N}^{\bullet+}$	C_6H_6	$A = 0.03; 10^4 B = 6-70$			k_A	56	3.2	-5					(30)
							50	7.9	-5					
							50	1.3	-5	$\Delta H^\ddagger \Delta S^\ddagger$				
							68	2.34	-4	12.4	-30			
							50	$k' = 9.9$	+3					
							50	$k'' = 1.05$	-1					
			$10^3 B > 7$											
			$10^3 B < 7$											
Aryl halides														
184	$\text{C}_6\text{H}_5\text{I} + \text{I}^{\bullet-}$	CH_3CN	$A = 0.74; B = 0.041$			k_A	157	5.0	-10				*	(14)
			0.74				157	1.0	-3					
			0.33				157	2.8	-9					
			0.72				185	8.1	-3					
			0.72				185	5.6	-9					
			0.32				185	6.9	-9					
			0.69				207	2.2	-8					
			0.69				207	3.1	-8					
			0.31				207	2.4	-8					

A = concentration of A + L and B = analytical concentration of B + M

18

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Order of reaction	Temperature		$k = k^0 \times 10^n$		k^0		n		$A = A^0 \times 10^n$		Reference
84	$\text{C}_6\text{H}_5\text{I} + \text{I}^{\bullet-}$ (continued)	CH_3CN	A = 0.66; B = 0.037	Na^+	= B	R A	238	238	2.5	-7							(14)
			0.66 0.074				236	236	3.0	-7							*
			0.39 0.147				238	238	1.4	-7							*
			A = 0.07; B = 0.010				240	240	1.9	-8							(20)
85	$p\text{-HOC}_6\text{H}_4\text{I} + \text{I}^{\bullet-}$	$\text{C}_6\text{H}_5\text{OH}$	0.030	Na^+	= B	R A	240	240	1.7	-8							(18)
			0.040				240	240	1.4	-5							
			0.10				240	240	1.0	-8							
			A = 0.02; B = 0.018				192	192	4.0	-6							
			0.01-0.02 0.01-0.1				230	230	7.5	-8							
			0.02 0.018				215	215	1.5	-5							
86	$o\text{-NO}_2\text{C}_6\text{H}_4\text{I} + \text{I}^{\bullet-}$	CH_3CN	0.02 0.02			R AB	231	231	4.2	-5							(14)
			0.04 0.04				231	231	3.6	-5							
			0.1				231	231	3.4	-5							
			A = 0.18; B = 0.04				100	100	1.3	-8							
			0.18 0.05				100	100	7.2	-7							
			0.04 0.18				100	100	1	-7							
			0.04 0.16				157	157	6.4	-6							
			0.08 0.33				157	157	5.0	-6							
			0.16 0.04				157	157	2.0	-5							
			0.16 0.08				157	157	1.2	-5							
			0.33 0.08				157	157	3.4	-5							
			0.04 0.16				185	185	3.8	-5							
			0.16 0.04				185	185	3.3	-5							
			0.16 0.08				185	185	7.1	-5							
			0.04 0.08				207	207	1.98	-4							
			0.04 0.15				207	207	1.8	-4							
			0.08-0.15 0.04-0.08				207	207	2.5	-4							

Homogeneous Reaction Kinetics

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A = concentration of A + I, and B = analytical concentration of B + M

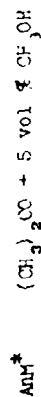
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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Reaction class	Temperature	$k^0 \times 10^7$	k^0	$k^0 \times 10^7$	B	$A^0 \times 10^7$	Comments	Literature
.66	$o\text{-NO}_2\text{C}_6\text{H}_4\text{I} + \text{I}^{*-}$ (continued)	$\text{CH}_3\text{C}_2\text{N}$	A = 0.04; B = 0.15 0.15 0.04			k AB	238 238	8.9 1.68	-4 -3		29		*	(14)
.67	$m\text{-NO}_2\text{C}_6\text{H}_4\text{I} + \text{I}^{*-}$	$\text{CH}_3\text{C}_2\text{N}$	A = 0.2-0.4; B = 0.04-0.16			k A	157 185 207 238	8 3.6 1.3 9.4	-9 -8 -7 -7		25		*	(14)
.68	$p\text{-NO}_2\text{C}_6\text{H}_4\text{I} + \text{I}^{*-}$	$\text{CH}_3\text{C}_2\text{N}$	A = 0.04; B = 0.09 0.09 0.04 0.04 0.08 0.08 0.04 0.04 0.08 0.08 0.04 0.04 0.08 0.08 0.04 0.2 0.04 0.04 0.08 0.07 0.04 0.01-0.02 0.02 0.02 0.06-0.12			k AB	100 100 157 157 185 185 207 207 202 238 238 240 240 240	8 4.4 1.4 2.1 9.7 1.3 4.81 5.7 5.0 3.6 5.0 4.8 3.8 1.46	-9 -7 -6 -6 -6 -5 -5 -5 -5 -4 -4 -4 -4				*	(14)
.69	$2,4,6\text{-(NO}_2)_3\text{C}_6\text{H}_2\text{Br} + \text{Br}^{*-}$	$2\text{-C}_6\text{H}_4\text{OH}$ $(\text{CH}_3\text{COOCH}_2)_2$	A = 0.05; B = 0.030			k A	-5 0 10 22	1.99 3.92 1.31 4.53	-4 -4 -3 -3		34		*	(19)
.90	$\text{HOOCH}(\text{NH}_2)\text{CH}_2\text{-4-HOC}_6\text{H}_2\text{-3,5-I}_2 + \text{I}^{*-}$ H_2O					k AB	63	(no exchange in 2 weeks)			18.2	9 10		(30)

A = concentration of A + L and B = analytical concentration of B + M

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of reagent	Reaction mass	Temperature	$k \times 10^n$		$A \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
191	$\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} + 3,5\text{-I}_2 + \text{H}_2\text{O}$	H_2O	$10^3 \text{ A} = 4-1500$ $10^3 \text{ B} = 1-40$	CH_3COOH CH_3COONa H_2SO_4 NaHSO_4	pH 2.5-5.2 1.3-2.5	$[\text{AB}(\text{H}^+)]^{-1}$	30 31 42	5.33 2.07 8.11	-4 -3 -3		8 23 13	*	(39)

SOLVENTS



COMMENTS

General. The halogens marked X^* are radioactive isotopes. Pseudo first order exchange rates are observed, and isotope effect, (appreciable difference between rate constants for forward and reverse reaction) is considered negligible. The kinetic rate law and the chemical reaction rate constant are calculated from the dependence of the exchange rate, $R = \frac{-d\text{X}^*}{(a+b)t \log(1-x/x_0)}$, upon the concentrations of A^*L and B^*L and any catalysts, where a is the stationary concentration A^*L , b is the stationary concentration B^*L , and x/x_0 is the measured ratio (at time t) of the concentration of the labeled isotope in the molecular species in which it

was not introduced to its concentration at infinite time in that same species. The exchange rate $R = f(a, b, \text{catalyst})$ such as A^*L , B^*L or more complex expressions. For a more complete treatment see (39) (21a). Rates of exchanges involving halogen salts in nonaqueous media in general parallel apparent degree of ionization from conductivity data. For this reason the reacting species is listed as the halogen ion, but the rate constants and concentrations are in terms of the total analytical, ionized and unionized salt concentration.

Reaction. (.20) (.22) Values of rate constants at concentration.

COMMENTS

(continued)

tration, (b), other than 0.024 M/l converted to this concentration by the empirical relation

$$\log(k_0/k_{0.024}) = -0.37 \log(t/0.024).$$

(³) found this transformation valid for each alkyl bromide studied over a temperature range from 26° to 65°C and for $k_0^{1/2} = 1.6$ to 100. (23) Values of rate constants by

(²⁴) corrected from erroneous values in 1951 Edition of Tables. Selected values listed from (⁷)(⁸). Negative salt effect observed by (⁴) who converted values of rate constants to the same concentration Na⁺ by empirical equation, see (20)(22). (24) Converted to sec. from original min.

(26) Negative salt effect observed by (³) who converted values of rate constants to the same concentration of LiBr by empirical equation, see (20)(22). (27) Negative salt effect. Rate constants converted by (³) to the same concentration of LiBr by empirical equation, see (20)(22).

(15) obtained straight line in plot of exchange rate divided by (A⁺), $R/(A^+)$, versus $\alpha(B^+)$ where α is the degree of dissociation of LiBr from conductivity measurements. Negligible intercept may be taken to indicate the low reactivity of undissociated salt. (28) Values of rate constants by

(24) corrected from erroneous values in 1951 Edition of

Tables. (29) Values of rate constants by (²⁸) corrected from erroneous values in 1951 Edition of Tables. Negative salt effect. Selected data of (²¹). (⁴) converted rate constants to same concentrations of NaI by empirical equation, see (20)(22). (30) Authors showed observed rate law to be consistent with mechanism involving fairly stable complex between reactants with K as the equilibrium constant for the dissociation of this complex.

(31) Selected data. (32) Negative salt effect. Values of rate constants converted to the same concentration of LiBr by empirical equation, see (20)(22). (33) Negative salt effect in acetone with LiBr. (³) converted values of rate constants to same concentration of LiBr by empirical equation, see (20)(22). (16) obtained straight line in plot of exchange rate divided by (A⁺), $R/(A^+)$, versus $\alpha(B^+)$ where α is the degree of dissociation of LiBr from conductivity measurements. The intercept and slope gave k_1 and k_2 respectively. A small positive salt effect observed by (⁶) in CH_3NO_2 with $(C_2H_5)_4NBr$ the halide salt. (34)

Selected data of (¹¹) and (²¹). (11) proposed results to indicate that I^- is the reacting species for the alkali halides, the undissociated molecule or a complex ion in the

COMMENTS

(continued)

case of ZnI_2 and an associated complex such as $CdCl_4$ in the case of CdI_2 which showed third order behavior on the basis of a single variation in concentration of CdI_2 by a factor of only two. Units of (11) converted to sec. from original hours. (.35) Reacting species in all solvents studied considered to be I^- and not HI , however in *n*-hexanol, *n*-dodecanol and acetic acid authors consider simultaneous reactions involving I^- and HI_2^- contribute to rate. By estimating degree of dissociation of HI and of formation of HI_2^- from conductivity data values of the reaction rate constants for each reacting species were estimated. Units converted to sec. from original hrs. (.37) (.38) Selected data (.39) Negative salt effect. (4) converted rate constants to same concentration of NaI by empirical equation, see (.20) (.22). Corrected for parallel reaction believed to be elimination with olefin formation. (.40) (.43) Negative salt effect. Rate constants were converted to same concentration of alkali halide by empirical equation, see (.20) (.22). (.44) E converted from original E_a of (34) by adding $\frac{1}{2}RT$. (.45) Rate constant at 25° extrapolated from measured values probably between 30° and $70^\circ C$. (.46) Selected data (.47) (.49) (.50) Rate constants

at $25^\circ C$ extrapolated from measured values probably between 30° and $70^\circ C$. (.51) (.52) Rate of deuterium exchange between DCl and camphene hydrochloride about 20% faster than halogen exchange, see 302,461. (.53) Rate constant at $25^\circ C$ extrapolated from measured values probably between 30° and $70^\circ C$. (.60) Units converted to sec. from original hrs. (.61) Units converted to sec. from original min. (.62) Units not stated and calculations not illustrated, assumed base e logarithms and sec. from calculations from illustrative curve. (.63) One hundred fifty fold variation in $B+H$ shows only first order rate with respect to I_2 thus indicating molecular I_2 rather than atoms to be the reacting species. Addition of small amount of water caused no effect. Slight inhibition by O_2 from air as 12% increase in rate observed on sweeping N_2 . (.64) Units converted to M/l from M/ml . 1 atoms produced photochemically and accuracy limited by estimation of concentration of atoms. (.65) (.66) Units converted to sec. from original min. (.67) (.68) Negative salt effect. Values converted to same concentration of $LiBr$. (.69) (.70) Units converted to sec. from original min. (.71) No difference observed in exchange rate for *cis*- and *trans*-isomers. Units converted

COMMENTS

(continued)

to M/l from M/ml. (.72) Values corrected from erroneous values in 1951 Edition of Tables. Units converted to M/l from original M/ml. (.73) Units converted to sec. from hrs. (.74) Iodine atoms produced photochemically and accuracy dependent upon the determination of the concentration of atoms. Units converted to M/l from original M/ml. (.76) Units converted to sec. from original min. (.77) Reaction inhibited by oxygen. Considered to involve chain mechanism and rate constants for the seven individual steps calculated by authors. (.78) (.79) E converted from E' of authors by adding $\frac{1}{2}RT$. (.80) In ethylene glycol diacetate E converted from E' of (.34) by adding $\frac{1}{2}RT$. (.81) Units converted to sec. from original min. (.82) E converted from E' of (.34) by adding $\frac{1}{2}RT$. (.84) First order constants erratic but show better agreement than calculated second order constants. Units converted to sec. from original hrs. Units and calculations not shown by (.20) but assumed to be hrs. from comparison with values by (.14). (.14) observed formation of black precipitate at higher tem-

peratures. Addition of free I_2 accelerated rate 10 to 15%. Addition of 0.5 gms. H_2O or Na_2SO_3 retarded rate about 15%. Selected data. (.85) No calculations shown, or units which were assumed to be hrs. and converted to sec. (.86) Free I_2 formed after about 30% exchange. I_2 made no noticeable effect on exchange rate. Units converted to sec. from original hrs. (.87) Units converted to sec. from original hrs. First order rate constants erratic but show less deviation than calculated second order constants. Appreciable free I_2 and black precipitate formed at 238°C. (.88) Units of (.14) converted to sec. from original hrs. Units of (.19) converted to M/l from original mM/l. First order rate constants showed less variation than calculated second order constants in 2-octanol. Second order rate constants showed less variation than calculated first order constants in acetonitrile. Method of calculation not indicated by (.19). (.89) E converted from E' of (.34) by adding $\frac{1}{2}RT$. (.91) No exchange observed in 24 hr. period at 52°C with CH_3OH or C_2H_5OH as solvent.

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ISOTOPE EXCHANGE
Hydrogen Isotope between Vth Group Element and Oxygen

Liquid phase

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

No.	Reaction	Solvent	Amount of reactant	Added	Amount of added	Defined mass action law	Temperature	Half-time	$k^0 \times 10^7$ k^0	η	Comments	Literature
1	$\text{H}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O}_2$	H_2O	$B = 11.6$				0	60-600				(1)
2	$\text{H}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O}_2$	H_2O	$B = 11.6$				0	130				(2)
3	$\text{NH}_4^+ + \text{CH}_3\text{COO}^- \longrightarrow \text{NH}_3 + \text{CH}_3\text{COOH}$	$\text{HClO}_4(\text{CH}_3)_2$	$A = 0.3-0.5$ $B = 0.1$ $A = 0.1$	HBr	0.001-0.1	$k^0[\text{H}^+]^{-1}$	0		2.5	-5	*	(3)
4	$\text{C}_2\text{H}_5\text{NH}_3^+ + \text{CH}_3\text{COO}^- \longrightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{CH}_3\text{COOH}$	B	$A = 0.1$	HCl	0.02		0	Rel. rate 1	0.07		*	(3)
5	$(\text{C}_2\text{H}_5)_2\text{NH}_2^+ + \text{CH}_3\text{COO}^- \longrightarrow (\text{C}_2\text{H}_5)_2\text{NH} + \text{CH}_3\text{COOH}$	B	$A = 0.1$	HCl	0.06		0		0.10		*	(3)
6	$(\text{CH}_3)_3\text{NH}^+ + \text{CH}_3\text{COO}^- \longrightarrow (\text{CH}_3)_3\text{N} + \text{CH}_3\text{COOH}$	B	$A = 0.1$	HCl	0.06		0		0.5		*	(3)
7	$(\text{CH}_3)_3\text{NH}^+ + \text{C}_6\text{H}_5\text{OT}^- \longrightarrow (\text{CH}_3)_3\text{N} + \text{C}_6\text{H}_5\text{OH}$	CHCl_3	$A = B = 0.1$	Cl ⁻			0	120				(2)
8	$(\text{C}_2\text{H}_5)_3\text{NH}^+ + \text{CH}_3\text{COO}^- \longrightarrow (\text{C}_2\text{H}_5)_3\text{N} + \text{CH}_3\text{COOH}$	B	$A = 0.1$	HCl	0.08		0		9		*	(3)
9	$(\text{C}_2\text{H}_5)_3\text{NH}^+ + \text{C}_6\text{H}_5\text{OT}^- \longrightarrow (\text{C}_2\text{H}_5)_3\text{N} + \text{C}_6\text{H}_5\text{OH}$	CHCl_3	$A = B = 0.1$	Cl ⁻			0	3.6×10^4				(2)
10	$\text{C}_6\text{H}_5\text{NH}_3^+ + \text{CH}_3\text{COO}^- \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{COOH}$	B	$A = 0.1$	HCl	0.08		0	> 100			*	(3)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Half-time	$k^0 \times 10^7$	Comments	Literature
.11	$\text{PH}_3 + \text{H}_2\text{O} \longrightarrow \text{PH}_2\text{D} + \text{H}_2\text{O}$	B	A = sat. at 100-500 mm.	X = H_3O^+ HCOOH CH_3COOH $(\text{CH}_3)_3\text{CCOOH}$ OH^-	+ buffering salt	k_{AX} k_{AX} k_{AX} k_{AX} k_{AX}	27 27 27 27 27		3.6 2.1 9.4 4.7 4.0	0 -3 -4 -4 -1	*

COMMENTS

Reactions: (.3) Rate constant calculated using rate law given by authors and half-time for exchange given at only one point. Exchange rate independent of which compound was labeled. This reaction used as reference for relative rates of alkyl substituted ammonium ions in methanol. No actual rates given. (.4)(.5)(.6) Relative rate with reference to (.3) as unity.

(.8) Relative rate with reference to (.3) as unity. Negative salt effect observed with 30 % decrease in rate constant in methanol on going from 0.05 to 0.4 M/l initial concentration of A. Increasing polarity of solvent observed to usually decrease rate of exchange. Reaction immeasurably fast in toluene with rates in $\text{C}_2\text{H}_5\text{OH}$ faster than in CH_3OH and slow in ethylene glycol. In organic acids as solvents, HCOOH or CH_3COOH , rate of exchange immeasurably fast. (.10) Rate relative to (.3) as unity. (.11) Reaction carried out in two phase system, gas and liquid, and rate constants corrected for amount of A in gas phase as exchange is limited to liquid phase. Conditions such that diffusion between phases was at least ten times faster than the reaction studied. General acid and base catalysis observed and rate of exchange is $\Sigma k_i A [\text{catalyst}]^i$. Catalyst constants for the acids were corrected for oxonium ion catalysis but no correction made for catalysis by conjugate base in buffer solution, (acid and conjugate base always equal.) Slight positive salt effect observed with NaCl at constant pH using benzoic acid, sodium benzoate buffer. Over temperature range 27-50°C activation energy for both H_3O^+ and OH^- catalysis is 17.6 Kcals. Preexponential term being 2.4×10^{13} and 2.7×10^{12} respectively.

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Homogeneous Reactions

372.508

ISOTOPIC EXCHANGE
H - D exchange on N in VIIIth Group Complex

Liquid phase

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

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k \times 10^2$ k^0 η	η	Comments
.1	$\text{Co}(\text{NO}_3)_6^{+++} + 18\text{H}_2\text{O} \longrightarrow \text{Co}(\text{NH}_3)_6^{+++} + 18\text{HOD}$	B	$10^3 \text{A} = 6-60$ $10^2 \text{A} = 4.8$	$\text{Na}_2\text{HPO}_4, \text{KH}_2\text{PO}_4$	4.7-5.6 4.81	$k \text{A}[\text{H}^+]^{-1} =$ $-d\text{A}/dt$	20 0 8 15 22	4.14 1.13 5.55 1.95 6.08	-9 -10 -10 -9 -9	*
.2	$\text{Co}(\text{ND}_2\text{CH}_2\text{CH}_2\text{ND}_2)_3^{+++} + 12\text{H}_2\text{O} \longrightarrow$ $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3^{+++} + 12\text{HOD}$	B	$10^3 \text{A} = 3-14$	$\text{Na}_2\text{HPO}_4, \text{KH}_2\text{PO}_4$	4.4-4.8	$k \text{A}[\text{H}^+]^{-1} =$ $-d\text{A}/dt$	0 8 15 22	2.46 9.7 3.38 1.05	-10 -10 -9 -8	*

COMMENTS

Reaction. (.1) Pseudo first order exchange rate constant independent of concentration of A or fraction of heavy isotope in A. Observed pseudo first order constant inversely proportional to corrected hydrogen ion activity. pH of buffer dependent upon concentration of trivalent cobaltic ion. If this correction is not made exchange rate appears to be dependent upon $\text{A}^{-0.54}$ power. Addition of KCl or NH_4NO_3 had no effect on rate constant. (.2) Rate constant calculated by multiplying observed pseudo first order exchange rate constant by corrected hydrogen ion activity. Observed pH of buffer corrected for influence of triply charged cobaltic ion.

LITERATURE

J. S. Anderson, H. V. A. Briscoe, N. L. Sidor, *CW* 1943, 361.

ISOTOPIC EXCHANGE
H - D exchange on nitrogen

Liquid phase

Amounts are in M/l
except where otherwise
indicated.Rate constants are in
M/l and sec.

SUPPLEMENT 1955

No.	Reaction	Method	Medium (Solvent)	Amount of reactants	Defined mass action law	Temperature	$k =$		Comments
							$k^0 \times 10^n$	n	
.1	$D_2 + NH_2^- \rightarrow HD + NHD^-$	mass sp.	NH ₃	A = (sat. at 50-60 mm of Hg); $10^3 B = 1.5-2.7$	k_{AB}	-50	8.2	+1	*
.2	$HD + NH_2^- \rightarrow H_2 + NHD^-$	mass sp.	NH ₃	A = (sat. at 0-30 mm of Hg); $10^3 B = 1.5-2.7$	k_{AB}	-50	4.7	+1	*
.3	$ArD + NH_2^- \rightarrow ArH + NHD^-$	Infra red	NH ₃	(See 302.402)					

COMMENTS

Reac ion. (.1) Pseudo first order rate as B undergoes rapid exchange with solvent. Reaction followed by (.2). Considered to follow same mechanism as para-hydrogen conversion catalyzed by NH_2^- , see 102.000. (.2) Determined from integrated form of differential rate equation involving two consecutive first order reactions.

LITERATURE

W.K. Wilmarth, J.C. Dayton, JCS 1953, 75, 4553.

EXCHANGE

Halogen replaced by H on aliphatic C

Gas phase

Reaction type: $RX + HX \longrightarrow RH + X_2$
 (A) (B) (L) (M)

Rate measured: dM/dt

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

No.	Reaction	Amount of reactant	Defined mass action law	Temperature, °C	$k = k^0 \times 10^n$		K	E	A = $A^0 \times 10^n$		Comments	Literature
					k^0	n			A^0	n		
1	$CH_3I + HI \longrightarrow CH_4 + I_2$	$10^3 A = 2-8; 10^3 B \sim 3$	$k_1 A_0 + k_2 AB/B_0$	270	k_1 8.0	-3					*	(2)
				280	1.5	-2						
				290	2.5	-2						
				300	4.4	-2						
				310	7.2	-2						
				320	1.14	-1		83.4	2.3	11		
					k_2							
				270	2.7	-5						
				280	5.2	-5						
				280	1.03	-4						
				300	2.00	-4						
				310	3.58	-4						
				320	7.0	-4		43.0	3.9	12		
				330	5.2	-4						
				320	5.7	-4						
				320	3.6	-4						
				320	2.4	-4						
		$10^3 A = 2-3; 10^3 B = 1-3$										
		0.4										
		0.9										
		0.3										

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k \times 10^n$		K	β	$A = A_0 \times 10^7$		Comments	Literature
					k_0	n			A_0	n		
.2	$C_2H_6I + HI \longrightarrow C_2H_6 + I_2$	$10^3 A = 1.1-2.5; 10^3 B = 4.2-5.0$	$k_1 AB + k_2 AB/B_0$	250	k_1 2.18	-2					*	(2)
				260	3.70	-2						
				280	1.02	-1						
				290	1.65	-1						
				300	2.83	-1		29.8	6.3	10		
				250	k_2 2.50	-5						
				260	5.5	-5						
				280	2.34	-4						
				290	4.7	-4						
				300	9.2	-4		43.0	1.8	13		
				300	9.1	-4						
				300	7.7	-4						
				300	6.6	-4						
.3	$n-C_3H_7I + HI \longrightarrow C_3H_8 + I_2$	$10^3 A = 0.45; 10^3 B = 1.1$ 1.0 0.45 0.12 0.34 0.11 0.25 0.13 0.20 0.22 0.14 0.13 0.17	$k_1 AB + k_2 AB/B_0$	260	k_1 1.67	-2					*	(2)
				270	2.84	-2						
				280	4.7	-2						
				290	7.6	-2						
				300	1.14	-1		29.2	1.6	10		
				260	k_2 8.3	-5						
				270	1.83	-4						
				280	3.7	-4						
				290	7.5	-4						
				300	1.40	-3		43.0	2.8	13		
				260	1.67	-2						
				270	2.84	-2						
				280	4.7	-2						

Homogeneous Reaction Kinetics

311.417

No.	Reaction	Amount of reactant	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$ k^0	n	K	β	$A^0 \times 10^n$ A^0	n	Comments	Literature
.4	$\text{Cl}_3\text{CBr} + \text{HBr} \longrightarrow \text{Cl}_3\text{CH} + \text{Br}_2$	$10^2 A = 1.1-2.5; 10^3 B = 0.5-39;$ $10^2 M = 1.7-4.1$	$k_{AB}^2 / (1 + K_{AB})$	147 169 182	3.64 2.55 7.57	-5 -4 -4	24.5 24.8 25.5				*	(3)
.4.1	$\text{Cl}_3\text{CBr} + \text{Br} \longrightarrow \text{Cl}_3\text{C} + \text{Br}_2$	$10^2 A = 1.1-2.5; 10^2 M = 1.7-4.1$	k_{AB}	147-182				10.2	8.1	10	*	(3)
.4.2	$\text{Cl}_3\text{C} + \begin{cases} \text{HBr} \longrightarrow \text{Cl}_3\text{CH} + \text{Br} & (1) \\ \text{Br}_2 \longrightarrow \text{Cl}_3\text{CBr} + \text{Br} & (2) \end{cases}$		$k_1 AB_1$ $k_2 AB_2$	~ 180 147 169 182	$k_1/k_2 = 1.4$ 4.1 4.0 3.9	1 0 0 0					*	(1) (3)

COMMENTS

Reaction. (.1)(.2)(.3) Reaction followed spectrophotometrically and homogeneity proved by packing. Values tabulated in original article in error by factor of ten which is corrected here. Pseudo second order rate law followed throughout 70% of the course. Values of k_1 and k_2 calculated from pseudo second order constants to include dependence of rate upon initial concentration of B. In all cases k_3 , the calculated first order constant, was found to fall off at lower pressures although it was reproducible and constant at higher pressures. (.4) Occurs simultaneously with reverse reaction, see 311.471. Thermal reaction in dark with equilibrium $\text{Br}_2 \xrightleftharpoons[k_2]{k_1} 2\text{Br}$ followed by 4.1 as rate controlling step in long chain

$\text{Cl}_3\text{C} + \text{HBr} \xrightleftharpoons[k_2]{k_1} \text{Cl}_3\text{CH} + \text{Br}$ and $\text{Cl}_3\text{C} + \text{Br}_2 \xrightleftharpoons[k_2]{k_1} \text{Cl}_3\text{CBr} + \text{Br}$.

$K = k_3/k_2$ also determined by independent kinetic study. Value of K determined by (2) does not agree with value of ~ 7 calculated by (1) from photo bromination of Cl_3CH at 110 to 130°C. Homogeneity proved by increasing S/V ratio six fold with

COMMENTS *(continued)*

- no effect on reaction rate. (.4.1) Rate controlling step in (.4) as well as in radioactive exchange, see 301.477.
(.4.2) Competing reactions for intermediate produced in rate controlling step.

LITERATURE

- (¹) V. V. Braunworth, H. J. Schunacher, *Kolloid Z.* 1939, 89, 184. (²) R. A. Ogg, *ACS* 1934, 56, 528. (³) J. H. Sullivan, N. Davidson, *JCP* 1951, 19, 143.

EXCHANGE

H replacement by halogen on aliphatic C

Gas phase

Reaction type: $RH + X_2 \longrightarrow RX + HX$

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

Rate measured: $-dR/dt$

Amounts are in M/l.

Rate constants are in

M/l and sec.

No.	Reaction	Amount of reactant	Added	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	k	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.1	$CH_4 + Br_2 \longrightarrow CH_3Br + HBr$	$10^3 A = 6-15$ $10^3 B = 6-15$			$k AB^{\frac{1}{2}} (v=0)$	297	7.85 -4			*	(7)
.1.1	$CH_4 + Br \longrightarrow CH_3 \cdot + HBr$	(From .1 and photochemical reaction)			$k AB$	~ 200			18 9		
.1.2	$CH_3 \cdot + \begin{cases} HBr \longrightarrow CH_4 + Br \\ Br_2 \longrightarrow CH_3Br + Br \end{cases}$ (1) (2)	(From .1 and photochemical reaction)			$k AB$	~ 200	k_1/k_2		2 0		
.2	$C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$	(Only photochemical studies)									(1)
.3	$(CH_3)_3CH + Br_2 \longrightarrow (CH_3)_3CBr + HBr$	$10^3 A = 5-15$ $10^3 B = 9-26$ $10^3 A \sim B$ $10^3 B \sim 1$			$k AB^{\frac{1}{2}} (v=0)$	112 130 130	9.7 -4 7.6 -3 7.6 -3	4	36	*	(5)
.3.1	$(CH_3)_3CH + Br \longrightarrow (CH_3)_3C \cdot + HBr$		H	0.0025	$k AB^{\frac{1}{2}} / (1 + KM/B)$				12 14		
.3.2	$(CH_3)_3C \cdot + \begin{cases} HBr \longrightarrow (CH_3)_3CH + Br \\ Br_2 \longrightarrow (CH_3)_3CBr + Br \end{cases}$ (1) (2)	(From .3 and photochemical reaction)			$k AB$		k_1/k_2		~ 5		

HOMOGENEOUS REACTION KINETICS

311.471

2

No.	Reaction	Amount of reactant	Amount added	Defined mass action law	Temperature	$k = k^0 \times 10^n$	k	$A = A^0 \times 10^n$	Comments	Literature
.4	$(CH_3)_3C + Br_2 \longrightarrow (CH_3)_3CBr + HBr$	$10^3 A = 5-14$ $10^4 B = 5-14$		$k AB^2 (v=0)$	197	k^0 6.3			*	(6) (8)
.4.1	$(CH_3)_3C + Br \longrightarrow (CH_3)_3CCH_2\cdot + HBr$	(From .4 and photochemical reaction)		$k AB$	197	k^0 3.6	18 ~12 ~10	9 ~10 ~10	*	(6) (6) (3) (6) (6)
.4.2	$(CH_3)_3CCH_2\cdot + \begin{cases} HBr \longrightarrow (CH_3)_3C + Br \\ Br_2 \longrightarrow (CH_3)_3CCH_2Br + Br \end{cases}$ (1) (2)			$k AB$		k_1/k_2				
.5	$C_6H_5CH_3 + Br_2 \longrightarrow C_6H_5CH_2Br + HBr$	$10^3 A = 4-7$ $10^4 B = 4-10$	0.0003	$k AB^2 (v=0)$	166 166	k^0 2.9 7			*	(2) (10)
.5.1	$C_6H_5CH_3 + Br \longrightarrow C_6H_5CH_2\cdot + HBr$	(From .5 and photochemical reaction)		$k AB$	166	k^0 3.7	7.6	2		(2) (10)
.5.2	$C_6H_5CH_2\cdot + \begin{cases} HBr \longrightarrow C_6H_5CH_3 + Br \\ Br_2 \longrightarrow C_6H_5CH_2Br + Br \end{cases}$ (1) (2)			$k AB$		k_1/k_2	5	1		(2) (10)
.6	$CH_3Br + Br_2 \longrightarrow CH_2Br_2 + HBr$	$10^3 A = 8-10$ $10^4 B = 7-15$		$k AB^2 (v=0)$	297	k^0 5.1			*	(7)
.6.1	$CH_3Br + Br \longrightarrow BrCH_2\cdot + HBr$	(From .6 and photochemical reaction)		$k AB$	~200		18	2		(7)
.7	$CH_3Br + Br_2 \longrightarrow CH_3OBr + HBr$	$10^2 A = 1.4-4$ $10^4 B = 2-38$	M	$k AB^2 / (1 + K_2/B)$	147 169 180	k^0 7.01 2.01 5.78	0.0402 0.0403 0.0302	1.4 1.4 1.4	*	(8) (9) (4) (9) (4)
.7.1	$CH_3CH + Br \longrightarrow CH_3C\cdot + HBr$	(From .7 and photochemical reaction)		$k AB$	147-182		9.3	2.3		(9)

Homogeneous Reaction Kinetics

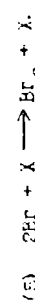
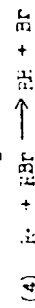
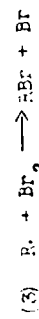
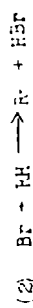
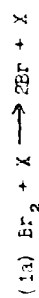
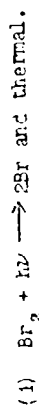
3

311.471

No.	Reaction	Amount of reactant	Added	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^n$	$\bar{A}$	$\bar{A}^0 \times 10^n$	Comments	Temperature
7.2	$\text{Cl}_2 + \text{HBr} \rightarrow \text{Cl}_2\text{H} + \text{Br} \quad (1)$ $\text{Cl}_2 + \text{Br}_2 \rightarrow \text{Cl}_2\text{Br} + \text{Br} \quad (2)$					147 109 152	4.08 4.03 3.92	-2 -2 -2			(°)

COMMENTS

General. Both thermal and photochemical reactions studied, but only thermal rate constants tabulated here. Halogenation assumed to proceed by the same mechanism as that for $\text{H}_2 + \text{Br}_2 \rightarrow$ see 311.700, with photochemical reaction differing from thermal reaction only in initiating step of the chain: Photochemical.



This leads the thermal rate being given by

$$-d\text{Br}/dt = \frac{k_2(k_3/k_4)^{1/2} \text{Br}_2^{1/2}}{1 + k_5/k_4}$$

Inhibition by HBr observed in all photochemical studies and ratio of rate constants for reactions (4) and (3) determined by varying initial concentration of HBr. Effectiveness of A as third body in recombination reaction (5) varies from a relative value of one for H_2 to 174 for neopentane.

Reaction. (1) Only initial (extrapolated to zero time) rate as reaction followed by (1a) which is almost ten times faster. Inhibition by X studied only for photochemical reaction. Mechanism indicates A to be 1.6 times more effective than H_2 for recombination of Br atoms. (3) Only initial rate (extrapolated to zero time.) Inhibition by H studied for both photochemical and thermal reaction with values of K disagreeing by 50%. It is possible that another competing reaction for $(\text{CH}_3)_3\text{C}^\cdot$ such as $(\text{CH}_3)_3\text{C}^\cdot \rightarrow$

December, 1955

COMMENTS

(continued)

$\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2$ should have been included in the reaction mechanism. Inhibition by oxygen demonstrated. (3.2)

Variation in ratio of k_1/k_2 by 50% depending upon whether thermal or photochemical reaction measured. (4.4) Only

initial rate, extrapolated to zero time as rate of further

bromination of H_2 not known. Inhibition by H and O_2 demon-

strated for the photochemical reaction. Reaction mechanism

indicates A to be 174 times more effective than H_2 for re-

combination of Br atoms. (4.1) Reaction mechanism

of (6) (8) does not include competing reaction $(\text{CH}_3)_3\text{COH}_2 \rightarrow$

$\text{CH}_3 + (\text{CH}_3)_2\text{COH}_2$. Inclusion of this would reduce k to

~ 12 Kcal/m. and give normal steric factor according to (9).

Product analysis not performed so this has not been con-

firmed. (5.3) Only initial rate, extrapolated to zero

time. Inhibition by oxygen shown and inhibition by H demon-

strated for the photochemical reaction. (6.6) Only

initial rate, extrapolated to zero time, although no appre-

ciable inhibition by H observed and subsequent bromination

appeared slow. Mechanism indicates A to be 1.2 times more

effective than hydrogen for recombination of Br atoms.

(7.7) Forward and reverse reaction simultaneously as well

as independently studied. See 211.477. Homogeneity proved

by increasing S/V ratio by factor of 8. (7.7.2) Ratio

of k_1/k_2 of (8) about one third the value reported by (4)

at -120°C but (8) studied both forward and reverse of reac-

tion (7.7).

LITERATURE

- (1) E. C. Andersen, E. R. Van Artsdalen, *JCP* 1944, 12, 478. (2) H. E. Anderson, H. A. Scheraga, E. R. Van Artsdalen, *JCP* 1953, 21, 1058. (3) S. M. Benson, H. Graff, *JCP* 1952, 20, 1182. (4) V. V. Braunworth, H. J. Schumacher, *Kolloid Z.* 1949, 59, 134. (5) B. H. Eckstein, H. A. Scheraga, E. R. Van Artsdalen, *JCP* 1954, 22, 28. (6) E. I. Hermans, E. R. Van Artsdalen, *JCP* 1951, 19, 779. (7) G. B. Kistiakowski, F. R. Van Artsdalen, *JCP* 1944, 12, 469. (8) F. E. Schweitzer, E. R. Van Artsdalen, *JCP* 1951, 19, 1028. (9) J. H. Sullivan, N. Davidson, *JCP* 1951, 19, 143. (10) E. H. Slegler, H. A. Scheraga, E. R. Van Artsdalen, *JCP* 1951, 19, 135.

Homogeneous Reactions

311.540

EXCHANGE

Hydrogen - Cyanogen

Hydrogen cyanide formation

Gas phase

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

No.	Reaction	Amount of reactant	Defined mass-action law	Temperature	$k \times 10^7$		α	β	
					k^0	n			
.1	$H_2 + (CN)_2 \longrightarrow 2 HCN$	$10^3 A = 3.6; 10^3 B = 3.6$	$k \frac{AB^2}{[1 + m(L/D)]}$	575	5.8	-5	0.25	72	
				600	2.0	-4			
				625	5.8	-4			
				650	1.9	-3			
				675	5.6	-3			
		1.8 3.6 5.4 5.4 1.8 5.4		625	1.5	-3			
				"	1.0	-3			
				"	8.2	-4			
				"	1.2	-3			
				"	7.6	-3			

COMMENTS

General. This rate law is taken over from the Bodenstein-Lind kinetics of $H_2 + Br_2$ (see 311.700) and has not been shown to apply to the $H_2 + (CN)_2$ reaction. The above values of k refer to late stages of the reaction; at early stages, k is, roughly, four times as high and falls with the progress of the reaction. Nor is k constant towards variations of A , B . Rate constants calculated on the assumption of a $k AB^2$ law behave in the same way. These data refer to a static system, in a silica vessel; the set of data at 575-675°C was obtained in an aged vessel; the data at 625°C, in a vessel treated with HNO_3 . Advance admixture of HCN , in amounts one-half to double the initial $(CN)_2$,

COMMENTS *(continued)*

at 625°C, lowers the rate by a factor of ~0.9. In pyrex at 550°C the rate is about 50% higher than in silica. Surface increase by a factor of 4 increased the rate (in the aged walls) by about 30% at ~600°C but has no appreciable effect at 650-675°C.

LITERATURE

C. N. Robertson, R. N. Pease, *ACE* 1942, 34, 1810

Homogeneous Reactions

312.421

EXCHANGE

H on Aliphatic C with flnd group metal

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	$k = k^0 \times 10^n$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Comments	Literature
.1	$\text{CH}_3\text{COOH} + \text{Hg}^{++} \longrightarrow$ (products not determined)	CH_3COOH	$B = 0.095$			$-dB/dt = k B$	50 70 90	9.5 1.03 8.0	-9 -6 -6		*	(1)
Metal replaced by H on aliphatic C												
.2	$(n\text{-C}_4\text{H}_9)_2\text{Hg} + \text{CH}_3\text{COOH} \longrightarrow n\text{-C}_4\text{H}_9 + \text{CH}_3\text{COOHC}_4\text{H}_9$	CH_3COOH	$10^2 A = 5-8$			$k A$	50 75	3.78 3.91	-5 -4	20 -16	*	(2)
.3	$[\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CH}]_2\text{Hg} + \text{CH}_3\text{COOH} \longrightarrow$ $n\text{-C}_4\text{H}_{10} + \text{CH}_3\text{COOHC}(\text{CH}_3)_2\text{H}_6$	CH_3COOH	$10^2 A = 5-8$			$k A$	25 50	2.30 1.47	-5 -4		*	(2)
.4	$[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{CH}]_2\text{Hg} + \text{CH}_3\text{COOH} \longrightarrow$ $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{COOHC}(\text{CH}_3)_2\text{C}_6\text{H}_5$	CH_3COOH	$10^2 A \sim 9$ 5 5-6 6 3	CH_3COONa HClO_4	0.05 0.0 0.022 0.045	$k A$ $k A[\text{HClO}_4]$	75 75 100 50 50	1.02 9.5 9.35 7.0 6.7	-5 -8 -5 -3 -3	23 -17	*	(2)

COMMENTS

Reaction: (.1) Appears to involve formation of one C-Hg bond per Hg^{++} reacting. Studied in order to correct for this simultaneous reaction to aromatic mercaptans in CH_3COOH . See 312.412. (.2) (.3) (.4) Rate law followed up to 85% reaction. Second alkyl mercury bond remaining after 10 to 20 half lives for first bond replacement. In presence of $HClO_4$, oxidation of solvent leads to increase in acidity and separation of metallic mercury after 40-50% reaction.

LITERATURE

- (¹) H.C. Brown, C.W. McGary, *ACS* 1955, 77, 2308. (²) S. Winstein, T.G. Traylor, *ACS* 1955, 77, 3747.

Homogeneous Reactions

31.422

EXCHANGE

H of Aromatic compound with Group II metal

Liquid phase

Reaction types: $ArH + M^{++} \xrightarrow{\text{slow}} ArM^{+} + H^{+}$

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

$$ArH + RM \xrightarrow{\text{A-M}} ArM + RH$$
$$\text{Ar}_2\text{M} + \text{ACH} \longrightarrow \text{ArH} + \text{ArMAC}$$

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined rate action law	Temperature	$k^o \times 10^n$	k^o	$k^o \times 10^n$	k^o	$A^o \times 10^n$	Comments	Literature
1	$C_6H_6 + Hg^{++} \rightarrow C_6H_5Hg^+ + H^+$	H_2O	$10^2 A = 1-4$ $10^2 B = 2-100$	HNO_3 $HClO_4$ $HClO_4$ $NaClO_4$ $LaClO_4$ ΣClO_4	$B: 0$ 3.4 $0.01-0.8$ $0-0.8$ $0-0.3$ $0.08-0.8$	k_{AB} $k = k_o + k_x X$ $X = ClO_4$	25 25 40 40 40 40	4.5 7.2	2.12 3.5	-5 -5	-5 -5	$A^o \times 10^n$	*	(6)
				HNO_3 $NaNO_3$ ΣNO_3	$0.05-5$ $0-6$ 0.1	$k = k_o + k_x X$ $X = NO_3$	40 40 40	2.12 2.2	2.0 1.5	-5 -5	-5 -5	$A^o \times 10^n$		
				Cl^-	6.0 0.0 0.05 0.2	k_B	40 40 40 40	2.5 1.03	2.5 1.03	-5 -5	-5 -5	$A^o \times 10^n$		
		$Ac97^*$	$A = 1.0; B = 0.1$	$NaClO_4$	0 0.20 0.40 0.60	k_{AB}	25 25 25 25	3.25 3.40 4.34 5.35	3.25 3.40 4.34 5.35	-5 -5 -5 -5	-5 -5 -5 -5	$A^o \times 10^n$	*	(6)

mono-alkyl substituted aromatic hydrocarbons

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined action law	Temperature	$k \times 10^n$		$A =$ $A^0 \times 10^n$	Comments	Literature
								k^0	n			
.4	$\text{CH}_3\text{C}_6\text{H}_5 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $\text{O-CH}_3\text{C}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.9; B = 0.09			k AB	50 70 90	1.18 7.9 4.14	-8 -6 -5	20.6 1.0 8	*	(2)
.5	$\text{CH}_3\text{C}_6\text{H}_5 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $\pi\text{-CH}_3\text{C}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	0.9; B = 0.09			k AB	50 70 90	4.98 3.57 1.99	-7 -8 -5	21.3 1.3 8	*	(2)
.6	$\text{CH}_3\text{C}_6\text{H}_5 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.9; B = 0.09			k AB	50 70 90	2.12 1.32 6.59	-8 -5 -5	19.9 6 7	*	(2)
.7	$\text{C}_2\text{H}_5\text{C}_6\text{H}_5 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.6; B $\approx$ 0.1			k AB	50	3.25	-6		*	(2)
.8	$(\text{CH}_3)_2\text{CHC}_6\text{H}_5 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_2\text{CHC}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.6; B $\approx$ 0.1			k AB	50	3.03	-6		*	(2)
.9	$(\text{CH}_3)_3\text{CC}_6\text{H}_5 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.6; B $\approx$ 0.1			k AB	50	2.48	-6		*	(2)
Di(tri) (tetra) (penta)-alkyl substituted aromatic hydrocarbons												
.10	$\text{O-}(\text{CH}_3)_2\text{C}_6\text{H}_4 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.5; B $\approx$ 0.1			k AB	50	1.26	-5		*	(2)
.11	$\pi\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_4 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.5; B $\approx$ 0.1			k AB	50	2.70	-5		*	(2)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined rate law	Temperature	$k \times 10^n$		δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.12	$p\text{-(CH}_3)_2\text{C}_6\text{H}_4 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_2\text{C}_6\text{H}_4\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.5; B $\geq$ 0.1			k AB	50	6.40	-6				*	(3)
.13	$1,2,3\text{-(CH}_3)_3\text{C}_6\text{H}_3 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.4; B $\geq$ 0.1			k AB	50	5.33	-5				*	(3)
.14	$1,2,4\text{-(CH}_3)_3\text{C}_6\text{H}_3 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.4; B $\geq$ 0.1			k AB	50	3.93	-5				*	(3)
.15	$1,3,5\text{-(CH}_3)_3\text{C}_6\text{H}_3 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.4; B $\geq$ 0.1			k AB	50	1.65	-4				*	(3)
.16	$1,2,3,4\text{-(CH}_3)_4\text{C}_6\text{H}_2 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_4\text{C}_6\text{H}_2\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.4; B $\geq$ 0.1			k AB	50	1.00	-4				*	(3)
.17	$1,2,3,5\text{-(CH}_3)_4\text{C}_6\text{H}_2 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_4\text{C}_6\text{H}_2\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.4; B $\geq$ 0.1			k AB	50	2.03	-4				*	(3)
.18	$1,2,4,5\text{-(CH}_3)_4\text{C}_6\text{H}_2 + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_4\text{C}_6\text{H}_2\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.4; B $\geq$ 0.1			k AB	50	2.36	-5				*	(3)
.19	$(\text{CH}_3)_6\text{C}_6\text{H} + \text{Hg}(\text{OOCCH}_3)_2 \longrightarrow$ $(\text{CH}_3)_6\text{C}_6\text{H}_2\text{HgOOCCH}_3 + \text{CH}_3\text{COOH}$	M	A = 0.5; B $\geq$ 0.1			k AB	50	1.75	-4				*	(3)

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^n$ k^0 n	β	$A = 10^n$ A^0 n	Comments	Literature
Mono-hydroxy (alkoxy) substituted benzene												
.20	$\text{HOC}_6\text{H}_5 + \text{Hg}^{++} \longrightarrow \text{HOC}_6\text{H}_4\text{Hg}^+ + \text{H}^+$	H_2O	$A = B = 0.3$	HNO_3	5% 10% 22% 34% 10%	k_{AB}	0 0 0 0 25	$k^0 \times 10^n$ k^0 n	-4 -4 -3 -3 -2		*	(⁸)
Metal replaced by hydrogen on aromatic-C												
.21	$(\text{C}_6\text{H}_5)_2\text{HS} + \text{HCOOH} \longrightarrow \text{C}_6\text{H}_5 + \text{HCOOHGC}_6\text{H}_5$	D_{10}x^*	$10^2 A = 5-10$; $B = 8.8$ $B = 5.5$	H_2O	1.4 1.7 6.3 2.4	k_A	29 30 30 30 30	$k^0 \times 10^n$ k^0 n	-4 -4 -4 -3 -3		*	(⁶) (⁴)
.22	$(\text{C}_6\text{H}_5)_2\text{HS} + \text{CH}_3\text{COOH} \longrightarrow \text{C}_6\text{H}_5 + \text{CH}_3\text{COOHGC}_6\text{H}_5$	B D_{10}x^*	$10^2 A \sim 5$ $A = 0.1$; $B = 8.8$ 9.8 10.2 11.2 11.8			k_A	25 42 42 42 42 42	$k^0 \times 10^n$ k^0 n	-4 -4 -4 -4 -4 -4	18.5 1.3 9	*	(⁷) (⁴) (⁵)

Homogeneous Reaction Kinetics

312.422

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^o n	$A \times 10^n$ A^o n	Comments	Literature
.23	$(C_6H_5)_2Hg + HgCl_2 \longrightarrow C_6H_5 + C_6H_5HgCl_2$	Et95*	$10^2 A = 1.3-3$ $10^2 B = 1.6-2$			k_{AB}	43 47 50 50 50 50 50 50	7.23 1.14 1.51 3.91 2.97 4.84 7.71 5.94 7.49	-3 -2 -2 -2 -2 -3 -3 -3 -3		(b)
		D1 97.2* D1 98.8* D1 89.5*	$10^2 A = 1.8$ $10^2 B = 2.7$	KClO ₄ KCl	0.0125 0.014 0.028				1 4	12 14	

CODED SOLVENTS

Ac97*	Acetic acid 97% + H ₂ O
Di0x*	Dioxane
D1 97.2(98.8) (89.5)*	Dioxane % indicated + H ₂ O
Et95*	C ₂ H ₅ OH 95% + H ₂ O

COMMENTS

Reaction. (.1) Selected data. Units converted from original minutes. First 10% reaction only. Second order rate constants calculated from measured pseudo first order constants by dividing by saturation concentration of benzene. Solution stirred vigorously and speed of stirring and volume of C_6H_6 did not effect measured rate. Correction made for slight extraction of L from H_2O layer. Rate apparently dependent upon total perchlorate ion and not upon ionic strength or perchloric acid. Similar behavior with sulfuric acid. Slight negative salt effect on catalytic constants of nitrates. Second order rate constants in presence of $(C_2H_5)_4NNO_3$, markedly low, may be due to complexing of C_6H_6 with positive ion, $(C_2H_5)_4N^+$. (.2) Second order rate law up to 80% reaction observed by ⁽¹⁾ indicates polymerization unimportant. Units converted from original minutes. (.3) Only early stages of reaction followed to avoid polymerization. Rate represents parallel mercuration at all available positions. For reactivity at each position see (.4)(.5)(.6). Reaction followed by titrimetric method for B and by infrared spectra analysis. Units converted from original minutes. (.4)(.5)(.6) Units converted from original minutes. Rate constants calculated for these three parallel reactions from

total rate (.3) and ratio of products formed For (.4)(.5) values are twice the partial rate constants per hydrogen of authors and represent the actual rate of formation of ortho and meta compound. (.7)(.8)(.9)(.10)(.11)(.12)(.13)(.14)(.15)(.16)(.17)(.18)(.19) Rate law followed from 30-70% reaction. Units converted from original minutes. All rate constants corrected for small parallel reaction with solvent. See 312.421. (.20) Units converted from original minutes. Small amount of urea added to remove oxides of nitrogen. (.21) Pseudo first order rate constants as B in large excess. Titrimetric method for L and spectrophotometric for A give consistent results. Dilatometric method of ⁽⁴⁾ gives appreciably higher values. (.22) Pseudo first order rate constant followed up to 85% reaction and second alkylmercury bond resistant to cleavage up to 30 half lives for first bond. In presence of $HClO_4$, oxidative side reaction occurs with solvent after about 40% reaction which increases acidity and metallic mercury separates. Dilatometric method of ⁽⁴⁾ gives appreciably higher values than ultrimetric method for L or spectrophotometric for A

LITERATURE

- (¹) H. C. Brown, C. W. McGary, *ACS* 1955, 77, 2300. (²) H. C. Brown, C. W. McGary, *ACS* 1955, 77, 2306. (³) H. C. Brown, C. W. McGary, *ACS* 1955, 77, 2310. (⁴) A. H. Corwin, M. A. Naylor, *ACS* 1947, 69, 1004. (⁵) F. Kaufman, A. H. Corwin, *ACS* 1955, 77, 6280. (⁶) R. M. Schramm, W. Klapproth, F. H. Westheimer, *JFC* 1954, 53, 843. (⁷) S. Winstein, T. G. Traylor, *ACS* 1955, 77, 3747. (⁸) F. H. Westheimer, E. Segel, R. Schramm, *ACS* 1947, 69, 773.

Homogeneous Reactions

312.451

EXCHANGE

Nitration of Aliphatic Compounds

Liquid phase

Amounts are in m/l.

No.	Reaction	Solvent	Amount of reactant	Added	Amount of addend	Defined mass action law	Order of reaction	$k = k^0 \times 10^n$	R
1	$\text{Cyclo-C}_6\text{H}_{12} + \text{N}_2\text{O}_5 \rightarrow \text{C}_6\text{H}_{11}\text{NO}_2, \text{C}_6\text{H}_{11}\text{NO}_2, \text{HNO}_3$ (L) (N) (N)	CCl_4	A = 0.05-0.4; B = 0.06-0.4	N_2O_5 (X)	0.004-0.2	$dL/dt = kAB / (0.02 + X^2)$ $dM/dt = kAB / (0.02 + X^2)$	20	6.4 -5 7.1 -5	21.5 21.5

COMMENTS

Authors suggest mechanism for reaction involving free radicals but not a chain reaction. The constant 0.02 in the rate law is a measure of the competition between solvent, CCl_4 , and NO_2 for reaction with $\text{C}_6\text{H}_{11}^\cdot$. The reaction with CCl_4 leading to formation of $\text{C}_6\text{H}_{11}\text{Cl}$ and oxidation of solvent with formation of CCl_3NO_2 or phosgene. $[\text{C}_6\text{H}_{11}\text{Cl}] / [\text{CCl}_3\text{NO}_2] = 2.5$.

LITERATURE

J. C. L. Brand, ACS 1955, 77, 2703.

EXCHANGE

Nitration of aromatic compounds

Liquid phase

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

Coded solvents and coded addends are at the end of the table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature degree	$k = k_0 \times 10^n$ k_0 n	δ	$A = A^0 \times 10^m$ A^0 m	Comments	Literature
.16	$C_6H_6 + HNO_3 \xrightarrow{C_6H_5NO_2 + H_2O}$	M + H ₂ SO ₄ 63.0 % 68.9 64.2 61.6 59.5 57.3 54.0 51.1	A << B = 0.61			kA	25 25 25 25 25 25 25 25	2.6 1.3 1.5 1.4 4.2 1.4 1.9 4	-2 -2 -3 -4 -5 -5 -6 -7		*	(⁹)
		CH ₃ COOH 99.6 %	A = 0.55; B = 12.4 0.10 8.0 0.10 9.7 0.17 9.7 0.21 9.7 0.34 9.7	HNO ₂	0.5 0.001-0.004 0.46 0.46 0.46 0.46	$k_0 = dL/dt$ kA	11 20 20 20 20 20	9.7 1.19 1.67 1.35 1.24 7.5	-4 -3 -3 -3 -3 -4		*	(¹¹)
		CH ₃ NO ₂	A = 0.1; B = 3.0	HNO ₂ + H ₂ SO ₄	0.0034 0-0.045	$-dA/dt = k_0 + k'[H_2SO_4]$	-10 -10	$k_0 = 1.64$ $k' = 1.45$	-6 -3		*	(¹⁴)
.17	$C_6H_6 + N_2O_5 \xrightarrow{C_6H_5NO_2 + HNO_3}$	CCl ₄	A = 2.56; B ~ 0.03 BzOH = 0.063 " " "	BzOH = Bz ₂ O	C ₆ H ₅ COOH; Bz ₂ O = (C ₆ H ₅ CO) ₂ O 0.035 0.075 0.145	k_B kB	20 20 20	2.11 1.25 9.35	-3 -3 -4		*	(¹¹)

Heterogeneous Reaction Kinetics

312.452

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$R = k^0 \times 10^n$ k^0 n	β	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
12		$C_6H_6 - N_2O_5 \longrightarrow$ (continued)	CCl_4	$BzOH = 0.127$ 0.127	Bz_2O	0.035 0.102	k_B	20 20	1.07 7.74	-3 -4		*	(11)
13	2	$C_6H_5CH_3 + HNO_3 \longrightarrow$ $CH_3C_6H_4NO_2 + H_2O$ $\longrightarrow 56.5\% (2); 3.5\% (3); 40.0\% (4)$	CH_3COOH 99.8 % CH_3COOH 90 % CH_3NO_2	$A = 0.33; B = 12.4$ $0.05-0.2$ 7.0 $A \ll B$ $A = 0.15; B = 3.0$	$HNO_3 + H_2SO_4$	0.50 $0.002-0.006$ 0.079 0 0.014 0.042 0.063 0.064 $0-0.08$	$-dA/dt = k_0$ k_0 $k_0 = (a + b[HNO_3]^{1/2})^{-1}$	11 20 45 (only relative rate)	1.03 6.3 (only relative rate)	-3 -5		*	(14)
				$A = 0.03; B = 7.0$	HNO_3	0.0038 0.076 0.170 0.420	k_0	-10 -10 -10 -10 -10	5.3 1.28 7.12 1.41 1.86	-7 -6 -6 -5 -5		*	(14)
				$A \sim 0.4; B = 7.0$	$HNO_3 + H_2O$	$0.001-0.002$ $0-1.6$	$k_0 = a(1 + b[H_2O])^{-1}$	-6 -6 -6 -6 -6	8.2 7.6 7.78 3.45 1.84	$+3$ $+4$ -5 -5 -5			
				$A = 0.1; B = 7.0$	$HNO_3 + KClO_4$	0.0046 0 0.011 0.0065 0.0123 $0.001-0.002$ 0	k_0	-10 -10 -10 -10 -10 -10	9.78 1.03 6.58 4.70 8.59	-5 -4 -5 -5 -5			

No.	Supplement No. 1961	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		$A = A^0 \times 10^n$	Comments	Literature
									k^0	n			
18	.2	$C_6H_5CH_3 + HNO_3 \longrightarrow$ (continued)	CH_3NO_2	$A = 0.1; B = 7.0$	HNO_3^+ KNO_3	0.001-0.002 0.0035 0.023 0.043 0.28 0.63	k_0	-10	-5	4.78	*	(14)	
								-10	-5	2.18			
								-10	-5	1.87			
								-10	-5	1.30			
								-10	-6	9.4			
19	.3	$C_6H_5C_2H_5 + HNO_3 \longrightarrow$ $C_6H_5C_2H_4NO_2 + H_2O$	CH_3COOH 99.8 %	$A = 0.04; B = 7.0$ 0.10 0.10	HNO_2	0.0027 0.0046 0.0143	$-dA/dt = k_0$	20	-5	6.00	*	(14)	
								20	-5	6.20			
								20	-5	5.65			
20		$C_6H_5C(CH_3)_3 + HNO_3 \longrightarrow$ $(CH_3)_3CC_6H_4NO_2 + H_2O$ $\longrightarrow$ 11.7 % (2); 6.5 % (3); 79.8 % (4)	CH_3COOH 90 %					45	-1 (rate relative to (.18)) (8)	6.4			
21		$C_6H_5OCH_3 + HNO_3 \longrightarrow$ $CH_3OCC_6H_4NO_2 + H_2O$	CH_3COOH M + H_2SO_4 62.8 % 59.6 57.3 53.5 49.5 45.2 41.3	$A = 0.026; B = 4.93$ $A \ll B = 0.61$	HNO_2 $(NH_4)_2CO_3$	0.691 0.07	k_A k_A	21	-3	4.14	*	(7) (9)	
								25	-2	3.0			
								25	-3	4.0			
								25	-4	9.8			
								25	-4	1.1			
								25	-5	1.5			
								25	-6	2			
								25	-7	4			
22		$C_6H_5COOCH_3 + N_2O_5 \longrightarrow$ $CH_3OCC_6H_4NO_2 + HNO_3$	CCl_4	$A = 1.50; B = 0.043$ 1.21 0.83 0.64 -0			k_{AB}	15	-3	1.34	*	(12)	
								15	-3	1.42			
								15	-3	1.53			
								15	-3	1.63			
								15	-3	1.82			

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature, °C	$k = k^0 \times 10^n$ k^0 n	B	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.23		$C_6H_5COOC_2H_5 + HNO_3 \longrightarrow$ $C_6H_5COOC_2H_5 + H_2O$	CH_3COOH 99.8 %	A = 0.10; B = 10.5	HNO_2	0.0029	k A	20	1.55	-4			(14)
.24		$C_6H_5COOC_2H_5 + N_2O_5 \longrightarrow$ $C_6H_5COOC_2H_5 + HNC$	CCl_4	A = 1.35; 1.08 0.80 0.55 → 0 = 0 0.5			k AB	15 15 15 15 15 20	1.44 1.53 1.70 1.87 2.17 4.41	-3 -3 -3 -3 -3 -3		*	(15)
.25		$C_6H_5COOC(CH_3)_3 + N_2O_5 \longrightarrow$ $(CH_3)_3COOC_2H_5 + HNO_3$	$CHCl_3$	A = 1.07; 0.73 0.57 → 0 = 0			k AB	15 15 15 15	2.07 2.38 2.54 3.02	-3 -3 -3 -3		*	(12)
.26		$C_6H_5CH_2SO_3Na + HNO_3 \longrightarrow$ $NaSO_3CH_2C_6H_4NO_2 + H_2O$ → 14 % (5)	M + H_2SO_4 18.7 mol %	A = 0.16; B = 7.0 mol %			k A	40	3.33	-4			(13)
.27		$C_6H_5CH_2CH_2SO_3Na + HNO_3 \longrightarrow$ $NaSO_3CH_2CH_2C_6H_4NO_2 + H_2O$	M + 17.2 mol % B	A = 0.169	$NaClO_4$ $NaNO_3$	Mol % 0.00 0.32 0.57 1.06 0.63 1.09 2.12	k A	30 30 30 30 30 30 30	2.48 2.80 3.15 3.93 2.22 2.13 1.87	-3 -3 -3 -3 -3 -3 -3		*	(13)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	$k \times 10^n$ k^0 n	$A \times 10^n$ A^0 n	Comments	Literature
.27		$C_6H_5CH_2SO_2Na + HNO_3 \rightarrow$ (continued) Mol % M	Mol % $HClO_4$	Mol % B; A = 0.168	M/B =	Mol ratio	k A						(13)
		75.5	7.6	16.7		82/18		30	1.16	-4			
		75.1	8.3	16.6		"		30	2.68	-4			
		74.0	9.6	16.4		"		30	7.48	-4			
		73.4	10.3	15.3		"		30	1.45	-3			
		73.0	10.9	15.1		"		30	3.00	-3			
		76.6	7.7	15.7		90.8/9.2		30	9.9	-5			
		74.1	7.5	16.4		"		30	2.33	-4			
		72.7	7.4	19.9		"		30	4.30	-4			
		71.3	7.2	21.5		"		30	7.18	-4			
		69.7	7.1	23.2		"		30	1.67	-3			
		67.8	6.8	25.4		"		30	4.81	-3			
		76.5	11.3	12.2		97.2/12.8		30	4.32	-4			
		74.9	11.0	14.1		"		30	9.33	-4			
		73.5	10.8	15.7		"		30	1.97	-3			
		72.5	10.6	16.9		"		30	3.30	-3			
		72.6	10.2	17.2		"		30	8.15	-4			
		"	"	"		"		30	2.46	-3			
		"	"	"		"		40	6.22	-4	8 9		(8)
		73.6	9.8	16.4; A = 0.08				25	4.53	-4			
		73.8	9.8	16.4 0.84				25	2.30	-4			
		60.0	0	40.0 0.53			$-dA/dt = k_0$	0	1.07	-4			
.28		$C_6H_5C_2N + HNO_3 \rightarrow$ $NCC_6H_4NO_2 + H_2O$	M + H_2SO_4 95.0 % 84.0 83.0 82.0 81.0 80.0	A << B = 0.61			k A	25	9.0	-3		*	(9)
								25	3.5	-3			
								25	1.5	-3			
								25	5.1	-4			
								25	1.9	-4			
								25	1.0	-4			

[illegible]

No.	Supplementing No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	k^0	n	$k = k^0 \times 10^n$	k^0	n	Comments	Literature
.30	.8	$C_6H_5NO_2 + HNO_3 \longrightarrow$ (continued)	B + M 5 % B + M	A = 0.20; M = 2.93 A = 0.07-0.1; M = 0	HNO ₂ HNO ₂	0.001-0.3 0.040 " " " "	k A k A	a [-13 b [-13	$k = (a + b[HNO_2]^{3/2})^{-1}$ 5.0 4.0 4.68 3.54 2.76 1.57 7.7		+2 +4 -3 -3 -3 -3 -4			*	(14)	
.31		$C_6D_5NO_2 + HNO_3 \longrightarrow$ $C_6D_5(NO_2)_2 + 2OH$	M + H ₂ SO ₄ 97.4 % 86.7	0.02 A = 0.05-0.1; B = 0.03	HNO ₂ + KNO ₃	0.02 0.0 0.11 0.21 0.32	k AB	-13 -13 -13 -13 25 25	6.00 5.32 4.11 2.96 1.58 2.23		-3 -3 -3 -3 -2 -2			*	(4) (5)	
.32	.4	$C_6H_5F + HNO_3 \longrightarrow$ $FC_6H_4NO_2 + H_2O$	M + H ₂ SO ₄ 70.0 % 68.4 68.0 66.4 64.4 62.8 59.6 54.0	A << B = 0.61 A = 0.05-0.1; B = 0.03			k A	25 25 25 25 25 25 25 20 20	1.3 7.0 4.0 9.9 2.0 5.3 8 4 2.6 1.1		-2 -3 -3 -4 -4 -5 -6 -7 -4 -3			*	(6)	
			CH ₃ COOH 99.8 %	A = 0.1-0.2; B = 8.0 9.0	HNO ₂	0.004 0.004	k A								*	(14)

[illegible]

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	B	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
Di-substituted-benzene													
.35	.7	$C_6H_5I + HNO_3 \longrightarrow$ $IC_6H_4NO_2 + H_2O$	CH_3COOH 99.8 %	A = 0.1-0.2; B = 8.0 9.0	HNO_2	0.004 0.0043	k_A	20 20	2.8 1.37			*	(14)
.36		$p-(CH_3)_2C_6H_4 + HNO_3 \longrightarrow$ $(CH_3)_2C_6H_3NO_2 + H_2O$	CH_3COOH 99.8 %	A = 0.01; B = 7.0 0.07 7.0 0.06 5.0	HNO_2	0.0046 0.0192 0.0096	$dL/dt = k_0$	20 20 20	6.17 5.70 4.33			*	(14)
.37		$p-CH_3C_6H_4COOCH_3 + N_2O_6 \longrightarrow$ $CH_3C_6H_4(COOCH_3)NO + HNO_3$	CCl_4	A = 1; B = 0.03 0.9 0.06 0.6 0.03 → 0			k_{AB}	15 15 15 15	1.52 1.81 1.86 2.18			*	(12)
.38		$o-(C_2H_5OOC)C_6H_4 + N_2O_6 \longrightarrow$ $(C_2H_5OOC)C_6H_3NO_2 + HNO_3$	CH_3CN CH_3NO_2 $CH_3NO_2 + CCl_4$ vol. ratio = 9:1 7:3 5:5 1:9	A = 1.1; B = 0.05 0.8 0.05			k_{AB}	20 20 20 20 20 20 20 20 20	2.9 3.07 2.70 2.27 2.02 1.40 1.43 1.39 1.31			*	(12)
.39		$p-CH_3C_6H_4N(CH_3)^+ + HNO_3 \longrightarrow$ $3-NO-4-CH_3C_6H_3N(CH_3)^+ + H_2O$	$H + H_2SO_4$ 81.7 % 75.8	A = B = 0.1			k_{AB}	25 25	1.08 4.07	13.7 17.6	2 8 8 9	*(16) (20)	

Homogeneous Reaction Kinetics

312.452

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature, °C	$k \times 10^n$ k^0 n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.40	$O-NO_2C_6H_4OH + HNO_3 \longrightarrow$ $(NO_2)_3C_6H_3OH + H_2O$	M + B 30 % 									

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined reaction law	Temperature, °C	$k^0 \times 10^n$ k^0 n	$k^0 \times 10^n$ k^0 n	Comments	Literature
.41	$p\text{-NO}_2\text{C}_6\text{H}_4\text{OH} + \text{HNO}_3 \longrightarrow$ (continued)	CH_3COOH	$10^2 A = 2.5; B = 2.70$ 1.38 $B = 1.4-5.8$	HNO_3	0.55 0.38 0.1-1.8	$k A [\text{HNO}_3]$ $k = a - b [\text{HNO}_3]$ a b	21 21	3.1 3.6	-3 -3	*	(7)
.42	$p\text{-ClC}_6\text{H}_4\text{OCH}_3 + \text{HNO}_3 \longrightarrow$ $4\text{-Cl-2-NO}_2\text{C}_6\text{H}_3\text{OCH}_3 + \text{H}_2\text{O}$	CH_3COOH	$A = 0.08; B = 4.44$ $(\text{CH}_3)_4\text{NNO}_2$ $(\text{C}_2\text{H}_5)_4\text{NNO}_2$ $10^2 A = 3-8; B = 4.14$ $10^2 A = 6; B = 4.2$	N_2O_4 N_2O_4 $(\text{CH}_3)_4\text{NNO}_2$ $(\text{C}_2\text{H}_5)_4\text{NNO}_2$ HNO_2 $\text{HNO}_2 + \text{LiNO}_3$	0.0375 0.01-0.03 0.007-0.08 0.01-0.02 0-0.34 0.04-0.08 0 0.040 0.081 0.18 0.24 0.38 0.1-0.16 0 0.055 0.076 0.114 0.152 0.228	$k A$ $k = [\text{N}_2\text{O}_4] (k_1 + k_2 [\text{NO}_2^-])$ k_1 k_2 k_1 $k A [\text{HNO}_2]$	35 35 35 35 25 35 35 35 35 35 35 35 35 35 35	2.61 1.3 2.5 5.2 1.59 1.33 1.03 1.24 1.45 1.77 1.40 1.27 1.22 1.12 1.09 1.18	-3 -2 -4 -3 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	*	(7)

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mechanism	Temperature	$k \times 10^n$	k^0	n	B	$A^0 \times 10^n$	Comments	Literature	
.42	$p\text{-ClC}_6\text{H}_4\text{OCH}_3 + \text{HNO}_3 \longrightarrow$ (continued)	CH_3COOH	$10^2 A = 6; B = 4.1$	$\text{HNO}_3 + \text{H}_2\text{O}$	0 0.11 0.22 0.44 0.89 1.11 0-0.14	$k A [\text{HNO}_3]$	35 35 35 35 35 35	1.31 1.21 1.11 1.01 0.93 0.94	-2 -2 -2 -2 -2 -2				*	(7)	
			$10^2 A = 5; B = 5.94$	HNO_3		$k_1 A + k A [\text{HNO}_3]$ k_1 k	25 25	1.8 5.8	-4 -2		(see comments)				
			$10^2 A = 2; B = 9.05$	HNO_3	3.5×10^{-4} 7.5×10^{-4} 0 0 2.5×10^{-4} 5.5×10^{-4} 8.5×10^{-4}	$dL/dt = k_0$	-15 -15 -11 -5 -5 -5 -5	9.1 9.6 2.2 3.5 2.4 2.0 1.7	-6 -6 -5 -5 -5 -5 -5						
.43	$m\text{-ClC}_6\text{H}_4\text{COOC}_2\text{H}_5 + \text{N}_2\text{O}_5 \longrightarrow$ $\text{Cl-NO}_2\text{C}_6\text{H}_4\text{COOC}_2\text{H}_5 + \text{HNO}_3$	CCl_4	$A = 0.6-1; B = 0.04-0.06$			$k AB$	15	8.7	-4				*	(12)	
.44	$p\text{-ClC}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{HNO}_3 \longrightarrow$ $\text{Cl-NO}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{H}_2\text{O}$	$\text{M} + \text{H}_2\text{SO}_4$ 99.4 % 98.4 95.8 93.1 90.8 88.4 $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ 0.52 % 2.87 4.21 6.21	$A = B = 0.025$			$k AB$	25 25 25 25 25 25 25 25 25	1.53 2.10 3.42 4.82 5.80 3.86 1.40 1.63 1.78 1.95	-3 -3 -3 -3 -3 -3 -3 -3 -3		17.4 17.0 16.3 17.5 15.8	1.6 1.8 7 1.1 1.1	-8 -8 -9 -8 -9	*	(10)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	$\log k$	$A = A^0 \times 10^n$	Comments	Literature
.45	$p\text{-Cl}_2\text{C}_6\text{H}_4\text{NO}_2 + \text{HNO}_3 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3(\text{NO}_2)_2 + \text{H}_2\text{O}$	B M + H ₂ SO ₄ 97.4 % 95.6 92.0 90.0 86.7 H ₂ SO ₄ + SO ₃ 0.0 % 2.80 5.38 10.93 14.6 19.7	A = 0.15 A = 0.05; B = 0.03 0.02 0.02 0.02 0.02 0.01 0.01 0.05 0.03 A = B = 0.025	HNO ₂	0.03	k A k AB	20 25 25 25 25 25 25 25 25 25 25	k^0 n -5 -3 -3 -3 -3 -3 -4 -4 -4 -4 -5		* (¹⁴) (⁵) (⁶) (⁵) (¹⁹) * (⁴) (⁵) (¹⁰)		
.46	$o\text{-Cl}_2\text{C}_6\text{H}_4 + \text{HNO}_3 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{H}_2\text{O}$	CH ₃ COOH 99.8 %	A = 0.10; B = 10.5	HNO ₂	0.0029	k A	20	2.57	-4			(¹⁴)
.47	$o\text{-Cl}_2\text{C}_6\text{H}_4 + \text{N}_2\text{O}_5 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{HNO}_3$	CCl ₄	A = 1.42; B = 0.043 1.11 0.043 0.88 0.043 0.61 0.043 -0 0.043			k AB	15 15 15 15 15	7.71 8.03 8.19 8.25 8.5	-4 -4 -4 -4 -4		* (¹²)	
.48	$m\text{-Cl}_2\text{C}_6\text{H}_4 + \text{HNO}_3 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{H}_2\text{O}$	CH ₃ COOH 99.8 %	A = 0.10; B = 10.5	HNO ₂	0.0029	k A	20	4.98	-4			(¹⁴)
.49	$m\text{-Cl}_2\text{C}_6\text{H}_4 + \text{N}_2\text{O}_5 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{HNO}_3$	CCl ₄	A = 0.6-1; B = 0.06			k AB	15	1.21	-3		* (¹²)	

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature, °C	$k = k^0 \times 10^n$ k^0 n	B	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.50	$p\text{-Cl}_2\text{C}_6\text{H}_4 + \text{HNO}_3 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{H}_2\text{O}$	CH_3COOH 99.8 %	A = 0.10; B = 10.5 12.0 12.0 12.2	HNO_2	0.0029 0.0030 0.0030 0.0034 0.0019 0.048 0.083 0.106 0.174 C-0.08	k_A	20 10 20 20 20 20 20 20 20 20	2.00 6.76 1.65 2.23 6.49 2.55 1.87 1.00 4.5			*	(14)
		CH_3NO_2	A = 0.1-0.2; B = 8.5	HNO_2		k_A	20	6.49				
			A = 0.1; B = 8.5; M = 0.3	$\text{HNO}_2 + \text{KNO}_3$	0.008 0 0.010 0.025 0.061 0.081	k_A	20 20 20 20 20 20	4.0 1.6 3.48 1.93 1.11 9.7				
.51	$p\text{-Cl}_2\text{C}_6\text{H}_4 + \text{N}_2\text{O}_5 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{HNO}_3$	CCl_4	A = 0.5-0.8; B = 0.05 0.7-1.9 0.04-0.06 0.5-1.8 0.04 A ~ 0.6; B ~ 0.04		0-0.25	k_{AB}	10 15 20	3.1 5.4 9.6			*	(12)
		CT/NH_4^+	A = 1.73; B = 0.055 1.28 0.040 0.56 0.047 ~0 ~0.05	HNO_3		$k_{AB}; k = a + b[\text{HNO}_3]^2$	20 20 10 10 10 10	1.1 8.0 5.79 6.67 8.04 9.04	17 1 10		*	(13)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mechanism	$k \times 10^n$	k^0	η	δ	$A = A^0 \times 10^n$	Comments	Literature
.51	$p\text{-Cl}_2\text{C}_6\text{H}_4 + \text{N}_2\text{O}_6 \longrightarrow$ $\text{Cl}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{HNO}_3$ (continued)	CT/NH ₉ *	A = 1.28; B = 0.05 0.63 0.05 -0 0.05 0.63 0.05 -0 0.05 A = 0.8; B = 0.05	TEAP*	0 1.8×10^{-3} 2.5×10^{-3} 4.0×10^{-3} 0 4.6×10^{-4} 1.2×10^{-3} 0 4.5×10^{-4} 6.0×10^{-4}	k _{AB}	15 15 15 20 20 10 10 10 10 20 20 20 25 25 25 10 10 10 10 20	1.18 1.38 1.85 2.49 2.65 7.99 1.25 2.28 3.06 2.44 3.26 4.31 3.39 3.75 4.48 1.08 1.24 1.50 1.85 4.3	-3 -3 -3 -3 -3 -4 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3			*	(12)
.52	$p\text{-Cl}_2\text{C}_6\text{H}_4\text{Br} + \text{N}_2\text{O}_6 \longrightarrow$ $\text{Cl}_2\text{BrC}_6\text{H}_3\text{NO}_2 + \text{HNO}_3$	CCl ₄	A = 1.30; B = 0.038 0.97 0.64 -0 0.71 0.06-0.1			k _{AB}	15	5.5	-4			*	(13)
.53	$p\text{-Cl}_2\text{C}_6\text{H}_4\text{Br}_2 + \text{N}_2\text{O}_6 \longrightarrow$ $\text{Br}_2\text{C}_6\text{H}_3\text{NO}_2 + \text{HNO}_3$	CCl ₄	A = 0.4-0.7; B = 0.04			k _{AB}	15	5.7	-4			*	(12)

No.	Supplementing 1951 401	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$	k^0	n	$A = 10^{12}$	Comments	Temperature
Tri-substituted Benzene														
.54		1,3,5-(CH ₃) ₃ C ₆ H ₃ + HNO ₃ → CH ₃ COOH 99.8 % (CH ₃) ₃ C ₆ H ₂ NO ₂ + H ₂ O		A = 0.05-0.1; B = 7.0 A = 0.07; B = 5.0	HNO ₂	0.004 0.007 0.014	dL/dt = k	20 20 20	5.62 5.48 4.17					(14)
.55		3,5-(CH ₃) ₂ C ₆ H ₃ SO ₃ ⁻ + HNO ₃ → H + 3 H ₂ O 100 % SO ₃ ⁻ CH ₂ -(CH ₃) ₂ C ₆ H ₂ NO ₂ + H ₂ O		39.7 0.23 38.9 0.32 17.6 0.07 17.6 0.14	HClO ₄	0.8 Mol %	k ₁ A dL/dt = k ₀ k ₁ A	0 0 0 25 25	4.60 1.81 1.47 5.9 3.8				*	(6)
.56	.12	2,4-(NO ₂) ₂ C ₆ H ₃ CH ₃ + HNO ₃ → H ₂ SO ₄ 100 % (NO ₂) ₂ C ₆ H ₂ CH ₃ + H ₂ O		A ~ 0.4; B ~ 0.2 ~0.6 ~0.8 ~0.4 ~0.2 0.4 0.1 0.2 0.4 0.6 ~0.4 ~0.2			k _{AB}	70 80 90 90 90 80 80 90 90 90 100 120 90 90 90 70	1.88 4.68 1.23 1.8 1.78 1.68 1.28 2.9 3.1 3.2 3.4 7.1 3.3 3.74 4.02 3.50 4.34	23.4 1.4 10			*	(1)
		M + H ₂ SO ₄ 88.7 % 95.0								23.5	4.7	10		
		93.0 92.0 91.0 89.5												

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No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined reaction law	Temperature	$k^0 \times 10^n$	k^0	n	$A^0 \times 10^n$	A^0	n	Comments	Literature	
.56	$2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CH}_3 + \text{HNO}_3 \rightarrow$ $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{CH}_3 + \text{H}_2\text{O}$ (continued)	$\text{H} + \text{H}_2\text{SO}_4$ 89.5% 87.4 $\text{H}_2\text{SO}_4 + \text{SO}_3$ 7.8 %	$A \approx 0.4; B \approx 0.2$			k_{AB}	90 110 90 70 80 90 90 90	2.82 1.40 1.15 1.3 3.7 9.4 9.0 8.2		-4 -3 -4 -5 -5 -5 -5 -5	1.0	11	*	(1)		
.57	$2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH} + \text{HNO}_3 \rightarrow$ $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH} + \text{H}_2\text{O}$	11.7 18.6	$A = 0.0012$	HNO_2	0.026	k_A	50	7		-7				*	(20)	
.58	$2,6-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH} + \text{HNO}_3 \rightarrow$ $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH} + \text{H}_2\text{O}$	30 % 60	$A = 0.001$	HNO_2	0.027 0.0065 0.029 0.108	k_A	50 50 50 50	2.3 1.7 5.7 1.8		-5 -5 -5 -4				*	(20)	
.59	$1-\text{NO}_2\text{C}_6\text{H}_4:(\text{CO})_2\text{C}_6\text{H}_4 + \text{HNO}_3 \rightarrow \text{B}$		$A = 0.24$ $\text{H}_2\text{SO}_4 = 0.044$ 0.101 0.176 0.234	HNO_2	0.0055 0.0065 0.0090 0.0065 0.0070	k_A	20 20 20 20 20	2.48 2.53 3.09 4.19 5.03		-3 -3 -3 -3 -3				*	(14)	
.60	$1,2,4-\text{Cl}_3\text{C}_6\text{H}_3 + \text{HNO}_3 \rightarrow$ $\text{Cl}_3\text{C}_6\text{H}_2\text{NO}_2 + \text{H}_2\text{O}$	CH_3COOH 99.6 % CH_3NO_2	$A = 0.10; B = 12.2$ $A = 0.10; B = 8.5$	HNO_2	0.0034 0.0018		20 20	1.80 5.44		-4 -4				*	(14)	
.61	$1,2,4-\text{Cl}_3\text{C}_6\text{H}_3 + \text{N}_2\text{O} \rightarrow$ $\text{Cl}_3\text{C}_6\text{H}_2\text{NO}_2 + \text{HNO}_3$	CT/NM 9*	$A = 0.55; B = 0.049$ 0.70			k_{AB}	15 15	6.82 6.19		-4 -4				*	(12)	

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No.	Reaction	Solvent	Amount of reactant	Amount of Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	k^0	n	$A = A^0 \times 10^n$	Comments	Literature
.61	1,2,4-Cl ₃ C ₆ H ₃ + N ₂ O ₂ → (continued)	CT/NH ₄ ⁺ CT/NH ₄ ⁺ CT/NH ₄ ⁺	A = 1.20; B = 0.049 0.71 0.049 0.62 0.043 1.15 A = 0 - 0			k AB	15 20 20 20 20 20	5.50 1.23 1.07 1.00 2.47 2.76	-4 -3 -3 -3 -3 -3		~10	*	(12)
Tetra-substituted benzene													
.62	2,4,6-(CH ₃) ₃ C ₆ H ₂ SO ₃ ⁻ + HNO ₃ → SO ₃ ⁻ CH ₂ -(CH ₃) ₃ C ₆ H ₂ NO ₂ + H ₂ O		M = 2 Mol % = 37.4; A = 0.28 39.4 0.27 36.4 0.17			$dl/dt = k_0$ $k_1 A$	0 0 0	1.09 1.60 7.28	-4 -4 -3			*	(6)

SOLVENTS

CT/NH₄⁺ 9 vol CCl₄ + 1 vol CH₃NO₂
 CT/NH₄⁺ 7 vol CCl₄ + 3 vol CH₃NO₂
 CT/NH₄⁺ 1 vol CCl₄ + 1 vol CH₃NO₂

ADDENDS

TEAP* Tetra ethyl ammonium picrate
 TEAHIS* Tetra ethyl ammonium hydrogen sulfate
 TEAN* Tetra ethyl ammonium nitrate

COMMENTS

Reaction. (.16) Pseudo first order rate constants measured by (9) as nitric acid in excess. Concentrations of benzene listed by (9) not true concentrations but refer to optical densities. In acetic acid at concentrations of nitric acid <12, mixed order observed by (14) with initial reaction being pseudo zero order tending to first order in latter stages. Zero order only at high nitric acid concentrations where large addition of HNO_2 necessary to depress rate to measurable value. HNO_2 shown by (14) to have no effect on reaction order. In CH_3NO_2 linear catalysis by H_2SO_4 only when $[\text{H}_2\text{SO}_4] > [\text{HNO}_2]$. (.17) Active nitrating species considered by (11) to be N_2O_5 which is involved in the following rapid equilibria:

$$\text{Bz}_2\text{O} + \text{N}_2\text{O}_5 \rightleftharpoons 2\text{BzNO}_3; \text{BzOH} + \text{N}_2\text{O}_5 \rightleftharpoons \text{BzNO}_3 + \text{HNO}_3;$$

$$\text{Bz}_2\text{O} + \text{HNO}_3 \rightleftharpoons \text{BzNO}_3 + \text{BzOH}. \text{ First equilibrium is catalyzed by acid. Only in extremely pure } \text{Bz}_2\text{O} \text{ is this equilibrium slower than the rate of nitration. Under these conditions nitration is so rapid that even the } \text{Bz}_2\text{O} \text{ is nitrated. In a mixture rate is comparable to rate using } \text{BzNO}_3. \text{ (.18) Pseudo zero order over entire course in contrast to (.16). In } \text{CH}_3\text{NO}_2 \text{ linear catalysis by } \text{H}_2\text{SO}_4 \text{ only when } [\text{H}_2\text{SO}_4] > [\text{HNO}_2]. \text{ Reciprocal of zero order rate constant linear with respect to } [\text{HNO}_2]^{\frac{1}{2}} \text{ up to } [\text{HNO}_2] = 0.08. \text{ At higher concentrations re-}$$

ciprocal of rate constant increases more rapidly. Reciprocal of zero order rate constant linear with respect to $[\text{H}_2\text{O}]$ over range studied. Initial concentration of H_2O used rather than average. (.19) Pseudo zero order over entire course in contrast to (.16). (.21) In CH_3COOH rate law pseudo first order only when sufficient HNO_2 present initially. Side reaction leading to dark colored products making up at least 10% of yield cause autocatalysis by the HNO_2 produced. Order with respect to HNO_2 varies with concentration of HNO_3 ranging from 0.65 when $[\text{HNO}_3] = 3.0$ to 0.2 when $[\text{HNO}_3] = 6.0$. In H_2SO_4 pseudo first order as HNO_3 in excess. Values of concentration of $\text{CH}_3\text{OC}_6\text{H}_5$ listed by (9) are not actually concentrations but functions of optical density. (.22) Second order rate constants calculated from pseudo first order initial rate constants dividing by concentration of N_2O_5 . At latter stages reaction shows autocatalysis by HNO_3 produced. Selected data. (.27) Selected data from large amount by (13). Relatively small depression of rate constants by NO_3^- considered to be caused by canceling of major effect by a large positive salt effect. (9) observe initial rate to tend toward zero order followed by a limiting first order reaction. Addition of NaNO_3 de-

COMMENTS

presses both zero and first order rate constants to the same extent. Addition of NaClO_4 increases first order rate constant more than it increases zero order constant. (.28) Pseudo first order as HNO_3 in excess. Values of concentrations of $\text{C}_6\text{H}_5\text{ON}$ listed by (9) are not actual concentrations but functions of optical density. (.29) Rate constants converted to seconds from original minutes. (.30) Addition of water tremendously increases the inhibiting effect of HNO_2 and changes it from a $\frac{1}{2}$ power effect in anhydrous media to a $\frac{3}{2}$ power of $[\text{HNO}_2]$. (.31) Lack of any measurable isotope effect shows that the rate determining step is not the removal of hydrogen. (.32) (.33) (.34) Rate constants pseudo first order as HNO_3 in excess. Concentrations of C_6H_5 listed by (9) are not actual concentrations but functions of optical density. Selected data of (14) who observe slight decrease in calculated first order constants with increase in initial concentration of $\text{C}_6\text{H}_5\text{F}$. (.35) Slight decrease in calculated first order constants observed with increase in initial concentration of A. (.36) Rate laws zero order over entire course of reaction in contrast to (.15) which is mixed first and second order and (.32) - (.35) which approach first order over entire course in this sol-

(continued)

vent. (.37) (.38) Second order rate constants calculated from initial pseudo first order constants by dividing by concentration of A which was in excess. At latter stages reaction shows autocatalysis by HNO_3 produced. (.39) Rate constants are in seconds converted from original minutes. (.40) Selected data. Rate constants converted to seconds from original minutes. (.41) Rate constants converted to seconds from original minutes of (10). In CH_3COOH (7) observed first order dependence upon HNO_2 up to $[\text{HNO}_2] = 5.0$ but some inhibiting effect of HNO_2 observed at $[\text{HNO}_2] = 10.0$. The linear dependence of the calculated second order constants upon $[\text{HNO}_2]$ from 1.4-5.8 considered to be due to a partial balancing of strong effects. (.42) In CH_3COOH (2) deduce dependence of pseudo first order rate constant k upon $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2^-]$ as $k = [\text{N}_2\text{O}_4](k_2 + k_3K/[\text{NO}_2^-])$ where k_2 is rate constant for nitrosation by N_2O_4 and k_3 for nitrosation by NO^+ . Nitrosation is assumed to be followed by the rapid reaction $\text{ArNO} + \text{HNO}_2 \rightarrow \text{ArNO}_2 + \text{HNO}$. k_2 determined from intercept of graph $k_2 = 1.3 \times 10^{-2}$. A lower limit for k_3 estimated from graph and upper limit for:

$$K = 1.9 \times 10^{-3} = [\text{NO}_2^-][\text{NO}^+]/[\text{N}_2\text{O}_4]$$

k_3 lower limit = 0.13. At $[\text{HNO}_2] = 5.94$ the rate law of

COMMENTS

(continued)

(⁷), $k_1 A + k_2 [\text{HNO}_2] = 0$. In absence of HNO_2 reaction is nearly zero order with respect to A. At $[\text{HNO}_3]$ in the range 6-9 M/l the kinetics are complicated having fractional non-constant reaction orders. At $[\text{HNO}_3] = 9-10$ simple orders are again observed if $[\text{HNO}_2]$ is not too large. Above $[\text{HNO}_3] = 10$ M/l the reaction is too fast to measure. (.43) Second order rate constants calculated from initial pseudo first order constants by dividing by the concentration of A. At latter stages reaction shows autocatalysis by HNO_3 formed. (.44) Rate constants converted to seconds from original minutes. (.45) Rate constants in $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ calculated by combining relative rates of (⁵) with rate constants for (.30) of (⁴) and (¹⁹). (.47) (.49) Second order rate constants calculated from initial pseudo first order constants by dividing by concentration of A. At latter stages reaction shows autocatalysis by HNO_3 formed. (.50) Reciprocal of rate constant linear with respect to $[\text{HNO}_2]^{\frac{1}{2}}$ only up to $[\text{HNO}_2] = 0.08$. At higher concentrations the reciprocal of the rate constant increases more rapidly. Excellent first order behavior over 97% reaction in CH_3NO_2 observed by (¹⁴). This is in contrast to (.16) (.18) and (.19) where zero order behavior over the

reaction course is found for this solvent. (.51) (.52)

(.53) Second order rate constants calculated from initial pseudo first order constants by dividing by concentration of A. At latter stages reaction shows autocatalysis by HNO_3 formed. (.55) Initial rate of reaction tends to zero order. This is followed by a limiting first order reaction. Addition of NaNO_3 depresses both first and second order rate constants to the same extent. Addition of NaClO_4 increases first order rate constant much more than it increases the zero order constant. (.56) Selected data. Rate constants in all H_2SO_4 media given by:

$$k = \{k_1 [\text{HSO}_4^-] + k_2 [\text{H}_2\text{SO}_4] + k_3 [\text{H}_2\text{S}_2\text{O}_7^-]\} Q$$

where $Q = [\text{NO}_2^-] / [\text{HNO}_2] = \{1 + [\text{OH}_3^+] [\text{HSO}_4^-]^2 / 33 [\text{H}_2\text{SO}_4]^2\}^{-1}$ at 90°C. $10^6 k_1 = 5.5$; $10^6 k_2 = 6.2$; $10^6 k_3 = 9.3$. Value of k_3 is in doubt as $[\text{HS}_2\text{O}_7^-]$ in oleum is uncertain. In excess SO_3 , Q approaches 1. Rate constants converted to seconds from original minutes. (.57) (.58) Rate constants converted to seconds from original minutes. (.59) Selected data. (.60) In CH_3NO_2 good first order rate through 97% reaction in contrast to zero order in this solvent for (.16) (.18) and (.19). (.61) Second order rate constants calculated by dividing initial pseudo first order constants

COMMENTS

(continued)

by concentration of A. At latter stages the reaction shows autocatalysis by HNO_3 formed. (.62) Initial rate of reaction tends to zero order. This is followed by a limiting first order reaction. Addition of NaNO_3 depresses both first

and zero order rate constants to the same extent. Addition of NaClO_4 increases the first order rate constant much more than it increases the zero order constant.

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EXCHANGE

Aryl Hydrogen substitution by Azo
(Diazocoupling reactions)

Liquid phase

Amounts are in M/l.
Rate constants are in
M/l and sec⁻¹.

Note: For compounds involving more than one aromatic ring, it is understood that the substitution take place in the ring written last. The position of substitution in the product, if given, is designated by a position number after the arrow counted in the same order as in the reactant.

No.	Reaction	Solvent	Amount of reactant	Acid	Ionic strength	pH	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	$I = I^0 \times 10^n$ I^0 n	Comments	Literature
.1	$\text{CH}_3\text{COCH}_2\text{CONHC}_6\text{H}_5 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$	H ₂ O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		6.4 6.7 7.0	k_{AB}	15 15 15	1.13 2.67 5.53	0 0 0		(⁵)
.2	$\text{CH}_3\text{COCH}_2\text{CONHC}_6\text{H}_5 + 3\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$	H ₂ O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		5.0 5.4	k_{AB}	15 15	1.65 4.09	+1 +1		(⁵)
.3	$\text{CH}_3\text{COCH}_2\text{CONHC}_6\text{H}_5 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$	H ₂ O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		5.62 6.12	k_{AB}	15 15	3.91 2.32	0 +1		(⁵)
.4	$1,3\text{-(HO)}_2\text{C}_6\text{H}_4 + 3\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$	H ₂ O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		5.82 6.04 6.28 6.48	k_{AB}	15 15 15 15	1.13 1.88 3.97 7.90	0 0 0 0		(⁵)
.5	$1,3\text{-(HO)}_2\text{C}_6\text{H}_4 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow$	H ₂ O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		6.0 6.4 6.8	k_{AB}	15 15 15	4.40 1.28 3.83	-1 0 0		(⁵)

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No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined base action law	Temperature	$k = k^0 \times 10^n$		$A = A^0 \times 10^n$		Comments	Literature
									k^0	n	A^0	n		
.6	$1,3-(\text{HO})_2\text{C}_6\text{H}_4 + 2\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow$	H_2O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		5.82 6.25 6.66 6.88	k_{AB}	15 15 15 15	1.57 6.12 2.22 4.47	-1 -1 0 0			*	(^b)
.7	$1,3-(\text{HO})_2\text{C}_6\text{H}_4 + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow$	H_2O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		6.58 6.80 7.00	k_{AB}	15 15 15	4.55 9.92 2.08	-1 -1 0			*	(^b)
.8	$1,3-(\text{HO})_2\text{C}_6\text{H}_4 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$	H_2O	$10^4\text{A} = 1-5$ $10^3\text{A} = 2$ $10^4\text{B} = 2$ $10^4\text{A} = 1-5$ $10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers	0.24	4.50 5.0 5.2 5.27 5.4	k_{AB}	15 15 15 15 15	1.97 4.90 8.80 1.35 1.52	0 0 0 +1 +1			* *	(^a) (^b) (^a) (^b)
.9	$4\text{-HOC}_6\text{H}_4\text{SO}_3\text{Na} + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$	H_2O	$10^4\text{A} = 1-5$	Buffers	0.24	8.17 9.15	k_{AB}	15 15	1.1 5.3	-1 -1			*	(^a)
Mono-substituted naphthalene														
.10	$\text{C}_{10}\text{H}_7-2\text{-OH} + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 2$ $10^4\text{B} = 2$	Buffers		6.4 6.6 7.0 7.4	k_{AB}	15 15 15 15	1.54 2.17 6.13 1.62	0 0 0 +1			*	(^b)

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No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k \times 10^n$		$A \times 10^n$		Comments	Literature
									k^o	n	A^o	n		
D1-substituted naphthalenes														
.11	1-HO-3-HSO ₃ C ₆ H ₄ + 2-NO ₂ C ₆ H ₄ N ₂ ⁺ → (2), (4)	H ₂ O	10 ⁵ A = 5; 10 ⁵ B = 1	Acetate buffers	0.5	4.59 4.61 4.64 5.60	k _{AB}	20	3.09 4.00 5.39 5.04	+5 +5 +5 +5				(7)
	" " → (2)					4.59 5.60	k _{AB}	20	2.9 4.2	+5 +5				
	" " → (4)					4.59 5.60	k _{AB}	20	2.1 8.8	+4 +2				
.12	1-HO-3-HSO ₃ C ₆ H ₄ + 4-ClC ₆ H ₄ N ₂ ⁺ → (2) ~75%, (4) ~25%	H ₂ O	10 ⁵ A = 5; 10 ⁵ B = 1	Phosphate buffers	0.25	6.35	k _{AB}	10	1.66	+3				(9)
.13	1-HO-3-HSO ₃ C ₆ H ₄ -2-D + 4-ClC ₆ H ₄ N ₂ ⁺ → → (2) ~80%, (4) ~20%	H ₂ O	10 ⁵ A = 5; 10 ⁵ B = 1	Phosphate buffers	0.25	6.35	k _{AB}	10	5.35	+2				(9)
.14	1-OH-4-NaSO ₃ C ₆ H ₄ + C ₆ H ₄ N ₂ ⁺ → (2)	H ₂ O	10 ⁴ A = 1-5; 10 ⁴ B = 1-5	Buffers	0.24	5.27 5.80	k _{AB}	15	5.9 2.10	-1 0			*	(4)
.15	1-OH-4-NaSO ₃ C ₆ H ₄ + p-CH ₃ C ₆ H ₄ N ₂ ⁺ → (2)	H ₂ O	10 ⁴ A = 1-5; 10 ⁴ B = 1-5	Buffers	0.24	6.30 6.73	k _{AB}	15	1.58 4.70	0 0			*	(4)
.16	1-HO-4-HSO ₃ C ₆ H ₄ + 2-CH ₃ OC ₆ H ₄ N ₂ ⁺ → (2)	H ₂ O	10 ³ A = 1; 10 ³ B = 1	Buffers + KCl	.005 .01 .02 .05	5.7 5.7 5.7 5.7	k _{AB}	10 10 10 10	4.6 4.5 4.6 3.7	-2 -2 -2 -2				(12)

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No.	Reaction	Solvent	Amount of reactant	Addend	Ionio strength	pH	Defined mass	Temperature	$k \times 10^n$ k^0 n	$k \times 10^n$ k^0 n	Comments	Literature
.16	1-HO-4-HSO ₃ C ₁₀ H ₆ + 2-CH ₃ OC ₆ H ₄ N ⁺ → (2) (continued)	H ₂ O	10 ³ A = 1; 10 ³ B = 1 10 ⁴ A = 5-10; 10 ⁴ B = 5	Buffers + KCl	.10 .25 .24 .24 .24 .24 .24 .24 .24 .24	5.7 5.7 5.80 6.30 6.73 7.08 5.90 6.30 6.73	k AB	10 10 15 15 15 15 25 25 25	3.2 2.8 1.37 5.09 1.22 2.64 3.28 1.28 3.08	-2 -2 -1 -1 0 0 -1 0 0		(12) (4)
.17	1-HO-4-HSO ₃ C ₁₀ H ₆ + 4-CH ₃ OC ₆ H ₄ N ⁺ → (2)	H ₂ O	10 ³ A = 1; 10 ³ B = 1	Buffers + KCl	.005 .01 .02 .05 .10 .25	5.7 5.7 5.7 5.7 5.7 5.7	k AB	10 10 10 10 10 10	7.2 7.4 8.0 8.1 8.9 9.8	0 0 0 0 0 0		(12)
.18	1-HO-4-NaSO ₃ C ₁₀ H ₆ + 4-HSO ₃ C ₆ H ₄ N ⁺ → (2)	H ₂ O	10 ⁴ A = 5; 10 ⁴ B = 1-5	Buffers	0.24	4.50 4.94 5.27 4.50	k AB	15 15 15 25	1.85 5.08 1.10 4.45	0 0 +1 0	*	(4)
.19	1-HO-4-HSO ₃ C ₁₀ H ₆ + 4-ClC ₆ H ₄ N ⁺ → (2)	H ₂ O	10 ⁵ A = 5; 10 ⁵ B = 1	Phosphate buffers	0.25	6.35	k AB	10	4.06	+2		(6)
.20	1-HO-4-HSO ₃ C ₁₀ H ₆ -2-D + 4-ClC ₆ H ₄ N ⁺ → (2)	H ₂ O	10 ⁵ A = 5; 10 ⁵ B = 1	Phosphate buffers	0.25	6.35	k AB	10	3.95	+2		(6)
.21	1-HO-5-H ₂ NSO ₃ C ₁₀ H ₆ + 4-CH ₃ C ₆ H ₄ N ⁺ → (2)	H ₂ O	10 ³ A = 2; 10 ⁴ B = 2	Buffers		6.4 6.7 7.0	k AB	15 15 15	1.33 2.53 4.26	0 0 0	*	(6)

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No.	Reaction	Solvent	Amount of reactant	Addend	Conc. of length	pH	Defined base	Temperature	$k = k^0 \times 10^n$	β	$A = A^0 \times 10^{12}$	Comments	Reference
.22	$2\text{-HO-6-HSO}_3\text{C}_3\text{H}_6 + \text{C}_6\text{H}_5\text{N}^+ \longrightarrow (1)$	H_2O	$10^2\text{A} = 1;$ $10^5\text{B} = 1$	Buffers	0.25	4.61	k AB	20	k^0 7.40 n +2			*	(10)
.23	$2\text{-HO-6-HSO}_3\text{C}_3\text{H}_6 + 3\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1;$ $10^5\text{B} = 1$	Buffers	0.25	6.34	k AB	20	k^0 2.88 n +2			*	(10)
.24	$2\text{-HO-6-HSO}_3\text{C}_3\text{H}_6 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1;$ $10^5\text{B} = 1$	Buffers	0.005 0.01 0.02 0.05 0.10 0.25	7.0 7.0 7.0 7.0 7.0 7.0	k AB	10 10 10 10 10 10	k^0 1.02 1.00 9.5 9.3 8.0 7.1	0 0 -1 -1 -1 -1			(12)
			$10^4\text{A} = 1-100;$ $10^5\text{B} = 1$		0.25 0.25 0.25 0.25 0.25 0.25	6.34 5.09 5.71 6.24 6.71 7.18		20 20 20 20 20 20	k^0 1.68 2.75 1.01 4.04 1.05 3.10	+2 -2 -1 -1 0 0		*	(10) (12)
.25	$2\text{-HO-6-HSO}_3\text{C}_3\text{H}_6 + 3\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^2\text{A} = 1;$ $10^5\text{B} = 1$	Buffers	0.25	4.61	k AB	20	k^0 1.20 n +3			*	(10)
.26	$2\text{-HO-6-HSO}_3\text{C}_3\text{H}_6 + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^2\text{A} = 1;$ $10^5\text{B} = 1$	Buffers	0.25	6.34	k AB	20	k^0 3.35 n +1			*	(10)
.27	$2\text{-HO-6-HSO}_3\text{C}_3\text{H}_6 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^5\text{A} = 1;$ $10^5\text{B} = 1$	Buffers	0.005 0.01 0.02 0.05 0.10 0.25	7.0 7.0 7.0 7.0 7.0 7.0	k AB	10 10 10 10 10 10	k^0 4.8 5.0 5.1 5.7 6.3 6.3	+1 +1 +1 +1 +1 +1		*	(12)

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k^0 \times 10^n$ k^0 n	g	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.28	$2\text{-HO-6-HSO}_3\text{C}_6\text{H}_4 + 3\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1$; $10^5\text{B} = 1$	Buffers	0.25	4.61	k_{AB}	20	1.07 +4			*	(10)
.29	$2\text{-HO-6-HSO}_3\text{C}_6\text{H}_4 + 4\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^4\text{A} = 1$; $10^5\text{B} = 1$	Buffers	0.25	5.60	k_{AB}	20	3.35 +3			*	(10)
.30	$2\text{-HO-6-HSO}_3\text{C}_6\text{H}_4 + 2.5\text{-(HSO}_3)_2\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^5\text{A} = 1$; $10^5\text{B} = 1$	Buffers	0.005 0.01 0.02 0.05 0.10 0.25	7.0 7.0 7.0 7.0 7.0 7.0	k_{AB}	10 10 10 10 10 10	4.8 0 5.1 0 6.0 0 6.3 0 1.28 +1 1.91 +1				(12)
.31	$2\text{-HO-6-HSO}_3\text{C}_6\text{H}_4 + 4\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1$; $10^5\text{B} = 1$	Buffers	0.25	6.35	k_{AB}	10	7.4 0				(6)
.32	$2\text{-HO-6-HSO}_3\text{C}_6\text{H}_4\text{-1-D} + 4\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1$; $10^5\text{B} = 1$	Buffers	0.25	6.35	k_{AB}	10	1.2 0				(6)
.33	$1\text{-NH}_2\text{-4-HSO}_3\text{C}_6\text{H}_4 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (2)$	H_2O	$\text{A:B} = (2:5)$	Buffers	0.24 0.24 0.24 0.24 0.24	2.04 3.43 3.49 4.51 5.18	k_{AB}	25 25 25 25 25	6.6 -1 1.0 0 2.8 0 2.3 0 2.3 0			*	(8)
.34	$1\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + \text{C}_6\text{H}_4\text{N}^+ \longrightarrow (2)$	H_2O	$\text{A:B} = (2:5)$	Buffers	0.24 0.24 0.24 0.24 0.24	2.43 3.49 4.32 4.95 6.25	k_{AB}	25 25 25 25 25	5.2 -1 6.9 0 1.1 +1 3.3 +1 5.0 +1			*	(8)

No.	Reaction	Solvent	Amount of reactant	Addend	ionic strength	pH	Defined reaction law	Temperature	$k \times 10^2$ k° n	$k \times 10^2$ k° n	$A = A^\circ \times 10^2$ A° n	Comments	literature
35	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + \text{C}_6\text{H}_5\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1; 10^3\text{B} = 1$	Buffers	0.25	5.60	k_{AB}	20	2.24	0		*	(10)
36	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 3\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1; 10^3\text{B} = 1$	Buffers	0.25	5.60	k_{AB}	20	8.5	-1		*	(10)
37	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^3\text{A} = 1; 10^3\text{B} = 1$	Buffers	0.005 0.01 0.02 0.05 0.10 0.25	5.70 5.69 5.67 5.62 5.58 5.53	k_{AB}	10 10 10 10 10 10	2.55 2.35 2.19 1.94 1.66 1.59	-1 -1 -1 -1 -1 -1			(9)
			$10^4\text{A} = 1-100;$ $10^5\text{B} = 1$		0.25 0.25 0.25	5.09 5.60 7.18		20 20 20	3.22 3.3 3.84	-1 -1 -1		*	(13) (10) (13)
38	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 3\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^4\text{A} = 1; 10^5\text{B} = 1$	Buffers	0.25	5.60	k_{AB}	20	4.80	0		*	(10)
39	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^2\text{A} = 1; 10^3\text{B} = 1$	Buffers	0.25	5.60	k_{AB}	20	7.80	-2		*	(10)
40	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 3\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^4\text{A} = 1; 10^5\text{B} = 1$	Buffers	0.25	2.09	k_{AB}	20	2.0	+3		*	(10)
41	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 4\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^5\text{A} = 1; 10^5\text{B} = 1$	Buffers	0.25	2.09	k_{AB}	20	2.24	+3		*	(10)
42	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_4 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}_2^+ \longrightarrow (1)$	H_2O	$10^6\text{A} = 1; 10^6\text{B} = 1$	Buffers	0.005 0.01 0.02 0.05 0.10 0.25 0.25	5.72 5.71 5.70 5.67 5.63 5.60 5.60	k_{AB}	10 10 10 10 10 10 20	6.81 6.74 6.81 6.67 6.85 6.87 1.05	+1 -1 +1 +1 +1 +1 +2		*	(9) (10)

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defining masses	Temperature	$k \times 10^n$		k	$A = A^0 \times 10^{12}$		Comments	Literature
									k^0	n		A^0	n		
.43	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_3 + 2\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^5\text{A} = 1; 10^5\text{B} = 1$	Buffers	0.25	5.60	k AB	20	8.78	+1				*	(10)
.44	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_3 + 4\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^4\text{A} = 1$	Buffers	0.25	5.60	k AB	20	1.64	+1				*	(10)
.45	$2\text{-NH}_2\text{-6-HSO}_3\text{C}_6\text{H}_3 + 2.5\text{-(HSO}_3\text{)}_2\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^5\text{A} = 1; 10^5\text{B} = 1$	Buffers	0.005 0.01 0.02 0.05 0.10 0.25 0.25	5.72 5.71 5.70 5.67 5.63 5.60 5.60	k AB	10 10 10 10 10 10 20	4.50 4.69 5.08 5.50 6.00 6.25 6.42	+1 +1 +1 +1 +1 +1 +1					(9)
Tri-substituted naphthalene															
.46	$1\text{-OH-3,8-(NaSO}_3\text{)}_2\text{C}_{10}\text{H}_6 + \text{C}_6\text{H}_5\text{N}^+ \longrightarrow (2)$	H_2O	$10^4\text{B} = 1\text{-5; A} \searrow \text{B}$	Buffers	0.24	6.30 7.08	k AB	15 15	1.35 8.36	-1 -1				*	(4)
.47	$1\text{-OH-3,8-(NaSO}_3\text{)}_2\text{C}_{10}\text{H}_6 + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (2)$	H_2O	$10^4\text{B} = 1\text{-5; A} \searrow \text{B}$	Buffers	0.24	7.08 8.17	k AB	15 15	3.28 3.73	-1 0				*	(4)
.48	$1\text{-OH-3,8-(NaSO}_3\text{)}_2\text{C}_{10}\text{H}_6 + 2\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (2)$	H_2O	$10^4\text{B} = 1\text{-5; A} \searrow \text{B}$	Buffers	0.24	7.08 8.17	k AB	15 15	9.3 1.04	-2 0				*	(4)
.49	$1\text{-OH-3,8-(NaSO}_3\text{)}_2\text{C}_{10}\text{H}_6 + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (2)$	H_2O	$10^4\text{B} = 1\text{-5; A} \searrow \text{B}$	Buffers	0.24	4.94 5.80	k AB	15 15	1.58 1.30	-1 0				*	(4)
.50	$1\text{-OH-3,8-(NaSO}_3\text{)}_2\text{C}_{10}\text{H}_6 + 4\text{-BrC}_6\text{H}_4\text{N}^+ \longrightarrow (2)$	H_2O	$10^4\text{B} = 1\text{-5; A} \searrow \text{B}$	Buffers	0.24	5.27 5.60	k AB	15 15	5.3 1.78	-1 0				*	(4)

Homogeneous Reaction Kinetics

312.455

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No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass	Temperature	$k \times 10^n$ k^0 n	δ	$A \times 10^n$ A^0 n	Comments	Literature
.51	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + C ₆ H ₅ N ⁺ → (2)	H ₂ O	10 ⁴ B = 1-5; A \ B	Buffers	0.24	5.27 5.90	k AB	15 15	1.75 -1 5.95 -1			*	(4)
.52	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 4-CH ₃ C ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ B = 1-5; A \ B	Buffers	0.24	5.90 6.73	k AB	15 15	2.12 -1 2.75 0			*	(4)
.53	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 2-CH ₃ OC ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ A = 1-5; 10 ⁴ B = 1-5	Buffers	0.24	6.3 7.08 7.08	k AB	15 15 25	2.08 -1 1.23 0 3.4 0		1 13	*	(4)
.54	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 4-HSO ₃ C ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ A = 1-5; 10 ⁴ B = 1-5	Buffers	0.24	4.94 5.27 5.80 5.27	k AB	15 15 15 25	6.64 -1 1.61 0 5.50 0 3.75 0		4 11	*	(4)
.55	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 4-BrC ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ B = 1-5; A \ B	Buffers	0.24	5.27 5.90	k AB	15 15	1.08 0 3.70 0			*	(4)
.56	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + C ₆ H ₅ N ⁺ → (1)	H ₂ O	B = 1-5; A \ B	Buffers	0.24	7.08 8.17	k AB	15 15	5.32 -2 5.64 -1			*	(4)
.57	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 4-CH ₃ C ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ B = 1-5; A \ B	Buffers	0.24	8.17 9.15	k AB	15 15	2.64 -1 1.20 0			*	(4)
.58	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 4-HSO ₃ C ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ B = 1-5; A \ B	Buffers	0.24	6.30 7.08	k AB	15 15	1.16 -1 5.92 -1			*	(4)
.59	2-OH-3,6-(NaSO ₃) ₂ C ₆ H ₃ + 4-NO ₂ C ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ⁴ A = 1; 10 ⁴ B = 1	Buffers		6.65	k AB	10	1.55 +3				(11)

Homogeneous Reaction Kinetics

312.455

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No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined reaction rates	Temperature	$k \times 10^n$ k^0 n	$k^0 \times 10^n$ k^0 n	Comments	Literature
.60	2-OH-6,8-(HSO ₃) ₂ C ₁₀ H ₄ -1-D + 4-NO ₂ C ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ³ A = 1; 10 ⁵ B = 1	Buffers		6.65	k AB	10	3.24	+2		(11)
.61	2-OH-6,8-(HSO ₃) ₂ C ₁₀ H ₃ + 3-ClC ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ³ A = 2; 10 ⁵ B = 1	Buffers		7.28	k AB	10	1.07	+1		(11)
.62	2-OH-6,8-(HSO ₃) ₂ C ₁₀ H ₄ -1-D + 3-ClC ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ³ A = 2; 10 ⁵ B = 1	Buffers		7.28	k AB	10	1.95	0		(11)
.63	2-OH-6,8-(HSO ₃) ₂ C ₁₀ H ₃ + 4-ClC ₆ H ₄ N ⁺ → (1)	H ₂ O	10 ³ A = 2-1; 10 ⁵ B = 1 10 ⁴ A = 5-20 Base catalyst C ₆ H ₅ N	Buffers [Base] .0234 .0487 .0931 .140 .232 .483 .687 .911 .0215 .0897 .221 .433 .0228 .0914 .225 .441 .0217 .0897 .222 .438		6.69 6.85 6.66 6.84 6.63 6.62 6.60 6.54 6.51 7.16 7.31 7.25 7.18 7.14 7.14 7.08 6.99 7.25 7.39 7.34 7.28	k AB k AB	10 10	6.2 1.54 6.03 1.10 2.24 2.95 4.68 8.01 1.02 1.15 4.79 1.29 2.82 4.37 8.32 2.57 5.50 8.25 1.10 3.47 7.41 1.10	-1 0 0 +1 +1 +1 +1 +1 +2 +2 0 +1 +1 +1 +1 +1 +1 +1 +1 +1 +1 +2		(11) (11) (11) (11)
			2-CH ₃ C ₆ H ₄ N					10	4.79	0		
			3-CH ₃ C ₆ H ₄ N					10	1.29	+1		
			4-CH ₃ C ₆ H ₄ N					10	2.82	+1		
								10	4.37	+1		
								10	8.32	0		
								10	2.57	+1		
								10	5.50	+1		
								10	8.25	+1		
								10	1.10	+1		
								10	3.47	+1		
								10	7.41	+1		
								10	1.10	+2		

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined reaction	Temperature	$k^o \times 10^2$	Comments	Literature
									k^o	n	
.63	$2\text{-OH-}6,8\text{-(HSO}_3\text{)}_2\text{C}_6\text{H}_3 + 4\text{-ClC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$ (continued)	H_2O $2,6\text{-(CH}_3\text{)}_2\text{C}_6\text{H}_3$	Base catalyst [Base] .071 .0364 .0739 .145 .205 .287			7.01 7.05 7.07 7.04 6.95 6.92	kAB	10 10 10 10 10 10	1.32 2.11 3.80 6.40 8.89 1.15	0 0 0 0 0 +1	(11)
.64	$2\text{-OH-}6,8\text{-(NaSO}_3\text{)}_2\text{C}_6\text{H}_3 + 4\text{-BrC}_6\text{H}_4\text{N}^+ \longrightarrow (1)$	H_2O	$10^4\text{B} = 1\text{-}5$ $\text{A} \approx \text{B}$	Buffers	0.24	5.80 6.73	kAB	15 15	9.40 6.00	-2 -1	(4)
Heterocyclic aromatic											
.65	$\text{C}_6\text{H}_4\text{CH:CHN:CH} + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}_2\text{C:NCH:CHN} + \text{H}^+$	H_2O	$10^4\text{A} = 1\text{-}10$ $10^5\text{B} = 1\text{-}5$	Buffers		7.10 8.15 9.15 10.0 11.0	kAB	25 25 25 25 25	3.0 1.20 9.1 3.52 4.89	-1 0 0 +1 +1	(3)
.66	$\text{C}_6\text{H}_4\text{CH:CHN:CH} + 4\text{-NO}_2\text{C}_6\text{H}_4\text{N}^+ \longrightarrow \text{C}_6\text{H}_4\text{NHCH:C-N}_2\text{C}_6\text{H}_4\text{-4-NO}_2 + \text{H}^+$ (indole)	H_2O	$10^4\text{A} = 1\text{-}10$ $10^5\text{B} = 2\text{-}5$	Buffers		4-6 6.7 7.6 8.6 9.2	kAB	0 0 0 0 0	2.3 3.1 3.9 5.2 4.5	0 0 0 0 0	(1)
.67	$\text{C}_6\text{H}_4\text{CH:CHN:CH} + 4\text{-NO}_2\text{C}_6\text{H}_4\text{N}^+ \longrightarrow \text{C}_6\text{H}_4\text{NHCH:C-N}_2\text{C}_6\text{H}_4\text{-4-NO}_2 + \text{D}^+$ (indole-D-substitute)	H_2O	$10^4\text{A} = 5$ $10^5\text{B} = 3$	Buffers		6.7	kAB	0	3.36	0	(1)

No.	Reaction	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k^0 \times 10^7$ k^0 η	Comments	Temperature
.68	$\text{C}_6\text{H}_4\text{CHN:NH} + p\text{-HSC}_6\text{H}_4\text{N}^+ \longrightarrow (3)$ (indazole)	H_2O	$10^3\text{A} = 2-10$; $10^4\text{B} = 2-20$	Buffers		8.50 8.65 9.00 9.15 9.60 10.10	kAB	25 25 25 25 25 25	1.0 1.0 1.8 5.0 1.4 4.6	-2 -2 -2 -2 -1 -1	(3)
.69	$\text{C}_6\text{H}_4\text{CHN:NH} + \text{HC}_6\text{H}_4\text{SO}_3\text{H} + 4\text{-HSO}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$	H_2O	$10^3\text{A} = 0-10$; $10^4\text{B} = 2-30$	Buffers		8.5 9.0 9.6 10.1	kAB	25 25 25 25	8.3 5 7 8	0 0 0 0	(3)
.70	$\text{C}_6\text{H}_4\text{CHN:NH} + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow \text{C}_6\text{H}_4\text{CHN:NH} + \text{H}^+$ (3-methyl-5-pyrazolone)	H_2O	$10^3\text{A} = 2$; $10^4\text{B} = 2$	Buffers		5.4 6.2 6.6	kAB	15 15 15	8.90 5.43 1.17	-1 0 +1	(5)
.71	$\text{C}_6\text{H}_4\text{CHN:NH} + 2\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (4)$ (3-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3\text{A} = 2$; $10^4\text{B} = 2$	Buffers		4.52 4.70 4.89 5.12	kAB	15 15 15 15	1.43 2.43 3.60 5.72	0 0 0 0	(5)
.72	$\text{C}_6\text{H}_4\text{CHN:NH} + 3\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (4)$ (5-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3\text{A} = 2$; $10^4\text{B} = 2$	Buffers		4.15 4.36 4.53 4.78	kAB	15 15 15 15	1.48 2.45 4.08 7.10	0 0 0 0	(5)
.73	$\text{C}_6\text{H}_4\text{CHN:NH} + 4\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow (4)$ (3-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3\text{A} = 2$; $10^4\text{B} = 2$	Buffers		4.6 5.0 5.4	kAB	15 15 15	2.47 5.92 1.40	0 0 +1	(5)

No.	Reaction.	Solvent	Amount of reactant	Addend	Ionic strength	pH	Defined mass action law	Temperature	$k^o \times 10^n$	Comments	Literature
									k^o n		
.74	$\text{C:ON}(\text{C}_6\text{H}_5)_2\text{N:C}(\text{CH}_3)_2\text{CH}_2 + 2\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow (4)$ (3-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3\text{A} = 2; 10^4\text{B} = 2$	Buffers		4.53 5.06 5.31	k AB	15 15 15	1.38 4.47 8.33	0 0 0	*
.75	$\text{C:ON}(\text{C}_6\text{H}_5)_2\text{N:C}(\text{CH}_3)_2\text{CH}_2 + 4\text{-CH}_3\text{OC}_6\text{H}_4\text{N}^+ \longrightarrow (4)$ (5-methyl-1-phenyl-5-pyrazolone)	H_2O	$10^3\text{A} = 2; 10^4\text{B} = 2$	Buffers		5.2 5.4 5.6	k AB	15 15 15	1.90 3.33 5.55	0 0 0	*

COMMENTS

General. In most of the coupling reactions listed, pseudo first order rate constants were determined with diazonium ion in smaller amount. Second order rate constants were calculated by dividing pseudo first order constants by analytical concentration of reactant in excess. In some cases authors also divided pseudo first order constants by calculated concentration of supposed reactive species. Such values have not been tabulated except where so stated under comments. Diazo coupling reactions are listed in order of the compound undergoing coupling, substituted benzene derivatives being listed first followed by mono-substituted naphthalene, then di- and tri-substituted naphthalene derivatives. These are followed by heterocyclic substances. In each group the compound with OH precedes NH_2 , NO_2 , HSO_3^- , Cl^- , Br^- , and I^- . Compounds with substituents in the 1-position precede, 2, 3, 4 etc. The diazonium ions are also arranged in a corresponding order.

Literature. (4) Units of rate constants converted to seconds from original minutes. A to B ratio varied from $\frac{1}{5}$ to 5. Plot of log of rate constant vs. pH observed to be linear with slope of unity. (5) Units converted to seconds from original minutes. Amperometric method used. Buffers used were Clark and Luba. Plot of log of rate constant vs. pH linear but slope varied from 0.6 to 1.3. (5) points out that similar plot by (4) had slope 0.9 not unity. (6) Units converted to seconds from original minutes. Concentrations of reactants not stated by authors. pH dependence concluded to indicate coupling involves diazonium ion with free amine.

COMMENTS

(continued)

Reaction. (.6) Rate constant converted to seconds from original minutes. Reaction followed potentiometrically. Authors calculate rate constants for paths involving $\text{HOC}_6\text{H}_4\text{O}^-$ and $\text{OC}_6\text{H}_4\text{O}^-$ ions. (.9) Calculated second order rate constants decreased with progress of reaction in this alkaline medium. Values approximate. (.11) Authors studied in detail influence of temperature, base catalysis and reaction medium upon ortho and para coupling. (.22) Rate constant corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield 98.8%. (.23) Rate constant corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield of product of coupling 82.2%. (.24) Rate constant at 20°C by (10^9) corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield 69.5%. (.25) Rate constant corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield 88.1%. (.26) Rate constant corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield 92.1%. (.26) Rate constant corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield 89.2%. (.29) Rate constant corrected for side reaction and calculated in terms of naphtholate ion as reactant. Yield 89.2%. (.33) (.34) Units converted to seconds from assumed minutes. (.35) Rate constant corrected for side reaction. Yield of product of coupling 89%. (.36) Rate constant corrected for side reaction. Yield of product of coupling 88%. (.37) Rate constant of (10^9)

corrected for side reaction. Yield of product of coupling 75.5%. Approximate value for activation energy calculated by editor. (.38) Rate constant corrected for side reaction. Yield of product of coupling 89.8%. (.39) Rate constant corrected for side reaction. Yield of product of coupling 82.8%. (.40) Rate constant corrected for side reaction. Yield of coupled product 73.7%. (.41) Rate constant corrected for side reaction. Yield of coupled product 68.1%. (.42) Rate constant of (10^9) corrected for side reaction. Yield of coupled product 87.3%. Approximate value for activation energy calculated by editor. (.43) Rate constant corrected for side reaction. Yield of coupled product 84.4%. (.44) Rate constant corrected for side reaction. Yield of coupled product 89.6%. (.45) Activation energy and frequency factor of doubtful accuracy as based on only two values ten degrees apart. (10^9) corrected rate constant for side reactions. Yield of coupled product 71%. (.65) Authors show reactive species is probably anion of A since plot of its concentration vs. pH has same shape as plot of rate constant vs. pH. (.68) Rate constant corrected for simultaneous zero order decomposition of B with $10^9 k_0 = 0.6, 9.0, 20.0, 5.0, 1.0$ and 25.0 at the pH's 8.5, 8.65, 9.0, 9.15, 9.60 and 10.1 respectively. Rate constant also corrected for consecutive reaction (.69) between Band L. (.69) A consecutive reaction to (.68) products not determined. Rate constant gives order of magnitude only.

LITERATURE

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EXCHANGE
Sulfonation of aromatic compounds

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	$k \times 10^n$ k^0 n	g	$A = k^0 \times 10^n$ k^0 n	Comments	Temperature
.2	$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			$k_{AB}R = k_0 [M + (k_1/k_0)^2]^{-1/2} - k_2 M/A(1 + q)$	40 40 40 40	k_0 1.55 k_1 1.68 k_2 4.83 q 3.89	-5 -6 -3 +3			(*)
.3	$CH_3C_6H_5 + H_2SO_4 \longrightarrow CH_3C_6H_4SO_3H + H_2O$	$C_6H_5NO_2$	A = 0.1-0.5; B = 0.1-0.3			$k_{AB}R = k_0 [M + (k_1/k_0)^2]^{-1/2} - k_2 M/A(1 + q)$	40 40 40 40	k_0 7.87 k_1 7.95 k_2 4.87 q 9.5	-5 -6 -3 +2			(*)
.4	$NO_2C_6H_5 + H_2SO_4 \longrightarrow m\text{-NO}_2C_6H_4SO_3H + H_2O$	A	B = 0.1-0.3			$k_{AB}R = k_0 [M + (k_1/k_0)^2]^{-1/2} - k_2 M/A(1 + q)$	40 40 40 40	k_0 2.4 k_1 2.5 k_2 1.13 q 1.53	-7 -8 -2 +3			(*)
		B + SO_3 (1-30%)	A < 0.1 [SO_3]		$k A[SO_3]/B$		25	6.3	-5	22	*	(*)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	E	$A = A^0 \times 10^m$	Comments	Literature
.5	$(\text{CH}_3)_3\text{N}^+\text{C}_6\text{H}_5 + \text{H}_2\text{SO}_4 \longrightarrow (\text{CH}_3)_3\text{N}^+\text{C}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$ (78% m, 22% o,p)	B + SO_3 (1-30%)	A < 0.1 [SO_3]	$\frac{1}{2} \text{SO}_3$ 4.1 11.5 20.1 24.2 33.1 (1-30)		kA	25 25 25 25 25	k^0 n 1.2 -5 2.3 -4 2.1 -3 3.0 -3 3.3 -2	16.3 14.9 14.9 15.2	1.1 7 2.0 7 1.9 8 5.3 8	*	(2)
.6	$\text{ClC}_6\text{H}_5 + \text{H}_2\text{SO}_4 \longrightarrow \text{ClC}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5; B = 0.1-0.3			kABR $k = k_1 \left[\frac{M + (k_1/k_0)^2}{1 + (k_1/k_0)^2} \right]^{-1/2} - k_2 M/A(1 + qM)$	40 40 40 40	k^0 n 1.06 -5 1.14 -6 8.5 -4 1.05 +3	8.9		*	(4)
.7	$\text{BrC}_6\text{H}_5 + \text{H}_2\text{SO}_4 \longrightarrow \text{BrC}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5; B = 0.1-0.3			kABR $k = k_1 \left[\frac{M + (k_1/k_0)^2}{1 + (k_1/k_0)^2} \right]^{-1/2} - k_2 M/A(1 + qM)$	40 40 40 40	k^0 n 9.5 -6 1.04 -6 8.2 -4 1.05 +3	8.9		*	(6)
.8	$4\text{-BrC}_6\text{H}_4\text{T} + \text{H}_2\text{SO}_4 \longrightarrow \text{Br-TC}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$ $\longrightarrow 4\text{-BrC}_6\text{H}_4\text{SO}_3\text{H} + \text{HOT}$	B + SO_3 (10-12%)	(k_1) (k_2)			k_B/k_T	0	k^0 n 1.82 0			*	(1)
Di-substituted Benzene												
.9	$m\text{-(CH}_3)_2\text{C}_6\text{H}_4 + \text{H}_2\text{SO}_4 \longrightarrow (\text{CH}_3)_2\text{C}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5; B = 0.1-0.3			kABR $k = k_1 \left[\frac{M + (k_1/k_0)^2}{1 + (k_1/k_0)^2} \right]^{-1/2} - k_2 M/A(1 + qM)$	40 40	k^0 n 1.17 -4 1.24 -5	6.4		*	(4)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass	Temperature	$k \times 10^7$ k^0 η	k k^0 η	Comments	Literature
.9		$m-(CH_3)_2C_6H_4 + H_2SO_4 \longrightarrow (CH_3)_2C_6H_4SO_3H + H_2O$ (continued)	$C_6H_5NO_2$	A = 0.1-0.5 B = 0.1-0.3				$k_{AB}; k = k_1[M + (k_1/k_2)^3]^{-1/2} - k_2M/A(1 + q)$			*	(⁴)
.10	.1	$p-CH_3C_6H_4NO_2 + H_2SO_4 \longrightarrow$ $1-CH_3-2-SO_3H-4-NO_2C_6H_3 + H_2O$	B + M	A = 0.2, M = 0.78 " 1.05 " 1.33 " 1.78 " 2.24 " 1.14 " 1.33 " 1.78 " 2.24 " 2.73 A = 0.1-0.2, M = 1.4-5.5 0.4 1.38 0.2 2.17 " 1.47 " 1.08 " " " " " " A = 0.2, $[SO_3] = 0.44$ " 1.1 " 2.2 " 0.2-0.8 " 1.2 " 0.7-1.5 A < 0.1 $[SO_3]$ $[SO_3] = 4.1$	$kA/M(M + [HSO_4^-])$			40 40 70 70 70 70 70 80 80 80 80 80 96 96 96 96 96 96 13 13 13 25 25 40 20 20	k_2 8.79 q 1.61 6.4 7.8 8.9 8.3 1.08 2.38 2.56 2.78 3.20 3.33 1.9 1.5 2.00 1.66 1.94 1.66 1.58 2.38 3.1 4.0 8.4 9.5 4.2 1.0 2.3	27 <		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rate action law	Temperature	$k^0 \times 10^n$	k^0	$k^0 \times 10^n$	k^0	$A =$ $A^0 \times 10^n$	Comments	Literature
.10	.1	$p\text{-CH}_3\text{C}_6\text{H}_4\text{NO}_2 + \text{H}_2\text{SO}_4 \longrightarrow$ (continued)	B + SO_3	A < 0.1 [SO ₃]	$\% \text{SO}_3 = 11.4$ 20.1 4-20		k_A $k'A([\text{SO}_3]/B)^{1.2}$	20 20 20	4.4 1.2	-4 -3	19.5	6 10	*	(2)	
			$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3			$k_{AB}; k = k_0 [M + (k_1/k_0)^3] - 1/3 - k_2 M/A(1 + Q)$	40 40 40 40	3.3 3.5 2.75 1.11	-6 -7 -3 +3	9.8		*	(4)	
.11		$p\text{-CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_3^+ + \text{H}_2\text{SO}_4 \longrightarrow$ $1\text{-CH}_3\text{-2-SO}_3\text{H-4-(CH}_3)_3\text{N}^+\text{C}_6\text{H}_3 + \text{H}_2\text{O}$	B + SO_3	A < 0.1 [SO ₃]	$\% \text{SO}_3 = 4.1$ 11.5 4-11		k_A $k'A([\text{SO}_3]/B)^{2.2}$	25 25 25	5.0 9.0	-3 -2	13.2	2.6 7	*	(3)	
.12		$p\text{-CH}_3\text{C}_6\text{H}_4\text{Cl} + \text{H}_2\text{SO}_4 \longrightarrow \text{CH}_3\text{-ClC}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3			$k_{AB}; k = k_0 [M + (k_1/k_0)^3] - 1/3 - k_2 M/A(1 + Q)$	40 40 40 40	1.71 1.85 4.59 3.36	-5 -6 -3 +3	7.4		*	(4)	
.13		$m\text{-Cl}_2\text{C}_6\text{H}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3			$k_{AB}; k = k_0 [M + (k_1/k_0)^3] - 1/3 - k_2 M/A(1 + Q)$	40 40 40 40	6.7 9.2 1.99 2.36	-6 -7 -3 +3	9.5		*	(4)	

Homogeneous Reaction Kinetics

312.462

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No.	Reaction	Solvent	Amount of reactant	Added	Amount of added	Defined mass	Temperature	$k = k^0 \times 10^n$	k^0	n	$A = A^0 \times 10^n$	Comments	Temperature
.14	$p\text{-Cl}_2\text{C}_6\text{H}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}_2\text{C}_6\text{H}_3\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3										
.15	$p\text{-Br}_2\text{C}_6\text{H}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Br}_2\text{C}_6\text{H}_3\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3										
Tri-substituted benzene													
.16	$1,2,4\text{-Cl}_3\text{C}_6\text{H}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Cl}_3\text{C}_6\text{H}_2\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3										
Substituted naphthalenes													
.17	$\text{C}_{10}\text{H}_8 + \text{H}_2\text{SO}_4 \longrightarrow \text{C}_{10}\text{H}_7\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3										

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	B	$A = A^0 \times 10^n$	Comments	Literature
13	$\alpha\text{-C}_{10}\text{H}_7\text{NO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{C}_{10}\text{H}_6\text{SO}_3\text{H} + \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{NO}_2$	A = 0.1-0.5 B = 0.1-0.3									
						$k_{AB}k = k_1[M + (k_1/k_0)^2]^{-1/3} - k_2M/A(1 + qM)$	40 40 40 40	k_0 2.61 k_1 2.98 k_2 8.17 q 3.57	-5 -6 -3 +3	8.4		(5)

COMMENTS

Reactions. (.2) (.3) Followed by turbidimetric method for H_2O by (4). Rate dependent upon concentration of water as given by expression for k which holds for first 5 to 7% reaction only, and for $[\text{H}_2\text{O}] < 0.15$. k_0 is measured rate constant for initial rate and the k_1 and k_2 terms are related to the forward and reverse reactions. Simultaneous sulfonation of solvent given by (.4). (.4) Reaction followed by turbidimetric method for H_2O by (4). See (.2) (.3). Reaction using spectrophotometric method in fuming sulfuric observed by (2) to be pseudo first order with respect to A as B in excess. Rate constant found to be proportional to first power of the ratio $[\text{H}_2\text{SO}_4]/[\text{H}_2\text{SO}_3]$ where $[\text{H}_2\text{SO}_4]$ was taken as equal to the SO_3 added. Rate constant calculated in terms of total $\text{C}_6\text{H}_5\text{NO}_2$ and $\text{C}_6\text{H}_5\text{NO}_2\text{H}^+$ rather than true $\text{C}_6\text{H}_5\text{NO}_2$ concentration. Units converted to seconds from

original minutes of (2). (.5) Analytical method for A with units converted to seconds from original minutes. First order with respect to A as B in excess. Rate constant found to be proportional to the ratio $[\text{H}_2\text{SO}_4]/[\text{H}_2\text{SO}_3]$ to the 2.4 power. $[\text{H}_2\text{SO}_4]$ taken as equal to the SO_3 added. Temperature dependence studied from 0 to 40°C . (.6) Followed by a turbidimetric method for H_2O . Expression for dependence of rate upon H_2O valid for first 5 to 7% reaction and for $[\text{H}_2\text{O}] < 0.15$. Measured rate constant for initial rate is k_0 . Terms for forward and reverse reactions involve k_1 and k_2 . For simultaneous sulfonation of solvent see (.4). (.8) Comparison of sulfonation at hydrogen and tritium studied in both fuming sulfuric and nitrobenzene as solvent. (.9) Followed by a turbidimetric method for H_2O . Expression for dependence of rate upon H_2O valid for first 5 to 7% reac-

COMMENTS

(continued)

tion and for $[H_2O] < 0.015$. Measured rate constant for initial rate is k_0 . Terms for forward and reverse reactions involve k_1 and k_2 . For simultaneous sulfonation of solvent see (.4). (.10) Integrated rate law of (3) gives linear plot up to 80% reaction for individual runs but calculated constants increase with increase in concentration of either H_2O , or SO_3 . Activation energy in presence of H_2O can be corrected by 20 kcal. for the heat of reaction of H_2O and SO_3 at infinite dilution in H_2SO_4 to give a value of 7 kcal. The rate law in excess H_2O or SO_3 consistent with mechanism involving simultaneous attack of both a sulfonating agent and a base to remove the proton. Units converted to seconds from original hours of (3). Pseudo first order with respect to A observed by (2) as SO_3 in larger excess. At these concentrations rate constant observed to be proportional to $[H_2S_2O_7]/[H_2SO_4]$ to the 1.2 power, where $[H_2S_2O_7]$ is taken as amount of SO_3 added. Units converted to seconds from original minutes of

(2). Turbidimetric method for H_2O in $C_6H_5NO_2$ used by (4). Expression for dependence of rate upon H_2O valid for first 5 to 7% reaction, and for $[H_2O] < 0.015$. Measured initial rate constant is k_0 and terms for forward and reverse reactions involve k_1 and k_2 . For simultaneous sulfonation of solvent see (.4). (.11) Pseudo first order with respect to A for at least 80% of reaction as B in excess. Rate found to be proportional to $[H_2S_2O_7]/[H_2SO_4]$ to the 2.2 power. $[H_2S_2O_7]$ taken as equal to the SO_3 added. Addition of a base such as H_2SO_4 reduces rate. Units converted to seconds from original minutes. (.12) (.13) (.14) (.15) (.16) (.17) (.18) Measured rate constant for initial reaction is k_0 . Net forward reaction given by k valid for 5-7% reaction and for $[H_2O] < 0.015$. Term involving k_1 is for forward reaction and term involving k_2 is for reverse reaction. For simultaneous sulfonation of solvent see (.4). Turbidimetric method used.

LITERATURE

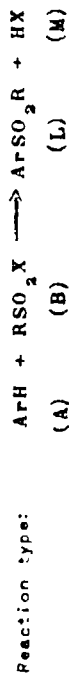
- (1) E. Berzlius-Larsson, L. Molander, *Arkiv. Kemi.* 1953, 6, 219. (2) J. C. Brand, *CSW* 1950, 100%.
- (3) W. A. Cowdrey, L. S. Davies, *CSW* 1949, 1871. (4) F. J. Stubbs, C. W. Williams, C. N. Hinshelwood, *CSW* 1948, 1035.

EXCHANGE

Aryl sulfone formation

Liquid phase

Amounts are in M/l.

Rate constants are in
M/l and sec.

No.	Reaction	Solvent	Amount of reactant	Added catalyst	Amount of added	Defined mass	Temperature	$k = k^0 \times 10^n$	n	E
1	$C_6H_6 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2C_6H_5 + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	3.5	-5	17
2	$C_6H_6 + p-CH_3C_6H_4SO_2Cl \longrightarrow p-C_6H_5SO_2C_6H_4CH_3 + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	1.08	-4	
3	$C_6H_6 + m-NO_2C_6H_4SO_2Cl \longrightarrow m-C_6H_5SO_2C_6H_4NO_2 + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	2.3	-6	
4	$C_6H_6 + p-ClC_6H_4SO_2Cl \longrightarrow p-C_6H_5SO_2C_6H_4Cl + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	1.8	-5	
5	$C_6H_6 + p-BrC_6H_4SO_2Cl \longrightarrow p-C_6H_5SO_2C_6H_4Br + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	1.8	-5	
							40	4.5	-5	
6	$C_6H_6 + p-IC_6H_4SO_2Cl \longrightarrow p-C_6H_5SO_2C_6H_4I + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	2.3	-5	
7	$CH_3C_6H_5 + p-BrC_6H_4SO_2Cl \longrightarrow CH_3C_6H_4SO_2C_6H_4Br + HCl$	A	B = 0.1	$AlCl_3$	0.1	k B	30	6.8	-5	
8	$NO_2C_6H_5 + p-BrC_6H_4SO_2Cl \longrightarrow$	A	B = 0.2	$AlCl_3$	0.2	(no measurable reaction)				
9	$ClC_6H_5 + p-BrC_6H_4SO_2Cl \longrightarrow ClC_6H_4SO_2C_6H_4Br + HCl$	A	B = 0.2	$AlCl_3$	0.2	k B	30	1.3	-5	
10	$BrC_6H_5 + p-BrC_6H_4SO_2Cl \longrightarrow BrC_6H_4SO_2C_6H_4Br + HCl$	A	B = 0.2	$AlCl_3$	0.2	k B	30	1.7	-5	

COMMENTS

Pseudo first order with respect to B as A in excess. Order with respect to catalyst, $AlCl_3$, not determined. Beyond 50% reaction calculated rate constants decrease. Units in seconds calculated from original minutes.

LITERATURE

S. C. J. Olivier, *RFC* 1914, 33, 146, 244.

Homogeneous Reactions

312.471

EXCHANGE

Replacement of H by halogen on aliphatic C

Liquid phase

 Reaction type: $RH + X_2 \longrightarrow RX + HX$ (unless otherwise stated)

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

(A) (B) (1) (30)

 Rate measured: $-dB/df$ unless otherwise stated

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

No.	Supplementing No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass	Temperature	$k = R^0 \times 10^n$	$A = A^0 \times 10^n$	Comments	Literature
Saturated aliphatic Derivatives												
.44		$C_2H_5(CH_2)_2COH + Br_2 \longrightarrow$ $CH_3CHBr(CH_2)_2COH + H_2O$	CCl_4	A = 0.046 0.095 0.191 0.381 0.762 1.52 4.57	H	0-0.05	R B	25 25 25 25 25 25 25	3.8 1.20 4.6 1.70 4.3 9.4 4.95	-6 -5 -5 -4 -4 -4 -3	*	(1)
.45		$(CH_3)_3CBr + Br_2$	CCl_4	A = B = 1.0	$[(CH_3)_3CO]_2$	0-2%	R AB ²	0	1.44	-8	*	(27)
Aliphatic-aliphatic mono Ketone												
.46	.1	$CH_3COCH_3 + 3ClO^- \longrightarrow$ $CH_3COO^- + CHCl_3 + 2OH^-$	H_2O	A = 0.31; $10^3 B = 1.5$	OH ⁻	0.034 0.071	R AB	0 0	1.02 1.55	-3 -3	*	(2)

Homogeneous Reaction Kinetic;

512.471

No.	Supplementing No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = \frac{k^0}{A^0 \times 10^n}$	δ	$A = \frac{A^0}{A^0 \times 10^n}$	Comments	Literature
.46	.1	$\text{CH}_3\text{COO}^- + \text{Br}_2 \rightarrow$ (cont.)	H_2O	$A = 0.31$ $10^3 B = 1.5$	OH^- Cl^-	$\left. \begin{matrix} 0.034 \\ 0.22 \end{matrix} \right\}$	k_{AB}	0	$k^0 = 1.24$ $n = -3$			*	(²)
.47	.2	$\text{CH}_3\text{COOCH}_3 + \text{Br}_2$	H_2O	$A = 0.1$ $B = 0.005$	HCl	0.5	k_A	5	$k^0 = 1.27$ $n = -6$			*	(¹¹)
			Ac_2S	"	"	"	"	15	$k^0 = 4.01$ $n = -6$				
				"	"	"	"	25	$k^0 = 1.53$ $n = -5$				
				"	"	"	"	35	$k^0 = 5.18$ $n = -5$	20.3			
				"	"	"	"	15	$k^0 = 5.72$ $n = -6$				
				"	"	"	"	25	$k^0 = 1.85$ $n = -5$				
				"	"	"	"	35	$k^0 = 5.76$ $n = -5$	20.0			
			Ac_5O	"	"	"	"	0	$k^0 = 1.14$ $n = -6$				
				"	"	"	"	15	$k^0 = 7.68$ $n = -6$				
				"	"	"	"	25	$k^0 = 2.49$ $n = -5$	19.7			
			Ac_7S	"	"	"	"	0	$k^0 = 2.26$ $n = -6$				
				"	"	"	"	15	$k^0 = 1.63$ $n = -5$				
				"	"	"	"	25	$k^0 = 5.27$ $n = -5$	20.1			
			H_2O	$A = 0.1$ $B = 0.005$	CH_3COO^-	0.147	k_A	35	$k^0 = 8.91$ $n = -7$			*	(¹¹)
				"	"	"	"	45	$k^0 = 2.58$ $n = -6$				
			Ac_2S	"	"	"	"	55	$k^0 = 7.05$ $n = -6$	20.7			
				"	"	"	"	35	$k^0 = 1.54$ $n = -6$				
				"	"	"	"	45	$k^0 = 4.32$ $n = -6$				
			Ac_5O	"	"	"	"	55	$k^0 = 1.12$ $n = -5$	19.0			
				"	"	"	"	35	$k^0 = 2.36$ $n = -6$				
				"	"	"	"	45	$k^0 = 6.40$ $n = -6$				
			Ac_7S	"	"	"	"	55	$k^0 = 1.68$ $n = -5$	19.4			
				"	"	"	"	35	$k^0 = 2.92$ $n = -6$				
				"	"	"	"	45	$k^0 = 7.66$ $n = -6$				
				"	"	"	"	55	$k^0 = 1.88$ $n = -5$	18.5			

Homogeneous Reaction Kinetics

312.471

No.	Supplying No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$k^0 \times 10^7$	k^0	n	$A = A^0 \times 10^7$	Comments	Literature
.47	.2	$\text{CH}_3\text{COCH}_3 + \text{Br}_2$ (cont.)	Ac_2O	$A = 0.1$; $B = 0.005$	CH_3COO^-	0.147	k_A	35	2.82		-6		*	(11)
.48	.2	$\text{CH}_3\text{COCH}_3 + 3\text{BrO}^- \longrightarrow$ $\text{CH}_3\text{COO}^- + \text{CHBr}_3 + 2\text{OH}^-$	H_2O	$10^4 A = 7-8$; $10^3 B = 1.5-5$	OH^-	0.007-0.07	$k_A[\text{OH}^-]$	0	6.7		-2		*	(2) (7)
.49	.4	$\text{CH}_3\text{COCH}_3 + \text{I}_2$	H_2O	$A = 0.27$; $10^3 B = 1-2$	(X_1) H_2O OH^- H_3O^+ $(\text{CH}_3)_3\text{CCOO}^-$ $(\text{CH}_3)_3\text{CCOOH}$ CH_3COO^- CH_3COOH $\text{CH}_2\text{OHCOO}^-$ CH_2OHCOOH $\text{CH}_2\text{ClCOO}^-$ CH_2ClCOOH $\text{C}_6\text{H}_5\text{Cl}_3\text{O}^-$ CH_3COO^- CH_3COOH	buffers 55.5 (5-20) 10^{-3} (2-20) 10^{-3} (2-10) 10^{-3} (4-100) 10^{-4} $\mu = 0.11$ $\mu = 0.11$ $\mu = 0.2$ $\mu = 0.2$ $\mu = 0.11$ 0.02-0.2 0.02-0.8 $\mu = 0.2$	$\sum k_1 A X_1$ k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1 k_1	25 25 25 25 25 25 25 25 25 25 25 25 25 25 25 25 25	8 2.5 2.74 4.08 7.3 2.44 1.01 3.85 3.25 5.0 1.27 7.58	-12 -1 -5 -7 -8 -7 -7 -8 -7 -6 -6 -6			*	(6)
.50	.4	$\text{CH}_3\text{COCH}_3 + 3\text{IO}^- \longrightarrow$ $\text{CH}_3\text{COO}^- + \text{CHI}_3 + 2\text{OH}^-$	H_2O	$10^4 A = 7-8$; $10^3 B = 1.5-5$	OH^-	0.007-0.035	$k_A[\text{OH}^-]$	0	6.9		-2		*	(2) (7)
									1.60		-1			
									3.12		-1			
									5.2		-1			
									13.4		-1			

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No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rates	Temperature	$k = k^0 \times 10^n$	ρ	$A = A^0 \times 10^7$	Comments	Literature
.51		$\text{CH}_3\text{COCH}_3 + 2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{N}(\text{C}_2\text{O}_2\text{H}_3)_2 \xrightarrow{\text{C}_6\text{H}_5\text{Cl}} \text{CH}_3\text{COCH}_2\text{Cl} + 2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{NHCOCCH}_3$	$\text{C}_6\text{H}_5\text{Cl}$	$10^2 B = 0.85$ 1.5 3.0 6.2 9.5 15.7 2.2 5.0 7.6 15.1	CH_2ClCOOH	0.0138 0.0138 0.0138 0.0138 0.0138 0.0072 0.0072 0.0072 0.0072 0.0072	$-\text{dB}^0/\text{dt}$	50 50 50 50 50 50 50 50 50 50	k^0 -8 -8 -7 -7 -7 -8 -7 -7 -7 -7		*	(⁶)	
.52		$\text{CH}_3\text{COCH}_3 + [(2,4,6\text{-Cl}_3\text{C}_6\text{H}_2)_2\text{N}]_2\text{C}(\text{O}_2\text{C}_6\text{H}_5)_2 \xrightarrow{\text{C}_6\text{H}_5\text{Cl}} \text{CH}_3\text{COCH}_2\text{Cl} + [(2,4,6\text{-Cl}_3\text{C}_6\text{H}_2)_2\text{N}]_2\text{C}(\text{O})$	$\text{C}_6\text{H}_5\text{Cl}$	$10^2 B = 3.4$ 5.5 10.5 17.6	CH_2ClCOOH	0.0072 0.0072 0.0072 0.0072	$-\text{dB}^0/\text{dt}$	50 50 50 50	k^0 -7 -7 -7 -7			*	(⁶)
.53		$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 + \text{Br}_2$	Ac75	$A = 0.1; B = 0.005$	HCl	0.5	k_A	15 25 35	k^0 -5 -5 -4	21.2 2.0	11	*	(¹⁷)
.54		$(\text{CH}_3)_3\text{CCOCH}_3 + \text{Br}_2$	Ac75	$A = 0.1; B = 0.005$	HCl	0.5	k_A	25 35 45	k^0 -5 -5 -4			*	(¹⁷)
.55		$\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_2\text{C}_6\text{H}_5 + \text{Br}_2$	Ac75	$A = 0.1; B = 0.005$	HCl	0.5	k_A	15 25 35	k^0 -5 -5 -4	20.6 6	10	*	(¹⁷)

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No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action	Temperature	$k = k^0 \times 10^7$	B	$A = A^0 \times 10^7$	Comments	Literature
.56		$(\text{CH}_3)_2\text{CHCOCH}(\text{CH}_3)_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	35 45 55	2.02 6.65 1.99	-5 -5 -4	3 11 22.8	*	(17)
.57		$(\text{CH}_3)_3\text{CCOCH}_2\text{CH}_3 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45	9.0 2.90 9.4	-6 -5 -5	9 10 21.8	*	(17)
.58		$(\text{CH}_3)_3\text{CCOCH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45	8.0 2.56 8.0	-6 -5 -5	3 10 21.3	*	(17)
.59		$(\text{CH}_3)_3\text{CCOCH}(\text{CH}_3)_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	35 45 55	1.74 5.98 1.72	-6 -6 -5	2 10 22.7	*	(17)
Halogen-substituted Ketones													
.60		$\text{CH}_3\text{COCH}_2\text{Cl} + \text{I}_2$	H_2O	$10^2 A = 2-6$	buffers $X = \text{H}_2\text{O}$ OH^- H_3O^+ $(\text{CH}_3)_3\text{CCOO}^-$ CH_3COO^- $\text{CH}_2\text{OHCOO}^-$ $\text{CH}_2\text{ClCOO}^-$	$\mu = 0.11$ " " " " " " $\mu = 0.2$	$\sum k_1 A_1$ $k_1 =$ $k_1 =$ $k_1 =$ $k_1 =$ $k_1 =$ $k_1 =$	25 25 25 25 25 25 25	4.8 2.0 < 3 2.64 1.87 2.52 4.59	-9 +2 -6 -4 -4 -5 -8		*	(6)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined Reaction	Temperature	$k \times 10^n$		ρ	$A \times 10^n$		Comments	Literature
									k^0	n		A^0	n		
.64		$\text{CH}_3\text{COCH}(\text{CH}_3)\text{COCH}_3 + \text{Br}_2$	H_2O	$10^2 A = 3.3$ $10^2 B = 3$			k_A	21 25 35	5.8 8.3 2.3	-5 -5 -4					(21)
.65		$\text{CH}_3\text{COCH}_2\text{COCH}_3 + \text{Br}_2$	H_2O	$10^2 A = 4-8$ $10^2 B = 4-8$	HCl	0 0 0-0.1 0.5 0 " " " " "	k_A	0 14 25 25 25 25 25 25 25 25	8.92 4.65 1.48 1.57 1.49 1.37 1.37 1.26 9.27 6.44	-4 -3 -2 -2 -2 -2 -2 -3 -3	18	1.2 9		*	(26)
.66		$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_2\text{COCF}_3 + \text{Br}_2$	Et6	$A \sim B \sim 0.015$			k_A	14 25	3.42 1.18	-3 -2	19	1 12		*	(26)
.67		$\text{C}_6\text{H}_5\text{COCH}_2\text{COCF}_3 + \text{Br}_2$	Et4	$A \sim B \sim 0.01$			k_A	14 25	3.72 8.55	-3 -3	13	3 7		*	(26)
.68		$\text{CH}-\text{CH}$ $\parallel \parallel$ $\text{CH}(\text{CH}_3)\text{COCH}_2\text{COCF}_3 + \text{Br}_2$	Et10	$A \sim B \sim 0.01$			k_A	14 25	2.96 1.01	-3 -2	19	8 11		*	(26)
Aromatic-aliphatic Ketone															
.69	.15	$\text{CH}_3\text{COCH}_2\text{H}_6 + \text{Br}_2$	Ac25	$A = 0.1$, $B = 0.005$	HCl	0.5	k_A	25 35	7.12 2.13	-6 -5				*	(11)

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No.	Supplement No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass	Temperature	$k^0 \times 10^n$	k^0	n	B	$A = k^0 \times 10^n$	Comments	Literature
.69	.13	$\text{CH}_3\text{COOC}_6\text{H}_5 + \text{Br}_2$ (cont.)	Ac25 Ac50	A = 0.1; B = 0.005	HCl	0.5	kA	45	5.77		-5	19.4		*	(¹¹)
			Ac50	"	"	"	"	25	9.16		-6				"
			Ac75	"	"	"	"	35	2.70		-5				"
			Ac75	"	"	"	"	45	7.34		-5	19.2			(¹¹) (¹⁵) (¹⁶)
			Ac75	"	"	"	"	15	6.25		-6				"
			Ac75	"	"	"	"	25	2.03		-5				"
			Ac75	"	"	"	"	35	6.28		-5				"
			Ac90	"	"	"	"	45	1.81		-4	20.2	1.3		(¹¹)
			Ac90	"	"	"	"	5	1.05		-5				"
			Ac90	"	"	"	"	15	3.72		-5				"
			Ac50	"	"	0.147	kA	25	1.20		-4	19.8		*	(¹¹)
			Ac50	"	"	"	"	35	1.28		-6				"
			Ac50	"	"	"	"	45	3.58		-6				"
			Ac75	"	"	"	"	55	9.91		-6	20.3			(¹¹) (¹⁶)
			Ac75	"	"	"	"	35	1.28		-6				"
			Ac75	"	"	"	"	45	4.0		-6				"
			Ac75	"	"	"	"	55	1.01		-5				"
			Ac90	"	"	"	"	65	2.75		-5	18.9	4		(¹⁶)
			Ac90	"	"	"	"	35	1.31		-6				"
			Ac90	"	"	"	"	45	3.52		-6				"
			Ac90	"	"	"	"	55	9.25		-6	19.3			"
.70	.14	$\text{CH}_3\text{CO}(\text{m-C}_6\text{H}_4\text{CH}_3) + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	kA	15	7.43		-6			*	(¹⁶)
			Ac75	"	"	"	"	25	2.47		-5				"
			Ac75	"	"	"	"	35	7.41		-5	20.0	1.2		(¹⁶)
.71	.15	$\text{CH}_3\text{CO}(\text{m-C}_6\text{H}_4\text{NO}_2) + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	kA	15	2.5		-6			*	(¹⁶)
			Ac75	"	"	"	"	25	8.2		-6				"
			Ac75	"	"	"	"	35	2.70		-5				"
			Ac75	"	"	"	"	45	7.96		-5	21.0	2.1		"

No.	Supplementing No. 1951	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^n$ k^0 n	β	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
.72	.16	$\text{CH}_3\text{CO}(\text{p-C}_6\text{H}_4\text{NO}_2)_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15 25 35 45	3.16 -6 9.8 -6 3.16 -5 9.5 -5	21.0	2.5 10	*	(16)
.73	.17	$\text{CH}_3\text{CO}(\text{m-C}_6\text{H}_4)_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45	1.38 -5 4.38 -5 1.28 -4	20.7	2.1 10	*	(16)
.74	.18	$\text{CH}_3\text{CO}(\text{p-C}_6\text{H}_4\text{F})_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45	1.49 -5 4.78 -5 1.36 -4	20.5	1.7 10	*	(16)
.75	.15	$\text{CH}_3\text{CO}(\text{m-C}_6\text{H}_4\text{Cl})_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15 25 35 45	3.58 -6 1.22 -5 3.92 -5 1.15 -4	20.8	2.2 10	*	(16)
.76		$\text{CH}_3\text{CO}(\text{p-C}_6\text{H}_4\text{Cl})_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15 25 35 45	4.7 -6 1.52 -5 4.73 -5 1.40 -4	20.6	2.0 10	*	(16)
.77	.20	$\text{CH}_3\text{CO}(\text{m-C}_6\text{H}_4\text{Br})_2 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15 25 35 45	3.63 -6 1.23 -5 3.89 -5 1.17 -4	20.8	2.2 10	*	(16)

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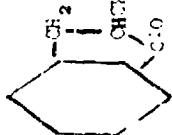
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No.	Supplementing No. 1951	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rate	Temperature	$k \times 10^n$	$k^0 \times 10^n$	g	$A = A^0 \times 10^n$	Comments	Temperature
.78	.21	$\text{CH}_3\text{CO}(\text{p-C}_6\text{H}_4\text{Br}) + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15 25 35 45	4.83 1.84 4.74 1.45	-6 -5 -5 -4	20.4	1.4 10	*	(16)
.79	.22	$\text{CH}_3\text{CO}(\text{m-C}_6\text{H}_4\text{I}) + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	15 25 35 45	3.71 1.25 4.03 1.17	-6 -5 -5 -4	20.7	1.9 10	*	(16)
.80	.23	$\text{CH}_3\text{CO}(\text{p-C}_6\text{H}_4\text{I}) + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45	1.82 4.97 1.47	-5 -5 -4	20.4	1.5 10	*	(16)
.81	.28	$\text{CH}_3\text{CH}_2\text{COC}_6\text{H}_5 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45 55 65	9.0 2.94 9.35 8.65 1.81 4.72	-6 -5 -5 -7 -6 -6	22.1	1.4 11	*	(14)
.82	.30	$\text{C}_6\text{H}_5\text{CH}_2\text{COC}_6\text{H}_5 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	k A	25 35 45 55 65	8.01 2.03 9.45 5.20 1.43 3.82	-6 -5 -5 -7 -6 -6	22.0	8 10	*	(14)
					CH_3COO^-	0.147	k A	45 55 65	5.20 1.43 3.82	-7 -6 -6	20.2	4 7	*	(15)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined base action	Temperature	$k \times 10^n$	g	$k \times 10^n$	Comments	Temperature
									k°	η	k°	η	
.83	.32	$(\text{CH}_3)_2\text{CHCOOC}_6\text{H}_5 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	kA	25	1.77	-6		*	(14)
			"	"	CH_3COO^-	0.147	kA	35	6.08	-6			
								45	1.92	-5	22.1	2.9	10
								45	1.27	-7		*	(15)
								55	3.70	-7			
								65	9.9	-7	20.9	3	7
.84	.34	$n\text{-C}_4\text{H}_9\text{CH}_2\text{COOC}_6\text{H}_5 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	kA	25	7.10	-6		*	(14)
			"	"	CH_3COO^-	0.147	kA	35	2.36	-5			
								45	7.30	-5	21.7	6	10
								45	5.86	-7			(15)
								55	1.57	-6			
								65	3.99	-6	20.1	4	7
.85	.35	$(\text{CH}_3)_2\text{CHCH}_2\text{COOC}_6\text{H}_5 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	kA	25	2.79	-6		*	(15)
			"	"	CH_3COO^-	0.147	kA	35	9.74	-6			
								45	2.89	-5	21.7	2.3	10
								45	2.54	-7			
								55	7.07	-7			
								65	1.87	-6	20.5	3.2	7
.86	.36	$n\text{-C}_4\text{H}_9\text{CH}_2\text{COOC}_6\text{H}_5 + \text{Br}_2$	Ac75	A = 0.1; B = 0.005	HCl	0.5	kA	25	6.81	-6		*	(15)
								35	2.22	-5			
								45	6.86	-5	21.4	3.4	10
Mono-carboxylic acids													
.87		$\text{CH}_3\text{COONa} + \text{Br}_2$	CH_3COOH	A = 2B = 0.025	NaBr	0.6f	kAB	25	1.53	-2		*	(15)
			Ac92			0.2		35	3.18	-2	16	~11	
			Ac9C			0.2		35	5.0	-2			
								35	1.4	-1			

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addenda	Defined mass action law	Temperature	$R =$		$A =$ $A^0 \times 10^n$	Comments	Literature
									$k^0 \times 10^n$	n			
Keto-carboxylate													
.63	.12	$\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 + \text{Br}_2$	H_2O	$10^3 A = 5-17$	KBr	0.05	A	0	1.35	-4		*	(23)
						"		18	6.85	-4			
						"		25	1.20	-3			
						0.10		18	6.85	-4			
						0.30		18	6.85	-4			
						0.60		18	6.26	-4			
						1.00		18	5.69	-4			
						2.00		18	4.35	-4			
						0.0		17	6.92	-4			
						0.042		18	7.08	-4			
.60		$\text{CH}_3\text{COCHBrCOOC}_2\text{H}_5 + \text{Br}_2$	H_2O	$10^3 A = 4-6; B < A$	Cu^{++} CH_3COONa CH_3COOH	0.099	$k A + k' A [\text{Cu}^{++}] + k'' A [\text{CH}_3\text{COO}^-] + k''' A [\text{Cu}^{++}] [\text{CH}_3\text{COO}^-]^{(24)}$	18	7.19	-4		*	(23)
						0.20		18	7.30	-4			
						0.37		18	7.54	-4			
						0-0.02		18	$k = 7.12$	-4			
						0.010		18	$k' = 1.03$	-1			
						0.10		18	$k'' = 3.15$	-1			
						"		18	$k''' = 4.4$	+1			
						0.05		0	1.59	-3			
						"		18	8.30	-3			
						0.10		25	1.47	-2			
.60		$\text{CH}_3\text{COCHBrCOOC}_2\text{H}_5 + \text{Br}_2$	H_2O	$10^3 A \sim 5$	KBr	0.05	k A	0	1.59	-3		*	(23)
						0.30		18	8.30	-3			
.60		$\text{CH}_3\text{COCHBrCOOC}_2\text{H}_5 + \text{Br}_2$	H_2O	$10^3 A \sim 5$	NaCl	0.10		18	8.26	-3			
						0.30		18	7.50	-3			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass	Temperature	$k^0 \times 10^n$	R	$A^0 \times 10^n$	Comments	Literature	
								k^0	n	A^0	n		
100	$CF_3COCHBrCOOCH_2H_5 + Br_2$ (cont.)	F_2O	$10^3 A \sim 5$	NaCl	0.60 1.00 2.00 0.0	KA	18	6.92	-3			*	(25)
				HCl	0.04-0.1		18	6.45	-3				
							18	5.65	-3				
							18	7.92	-3				
							18	7.19	-3				
							18	7.35	-3				
							18	7.54	-3				
				Cu^{++}	0.37 0-0.02		18	8.0	-3			*	(24)
101	$CH_3COCH(ClCH_2H_5)COOCH_2H_5 + Br_2$	H_2O	$A = 0.03$ $B = 0.001$			KA	20	4.8	-6				(21)
							25	7.6	-6				
							35	1.73	-5	15.5	1.0	6	
102	$CH_2BrCH_2ClOCHCOOCH_2H_5 + Br_2$	H_2O	$10^3 A = 3-7; B < A$	Acids + salts $X_1 = Cu^{++}$ Ni^{++} La^{+++} Zn^{++} Pb^{++} Mn^{++} Cd^{++} Mg^{++} Ca^{++} Ba^{++} H^+ Be^{++} Al^{+++} Na^+ K^+	0-0.1 0-0.3	KA + $\sum R_i X_i$	18	$k = 1.34$	-3			*	(26)
							18	$k_1 = 1.22$	-1				
							18	$k_1 = 6.25$	-2				
							13	$k_1 = 5.65$	-2				
							18	$k_1 = 2.11$	-2				
							18	$k_1 = 1.07$	-2				
							18	$k_1 = 6.5$	-3				
							18	$k_1 = 6$	-3				
							18	$k_1 = 4.3$	-3				
							18	$k_1 = 4.1$	-3				
							18	$k_1 = 1.1$	-3				
							18	$k_1 = 7.1$	-4				
							19	$k_1 = 5$	-4				
							18	$k_1 \sim 4$	-4				
							16	$k_1 = 5$	-5				
							16	$k_1 = (0.0)$					

No.	Supplementing 751 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rate action law	Temperature	$k \times 10^n$ k^0 n	B	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
94		 (2-O-carboxybenzyliden-1 one)	Ac2O (16 M/D)	$10^2 A = 4.2$ $10^3 B = 6.8$ $10^4 C = 2.6$ $10^5 D = 3.5$ $A = 4$	HBr	0.245 0.245 0.253 0.352	k_A	25 25 25 25	2.77 2.93 3.85 5.36	-4 -4 -4 -4			(18)
Dicarboxylic acid (ester)													
95		$B_2(COOCH_2)_2 + 2Br_2$	H ₂ O	$10^3 A = 5-25$ $10^3 B = 1-3$	HClO ₄	$(2-8 \cdot 10) \times 10^{-3}$	$-dA/dt = k_A$	25	3.0	-5		*	(9) (21)
95.1		$m_2(COOCH_2)_2 + 5Br_2$	H ₂ O	$10^4 A = 4-70$ $10^4 B = 2-300$ $10^4 [H]^+ = 8.4-26$ 81 25 $10^5 [H]^+ = 3-19$	CH_2ClCOO^- CH_3COO^-	0.050 0.028 0.022 0.020	k_A	25 25 25 25	2.38 2.0 4.37 3.95 4.93	-5 -5 -5 -5 -4	*	(9)	
96		$B_2H_2(COOCH_2)_2 + Br_2$	H ₂ O	$10^4 A \sim 4$ $10^2 B = 2$	HClO ₄ CH_2ClCOO^- $CH_2ClCOOH$ CH_3COO^- CH_3COOH $X = CH_2ClCOO^-$ CH_3COO^-	0.0011 0.05 0.05 0.002 0.002	k_A	25 25 25 25 25 25	2.8 6.2 6.0 6.9 1.7	-4 -4 -4 -3 -1	*	(9) (21)	

Heterogeneous Reaction Kinetics

312.471

18

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rate law	Temperature	$k \times 10^n$	k^0	n	β	$A = A^0 \times 10^n$	Comments	Literature
Nitriles															
.09		$C_2H_5C \equiv N + 2Br_2$	H_2O	$10^3 A = 2-3$ $10^3 B = 6-23$ $10^3 = 2.5$ 11.8 2.5 5.9	HBr	0.0014 0.0089 0.0027 0.0089	$-dA/dt = kA$	0 10 0 0 0	1.00 2.9 6.0 5.6 3.4 3.2	-3 -3 -4 -4 -4 -4	-3 -3 -4 -4 -4 -4	18	2 11	*	(20)
.09		$CH_3C \equiv N + Br_2$	H_2O	$B \gg A$			kA	0	> 2	-1	-1			*	(20)
.100		$C_2H_5OC \equiv CH_2CN + Br_2$	H_2O				$-dA/dt = kA$	0 10	7.1 2.3	-5 -4	-5 -4	17	2 9	*	(20)
.101		$C_2H_5OC \equiv CHBrCN + Br_2$	H_2O					0	8	-2	-2			*	(20)
Nitro-compounds															
.102		$CH_3CHNO_2 + 5Br_2$	H_2O	$A = 0.3-0.4$ $B = 0.02$			kA	26 35	4.1 1.23	-8 -7	-8 -7	23	1 9	*	(19)
.103		$CH_3CHNO_2 + I_2$	H_2O	$A = 0.3-0.4$ $10^3 B = 2-7$	(X) C_6H_5N		kA	15 26 35	9.1 4.0 1.27	-9 -8 -7	-9 -8 -7	22.9	1.2 9	*	(19)
			"	$A = 0.1-0.2$ $10^3 B = 2-4$		$= A$	kAX	17 25 35	6.07 1.49 3.57	-5 -4 -4	-5 -4 -4	16.8 $\Delta S^\ddagger = -25$		*	(22)

No.	Supplementing No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rates	Temperature	$k \times 10^n$	k^0	n	$\log A$	Comments	Literature
103		$\text{CH}_3\text{CH}_2\text{NO}_2 + \text{I}_2$ (cont.)	Et ₂ O	A = 0.1-0.2; 10 ³ B = 2-4	(X) C_6H_6	= A	k _{AX}	0	8.61		-6		*	(22)
			Et ₂ O	"	"	"	k _{AY}	25	1.08		-4			
			Et ₂ O	"	"	"	k _{AX}	35	2.32		-4	15.8	$\Delta S^\ddagger = -28$	
			Et ₂ O	"	"	"	k _{AX}	0	4.6		-7			
			Et ₂ O	"	"	"	k _{AX}	25	5.87		-8			
			Et ₂ O	"	"	"	k _{AX}	35	1.62		-5	17.1	$\Delta S^\ddagger = -30$	
			Et ₂ O	"	"	"	k _{AX}	25	4.1		-4			
			Et ₂ O	"	"	"	k _{AX}	25	2.20		-4			
			Et ₂ O	"	"	"	k _{AX}	25	3.03		-4			
			Et ₂ O	"	"	"	k _{AX}	25	3.47		-4			
			Et ₂ O	"	"	"	k _{AX}	25	7.5		-5			
			Et ₂ O	"	"	"	k _{AX}	25	1.27		-4			
			Et ₂ O	"	"	"	k _{AX}	25	1.28		-4			
104		$\text{CH}_3\text{COCH}_2\text{NO}_2 + 2\text{Br}_2$	H ₂ O				$-dA/dt = kA$	0	2.0		-3		*	(20)
			H ₂ O				$-dA/dt = kA$	10	6.4		-3	12		
105		$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{NO}_2 + 2\text{Br}_2$	H ₂ O				$-dA/dt = kA$	0	5.3		-4		*	(20)
			H ₂ O				$-dA/dt = kA$	10	1.52		-3	9		
106		$\text{CH}_2(\text{NO}_2)_2 + 2\text{Br}_2$	H ₂ O				$-dA/dt = kA$	0	4.5		-2		*	(20)
107		$\text{CH}_3\text{CHClNO}_2 + \text{Br}_2$	H ₂ O	A > B; A < B			k _A	35	1.7		-6		*	(20)
			H ₂ O				k _A	48	6.2		-6	8		

SOLVENTS

Ac₂S (50, 75, 80, 90, 92) vol of CH₃COOH + H₂O to make 100 volumes.Et₄ (6, 10, 16, 20, 33, 50, 67, 70, 83, 95) H₂O + C₂H₅OH vol %

COMMENTS

General. See comments 1951 edition. For ketones and keto-acids rate determining step considered to be enolization and or ionization of C-H bond. The rates and rate constants listed are for rate of disappearance of halogen, unless otherwise specified. Since replacement of first hydrogen by halogen is generally slower than replacement of second or third hydrogen on the same carbon the measured rate of disappearance of halogen may be two or even three times that of the rate controlling enolization or ionization. Since organic compound usually is in excess of halogen measured rates are pseudo zero order, and first order rate constants are obtained by dividing pseudo zero order rate of disappearance of halogen by concentration of compound being halogenated.

Literature. (1) (2) (3) (4) (5) (6) (7) (8) (9) converted from original minutes. (11) (14) (15) (16) (17) converted from original minutes and from ml. of N/50 thiosulfate per 20 ml. (18) (19) (20) (21) (22) (23) (24) (26) converted from original minutes. (27) converted from original hours.

Reactions. (.44) Pseudo first order with respect to B over about 85% of reaction as A in sufficient excess. At the higher concentrations of A reaction approximately first order with

respect to A as k/A almost constant. At lower concentrations reaction more nearly second order with respect to A and k/A^2 almost constant. Authors suggest mechanism involving an intermediate A-B complex consistent with data. Decomposition of complex found to be first order and rate law determined. (.45) Rate law not confirmed, except that it is an over-all third order, as $A = B$ in all cases. Addition of *t*-butylperoxide reduces rate about 25%. (.46) Rate controlling step considered to involve reaction of $OC_2H_5^-$ with enol or enolate ion rather than rate of formation of enol and enolate ion. Hydroxyl ion effect attributed to shift of enolate ion equilibrium as doubling OH^- increases rate by only 50%. (.47) First order constants calculated from pseudo zero order rates corrected from 1951 edition in which rates were in equivalents of halogen per liter rather than M/l as stated. (.48) Rate of enolization, considered to be rate controlling step, would be one third calculated rate as second and third hydrogen replaced more rapidly. (.49) Data may be represented by sum of second and third order terms with respective catalytic constants or in terms of concerted termolecular mechanism of (28). (.50) Rate of enolization, considered to be rate controlling step,

COMMENTS

(cont.)

would be one third calculated rate as second and third hydrogen replaced more rapidly. (.51) (.52) Consecutive mechanism involving reversible enolization followed by reaction with N-halide consistent with data. Rates are expressed in equivalents of oxidizing power of N-halide per liter. (.60) (.61) (.62) (.63) Acidity nearly constant in buffered solutions but where change occurred rate constants calculated for average acidity. (.65) (.66) (.67) (.68) First order rate law observed up to 80% reaction for all concentrations of A and B studied. Replacement of second hydrogen apparently much slower than first. Longer time intervals however did lead to more than 100% absorption of bromine on basis of amount of A present. (.89) (.70) (.71) (.72) (.73) (.74) (.75) (.76) (.77) (.78) (.79) (.80) (.81) (.82) (.83) (.84) (.85) (.86) First order rate constants calculated from pseudo zero order data in terms of ml of N/50 thiosulfate per 30 ml. Corrected from 1951 edition which has rates in equivalents of halogen per liter instead of M/l as listed. (.87) Induction period observed. Reaction accelerated (up to a maximum) with H_2O_2 . With different alkali acetates rate are found to vary in the order $K > Na > Li$. No measurable reaction in pure H_2O . (.96) Reaction

tion inhibited by I^- . With different alkali acetates the rate varies in the order $K > Na > Li$. (.89) (.90) Reactions occur consecutively and rate constants calculated for each by analysis of composite data of both reactions. (.92) For calculation of catalytic effect of ions K^+ arbitrarily taken as reference ion with $K_I = 0.00$. Where complexing occurs as with Cd^{++} with Br^- simple summation equation is not valid. Catalytic constant for Ni^{++} in CH_3COO^- buffers based upon no complex formation. Assumed complex formation increases value. Variation of concentration of H^+ , Cu^{++} and Ni^{++} with time complicates analysis of rates which also vary with time and results of (.26) are extrapolated to $t = \infty$. No appreciable acid catalysis observed by (.8). (.93) Reaction reversible but measured under conditions leading to almost complete reaction. (.95) Composite reaction consisting of consecutive steps (.95.1) and (.96). Rate constants calculated by (.3) low as the second step. (.96), assumed extremely rapid. (.95.1) Replacement of first hydrogen followed by consecutive reaction involving second hydrogen (.96). (.96) Value calculated by (.21) low probably due to error in assumed concentration of A. (.97) Decrease in rate with progress of reaction attributed

COMMENTS

(continued)

to acid hydrolysis of ester occurring simultaneously.
 (.98) Rate determining step probably ionization with ionization of monohalogenated nitrile more rapid than first step.
 Dependence of rate upon concentration of Br_2 and HBr may be related to a lower reactivity for Br_3^- . (.99) Reaction measured in presence of $\text{CH}_3(\text{CN})_2$, see (.98) and only one determination. (.100) (.101) Consecutive reactions with (.101) determined in presence of some $\text{C}_2\text{H}_5\text{OOCCH}_2\text{CN}$ and only

one determination. (.102) (.103) Assumed to proceed through rate determining ionization. One drop of strong acid added to minimize competition by OH^- . In presence of RN reaction assumed to proceed through slow bimolecular ionization, $\text{RN} + \text{CH}_3\text{CH}_2\text{NO}_2 \longrightarrow \text{RNH}^+ + \text{CH}_3\text{CHNO}_2^-$, as rate controlling step followed by rapid reaction between I_2 and the carbanion. (.104) (.105) (.106) (.107) Rate determining step assumed to be ionization.

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EXCHANGE

Replacement of H by halogen on aromatic C

Liquid phase

Reaction types:



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

* Coded solvents, Com-
ments, Literature at
the end of the table.

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

No.	Supplementing No. 1957	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action time	Temperature	$k =$ $k^0 \times 10^7$ k^0	$A =$ $A^0 \times 10^7$ A^0	Comments	Literature
Unsubstituted aromatic hydrocarbons												
.272	.2	$\text{C}_6\text{H}_6 + \text{Br}_2$	Ac^*	$A = 0.095$	ZnCl_2	0.50	k_{AB}	25	2.2	-4	*	(1)
.272.1	.3	$\text{C}_6\text{H}_6 + \text{HOBr}$	DI SO^*	$10^2 A = 1-1.6;$ $10^4 B = 9-13$	HClO_4	0.03-0.14	$k_{AB}[\text{H}^+]$	25	5.98	-1		(1a)
.272.2		$\text{C}_6\text{H}_6 + \text{ICl}$	Ac SO^*	$A = 0.2; 10^3 B = 3-7$	ZnCl_2	1.40	$k_{AB}[\text{ZnCl}_2]$	25	<1.6	-7		(2a)
.273		$\text{C}_{10}\text{H}_8 + \text{Br}_2$	Ac SO^*	$10^3 A = 9-16;$ $10^4 B = 9-60$	KBr KBr	0.20 0.1-0.5 0.4-6.0 $\mu = 0.5$	k_{AB} $k = k'k''/(k_1 + [\text{Br}^-])$	25 k'/K_1 K_1	1.0 3.41 1.64	-1 -2	*	(4a)

No.	Supplementing No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined reaction	Temperature	$k \times 10^n$	k^0	n	$A \times 10^n$	A^0	n	Comments	Literature
Alkyl substituted Benzene																
.273		$C_{10}H_8 + Br_2$ (continued)	Ac 50*	$10^3 A = 8-16$; $10^4 B = 3-90$	$\left. \begin{array}{l} XBr \\ NaClO \end{array} \right\}$	0.2 0.1 0.2 0.4 0.6	k_{AB}	25	k^0	n	A^0	n				(4a)
.274.1	.7	$CH_3C_6H_5 + Br_2$	CCl_4	$10^2 A = 3-37$; $10^2 B = 4-10$	I_2	0.035	$k_{AB}[I_2]$	25	3.5	-3					*	(1)
.274.2		$CH_3C_6H_5 + HOBr$	DI 50*	$10^3 A = 5-17$; $10^4 B = 8-18$	$HClO_4$	0.002-0.01	$k_{AB}[H^+]$	25	2.2	+1					*	(14b)
.274.3		$CH_3C_6H_5 + ICl$	Ac 99*	$A = 0.2$; $10^3 B = 3-7$	$ZnCl_2$	1.40	$k_{AB}[ZnCl_2]$	25	1.8	-5						(20a)
.275	.9	$C_7H_7C_6H_5 + Br_2$	CF_3COOH	$A = 0.24$; $10^3 B = 4$ 0.22 0.11 0.056 4-15	$ZnCl_2$	0.125 0.25 0.50	k_{AB}	2	1.14	-3						(1a)
.275		$C_7H_7C_6H_5 + Br_2$	Ac*	$10^3 A = 4-9$	$ZnCl_2$	0.125 0.25 0.50	k_{AB}	25	3.2	-3					*	(1)

Homogeneous Reaction Kinetics

512.475

3

No.	Supplementing 1956	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined base action law	Temperature	$k = A^0 \times 10^n$ k^0 n	β	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.276		$n\text{-C}_4\text{H}_9\text{C}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	time 24,800	% reacted 10		*	(5)
.277	.11	$(\text{CH}_3)_2\text{CHC}_2\text{H}_5 + \text{Br}_2$	Ac*	$10^2 A = 5-9$	ZnCl ₂	0.125 0.25 0.50	k AB	25 25 25	2.08 -3 9.3 -3 2.04 -2			*	(1)
.278		$n\text{-C}_4\text{H}_9\text{C}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	time 23,400	% reacted 10		*	(5)
.279		$(\text{CH}_3)_2\text{CHC}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	37,200	10		*	(5)
.280	.15	$(\text{CH}_3)_3\text{CC}_2\text{H}_5 + \text{Br}_2$	Ac*	A = 0.095	ZnCl ₂	0.25 0.50		25 25	6.7 -3 2.84 -2			*	(1)
.281		$\text{C}_2\text{H}_5(\text{CH}_3)\text{CHC}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	time 42,800	% reacted 10		*	(5)
.282		$n\text{-C}_4\text{H}_9\text{C}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	36,400	10		*	(5)
.283		$(\text{CH}_3)_2\text{CHC}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	66,800	10		*	(5)
.284		$(\text{CH}_3)_2\text{CH}(\text{CH}_3)\text{CHC}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	48,400	10		*	(5)
.285		$\text{C}_2\text{H}_5(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = B = 0.02	NaOAc	0.15		25	60,000	10		*	(5)
.286		$\text{C}_2\text{H}_5\text{CH}_2\text{C}_2\text{H}_5 + \text{Br}_2$	Ac 85*	A = 0.1; B = 0.05				35	17,500	10		*	(23)
.287	.10	$1,2\text{-(CH}_3)_2\text{C}_2\text{H}_4 + \text{Br}_2$	Ac*	A = 0.097	ZnCl ₂	0.25 0.50	k AB	25 25	1.18 -1 2.14 -1			*	(1)
.287.1		$1,2\text{-(CH}_3)_2\text{C}_2\text{H}_4 + \text{ICl}$	Ac 99*	A = 0.1; $10^3 B = 5-7$	ZnCl ₂	0.8 1.4 1.4	k AB [ZnCl ₂]	25 25 45	1.06 -4 1.80 -4 1.39 -3	19	1.3 10		(267)

No.	Supplement No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$	k^0	n	$k \times 10^n$	k^0	n	Comments	Literature
288	17	1,3-(CH ₃) ₂ C ₆ H ₄ + Br ₂	Ac [*]	A = 0.04-0.1	ZnCl ₂	0.0312 0.0825 0.125	k AB	25	6.4	-7					*	(1)
288.1		1,3-(CH ₃) ₂ C ₆ H ₄ + Br ₂	Ac ^{99*}	A = 0.1-0.25 10 ³ B = 3-7	ZnCl ₂	0.40 0.20 1.40 0.40 0.80	k AB[ZnCl ₂] ²	25	1.18	-3						(28a)
289		1,4-(CH ₃) ₂ C ₆ H ₄ + Br ₂	Ac [*]	A = 0.036	ZnCl ₂	0.125 0.25 0.50	k AB	25	1.43	-2					*	(1)
289.1		1,4-(CH ₃) ₂ C ₆ H ₄ + Br ₂	CF ₃ COOH	10 ² A = 5.2; 10 ³ B = 4 2.6 4-8 1.3 4			k AB	25	7.8	-2						(1a)
290		1,2,4-(CH ₃) ₃ C ₆ H ₃ + Br ₂	Ac ^{99*}	A = 0.2; 10 ³ B = 4-7	ZnCl ₂	0.80 1.40	k AB[ZnCl ₂] ²	25	5.2	-5						(23a)
291		1,2,4-(CH ₃) ₃ C ₆ H ₃ + Br ₂	Ac ^{80*}	A = 0.55; B = 0.12				25	1.31	-4					*	(3a)
292		1,2,4-(CH ₃) ₃ C ₆ H ₃ + Br ₂	Ac [*]	A = 0.08	ZnCl ₂	0.50	k AB	25	1.97	-2					*	(1)
292		1,2,4-(CH ₃) ₃ C ₆ H ₃ + Br ₂	Ac [*]	A = 0.10; B = 0.10 0.10 0.10 0.02 0.02 0.005 0.01				25	144						*	(1b)
								25	390							(14a)
								25	51.2							
								25	18.4							

No.	Supplement No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		B	$A \times 10^n$		Comments	Literature
									k^0	n		A^0	n		
.294	.13	1,3,5-(CH ₃) ₃ C ₆ H ₃ + Br ₂ (continued)	Ac*	A = 0.05; 10 ³ B = 4	NaOAc	0.25	$k_1AB + k_2AB^2$	25	k_1 2	-4				* (26) (28)	(28)
						"		25	k_2 5.83	0					
						0.10		25	k_1 5.8	-3					
						"		25	k_2 1.07	+1					
						0.25		25	k_1 1.25	-2					
						"		25	k_2 3.83	+1					
						0.10		25	k_1 1.0	-3					
						"		25	k_2 1.17	+1					
						0.25		25	k_1 2.5	-3					
						"		25	k_2 3.75	+1					
			Ac90*	0.05-0.14	ZnCl ₂	0.001		25	k_1 1.80	-2	7.1			* (1) (26)	(26)
						"		25	k_2 4.00	0	6.5				
						0.002		25	k_1 3.73	-2					
						"		25	k_2 5.50	0					
						0.004		25	k_1 7.87	-2					
						"		25	k_2 3.33	0					
						0.010		25	k_1 1.95	-1					
						"		25	k_2 5.00	0					
						0.0125		25	1.72	-1					
						0.0313		25	5.55	-1					
			Ac90*	10 ³ A = 1-2; 10 ³ B = 4	ZnCl ₂	7.4	$k_1AB + k_2AB^2$	25	k_1 6.70	-1				(26)	(26)
						"		25	k_2 1.80	+2					
						"		25	k_1 1.33	-4					
						"		25	k_2 2.35	0					
						0.245		25	k_1 2.0	-2					
						"		25	k_2 1.92	+1					
						"		25	k_1 3.65	-1					
						"		25	k_2 1.92	+2					
						"		25							
						"		25							
						"		25							

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined Reaction	Temperature	$k \times 10^n$ k^0 n	$A =$ $A^0 \times 10^n$ E n	Comments	Literature
.224	.18	1,3,5-(CH ₃) ₃ C ₆ H ₃ + Br ₂ (continued)	Ac ₂ O*	$10^3 A = 3.8; 10^3 B = 1.2$	NaOAc	0.009	$k_1 AB + k_2 AB^2$	25	$k_1 2.97$ -1		*	(26)
			C ₆ H ₅ Cl	"	"		$k AB^2$	25	$k_2 2.05$ +2			
				$A = 0.19; 10^3 B = 3.8$				25	2.45 -1			
				19				25	2.98 -1			
				36				25	3.10 -1			
			Ac ₂ O*	$A = 0.12; 10^3 B = 4$	H ₂ O	~50 % sat	$k ABH^A$	25	1.73 0		(28)	(27)
			Ac ₂ O*	"	"	0 % sat		25	1.47 0			
			CCl ₄	$A = 0.7; 10^3 B = 1-2$	"	40 % sat		17	1.27 -2			
				"	"	80 % sat		25	3.0 -4			
				"	"	0.01-0.06		25	2.6 -3			
				~0.1	0.5			25	1.23 -2			
								25	6.8 -3			
								25	4.5 -3			
								25	3.7 -3			
.224.1		1,3,5-(CH ₃) ₃ C ₆ H ₃ + ICl	CCl ₄	$A = 0.2; 10^3 B = 11$	H ₂ O IBr	~50 % sat	$k AB[IBr]^2$	34	4.7 -3	-11	(10), (32), (10)	(26a)
						0.001		14	9.2 +2			
						0.0008		25	9.8 +2			
						"		25	9.2 +2			
						"		25	7.3 +2			
						"		25	5.5 +2			
						"		25	3.6 +2			
						0.0004		25	9.7 +2			
						0.002		25	7.8 +2			
						0.001		36	8.2 +2	~0		
						0.06-0.1	$k AB[ZnCl_2]$	25	6.1 -2			
						0.2		25	7.2 -2			
						0.30		25	6.7 -2			
						0.40		25	9.2 -2			
						0.80		25	1.46 -1	4 10		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defining base	Temperature	$k \times 10^n$		$\bar{g}$	$A = A^0 \times 10^{17}$		Comments	Literature
									k^0	n		k^0	n		
.294.1		1, 1, 5-(CH ₃) ₃ C ₆ H ₃ + ICl <i>continued</i>	Ac 99*	A = 0.1-0.2; 10 ³ B = 7	ZnCl ₂	0.08-0.1	$k_{AB}[ZnCl_2]$	45	3.22	-1	18				(28a)
				10 ² A = 1.2; 10 ³ B = 3-10				25	7.37	0					(1a)
				3.2; 5				25	2.16	+1					
				14.2				25	5.76	+1					
				7.12				25	9.34	+1					
.295		1, 3, 5-(CH ₃) ₃ C ₆ H ₃ + Br ₂	Ac*	10 ² A = 2-4	ZnCl ₂	0.0125 0.0312	k_{AB}	25	6.3	-2				*	(1)
								25	1.94	-1					
								25	1.13	-2					(28a)
.295.1		1, 3, 5-(CH ₃) ₃ C ₆ H ₃ + ICl	Ac 99*	A = 0.1; 10 ³ B = 4	ZnCl ₂	0.40 0.80	$k_{AB}[ZnCl_2]$	25	1.83	-2					(1)
								25	1.7	-3				*	(14a)
.296		1, 3, 5-[(CH ₃) ₃ C] ₃ C ₆ H ₃ + Br ₂	Ac*	A = 0.088	ZnCl ₂	0.50	k_{AB}	25	time						
									63.4		% reacted				
.296.1		1, 2, 3, 4-(CH ₃) ₄ C ₆ H ₂ + Br ₂	Ac*	10 ² A = 2; 10 ² B = 1.0	ZnCl ₂	0.0312	k_{AB}	25	155						
									1.23	C				*	(1)
.297		1, 2, 3, 5-(CH ₃) ₄ C ₆ H ₂ + Br ₂	Ac 90*	10 ² A = 2-10; 10 ³ B = 9-3.6	NaOAc	0.1	$k_{1AB} + k_{2AB}^2$	25	k_1 8.6	-1					(28)
									k_2 5.2	+2					
								25	6.13	-2					(28a)
.297.1		1, 2, 3, 5-(CH ₃) ₄ C ₆ H ₂ + ICl	Ac 99*	A = 0.08; 10 ³ B = 4-7	ZnCl ₂	0.05 0.20 0.40	$k_{AB}[ZnCl_2]$	25	7.80	-2					
								25	8.8	-2					

No.	Supplementing No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k \times 10^7$	k^0	k^0	$k^0 \times 10^7$	E	$A = 10^7$	Comments	Temperature
.297.1		1,2,3,5-(CH ₃) ₄ C ₆ H ₂ + ICl ₂ (continued)	Ac 99*	A = 0.03; 10 ³ B = 4-7	ZnCl ₂	0.08 0.05	$k_{AB}[ZnCl_2]$	25 45	-1 -1	1.29 3.54	1.0	11	16			(28a)
.298		1,2,4,5-(CH ₃) ₄ C ₆ H ₂ + Br ₂	Ac*	10 ³ A = 4-8	ZnCl ₂	0.0312 0.0625	k_{AB}	25 25	-2 -1	6.7 2.42					*	(1) (10)
.296.1		1,2,4,5-(CH ₃) ₄ C ₆ H ₂ + ICl	Ac 99*	10 ² A = 7-15 10 ³ B = 4-7	ZnCl ₂	0.40 0.80 1.40 0.78	$k_{AB}[ZnCl_2]$	25 25 25 45	-3 -3 -3 -2	1.79 1.87 3.14 1.25		10	17			(28a)
.299		(CH ₃) ₅ C ₆ H + Br ₂	Ac* Ac 9C*	A = 0.011 10 ³ A = 3-11; 10 ³ B = 1-4	ZnCl ₂ NaOAc	0.0312 0.1	k_{AB} $k_1AB + k_2AB^2$	25 25 25	0 0 +3	2.35 k_1 1.81 k_2 1.86					*	(1) (28)
.300		(CH ₃) ₆ C ₆ H + ICl $\rightarrow$ (CH ₃) ₆ C ₆ I, (CH ₃) ₅ C ₆ Cl, HCl, HI (75%) (25%)	Ac* AC 99*	A = B = 0.01-0.02 10 ² A = 5-20; 10 ³ B = 2-7	ZnCl ₂	0.056 0.11 0.21 0.40 0.82 0.055 0.11	$k_{AB}[ZnCl_2]$	25 25 25 25 25 45 45	-2 -2 -2 -2 -2 -1 -1	2.91 3.04 3.73 4.23 6.10 1.67 1.73		5	10		*	(28a)
			CCl ₄	10 ³ A = 244; 10 ³ B = 5 97 2-7 49 3			k_{AB}^3	25 25 25	-1 0 0	4.92 1.65 3.18			16			(1a)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k'' n	$k \times 10^n$ k'' n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.304	$C_6H_5OH + I_2$	H_2O	$A = 0.01; B = 0.001$	$\left. \begin{array}{l} HOAc \\ NaOAc \\ " \\ " \\ " \\ " \\ " \\ " \\ H_2PO_4^- \\ HPO_4^- \end{array} \right\}$	pH 4.68 " 4.96 " 5.28 " 6.00 " 6.40 " 6.70 " 7.12 " $\left. \begin{array}{l} 0.024 \\ 0.008 \end{array} \right\}$ $\left. \begin{array}{l} 0.045 \\ 0.015 \end{array} \right\}$ $\left. \begin{array}{l} 0.60 \\ 0.020 \end{array} \right\}$ $\left. \begin{array}{l} 0.032 \\ 0.008 \end{array} \right\}$ $\left. \begin{array}{l} 0.064 \\ 0.016 \end{array} \right\}$ $\left. \begin{array}{l} 0.080 \\ 0.020 \end{array} \right\}$	$k_{AB}; k = k_0 + k_1 [HOAc]$ $k_{A3}; k = k_0 + k_1 [H_2PO_4^-]$ k_{AB}	25 25 25 25 25 25 25 25 25 25 25 25 25 25 25	k_0 2.90 k_1 3.86 k_0 5.56 k_1 1.46 k_0 1.10 k_1 5.96 k_0 6.7 k_1 3.3 k_0 1.5 k_1 2.2 k_0 3.0 k_1 8.0 k_0 9.5 k_1 6.1 k_0 1.20	-4 -3 -4 -2 -3 -2 -5 -4 -4 -3 -4 -3 -4 -2 -2	$A^0 \times 10^n$ A^0 n	$*$ (30) (34)	(3)

No.	Reaction	Solvent	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^{12}$	k	$A^0 \times 10^{12}$	A^0	n	Comments	Literature
.304	$C_6H_5OH + I_2$ (continued)	H_2O	$10^3 A = 8; 10^3 B = 2$ Ionic strength = 0.3	$\left. \begin{matrix} KH_2PO_4 \\ Na_2HPO_4 \end{matrix} \right\}$ " 										

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass action law	Temperature	$k \times 10^n$		$A \times 10^n$		Comments	Literature
									k^0	n	A^0	n		
.505		$C_6H_5OCH_3 + HCl$ (continued)	H_2O	$10^3 A = 7.7; 10^3 B = 6.0$	$HClO_4$	0.012	$k B$	25	7.02	-4			*	(17)
				" 12.0	"	0.012		25	1.06	-3				(16)
				3	"	0.1		25	6.3	-4				(17)
				6.6 0.2-1	"	0.6		25	1.3	-3				(34)
				10	HCl	0.0002	$k B[HCl]^2$	25	3.57	+4			*	(17)
				$10^3 A = 6.6; 10^4 B = 7$	$AgClO_4 + HClO_4$	0.16	$k B$	0	5.00	-5				
				"	"	0.012		25	1.55	-4				
				8.0 5	"	0.065		25	2.35	-4				
				15 5	"	0.05		25	2.65	-4				
				28 5	"	"		25	3.25	-4				
.506	.19	$C_6H_5OCH_3 + Br_2$	Ac^*	$10^2 A = 2.5; 10^2 B = 1$	$NaAc$	0.068	$k AB$	25	1.6	-2			*	(33)
				$A = B = 0.00625$	$LiBr$	0.035		25	Time		t reacted			(19)
									84		10			
.507		$C_6H_5OCH_3 + ICl \rightarrow$ $p-IC_6H_4OCH_3, p-ClC_6H_4OCH_3$ (85%) (15%)	Ac^*	$A = B = 0.0125$				24	12,960	-4			*	(29)
				0.025				24	2,790	-4				
				0.05				24	708	-4				
				0.0125				40	4,620	-4				
				0.025				40	1,140	-4				
				0.05				40	288	-4				
.508		$C_6H_5OC_2H_5 + HCl$	H_2O	$10^3 A = 4; 10^3 B = 1$	HCl	0.0002	$k B[HCl]^2$	25	3.60	+4			*	(34)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass	Temperature	$k \times 10^2$ k^0 n	$k \times 10^2$ k^0 n	$A \times 10^2$ A^0 n	Comments	Literature
Carboxyl substituted benzene													
.308.1		$C_6H_5OC_2H_5 + Br_2$	Ac^*	$A = 0.01; 10^3B = 1$			k AB	20	time 86.5	% reacted 20			(1b)
.308.2		$C_6H_5OCH(CH_3)_2 + Br_2$	Ac^*	$A = 0.01; 10^3B = 1$			k AB	20	143	20			(1b)
.308.3		$C_6H_5OC(CH_3)_3 + Br_2$	Ac^*	$A = 0.01; 10^3B = 1$			k AB	20	390	20			(1b)
.309		$C_6H_5OC_2H_5 + Br_2$	Ac^*	$A = B = 0.0125$				25	2,700	10		*	(23)
Amine (Amide)-substituted benzene													
.310		$C_6H_5COOH + HOBr$	Ac_4O^*	$10^3A = 3; 10^3B = 3.4$	$HClO_4$	0.119 0.224 0.448 0.7 0.9 0.224 0.672	k AB	22	5.1 1.2 3.2 8.2 1.7 2.42	-3 -2 -2 -2 -1 -2			(24)
.311		$C_6H_5COOC_2H_5 + Cl_2$	Ac^*	$A = 0.10; B = 0.01$	H_2SO_4	0.448 0.442 0.294 0.59 1.17		22	5.47 1.63 4.6 2.65	-2 -2 -2 -1			(23)
.312		$C_6H_5COOC_2H_5 + Cl_2$	Ac_4O^*	$A = 0.5; B = 0.05$				25	46,000	10		*	(23)
.313		$C_6H_5NH_2 + I_2 \rightarrow (p)$	H_2O	$10^3A = 2-9; 10^3B = 1-4$ Ionic strength = 0.3 $KI = 0.12$	KH_2PO_4 Na_2HPO_4	0.61 0.61	k AB	25	6.95	-3		*	(2)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined Basis Reaction	Temperature	$k \times 10^3$	n	g	$A \times 10^3$	Comments	- Temperature					
-217		$C_6H_5NH_2 + I_2 \longrightarrow (p)$ (continued)	H_2O	$10^3 A = 2-8; 10^3 B = 1-4$ Ionic strength = 0.3	KH_2PO_4 Na_2HPO_4 " " " "	$C. 0.03-0.002$ 0.005 $C. 0.04-0.003$ 0.02 0.03 0.045	k_{AB}	25	1.42		-2			*	(2)				
									1.39			-2							
									2.43			-2							
									$k = k_0 + k_1 [H_2PO_4^-] + k_2 [HPO_4^-]$										
												25	k_0 2.05			-3			
												25	k_1 4.89			0			
												25	k_2 5.0			-3			
												35	k_0 7.59			-3			
												35	k_1 1.42			+1	24		
			H_2O	$10^3 A = 2-8; 10^3 B = 1-4$ $KH_2PO_4 = 0.05$ $Na_2HPO_4 = 0.05$ Ionic strength = 0.8	KI	0.1 0.15 0.2 0.3 0.4 0.5	k_{AB}	25	3.46		-2			*	(3)				
									1.52			-2							
									8.56			-3							
									3.82			-3							
									2.15			-3							
									1.36			-3							
									1.81			-2							
									2.50			-2							
									3.93			-2							
									$k = k_0 + k_1 [HPO_4^-]$										
			H_2O	$10^3 A = 2-8; 10^3 B = 1-4$ $KH_2PO_4 = 0.05$ $Na_2HPO_4 = 0.05$ Ionic strength = 0.3	KI	0.02 0.005 0.03 0.075 0.05 0.0125	k_{AB}	25	1.81		-2			*	(6)				
									2.50			-2							
									3.93			-2							
									$k = k_0 + k_1 [HPO_4^-]$										
													25			k_0 2.05	-3		
													25			k_1 4.89	0		
													25			k_2 5.0	-3		
													35			k_0 7.59	-3		
													35			k_1 1.42	+1	24	
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														
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			25	k_1 4.89	0														
			25	k_2 5.0	-3														
			35	k_0 7.59	-3														
			35	k_1 1.42	+1	24													
			25	k_0 2.05	-3														

No	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass	Temperature	$k = k^0 \times 10^n$	B	$A = A^0 \times 10^n$	Comments	Literature
.314	$\text{CH}_3\text{CONHC}_6\text{H}_5 + \text{HCl} \longrightarrow \text{CH}_3\text{CONHC}_6\text{H}_4\text{I} + \text{HCl} + \text{HI}$ (90%) (10%)	Ac^*	$A = B = 0.025$				24	time	η reacted		*	(29)
			0.05				24	40,800	10			
			0.025				50	9,800	10			
			0.05				50	6,700	10			
.315	$\text{CH}_3\text{CON}(\text{CH}_3)_2 + \text{Br}_2$	Ac^*	$A = B = 0.05$				25	10,900	10	*	(33)	
Sulfo-alkyl substituted benzene												
.316	$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na} + \text{HCl}$	H_2O	$10^3 A = 1-7; 10^3 B = 4$	HClO_4	2.0	k_{AB}	22	1.0	-3			(21)
					3.0		22	3.5	-3			
					4.0		22	1.0	-2			
					1.13		22	1.85	-3			
					2.25		22	9.12	-3			
					3.0		22	2.9	-2			
.317	$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na} + \text{HCl}$	H_2O	$10^3 A = 7-14; 10^3 B = 3-5$	$\text{H}_2\text{SO}_4 + \text{KCl}$ " " " "	2.25	k_{AB}	22	1.21	-2			(20)
					0.0001		22	2.01	-2			
					0.0004		22	2.01	-2			
					0.0006		22	2.6	-2			
					0.0047		22	7.23	2			
					0.0094		22	1.46	-1			
.318	$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na} + \text{HCl}$	H_2O	$10^3 A = 7-14; 10^3 B = 3-5$	HClO_4	0.024	k_{AB}	22	3.4	-1			
					0.047		22	6.7	-1			
					0.094		22	1.38	0			

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined rate action law	Temperature	$k = k^0 \times 10^n$	δ	$A = A^0 \times 10^n$	Comments	Literature
Disubstituted Benzene												
Alkyl, Hydroxyl (Alkoxy)												
.318	$o\text{-CH}_3\text{C}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3 A = 2-10; 10^3 B \sim 1$	NaOH	0-0.01	R_{AB}	25	2.08	+4		*	(³⁴)
.319	$m\text{-CH}_3\text{C}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3 A = 2-10; 10^3 B \sim 1$	NaOH H^+	0-0.5 3×10^{-6}	R_{AB}	25 25	7.3 5.6	+4 +4		*	(³⁴)
.320	$p\text{-CH}_3\text{C}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3 A = 2-10; 10^3 B \sim 1$ ~ 2	NaOH HCl	0-0.01 0.0002	R_{AB} $k_B[\text{HCl}]^2$	25 25	1.50 3.62	+4 +4		*	(³⁴)
.321	$4\text{-CH}_3\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	$\text{Ac } 10^*$	$10^2 A = 8; 10^2 B = 4$	NaOAc KI KH_2PO_4 Na_2HPO_4 KI	1 0.03 0.02 0.01 0.1	R_{AB}	25	1.97	-2		*	(⁷)
				KH_2PO_4 Na_2HPO_4 KI	0.025 0.012 0.12		25	1.33	-2		*	(⁷)
				KH_2PO_4 Na_2HPO_4 KI	0.02 0.01 0.1	R_{AB}	25	1.45	-3		*	(¹⁷)
.322	$m\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3 + \text{HOCl}$	D_2O^*	$10^3 A = 8; 10^3 B = 2$	AgClO_4 HClO_4	0.012 " "	$R_B; k = R + k'[\text{H}^+] + k''[\text{H}^+]^2$	25	2.2 2.8 3.5	-4 -4 -4		*	(¹⁷)
.323	$m\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3 + \text{H}_2\text{O}_2$	Ac^*	$10^2 A = 1; 10^2 B = 1$			R_{AB}	20	2.2	-1			(^{1b})

No.	Reaction	Solvent (medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^7$ k^0	δ n	$k^0 \times 10^7$ k^0	δ n	Comments	Literature
323	$p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3 + \text{HCl}$	DI 62, 5*	$10^2 A = 4.4; 10^4 B = 8$	HClO_4 AgClO_4	$\left. \begin{matrix} 0.50 \\ 0.05 \end{matrix} \right\}$	$k_B [\text{H}^+]$	25	8.2	-4			*	(35)
324	$p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3 + \text{DCl}$	DIW 50*	5-8	HClO_4 AgClO_4	$\left. \begin{matrix} 0.05 \\ 0.027 \end{matrix} \right\}$	$k_B; k = k_0 + k'[\text{H}^+] + k''[\text{H}^+]^2$	25	1.9	-4			*	(17)
325	$p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3 + \text{JCl} \longrightarrow$ $2\text{-I-4-CH}_3\text{C}_6\text{H}_3\text{OCH}_3, 2\text{-Cl-4-CH}_3\text{C}_6\text{H}_3\text{OCH}_3$ (50%) (50%)	DI 62*	$A = 0.044; 10^3 B = 8$	HClO_4 AgClO_4	$\left. \begin{matrix} 0.50 \\ 0.05 \end{matrix} \right\}$	$k_B [\text{H}^+]$	25	1.58	-3			*	(35)
326	$p\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	Ac*	$A = B = 0.0125$ 0.025 0.05				24	83, 400	20			*	(28)
327	$4\text{-CH}_3\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	Ac 10*	$10^3 A = 8; 10^3 B = 4$	NaOAc KI	$\left. \begin{matrix} 1 \\ 0.03 \end{matrix} \right\}$	k_{AB}	25	2.40	-2			*	(7)
		M 25*	8	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.02 \\ 0.01 \\ 0.1 \end{matrix} \right\}$		25	2.80	-2				
		M 30*	8	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$		25	1.51	-2				
		DI 30*	8	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.02 \\ 0.01 \\ 0.1 \end{matrix} \right\}$		25	1.50	-3				
328	$4\text{-CH}_3\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	Ac 10*	$10^3 A = 8; 10^3 B = 4$	NaOAc KI	$\left. \begin{matrix} 1 \\ 0.03 \end{matrix} \right\}$	k_{AB}	25	2.38	-2			*	(7)

No.	Reaction.	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined base	Temperature	$k = k^0 \times 10^n$	$k = k^0 \times 10^n$	$A = A^0 \times 10^n$	Comments	Literature
327	$4\text{-CH}_3\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$ (continued)	M 30*	$10^3\text{A} = 8; 10^3\text{B} = 2$	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$	k AB	25	k^0	k^0	A^0	*	(7)
328	$4\text{-(CH}_3)_2\text{CHC}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	Ac 10*	$10^3\text{A} = 8; 10^3\text{B} = 4$	NaOAc KI	$\left. \begin{matrix} 1 \\ 0.03 \end{matrix} \right\}$	k AB	25	1.57	2.82		*	(7)
		M 25*	8 2	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.02 \\ 0.01 \\ 0.1 \end{matrix} \right\}$		25	3.18				
		M 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$		25	1.76				
		D1 30*	8 2	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.02 \\ 0.01 \\ 0.1 \end{matrix} \right\}$		25	1.58				
329	$4\text{-(n-C}_4\text{H}_9)_2\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	M 30*	$10^3\text{A} = 8; 10^3\text{B} = 2$	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$	k AB	25	1.80			*	(7)
330	$4\text{-C}_2\text{H}_5(\text{CH}_3)_2\text{C}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	M 30*	$10^3\text{A} = 8; 10^3\text{B} = 2$	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$	k AB	25	1.80			*	(7)
331	$4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	Ac 10*	$10^3\text{A} = 8; 10^3\text{B} = 4$	NaOAc KI	$\left. \begin{matrix} 1 \\ 0.03 \end{matrix} \right\}$	k AB	25	3.80			*	(7)
		M 25*	8 2	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.02 \\ 0.01 \\ 0.1 \end{matrix} \right\}$		25	4.05				

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass action law	Temperature	$k \times 10^n$		$A \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
.331	$4-(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2) \text{ (cont.)}$	H_2O^*	$10^3 A = 8; 10^3 B = 2$	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$	k_{AB}	25	2.27	-2			*	(7)
		D_2O^*	8	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.02 \\ 0.01 \\ 0.1 \end{matrix} \right\}$		25	1.90	-3				
.332	$4-\text{C}_2\text{H}_5(\text{CH}_3)_2\text{CC}_6\text{H}_4\text{OH} + \text{I}_2 \longrightarrow (2)$	H_2O^*	$10^3 A = 8; 10^3 B = 2$	KH_2PO_4 Na_2HPO_4 KI	$\left. \begin{matrix} 0.025 \\ 0.012 \\ 0.12 \end{matrix} \right\}$	k_{AB}	25	2.72	-2			*	(7)
Disubstituted Benzene Di-Alkoxy													
.333	$o-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_4 + \text{Br}_2$	Ac^*	$A = B = 0.0031$				25	time 91.3 221	% reacted 10 20			*	(19)
.334	$p-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_4 + \text{HOCl}$	H_2O	$10^3 A = 4; 10^3 B = 2$	H_2SO_4 Ag^+	$\left. \begin{matrix} 0.011 \\ 0.005-0.1 \end{matrix} \right\}$	k_B	25	3.1 -4				*	(15)
.335	$p-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_4 + \text{Br}_2$	Ac^*	$A = B = 0.0125$ 0.00625				25	time 336 763 1,220 2,730	% reacted 10 20 10 20			*	(19)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$ k^0 n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
Disubstituted Benzene Alkoxy, Carboxyl											
.336	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{COONa} + \text{HOBr}$	H_2O	$10^3 A = 7\text{--}14; 10^3 B = 4\text{--}5$	$\left. \begin{array}{l} \text{Na}_2\text{HPO}_4 \\ \text{KH}_2\text{PO}_4 \end{array} \right\}$	$\left. \begin{array}{l} 0.01\text{--}0.03 \\ 0.002 \\ 0.004 \\ 0.006 \end{array} \right\}$	k_{AB}	22	1.1 1.6 2.2 1.32	-1 -1 -1 0	*	(20)
				$\left. \begin{array}{l} \text{Na}_2\text{HPO}_4 \\ \text{KH}_2\text{PO}_4 \\ \text{KBr} \end{array} \right\}$	$\left. \begin{array}{l} 0.011 \\ 0.002 \\ 0.0017 \end{array} \right\}$	k_{AB}	22				
Disubstituted Benzene Alkyl, Amino											
.337	$4\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2 + \text{I}_2 \rightarrow (2)$	H_2O^*	$10^3 A = 8; 10^3 B = 1$	Na_2HPO_4	$\left. \begin{array}{l} 0.02 \\ 0.04 \\ 0.06 \\ 0.08 \end{array} \right\}$	k_{AB}	25	3.37 4.25 5.27 6.29 1.12 1.43 1.75 2.08	-3 -3 -3 -3 -2 -2 -2 -2	*	
				$\left[\text{KI} \right] = 0.05$ $\left[\text{Na}_2\text{HPO}_4 \right] / \left[\text{C}_6\text{H}_5\text{PO}_4 \right] = 0.28$ $\mu = 0.28$		$k = k_0 + k_1 [\text{Na}_2\text{HPO}_4]$	25 25 25 35 35 35 35	$\left. \begin{array}{l} k_0 \\ k_1 \end{array} \right\}$ 2.35 4.89 7.94 1.59	-3 -2 -3 -1	5 13 3 14	

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass	Temperature	$k \times 10^n$ k^0	n	$A = A^0 \times 10^n$	Comments	Literature
.338	$4\text{-C}_6\text{H}_4\text{CH}_2\text{NH}_2 + \text{I}_2 \longrightarrow (2)$	H_2O^*	$10^3 A = 6; 10^3 B = 1$ $\mu = 0.28$	Na_2HPO_4 KH_2PO_4 KI	$\left. \begin{array}{l} 0.04 \\ 0.01 \\ 0.05 \end{array} \right\}$	k_{AB}	25 35	4.76 1.54	-3 -2		*	(⁶)
.339	$4\text{-(CH}_3)_2\text{CHC}_6\text{H}_4\text{NH}_2 + \text{I}_2 \longrightarrow (2)$	H_2O^*	$10^3 A = 8; 10^3 B = 1$ $\mu = 0.28$	Na_2HPO_4 KH_2PO_4 KI	$\left. \begin{array}{l} 0.04 \\ 0.01 \\ 0.05 \end{array} \right\}$	k_{AB}	25 35	5.12 1.60	-3 -2		*	(⁶)
.340	$4\text{-(CH}_3)_3\text{CC}_6\text{H}_4\text{NH}_2 + \text{I}_2 \longrightarrow (2)$	H_2O^*	$10^3 A = 8; 10^3 B = 1$	Na_2HPO_4	$\left. \begin{array}{l} 0.02 \\ 0.04 \\ 0.06 \\ 0.08 \\ 0.02 \\ 0.04 \\ 0.06 \\ 0.08 \end{array} \right\}$	k_{AB}	25 25 25 25 35 35 35 35	5.97 7.02 8.06 8.98 1.74 2.04 2.39 2.72	-3 -3 -3 -3 -2 -2 -2 -2		*	(⁶)
				$[\text{KI}] = 0.05$ $[\text{Na}_2\text{HPO}_4] / [\text{KH}_2\text{PO}_4] = 4$ $\mu = 0.28$		$k = k_0 + k_1 [\text{Na}_2\text{HPO}_4]$	35	2.72	-2			
							25 25 35 35	k_0 4.90 k_1 5.30 k_0 1.40 k_1 1.66	-3 -2 -2 -1	5 9 11 14		
Disubstituted benzene												
Hydroxyl, Nitro												
.341	$\text{O-NC}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3 A = 2\text{-}10; 10^3 B = 1$	NaOH	0.015	k_{AB}	25	1.68	+1		*	(³⁴)
.342	$\text{m-NO}_2\text{C}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3 A = 2\text{-}10; 10^3 B = 1$	NaOH	0-0.01	k_{AB}	25	9.8	+1		*	(³⁴)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined reaction	Temperature	$k \times 10^n$ k n	$A = A^0 \times 10^n$ A^0 n	Comments	Temperature
Disubstituted benzene											
Hydroxyl, Halogen											
343	$m\text{-NO}_2\text{C}_6\text{H}_4\text{OH} + \text{Br}_2$	H_2O	$10^6\text{B} = 5\text{--}25$	Ag_2SO_4	sat.	k_{AB}	25	~ 9 +3		*	(22)
344	$m\text{-NO}_2\text{C}_6\text{H}_4\text{OH} + \text{HOBr}$	H_2O	$A = B = 0.01\text{--}0.3$	Ag_2SO_4	sat.	k_{AB}	25	~ 1.0 +1		*	(22)
345	$p\text{-NO}_2\text{C}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3\text{A} = 2\text{--}10$; $10^3\text{B} = 1$	NaOH HCl	0.015 0.0002	k_{AB} $k_{B[\text{HCl}]}^2$	25 25	1.14 3.44 +1 +4		*	(24)
Disubstituted benzene											
Alkoxy, Nitro											
346	$o\text{-ClC}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3\text{A} = 2\text{--}10$; $10^3\text{B} = 1$	NaOH	0.1	k_{AB}	25	9.8 +2		*	(24)
347	$p\text{-ClC}_6\text{H}_4\text{O}^- + \text{HOCl}$	H_2O	$10^3\text{A} = 2\text{--}10$; $10^3\text{B} \sim 1$	NaOH	0-0.01	k_{AB}	25	8.2 +2		*	(24)
348	$o\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_3 + \text{Cl}_2$	$\text{Ac}99^*$	$10^2\text{A} = 5$; $10^3\text{B} = 5$	HCl	0.02	k_{AB}	20	3.00 -4		*	(25)
349	$p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_3 + \text{HOBr}$	H_2O $\text{AcW}10^*$ $\text{AcW}25^*$ $\text{AcW}50^*$ $\text{AcW}65^*$ $\text{AcW}75^*$	$10^3\text{A} = 5$; $10^3\text{B} \sim 6$			k_{AB}	20 20 20 20 20 20 20	2.1 1.83 1.92 1.89 1.79 1.62 2.48 3.24 4.34 -2 -1 -1 -1 -1 -1 -1 -1 -1		*	(13)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$		β	$A =$ $A^0 \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.349	$p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_3 + \text{HOBr}$ (continued)	AcW75*	$10^3\text{A} = 5; 10^3\text{B} \sim 6$	H_2SO_4	0.030 0.043 0.088	k_{AB} $k = k_0 + k_1[\text{H}_2\text{SO}_4]$	20 20 20	6.80 8.20 1.61	-1 -1 0				*	(13)
				Na_2HPO_4 Na_2SO_4 Li_2SO_4 NaOAc	0.005 0.020 0.030 0.010 0.050 sat.		20 20 20 20 20 20	1.84 1.64 1.70 1.76 1.35 1.22 8.5 1.35	+1 -1 -1 -1 -1 -2 -1					
.350	$o\text{-NO}_2\text{C}_6\text{H}_4\text{OC}_2\text{H}_5 + \text{Cl}_2$	AcW85*	$10^2\text{A} = 5; 10^3\text{B} = 5$	HCl	0.020	k_{AB}	20	6.03	-4				*	(25)
.351	$4\text{-NO}_2\text{C}_6\text{H}_4\text{OC}_2\text{H}_5 + \text{HOBr} \longrightarrow (2)$	Ac75*	$10^3\text{A} = 2\text{-}8; 10^3\text{B} = 3\text{-}8$			k_{AB}	20	3.22	-1				(13), (13), (14)	
.352	$o\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac99*	$10^2\text{A} = 5; 10^3\text{B} = 5$	HCl	0.020	k_{AB}	20	2.90	-4				*	(25)
.353	$p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}_3 + \text{HOBr}$	Ac75*	$10^3\text{A} = 2\text{-}10; 10^3\text{B} = 2\text{-}10$			k_{AB}	20	3.53	-1				(14)	
.354	$p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}(\text{CH}_3)_2 + \text{HOBr}$	Ac75*	$10^3\text{A} = 2\text{-}10; 10^3\text{B} = 2\text{-}10$			k_{AB}	20	6.42	-1				(14)	
.355	$p\text{-NO}_2\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_3\text{CH}_3 + \text{HOBr}$	Ac75*	$10^3\text{A} = 2\text{-}10; 10^3\text{B} = 2\text{-}10$			k_{AB}	20	3.80	-1				(14)	
.356	$p\text{-NO}_2\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_4\text{CH}_3 + \text{HOBr}$	Ac75*	$10^3\text{A} = 2\text{-}10; 10^3\text{B} = 2\text{-}10$			k_{AB}	20	3.59	-1				(14)	

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	$k = k^0 \times 10^n$	Comments	Literature
Disubstituted Benzene											
Aryl alkoxyl, Nitro											
.337	$p\text{-NO}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5 + \text{HOBr}$	Ac 75*	$10^2 A = 1\text{-}2; 10^3 B = 5\text{-}8$			k_{AB}	20	1.14	-1	(11) (13) (14)	*
Disubstituted Benzene											
Amino (Amide), Nitro											
.356	$m\text{-NO}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{Br}_2$	Ac*	$10^3 A = 1; 10^4 B = 1$	NaOAc LiBr	0.068 0.035	k_{AB}	25	1.42	+1	(33)	*
.359	$m\text{-NO}_2\text{C}_6\text{H}_4\text{NHCOCH}_3 + \text{Cl}_2$	Ac*	$A = 0.1; B = 0.07$			k_{AB}	25	6.7	-5	(33)	*
Disubstituted Benzene											
Alkoxyl, Halogen											
.360	$p\text{-FC}_6\text{H}_4\text{OCH}_2\text{COOH} + \text{HOBr}$	AcW 75*				k_{AB}	20	9.5	0	(14)	
.361	$o\text{-ClC}_6\text{H}_4\text{OCH}_3 + \text{Br}_2$	AcW 75*	$10^3 A = 7.5; 10^2 B = 1.5$		HBr	$k_{AB} + k' AB^2$	20	5.52	-2	(8)	*
						0.0075	20	5.37	-2		
.362	$p\text{-ClC}_6\text{H}_4\text{OCH}_3 + \text{Br}_2$	Ac 50* AcW 75*	$10^2 A = 4\text{-}8; 10^3 B = 7.5$ $A = B = 0.02$			k_{AB}	20	4.50	-2	(12)	
						$k_{AB} + k' AB^2$	20	2.20	-4	(11)	*
						k'/k	k'/k	6.35	+1		
						k'/k	k'/k	1.12	-2		
						k'/k	k'/k	3.19	+2		

No.	Reaction	Solvent (medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass action law	Temperature	$k \times 10^n$		β	$A \times 10^n$		Comments	Temperature
								k^0	n		A^0	n		
.363	$p\text{-ClC}_6\text{H}_4\text{OC}_6\text{H}_4\text{Br}_2$	Ac 50* AcW75*	$10^2 A = 4-8; 10^2 B = 7.5$ $A = B = 0.02$			k_{AB} $k_{AB} + k'_{AB^2}$	20 k'/k	2.55 5.88 3.19	-2 -4 +2				*	(12) (11)
.364	$p\text{-ClC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2$	AcW75*	$A = B = 0.02$			$k_{AB} + k'_{AB^2}$	20 k'/k	7.45 3.19	-4 +2				*	(11)
.365	$p\text{-ClC}_6\text{H}_4\text{OCH}(\text{CH}_3)_2 + \text{Br}_2$	Ac 50* AcW75*	$10^2 A = 4-8; 10^2 B = 7.5$ $10^2 A = 2-4; 10^2 B = 2$ $10^3 A = 7.5; 10^2 B = 4$	HBr	0.0075 0.0225 0.0375 0.075	k_{AB} $k_{AB} + k'_{AB^2}$	20 k'/k	8.0 1.91 1.63 2.00 2.17 2.57 3.19	-2 -3 -3 -3 -3 -3 +2				*	(12) (11)
.366	$p\text{-ClC}_6\text{H}_4\text{OCH}_2\text{COOH} + \text{HOBr}$	AcW75*				k_{AB}	20	4.1	0					(14)
.367	$p\text{-ClC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{COOH} + \text{HOBr}$	AcW75*				k_{AB}	20	3.5	+1					(14)
.368	$p\text{-ClC}_6\text{H}_4\text{OCH}(\text{CH}_3)\text{COOH} + \text{HOBr}$	AcW75*				k_{AB}	20	5.0	0					(14)
.369	$p\text{-BrC}_6\text{H}_4\text{OCH}_3 + \text{Br}_2$	Ac 50*	$10^2 A = 4-8; 10^2 B = 7.5$			k_{AB}	20	1.20	-2				*	(12)
.370	$p\text{-BrC}_6\text{H}_4\text{OC}_6\text{H}_4 + \text{Br}_2$	Ac 50*	$10^2 A = 4-8; 10^2 B = 7.5$			k_{AB}	20	2.80	-2				*	(12)
.371	$p\text{-BrC}_6\text{H}_4\text{OCH}(\text{CH}_3)_2 + \text{Br}_2$	Ac 50*	$10^2 A = 4-8; 10^2 B = 7.5$			k_{AB}	20	8.49	-2				*	(12)
.372	$p\text{-BrC}_6\text{H}_4\text{OCH}_2\text{COOH} + \text{HOBr}$	AcW75*				k_{AB}	20	5.6	0					(14)
.373	$p\text{-BrC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{COOH} + \text{HOBr}$	AcW75*				k_{AB}	20	5.1	1					(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass	Temperature	$k^0 \times 10^n$	k^0	$k^0 \times 10^n$	k^0	Comments	Literature
Disubstituted benzene													
Aryl-alkoxyl, Halogen													
.374	$p-(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{F} + \text{Cl}_2$	Ac 99*	$A = 3B \sim 10^{-2}$	HCl		k AB	20	5.00	-3			*	(24)
.375	$p-(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{F} + \text{HOBr}$	AcW 75*				k AB	20	1.56	+1				(14)
.376	$p-(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{Cl} + \text{Cl}_2$	Ac 99*	$A = 3B \sim 10^{-2}$	HCl		k AB	20	2.97	-3			*	(24)
.377	$p-(o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{Cl} + \text{HOBr}$	AcW 75*				k AB	20	9.5	0				(14)
.378	$p-(p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{Cl} + \text{HOBr}$	AcW 75*				k AB	20	1.17	+1				(14)
.379	$p-(2',6'\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{Cl} + \text{Cl}_2$	Ac 99*	$A = 3B \sim 10^{-2}$	HCl		k AB	20	4.58	-3			*	(24)
.380	$p-(o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{Br} + \text{Cl}_2$	Ac 99*	$A = 3B \sim 10^{-2}$	HCl		k AB	20	1.83	-2			*	(24)
Disubstituted benzene													
Amino, Halogen													
.381	$4\text{-ClC}_6\text{H}_4\text{NH}_2 + \text{ICl} \longrightarrow$ $4\text{-Cl-2-IC}_6\text{H}_3\text{NH}_2 + \text{HCl}$	H_2O	$10^3 A = 4; 10^3 B = 1$	HClO_4 NaCl	$\left. \begin{matrix} 0.4 \\ 0.4 \end{matrix} \right\}$	k AB	11 18 25 35 25 25 25 25 25	1.48 2.86 5.61 1.37 2.27 5.80 1.61 4.27 1.07	-2 -2 -2 -1 -1 -2 -2 -3 -3		7 10	*	(4)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$ k^0 n	δ	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
.381	$4\text{-Cl-C}_6\text{H}_4\text{NH}_2 + \text{ICl} \longrightarrow$ $4\text{-Cl-2-IC}_6\text{H}_3\text{NH}_2 + \text{HCl}$ (continued)	H ₂ O	$10^3\text{A} = 5; 10^3\text{B} = 1$	NaCl $\mu = 1.00$ $\mu = 0.80$ HClO ₄ HCl HClO ₄ NaCl NaClO ₄ $\mu = 0.8$	0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.4 0.4	k AB	25 25 25 25 25 25 25 25 25 25 25 25	-1 -1 -1 -2 -2 -2 -2 -2 -2 -2 -2 -2		*	(*)	
Disubstituted benzene Aryl (diphenyl), alkoxyl												
.392	$p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{OCH}_3 + \text{Cl}_2$	Ac 99*	$10^3\text{A} = 5; 10^3\text{B} = 2.5$ 10 5	HCl	0.01 0.02	k AB	20 20	1.24 1.27	0 0		*	(25)
.393	$2'\text{-NO}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{-4-OCH}_3 + \text{Cl}_2$	Ac 99*	$10^2\text{A} = 1; 10^3\text{B} = 5$	HCl	0.02	k AB	20	3.72	-1		*	(25)
.394	$4'\text{-NO}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{-4-OCH}_3 + \text{Cl}_2$	Ac 99*	$10^3\text{A} = 5; 10^3\text{B} = 2.5$ 10 5	HCl	0.01 0.02	k AB	20 20	1.32 1.38	-1 -1		*	(25)
.395	$p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}_2\text{H}_5 + \text{Cl}_2$	Ac 99*	$10^2\text{A} = 1; 10^3\text{B} = 5$	HCl	0.02	k AB	20	2.40	0		*	(25)

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$	ρ	$A = A^0 \times 10^n$	Comments	Reference
.336	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	7.16	-1		*	(25)
.337	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	2.61	-1		*	(25)
.338	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	2.72	0		*	(25)
.339	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	7.98	-1		*	(25)
.340	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	2.83	-1		*	(25)
.341	$p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	4.72	0		*	(25)
.342	$2\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	1.55	0		*	(25)
.343	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	5.48	-1		*	(25)
.344	$p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	2.70	0		*	(25)
Disubstituted benzene												
Aryl (diphenyl), Aryl-alkoxyl												
.345	$1\text{-C}_6\text{H}_4\text{CH}_2\text{O}-4\text{-C}_6\text{H}_4\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^3 A = 5; 10^3 B = 2.5$	HCl	0.01	k AB	20	9.05	-1		*	(25)
.346	$1\text{-C}_6\text{H}_4\text{CH}_2\text{O}-4\text{-(4'-NO}_2\text{C}_6\text{H}_4\text{)CH}_3 + \text{Cl}_2$	Ac 99*	$10^3 A = 5; 10^3 B = 2.5$	HCl	0.01	k AB	20	8.92	-2		*	(25)
.347	$1\text{-(4'-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O)-4-C}_6\text{H}_4\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^3 A = 5; 10^3 B = 2.5$	HCl	0.01	k AB	20	1.73	-1		*	(25)
Disubstituted diphenyl												
Alkoxyl, Halogen												
.348	$4\text{-C}_6\text{H}_4\text{CH}_2\text{O}-4'\text{-C}_6\text{H}_4\text{CH}_3 + \text{Cl}_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	7.90	-1		*	(25)

No.	Reaction	Solvent (Mole %)	Amount of reactant	Acid (Catalyst)	Amount of addend	Defined base	Temperature	$k \times 10^7$		$\bar{r}$	$A = A^0 \times 10^7$		Comments	Literature
								k^0	η		A^0	η		
.399	4-Cl-C ₆ H ₄ -4'-OCH ₃ + Cl ₂	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	6.12	-1			*	(25)	
.400	4-Br-C ₆ H ₄ -4'-OCH ₃ + Cl ₂	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	5.70	-1			*	(25)	
.401	4-F-C ₆ H ₄ -4'-OCH ₃ + Cl ₂	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	1.53	0			*	(25)	
.402	4-Cl-C ₆ H ₄ -4'-OC ₂ H ₅ + Cl ₂	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	1.18	0			*	(25)	
.403	4-Br-C ₆ H ₄ -4'-OC ₂ H ₅ + Cl ₂	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	1.09	0			*	(25)	
.404	4-Cl-C ₆ H ₄ -4'-OCH(CH ₃) ₂ + Cl ₂	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	2.47	0			*	(25)	
Heterocyclic substituted benzene														
.404.1	1,2-CH ₂ CH ₂ OCH ₃ + Br ₂ (coumaran)	Ac*	$10^2 A = 1; 10^3 B = 1$			k AB	20	2.5	0				(1b)	
.404.2	1,2-CH ₂ CH ₂ CH ₂ OCH ₃ + Br ₂ (chroman)	Ac*	$10^2 A = 1; 10^3 B = 1$			k AB	20	9.9	-1				(1b)	
.404.3	1,2-CH ₂ CH ₂ CH ₂ CH ₂ OCH ₃ + Br ₂ (phenochroman)	Ac*	$10^2 A = 1; 10^3 B = 1$			k AB	20	4.85	-2				(1b)	
Three substituents on Benzene														
Dialkyl, Hydroxyl														
.405	1,2-(CH ₃) ₂ -4-OCH ₃ + HOCt	H ₂ O	$10^3 A = 2-10; 10^3 B \approx 1$	NaOH	0-0.01	k AB	25	3.37	+4			*	(35)	

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass	Temperature	$k \times 10^n$ k^0 n	k	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
.405.1	1,3-(CH ₃) ₂ -2-CH ₃ OC ₆ H ₃ + Br ₂	Ac*	10 ² A = 4; 10 ² B = 1			k AB	20	1.3 -2				(1b)
Three substituents on Benzene Dialkyl, Halogen												
.405.2	1,4-(CH ₃) ₂ -2-IC ₆ H ₃ + ICl	CF ₃ COOH	10 ² A = 4.7; 10 ² B = 4 2.3 4			k AB	25 25	3.2 -2 3.7 -2				(1a)
Three substituents on Benzene Alkyl, Hydroxyl, Halogen												
.406	1-CH ₃ -4-O ⁻ -6-Cl-C ₆ H ₃ + HOCl	H ₂ O	10 ³ A = 2-10; 10 ³ B ≈ 1	NaOH	0-0.01	k AB	25	2.78 +3			*	(24)
Three substituents on Benzene Alkoxy, Carboxyl, Halogen												
.407	1-CH ₃ O-2-COOCH ₃ -4-Cl-C ₆ H ₃ + HOBr	AcW75*				k AB	20	2.56 -1				(14)
.408	1-CH ₃ O-4-COO(CH ₃)-6-Cl-C ₆ H ₃ + HOBr	AcW75*				k AB	20	6.26 -2				(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass action law	Temperature	$k \times 10^n$		$A = A^0 \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
.409	$1-\text{CH}_3\text{O}-4-\text{COOC}_2\text{H}_5-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	6.45	-2				(14)
.410	$1-\text{C}_2\text{H}_5\text{O}-4-\text{COOCH}_3-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.24	-1				(14)
.411	$1-\text{C}_2\text{H}_5\text{O}-4-\text{COOC}_2\text{H}_5-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.30	-1				(14)
.412	$1-\text{CH}_3\text{CH}_2\text{O}-4-\text{COOCH}_3-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.40	-1				(14)
.413	$1-\text{CH}_3\text{CH}_2\text{O}-4-\text{COOC}_2\text{H}_5-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.45	-1				(14)
.414	$1-(\text{CH}_3)_2\text{CHO}-2-\text{COOCH}_3-4-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	8.40	-1				(14)
.415	$1-(\text{CH}_3)_2\text{CHO}-4-\text{COOCH}_3-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	2.08	-1				(14)
.416	$1-(\text{CH}_3)_2\text{CHO}-4-\text{COOC}_2\text{H}_5-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	2.24	-1				(14)
.417	$1-\text{CH}_3(\text{CH}_2)_3\text{O}-4-\text{COOC}_2\text{H}_5-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.53	-1				(14)
.418	$1-\text{CH}_3(\text{CH}_2)_4\text{O}-4-\text{COOC}_2\text{H}_5-6-\text{Cl}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.53	-1				(14)
.419	$1-\text{CH}_3\text{O}-2-\text{COOCH}_3-4-\text{Br}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	3.45	-1				(14)
.420	$1-\text{CH}_3\text{O}-4-\text{COOCH}_3-6-\text{Br}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	8.40	-2				(14)
.421	$1-\text{CH}_3\text{O}-4-\text{COOC}_2\text{H}_5-6-\text{Br}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	8.81	-2				(14)
.422	$1-\text{C}_2\text{H}_5\text{O}-2-\text{COOCH}_3-4-\text{Br}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	6.86	-1				(14)
.423	$1-\text{C}_2\text{H}_5\text{O}-4-\text{COOCH}_3-6-\text{Br}-\text{C}_6\text{H}_3 + \text{HOBr}$	AcW 75*				k AB	20	1.66	-1				(14)

Homogeneous Reaction Kinetics

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No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass	Temperature	$k = k^0 \times 10^n$	B	$A = A^0 \times 10^n$	Comments	Literature
.424	$1-C_2H_5O-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	1.77	-1			(14)
.425	$1-CH_3CH_2CH_2O-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	1.92	-1			(14)
.426	$1-CH_3CH_2CH_2O-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	2.00	-1			(14)
.427	$1-(CH_3)_2CHO-2-COOC_2H_5-4-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	1.02	0			(14)
.428	$1-(CH_3)_2CHO-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	3.05	-1			(14)
.429	$1-(CH_3)_2CHO-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	3.19	-1			(14)
.430	$1-CH_3(CH_2)_3O-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	2.05	-1			(14)
.431	$1-CH_3(CH_2)_4O-4-COOC_2H_5-6-Br-C_6H_3 + HOBr$	AcW75*				k AB	20	2.06	-1			(14)
Three Substituents on Benzene Alkyl, Aryl-alkoxyl, Halogen												
.432	$1-CH_3-2-C_6H_4CH_2O-5-Cl-C_6H_3 + Cl_2$	Ac99*	$A = 3B \sim 0.01$	HCl		k AB	20	3.88	-2		*	(24)
.433	$1-CH_3-2-(o-NO_2C_6H_4CH_2O)-5-Cl-C_6H_3 + Cl_2$	Ac99*	$A = 3B \sim 0.01$	HCl		k AB	20	6.03	-3		*	(24)
.434	$1-CH_3-2-(2',6'-Cl_2C_6H_4CH_2O)-5-Cl-C_6H_3 + Cl_2$	Ac99*	$A = 3B \sim 0.01$	HCl		k AB	20	1.43	-2		*	(24)
.435	$1-CH_3-4-C_6H_4CH_2O-5-Br-C_6H_3 + Cl_2$	Ac99*	$A = 3B \sim 0.01$	HCl		k AB	20	6.65	-2		*	(24)
.436	$1-CH_3-2-(o-CH_3C_6H_4CH_2O)-5-Br-C_6H_3 + Cl_2$	Ac99*	$A = 3B \sim 0.01$	HCl		k AB	20	5.48	-2		*	(24)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$		$A = A^0 \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
.437	$1-\text{CH}_3-4-(\text{o}-\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	7.63	-2			*	(24)
.438	$1-\text{C}_2\text{H}_5-4-(\text{o}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	1.50	-2			*	(24)
.439	$1-\text{C}_2\text{H}_5-4-(\text{p}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	1.63	-2			*	(24)
.440	$1-\text{CH}_3\text{CH}_2\text{CH}_2-4-(\text{o}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	1.08	-2			*	(24)
.441	$1-\text{CH}_3\text{CH}_2\text{CH}_2-4-(\text{p}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	1.23	-2			*	(24)
.442	$1-(\text{CH}_3)_3\text{C}-4-(\text{o}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	5.60	-3			*	(24)
.443	$1-(\text{CH}_3)_3\text{C}-4-(\text{p}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	6.55	-3			*	(24)
.444	$1-(\text{CH}_3)_3\text{C}-4-(2',6'-\text{Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	1.16	-2			*	(24)
.445	$1-(\text{CH}_3)_2\text{CH}(\text{CH}_3)-4-(\text{p}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	2.63	-2			*	(24)
.446	$1-(\text{CH}_3)_2\text{CH}(\text{CH}_3)-4-(\text{o}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	4.28	-3			*	(24)
.447	$1-(\text{CH}_3)_2\text{CH}(\text{CH}_3)-4-(\text{p}-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{O})-5-\text{Br}-\text{C}_6\text{H}_3 + \text{Cl}_2$	Ac 99*	A = 3B $\approx$ 0.01	HCl		k AB	20	5.55	-3			*	(24)
Three Substituents on Benzene													
Hydroxyl, Halogen, Halogen													
.448	$1-\text{OH}-2,4-\text{Br}_2-\text{C}_6\text{H}_3 + \text{Br}_2$	AcW 72*	$10^3 A = 5; 10^3 B = 4$	HClO_4 LiBr	$\left. \begin{matrix} 0.10 \\ 0.10 \end{matrix} \right\}$	k AB	20	5.3	-1			*	(23)
		AcW 80*	7	HClO_4 LiBr	$\left. \begin{matrix} 0.10 \\ 0.137 \end{matrix} \right\}$		20	2.4	-1				

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$		$A = A^0 \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
.449	1-OH-2,6-Br ₂ -C ₆ H ₃ + Br ₂	AcW90*	$10^3 A = 2.5; 10^3 B = 4$	HBr HClO ₄	0.30 0.20 0.10	k AB	20	1.80 2.44	-1 -1			*	(25)
				HBr HClO ₄	0.10 0.20		20	5.13	-1				
				HBr LiBr	0.20 0.10		20	1.99	-1				
				HBr LiBr	0.10 0.20		20	3.02	-1				
Three Substituents on Benzene													
Alkoxy, Halogen, Halogen													
.450	1-CH ₃ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	2.83	-1				(14)
.451	1-C ₂ H ₅ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	5.66	-1				(14)
.452	1-CH ₃ CH ₂ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	6.34	-1				(14)
.453	1-(CH ₃) ₂ CHO-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	1.03	0				(14)
.454	1-CH ₃ (CH ₃) ₂ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	6.45	-1				(14)
.455	1-CH ₃ (CH ₃) ₂ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	6.52	-1				(14)
.456	1-HOCCCH ₂ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	2.30	-2				(14)
.457	1-HOCC(CH ₃) ₂ O-2,4-Cl ₂ -C ₆ H ₃ + HOBr	AcW75*				k AB	20	1.36	-1				(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined action law	Temperature	$k \times 10^n$		Δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.458	$1-\text{HOOC}(\text{CH}_3)_2\text{CHO}-2,4\text{-Cl}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	2.74	-2					(14)
.459	$1-\text{HOOC}(\text{CH}_3)_2\text{CHO}-2,6\text{-Cl}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	3	-3					(14)
.460	$1-\text{C}_6\text{H}_5\text{CH}_2\text{O}-2,4\text{-Cl}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	2.05	-1					(14)
.461	$1-\text{Br}(\text{CH}_3)_2\text{O}-2,4\text{-Cl}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	4.55	-2					(14)
.462	$1-\text{Br}(\text{CH}_3)_3\text{O}-2,4\text{-Cl}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	1.60	-1					(14)
.463	$1-\text{CH}_3\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	3.73	-1					(14)
.464	$1-\text{CH}_3\text{O}-2,6\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	8	-3					(14)
.465	$1-\text{C}_2\text{H}_5\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	7.47	-1					(14)
.466	$1-\text{CH}_3\text{CH}_2\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	8.52	-1					(14)
.467	$1-(\text{CH}_3)_2\text{CHO}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	1.36	0					(14)
.468	$1-\text{CH}_3(\text{CH}_3)_3\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	8.60	-1					(14)
.469	$1-(\text{CH}_3)_2\text{CHCH}_2\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	1.01	0					(14)
.470	$1-\text{CH}_3(\text{CH}_3)_4\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	8.80	-1					(14)
.471	$1-(\text{CH}_3)_2\text{CH}(\text{CH}_3)_2\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	9.74	-1					(14)
.472	$1-\text{C}_6\text{H}_5\text{CH}_2\text{O}-2,4\text{-Br}_2\text{-C}_6\text{H}_3 + \text{HOBr}$	AcW75*				k AB	20	2.65	-1					(14)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^3$ k^0 n	$A =$ $A^0 \times 10^3$ A^0 n	Comments	Literature
Three Substituents on Diphenyl											
Alkoxy, Halogen, Nitro											
.473	4'-NO ₂ -2-Cl-4-CH ₃ O-C ₆ H ₄ C ₆ H ₅ + Cl ₂	Ac 99*	10 ² A = 1; 10 ³ B = 5	HCl	0.02	k AB	20	3.2 -4		*	(25)
.474	4'-NO ₂ -3-Cl-4-C ₂ H ₅ O-C ₆ H ₄ C ₆ H ₅ + Cl ₂	Ac 99*	10 ² A = 1; 10 ³ B = 5	HCl	0.02	k AB	20	6.45 -4		*	(25)
.475	4'-NO ₂ -3-Cl-4-CH ₃ CH ₂ O-C ₆ H ₄ C ₆ H ₅ + Cl ₂	Ac 99*	10 ² A = 1; 10 ³ B = 5	HCl	0.02	k AB	20	6.92 -4		*	(25)
.476	4'-NO ₂ -3-Cl-4-(CH ₃) ₂ CHO-C ₆ H ₄ C ₆ H ₅ + Cl ₂	Ac 99*	10 ² A = 1; 10 ³ B = 5	HCl	0.02	k AB	20	9.40 -4		*	(25)
Four Substituents on Benzene											
Alkyl, Alkyl, Alkyl, Halogen											
.477	1,3,5-(CH ₃) ₃ -2-F-C ₆ H ₄ + Br ₂	CH ₃ NO ₂	A = B = 0.01				30	time 1,700	% reacted 10	*	(23a)
.478	1,3,5-(CH ₃) ₃ -2-Cl-C ₆ H ₄ + Br ₂	CH ₃ NO ₂	A = B = 0.01 0.02 0.01				30	2,920 720 9,000	10 10 10	*	(23a)
.479	1,3,5-(CH ₃) ₃ -2-Br-C ₆ H ₄ + Br ₂	AcNm*	A = B = 0.01 0.01				30	3,230 15,800	10 10	*	(23a)
.480	1,3,5-(CH ₃) ₃ -2-I-C ₆ H ₄ + Br ₂	CH ₃ NO ₂	A = B = 0.01				30	1,270	10	*	(23a)
Four Substituents on Diphenyl											
.481	3,3'-Cl ₂ -4,4'-(OH ₃) ₂ -(C ₆ H ₃) ₂ + Cl ₂	Ac 99*	10 ² A = 1; 10 ³ B = 5	HCl	0.02	k AB	20	6.03 -3		*	(27)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Defined mass action law	Temperature	$k = k^0 \times 10^n$	ρ	$A = A^0 \times 10^n$	Comments	Literature
					Amount of addend		k^0	n			
Five Substituents on Benzene											
Alkyl, Alkyl, Alkyl, Alkyl, Halogen											
.485	1, 2, 3, 5- (CH ₃) ₄ - 4- I- C ₆ H + Br ₂	CH ₃ NO ₂	A = B = 0.01			30	time 870	10	% reacted	*	(23 ^a)
.486	1, 2, 4, 5- (CH ₃) ₄ - 3- I- C ₆ H + Br ₂	Ac [*]	A = B = 0.01 0.02			30	8,820 2,100	10 10		*	(23 ^a)
.487	1, 2, 3, 5- (CH ₃) ₄ - 4- Cl- C ₆ H + Br ₂	CH ₃ NO ₂	A = B = 0.01			30	1,650	10		*	(23 ^a)
.488	1, 2, 4, 5- (CH ₃) ₄ - 3- Cl- C ₆ H + Br ₂	CH ₃ NO ₂ AcNm [*]	A = B = 0.01 0.01			30	830 4,520	10 10		*	(23 ^a)
.489	1, 2, 3, 5- (CH ₃) ₄ - 4- Br- C ₆ H + Br ₂	CH ₃ NO ₂	A = B = 0.01			30	1,690	10		*	(23 ^a)
.490	1, 2, 4, 5- (CH ₃) ₄ - 3- Br- C ₆ H + Br ₂	CH ₃ NO ₂	A = B = 0.01 0.02 0.01			30	1,980 515 10,400	10 10 10		*	(23 ^a)
.491	1, 2, 3, 5- (CH ₃) ₄ - 4- I- C ₆ H + Br ₂	AcNm [*]	A = B = 0.01			30	320	10		*	(23 ^a)
.492	1, 2, 4, 5- (CH ₃) ₄ - 3- I- C ₆ H + Br ₂	CH ₃ NO ₂	A = B = 0.01			30	1,500	10		*	(23 ^a)

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined rate action law	Temperature	$k = k^0 \times 10^n$ k^0 n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
Five Substituents on Benzene												
Alkoxy, Alkyl, Nitro, Halogen												
.493		1-CH ₃ O-3,5-(CH ₃) ₂ -2-NO ₂ -4-Cl-C ₆ H + HOBr	AcW75*				k AB	20	7.42 -1			(14)
.494		1-C ₂ H ₅ O-3,5-(CH ₃) ₂ -2-NO ₂ -4-Cl-C ₆ H + HOBr	AcW75*				k AB	20	1.42 0			(14)
.495		1-C ₆ H ₅ CH ₂ O-3,5-(CH ₃) ₂ -2-NO ₂ -4-Cl-C ₆ H + HOBr	AcW75*				k AB	20	4.93 -1			(14)
Five Substituents on Benzene												
Alkoxy, Alkyl, Halogen, Halogen												
.496		1-HOOCCH ₂ O-3,5-(CH ₃) ₂ -2,4-Cl ₂ -C ₆ H + HOBr	AcW75*				k AB	20	3.1 0			(14)
.497		1-(o-CH ₃ C ₆ H ₄ CH ₂ O)-3,5-(CH ₃) ₂ -2,4-Cl ₂ -C ₆ H + Cl ₂	Ac 99*	A = 3B ~ 0.01	HCl		k AB	20	1.72 -1		*	(24)
.498		1-(o-NO ₂ C ₆ H ₄ CH ₂ O)-3,5-(CH ₃) ₂ -2,4-Cl ₂ -C ₆ H + Cl ₂	Ac 99*	A = 3B ~ 0.01	HCl		k AB	20	2.05 -2		*	(24)
.499	.288	1-(o-ClC ₆ H ₄ CH ₂ O)-3,5-(CH ₃) ₂ -2,4-Cl ₂ -C ₆ H + Cl ₂	Ac 99*	A = 3B ~ 0.01	HCl		k AB	20	4.95 -2		* (23b), (24)	(24)
Monosubstituted Naphthalene												
Halogen												
.500		1-FC ₁₀ H ₇ + Cl ₂ → (4)	Ac*	A = B = 0.025				25	time 150	1 reacted 20	*	(18)
.501		1-FC ₁₀ H ₇ + Br ₂ → (4)	Ac*	A = B = 0.10 0.20				25	2,240 10	10 10	*	(18)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^n$		$A = A^0 \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
.501	1-FC ₁₀ H ₇ + Br ₂ → (4) (continued)	Ac*	A = B = 0.10 0.20 0.05 0.10	HClO ₄	0.50 0.50 0.50 0.50		25 25 52 52	time	144 30 284 60	% reacted	10 10 10 10	*	(18)
.502	1-ClC ₁₀ H ₇ + Cl ₂ → (4)	Ac*	A = B = 0.025 0.20				25 25	2,700 278		20 20		*	(18)
.503	1-ClC ₁₀ H ₇ + Br ₂ → (4)	Ac*	A = B = 0.10 0.20 0.10 0.20 0.05 0.10 0.05 0.10 0.05 0.10 0.20	HClO ₄	0.50 0.50 0.50 0.50 0.50 0.50 0.169		25 25 25 25 52 52 25 25 25 52 52	70,200 8,340 4,860 840 7,200 1,680 6,800 1,290 210 960 488	10 10 10 10 10 10 10 10 10 20 20		*	(18)	
.504	1-BrC ₁₀ H ₇ + Cl ₂ → (4)	Ac*	A = B = 0.025				25	3,240		20		*	(18)
.505	1-BrC ₁₀ H ₇ + Br ₂ → (4)	Ac*	A = B = 0.10 0.20 0.10 0.20 0.05 0.10	HClO ₄	0.50 0.50 0.50 0.50		25 25 25 25 52 52	108,000 13,320 7,320 1,320 8,880 2,160	10 10 10 10 10 10			*	(18)

Homogeneous Reaction Kinetics

312.472

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No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (Catalyst)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		$A = A^0 \times 10^n$		Comments	Literature
								k^0	n	A^0	n		
.506	$1\text{-IC}_{10}H_7 + Br_2 \longrightarrow (4)$	Ac*	A = B = 0.10 0.20 0.10 0.20 0.05 0.10	HClO ₄	0.50 0.50 0.50 0.50		25 25 25 25 52 52	time 37,200 5,460 3,780 300 3,840 840		% reacted 10 10 10 10 10 10		*	(18)
Disubstituted Naphthalene													
Alkoxy, Nitro													
.507	$1\text{-CH}_3\text{O-2-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	1.21	-2			*	(25)
.508	$1\text{-CH}_3\text{O-4-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	7.08	-1			*	(25)
.509	$1\text{-C}_2H_5\text{O-2-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	1.68	-2			*	(25)
.510	$1\text{-C}_2H_5\text{O-4-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	1.25	0			*	(25)
.511	$1\text{-CH}_3\text{CH}_2\text{O-4-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	1.20	0			*	(25)
.512	$1\text{-C}_2H_5\text{O-4-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	4.20	-1			*	(25)
.513	$1\text{-(p-NO}_2\text{C}_6H_4\text{CH}_2\text{O)-2-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	1.62	-3			*	(25)
.514	$1\text{-(p-NO}_2\text{C}_6H_4\text{CH}_2\text{O)-4-NO}_2\text{-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	1.03	-1			*	(25)
Disubstituted Naphthalene													
Alkoxy, Halogen													
.515	$1\text{-CH}_3\text{O-2-Cl-C}_{10}H_6 + Cl_2$	Ac 99*	$10^2A = 1; 10^3B = 5$	HCl	0.02	k AB	20	2.44	-1			*	(25)

No.	Reaction	Solvent (medium)	Amount of reactant	Added (catalyst)	Amount of added	Defined mass	Temperature	$k = k^0 \times 10^n$	k^0	n	Comments	Literature
.516	$1-C_2H_5O-2-Cl-C_{10}H_6 + Cl_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	3.81		-1	*	(25)
.517	$1-CH_3CH_2CH_2O-2-Cl-C_{10}H_6 + Cl_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	4.51		-1	*	(25)
.518	$1-C_6H_5CH_2O-2-Cl-C_{10}H_6 + Cl_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	1.79		-1	*	(25)
.519	$1-(p-NO_2C_6H_4CH_2O)-2-Cl-C_{10}H_6 + Cl_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	4.00		-2	*	(25)
.520	$1-(p-NO_2C_6H_4CH_2O)-4-Cl-C_{10}H_6 + Cl_2$	Ac 99*	$10^2 A = 1; 10^3 B = 5$	HCl	0.02	k AB	20	~ 1.1		+1	*	(25)

CODED SOLVENTS

Ac*	CH ₃ COOH
Ac 85, (80)...*	CH ₃ COOH % designated + H ₂ O
DIW 50*	Dioxane 50 wt % + H ₂ O
AcC 90*	CH ₃ COCH + 10 vol % CCl ₄
AcB 90*	CH ₃ COCH + 10 vol % C ₆ H ₆
M 30, (25)...*	CH ₃ OH vol % designated + H ₂ O
DI 30*	Dioxane 30 vol % + H ₂ O
AcH 75* (10) (25) (50) (65) (85)	CH ₃ COOH weight % designated + H ₂ O
AcD*	Deuterium substituted CH ₃ COOH
AcD 90*	90 vol % deuterium substituted CH ₃ COOH + D ₂ O
AcNm*	CH ₃ COOH + CH ₃ NO ₂ (1:1 by volume)

COMMENTS

(.272) - (.273)	Unsubstituted aromatic hydrocarbons	(.405) - (.472)	Three Substituents on Benzene
(.274) - (.300)	Alkyl substituted benzene	(.405)	Alkyl, Alkyl, Hydroxyl
(.301) - (.317)	Monosubstituted benzene	(.406)	Alkyl, Hydroxyl, Halogen
(.301) - (.308)	Alkoxy(hydroxyl) substituted benzene	(.407) - (.431)	Alkoxy, Carboxyl, Halogen
(.310) - (.312)	Carboxyl substituted benzene	(.432) - (.447)	Alkyl, Arylalkoxy, Halogen
(.313) - (.315)	Amino(amide) substituted benzene	(.448) - (.449)	Hydroxyl, Halogen, Halogen
(.316) - (.317)	Sulfo-alkyl substituted benzene	(.450) - (.472)	Alkoxy, Halogen, Halogen
(.318) - (.336)	Disubstituted benzene	(.473) - (.478)	Three Substituents on Diphenyl
(.318) - (.332)	Alkyl, Hydroxyl(alkoxy)		Alkoxy, Halogen, Nitro
(.333) - (.335)	Di-alkoxy	(.477) - (.480)	Four Substituents on Benzene
(.336)	Alkoxy, carboxyl		Alkyl, Alkyl, Alkyl, Halogen
(.337) - (.340)	Alkyl, Amino	(.481) - (.484)	Four Substituents on Diphenyl
(.341) - (.347)	Hydroxyl, Nitro		Alkoxy, Alkoxy, Halogen, Halogen
(.348) - (.356)	Alkoxy, Nitro	(.485) - (.499)	Five Substituents on Benzene
(.357)	Aryl alkoxy, Nitro	(.485) - (.492)	Alkyl, Alkyl, Alkyl, Alkyl, Halogen
(.358) - (.359)	Amino(amide), Nitro	(.493) - (.495)	Alkoxy, Alkyl, Alkyl, Nitro, Halogen
(.360) - (.373)	Alkoxy, Halogen	(.496) - (.499)	Alkoxy, Alkyl, Alkyl, Halogen, Halogen
(.374) - (.380)	Arylalkoxy, Halogen	(.500) - (.506)	Monosubstituted Naphthalene
(.381)	Amino, Halogen	(.500) - (.506)	Halogen
(.382) - (.397)	Aryl(diphenyl), Alkoxy	(.507) - (.520)	Disubstituted Naphthalene
(.398) - (.404)	Disubstituted diphenyl-	(.507) - (.514)	Alkoxy, Nitro
	Alkoxy, Halogen	(.515) - (.520)	Alkoxy, Halogen

COMMENTS

Reaction. (.272) Rate law does not include dependence on $[\text{ZnCl}_2]$. HBr inhibits probably by complexing with ZnCl_2 . Plot of $1/k$ vs. $[\text{HBr}]$ is linear. (.273) Selected data, units, seconds converted from original minutes. (.274) Rate law of (1) does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear for ZnCl_2 catalyzed reaction. Attributed to the formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. Time for 10% reaction given by $(5)^{(23)}$. Detailed study by (36) on dependence of rate upon $\text{C}_6\text{H}_5\text{CH}_2$, Br_2 and I_2 shows rate determining step may be expressed as first order with respect to $\text{C}_6\text{H}_5\text{CH}_2 \cdot \text{HBr}$ and third order with respect to I_2 . (.275) Rate law does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to the formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. (.276) Units, seconds converted from original minutes. (.277) Rate law does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to the formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. (.278) (.279) Units, seconds converted from original minutes. (.280) Rate law does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. (.281) (.282) (.283) (.284) (.285) (.286)

(continued)

Units, seconds converted from original minutes. (.287) (.288) (.289) Rate law does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. (.290) Units, seconds converted from original minutes. (.291) Rate law does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. (.292) Units, seconds converted from original minutes of (19) . Rate law of (1) does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. (.293) Selected data. Units, seconds converted from original minutes. Rate law holds up to 50% reaction. $k = k_0 + k'[\text{H}^+] + k''[\text{H}^+]\text{A}$ over range studied $k_0 = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$, $k'' = 0.193$. Values of k_0 and k' identical for mesitylene, phenol, anisole, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. See (.301) (.305) (.322) (.323). (.294) Selected data of (26) (28) . Units, seconds converted from original minutes of (28) . Original units of (26) mixed, both seconds and minutes used. Rate law followed to 75% reaction. (31) gives rate dependence upon HBr but no rate constants. Selected data of (27) in

COMMENTS

(continued)

CCl_4 . Seconds converted from original minutes. Induction period 1f HBr not introduced initially. Rate law followed to 90% reaction. Pseudo first order with respect to B, one-half order with respect to HBr and zero order with respect to A since A in sufficient excess. Rate constant calculated by dividing pseudo 3/2 order constant by concentration of A. Reaction carried out in dark to avoid side chain bromination. Strong catalysis by impurities in commercial mesitylene. Selected data of ⁽¹⁰⁾ in CCl_4 . ⁽³²⁾ gives rate law in agreement with ⁽¹⁰⁾ and times for fractional reaction. ⁽²³⁵⁾ ^(.236) ^(.237) Rate law does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to the formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. ^(.238) ^(.239) Rate law of ⁽¹⁾ does not include dependence on $[\text{ZnCl}_2]$. Plot of $1/k$ vs. $[\text{HBr}]$ is linear, which is attributed to the formation of an inactive $\text{ZnCl}_2 \cdot \text{HBr}$ complex. ⁽¹⁹⁾ gives times for 10% reaction. ^(.300) Units, seconds converted from original minutes. Ratio of $(\text{CH}_3)_3\text{COI}$ to $(\text{CH}_3)_3\text{CCl}$ estimated from amount of I_2 at infinite time. The HI formed on chlorination reacts with ICl to form unreactive I_2 . ^(.301) Selected data of ⁽¹⁷⁾, units, seconds converted from original. Pseudo first order rate

law followed up to 50% reaction. Pseudo first order constant expressed by ⁽¹⁷⁾ by the equation $k = k_0 + k'[\text{H}^+] + k''[\text{H}^+]^2$ with values $k_0 = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 0.475$ in the range studied. Values of k_0 and k' identical for mesitylene, phenol, anisole, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. See ^(.293) ^(.305) ^(.322) ^(.323). In presence of HCl rate constant observed by ⁽³⁴⁾ had identical values for phenols and phenolic ethers studied at phenol concentrations greater than value listed. See ^(.305) ^(.308) ^(.320). Rate determining step may be $\text{HCl} + \text{HOCl} \longrightarrow \text{Cl}_2 + \text{H}_2\text{O}$. ^(.302) $\text{C}_6\text{H}_5\text{O}^-$ and HOCl considered to be reactive species by ⁽³⁴⁾ rather than $\text{C}_6\text{H}_5\text{OH}$ and OCl^- based on study of OH^- dependence of rate of chlorination of salicylic acid. Units, seconds converted from original minutes. ^(.303) Units, seconds converted from original minutes. ^(.304) Selected data of ⁽³⁾, ⁽³⁰⁾. Units, seconds converted from original minutes of ⁽³⁾, ⁽⁷⁾, ⁽³⁰⁾. Rate law followed up to about 50% reaction by ⁽⁴⁾ and 60% reaction by ⁽⁷⁾. KI also added 0.1 M/l by ⁽³⁰⁾, 0.12 by ⁽³⁾ and 0.03-0.12 by ⁽⁷⁾. Empirical expression for k developed by ⁽³⁾ at pH 5.7-6.8 and 4.5-6.0 respectively: at 25° $k = 10^{-9} \times [\text{H}^+]^{-1} \{0.557 + 37.5[\text{Na}_2\text{HPO}_4] + 1[\text{KH}_2\text{PO}_4]\}$ at 35° $k = 10^{-9} [\text{H}^+]^{-1} \{2.22 + 153[\text{Na}_2\text{HPO}_4] + 9.0[\text{KH}_2\text{PO}_4]\}$.

COMMENTS

Phenoxide ion considered to be reacting species and rate constant also calculated in terms of it. (.305) Ag^+ introduced by (¹⁵), (¹⁶) and (¹⁷) to keep Cl^- concentration low. (¹⁶) observes rate to be identical to rate for $\text{C}_6\text{H}_5(\text{OCH}_3)_2$ and $\text{C}_6\text{H}_5\text{OH}$. See (.301) and (.334). Selected data of (¹⁷). Units, seconds converted from original minutes. Rate constant expressed by (¹⁷) by the equation $k = k_0 + k'[\text{H}^+] + k''[\text{H}^+]^2$ with values $k_0 = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 0.109$ in the range studied. Values of k_0 and k' identical for mesitylene, phenol, anisole, methyl *m*-tolyl ether, and methyl *p*-tolyl ether. See (.293) (.301) (.322) (.323). In presence of HCl rate constant observed by (³⁴) had identical values for phenols and phenolic ethers studied at phenol or ether concentrations greater than value listed. See (.301) (.308) (.320). (.306) (.307) Units, seconds converted from original minutes. (.308) Units, seconds converted from original minutes. Rate constant identical to value observed by author for phenols and phenolic ethers studied in presence of HCl at phenol or ether concentration greater than value listed. See (.301) (.305) (.320). (.303) (.311) (.312) Units, seconds converted from original minutes. (.313) Pseudo second order rate law valid only under specified conditions as rate

(continued)

dependent upon $[\text{KI}]$ and buffer constituents. From pH 5.4 to 7.6 k_0 is independent of pH. Below pH 5.4 calculated value of k_0 (extrapolated to zero buffer concentration) falls to 9.8×10^{-4} at pH = 4.57. Units, seconds converted from original minutes. Rate law followed to about 50% reaction. (.314) HI formed on chlorination reacts rapidly with ICl to form I_2 which is unreactive at stated conditions. Units, seconds converted from original minutes. (.315) Units, seconds converted from original minutes. (.318) (.319) Units, seconds converted from original minutes. Mechanism considered to involve ArO^- and HOCl see (.302). (.320) Units, seconds converted from original minutes. In presence of HCl and sufficient phenol rate identical for phenols and phenolic ethers studied by (³⁴). See (.301) (.305) (.308). (.321) Rate law followed up to about 60% reaction. Units, seconds converted from original minutes. (.322) Rate law followed up to 50% reaction. Units, seconds converted from original minutes. Pseudo first order constant expressed by the equation $k = k_0 + k'[\text{H}^+] + k''[\text{H}^+]^2$ with values $k_0 = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 1.30$ in the range studied. Values of k_0 and k' identical for mesitylene, phenol, anisole and *m*- and *p*-tolyl methyl ether. See (.293) (.301)

COMMENTS

(continued)

(.305) (.323). (.323) Units, seconds converted from original minutes. Pseudo first order constant expressed by (17) by the equation $k = k_0 + k'[\text{H}^+] + k''[\text{H}^+]^2$ with values $k_0 = 1.25 \times 10^{-4}$, $k' = 1.18 \times 10^{-3}$ and $k'' = 9 \times 10^{-2}$ in the range studied. Values of k_0 and k' identical for mesitylene, phenol, anisole and *m*- and *p*-tolyl methyl ether. See (.293) (.301) (.305) (.322). (.305) compares rate in deuterium substituted solvent see (.324). (.324) Units, seconds converted from original minutes. Since rate in D_2O is faster than in H_2O a rate controlling step is considered to be fission of $\text{H}_2\text{OCl}^+ \rightarrow \text{Cl}^+ + \text{H}_2\text{O}$. (.325) HI formed in chlorination reacts with ICl to form I_2 which is unreactive at stated conditions. Percent of chlorination was estimated from iodine left at infinite time. Units, seconds converted from original minutes. (.326) (.327) (.328) Rate law followed to about 80% reaction. Units, seconds converted from original minutes. (.329) Calculated rate constants drift upward after 40% reaction. Units, seconds converted from original minutes. (.330) (.331) (.332) Rate law followed to about 80% reaction. Units, seconds converted from original minutes. (.333) Units, seconds converted from original minutes. (.334) Rate observed to be

identical to rate for $\text{C}_6\text{H}_5\text{OH}$, and $\text{C}_6\text{H}_5\text{OCH}_3$, see (.304) (.305). (.335) Units, seconds converted from original minutes. (.336) Authors observe that plot of calculated k vs. $[\text{Br}^-][\text{H}^+]$ is linear. They suggest rate equation of the form $-d\text{B}/dt = k_1\text{AB} + k_2\text{A}[\text{Br}_2]$ and using the equilibrium constant for the reaction $\text{Br}_2 + \text{H}_2\text{O} = \text{HOBr} + \text{Br}^- + \text{H}^+$ calculate $k_1 = 0.108$ and $k_2 = 119$. (.337) (.338) (.339) (.340) Units, seconds converted from original minutes. Rate constants valid only under conditions specified. (.341) (.342) Units, seconds converted from original minutes. (.343) (.344) Simultaneous reactions. Units, seconds converted from original minutes, and M/l converted from original equivalents per liter. (.345) (.346) (.347) Units, seconds converted from original minutes. (.348) Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.349) Rate law followed to 80% reaction and shown to be valid over two-fold variation in initial concentrations of A and B. Values of concentrations not stated. (.350) (.352) Cl_2 produced in reaction media from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.357) Ring in which substitution occurs not specified. (.358) (.359) Units, seconds converted from

COMMENTS

(continued)

original minutes. (.361) (.362) (.363) (.364) (.365) (.366) (.370) Rate law in terms of free Br_2 as calculated using equilibrium constant for dissociation of Br_3^- . Units, seconds converted from original minutes. (.374) (.376) (.379) (Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.381) Rate law followed up to 85% reaction. Plot of rate constant vs. $[\text{H}^+]^{-1}$ is linear. Rate proportional to $k_1/(\text{H}^+ + [\text{Cl}^-])[\text{Cl}^-]$ where k_1 is equilibrium constant for $\text{ICl}_2^- \rightleftharpoons \text{ICl} + \text{Cl}^-$. Rate constant corrected for change of volume with temperature. (.382) through (.404) Position of substitution not specified by (^{2b}). Classification based upon ring in which substitution thought to occur, (written last). Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.405) (.406) Rate law in terms of phenolate ion and HOCl which authors consider to be involved in rate controlling step. Units, seconds converted from original minutes. (.432) through (.447) Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.448) (.449) In absence of initial Br^- rate constant decreases with progress of reaction

due to inhibition by Br^- formed. In reaction (.448) rate constant may be expressed by equation $k[\text{Br}_3^-][\text{H}^+]/(\text{Br}_2) = (3.2[\text{H}^+] + 0.63)/(0.28[\text{Br}^-] + 1.32[\text{H}^+][\text{Br}^-])$, where $[\text{Br}_2^-]$ represents total Br_3^- and (Br_2^-) represents only free Br_3^- . (.473) (.474) (.475) (Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.477) (.478) (.479) (.480) Units, seconds converted from original minutes. (Relative rates to parent hydrocarbons also given). (.481) (.482) (.483) (Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. (.485) through (.492) Units, seconds converted from original minutes. (Relative rates to parent hydrocarbons also given.) (.497) (.498) (.499) Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes. Rate constant for (.499) replaces the value listed in 1951 Tables which should have been 5.3×10^{-2} not 2.35×10^{-1} . (.500) through (.506) Units, seconds converted from original minutes. (.507) through (.530) Cl_2 produced in reaction medium from $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCl}_2$. Units, seconds converted from original minutes.

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Homogeneous Reactions

EXCHANGE

Liquid phase

312.473

H replacement by halogen on heterocyclic ring



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

Rate measured: $-dE/dt$

No.	Reaction	Solvent (medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^{12}$ k^0	f	Comments	Literature
.1	$\begin{array}{c} (C_2H_5OOC)C-CCH_3 \\ \\ CH_3CCH \\ \\ N \\ \\ H \end{array} + I_2 \longrightarrow \begin{array}{c} (C_2H_5OOC)C-CCH_3 \\ \\ CH_3CCH \\ \\ N \\ \\ H \end{array} + HI$	H ₂ O + 28 wt% dioxane	$10^3 A = 5-6$; $10^3 B = 7-9$	KI	0.5-0.8	$\frac{k_{AB}}{1 + K[I^-]}$	28	1.57 +1	710	*	(¹)
.2	$\begin{array}{c} CH_3C-CH \\ \\ (C_2H_5OOC)C-CCH_3 \\ \\ N \\ \\ H \end{array} + I_2 \longrightarrow \begin{array}{c} CH_3C-CH \\ \\ (C_2H_5OOC)C-CCH_3 \\ \\ N \\ \\ H \end{array} + HI$	H ₂ O + 28 wt% dioxane	$10^3 A = 5-6$; $10^3 B = 6-9$	KI	0.6-0.9	$\frac{k_{AB}}{1 + K[I^-]}$	28	6.0 -1	710	*	(¹)
.3	$\begin{array}{c} (C_2H_5OOC)C-CCH_3 \\ \\ CH_3CCH \\ \\ N \\ \\ CH_3 \end{array} + I_2 \longrightarrow \begin{array}{c} (C_2H_5OOC)C-CCH_3 \\ \\ CH_3CCH \\ \\ N \\ \\ CH_3 \end{array} + HI$	H ₂ O + 28 wt% dioxane	$10^3 A \sim 9$; $10^3 B \sim 6$	KI	0.5-0.8	$\frac{k_{AB}}{1 + K[I^-]}$	26	1.7 +1	710	*	(¹)

Homogeneous Reaction Kinetics

312.473

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k = k^0 \times 10^7$ k^0 η	k	Comments	Literature
3.	$\begin{array}{c} \text{H}_6\text{OOC} \text{---} \text{C} \text{---} \text{CCH}_3 \\ \quad \\ \text{CH}_3 \text{C} \text{---} \text{N} \\ \\ \text{CH}_3 \end{array} + \text{H}^+ + \text{I}_2^- \longrightarrow \begin{array}{c} \text{H}_6\text{OOC} \text{---} \text{C} \text{---} \text{CCH}_3 \\ \quad \\ \text{CH}_3 \text{C} \text{---} \text{N} \\ \\ \text{CH}_3 \end{array} + \text{I}_2$	H ₂ O + 28 wt % dioxane		HCl KI	0.5-0.8	k_{ABC}	28	1.40 -2		*	(1)
4.	$\begin{array}{c} \text{CH}_3 \text{C} \text{---} \text{CH} \\ \quad \\ \text{C} \text{---} \text{N} \\ \\ \text{CH}_3 \end{array} + \text{I}_2 \longrightarrow \begin{array}{c} \text{CH}_3 \text{C} \text{---} \text{CH} \\ \quad \\ \text{C} \text{---} \text{N} \\ \\ \text{CH}_3 \end{array} + \text{HI}$	H ₂ O + 28 wt % dioxane	$10^3 A \sim 6$ $10^3 B = 6-8$	KI	0.5-0.8	$\frac{k_{AB}}{1 + K[I^-]}$	28	6.9 -1	7.10	*	(1)
4.1	$\begin{array}{c} \text{CH}_3 \text{C} \text{---} \text{CH} \\ \quad \\ \text{C} \text{---} \text{N} \\ \\ \text{CH}_3 \end{array} + \text{H}^+ + \text{I}^- \longrightarrow \begin{array}{c} \text{CH}_3 \text{C} \text{---} \text{CH} \\ \quad \\ \text{C} \text{---} \text{N} \\ \\ \text{CH}_3 \end{array} + \text{I}_2$	H ₂ O + 28 wt % dioxane		HCl KI	0.5-0.8	k_{ABC}	28	6.9 -4		*	(1)
5.	$\begin{array}{c} \text{CH-N} \\ \quad \\ \text{HC} \text{---} \text{N} \\ \\ \text{H} \end{array} + 2\text{I}_2 \longrightarrow \text{C}_2\text{H}_4\text{N}_2\text{I}_2 + 2\text{HI}$	H ₂ O	$10^2 A = 1.5-8$ $10^4 B = 4-5$ $\mu = 0.05$	HClO ₄ KI $10^8 [H^+] =$	0.007-0.02 0.007-0.02 3-20	$-2dA/dt =$ $k_{AB}[H^+]^{-1}[I^-]^{-2} +$ $k'A^2B[H^+]^{-1}[I^-]^{-2}$	25	1.10 -13 6.9 -12		*	(2)

COMMENTS

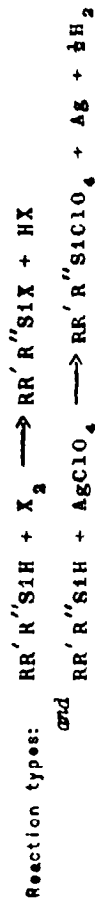
Reaction. (.1)(.2)(.3) In buffered solution pH = 6.8 to 6.9. Reverses in presence of strong acid. (.3.1) Reverse of reaction (.3) in presence of acid. (.4) In buffered solution pH = 6.8-6.9. (.4.1) Reverse of (.4) in presence of acid. (.5) Observed rate pseudo first order as A and I^- both in large excess. Calculated values of k and k' based upon free glyoxaline for A (total glyoxaline minus perchloric acid), stoichiometric I_2 assumed to be predominantly I_3^- . Authors consider reactive form to be either I^+ or H_2OI^+ . Rate determining step probably replacement of first hydrogen since moniodide reacts very much more rapidly even though A in twenty fold excess.

LITERATURE

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EXCHANGE
Replacement of H by halogen on Si

Liquid phase



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

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined Rate Equation	Temperature	$k =$		Comments	Literature
						$k^0 \times 10^n$	n		
.1	$(C_2H_5)_3SiH + I_2 \longrightarrow (C_2H_5)_3SiI + HI$	CCl_4	$10^3 A = 5-33; 10^3 B = 5-33$	k_{AB}^2	-18	1.28	0	*	(1)
					-9	1.30	0		
					1	1.28	0		
					10	1.78	0		
					25	3.14	0		
.2	$(C_2H_5)_3SiH + AgClO_4 \longrightarrow (C_2H_5)_3SiClO_4 + Ag + \frac{1}{2}H_2$	C_6H_6 $CHCl_3$	$10^3 A = 5-26; E = 0.17-0.36$ $B = 0.4$ $10 A = 1.1; 10 B = 1.2-1.7$	k_{AB}^2	25	7.7	+1	*	(2)
					25	5.9	+2		
					25	1.2	-2		
					23	1.6	-2		
					23	2.2	-2		
.3	$(n-C_3H_7)_3SiH + I_2 \longrightarrow (n-C_3H_7)_3SiI + HI$	CCl_4 C_6H_6	$A = B = 0.01-0.05$	k_{AB}^2	25	3.0	0	*	(1)
					25	1.77	+1		
.4	$(n-C_3H_7)_3SiH + AgClO_4 \longrightarrow (n-C_3H_7)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.14; B = 0.31$	k_{AB}^2	23	8.3	-3	*	(2)
.5	$[(CH_3)_2CH]_3SiH + I_2 \longrightarrow [(CH_3)_2CH]_3SiI + HI$	C_6H_6	$A = B = 0.01-0.05$	k_{AB}^2	25	4.0	0	*	(1)

Homogeneous Reaction Kinetics

312.474

2

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined mass action law	Temperature	$k = k^0 \times 10^n$	Comments	Temperature
.6	$[(CH_3)_2CH]_3SiH + AgClO_4 \longrightarrow [(CH_3)_2CH]_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.14; B = 0.43$	$k_0 AB^2$	23	1.2	-5	(2)
.7	$(n-C_4H_9)_3SiH + I_2 \longrightarrow (n-C_4H_9)_3SiI + HI$	CCl_4 C_6H_6 $CHCl_3$	$A = B = 0.01-0.05$	$k_0 AB^3$	25	5.0	0	(1)
					25	2.09	+1	
					25	1.66	+3	
.8	$(n-C_4H_9)_3SiH + AgClO_4 \longrightarrow (n-C_4H_9)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.14; B = 0.51$ 0.43	$k_0 AB^2$	23	4.7	-3	(2)
					23	5.2	-3	
.9	$[(CH_3)_2CHCH_2]_3SiH + I_2 \longrightarrow [(CH_3)_2CHCH_2]_3SiI + HI$	CCl_4 C_6H_6	$A = B = 0.01-0.05$	$k_0 AB^3$	25	3.9	-1	(1)
					25	9.7	-1	
.10	$[(CH_3)_2CHCH_2]_3SiH + AgClO_4 \longrightarrow [(CH_3)_2CHCH_2]_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.14; B = 0.43$	$k_0 AB^2$	23	1.8	-4	(2)
.11	$(C_6H_5CH_2)_3SiH + AgClO_4 \longrightarrow (C_6H_5CH_2)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.08; B = 0.08$	$k_0 AB^2$	23	~2.6	0	(2)
.12	$(p-CH_3C_6H_4CH_2)_3SiH + AgClO_4 \longrightarrow (p-CH_3C_6H_4CH_2)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.08; B = 0.08$	$k_0 AB^2$	23	~4.4	0	(2)
.13	$(p-ClC_6H_4CH_2)_3SiH + AgClO_4 \longrightarrow (p-ClC_6H_4CH_2)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.08; B = 0.08$	$k_0 AB^2$	23	9.2	-2	(2)
Aryl-silanes								
.14	$C_6H_5(CH_3)_2SiH + AgClO_4 \longrightarrow C_6H_5(CH_3)_2SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.14; B = 0.21$ 0.06	$k_0 AB^2$	23	1.1	-1	(2)
					23	4.9	-1	
.15	$p-CH_3C_6H_4(CH_3)_2SiH + AgClO_4 \longrightarrow p-CH_3C_6H_4(CH_3)_2SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3C_6H_5$	$A = 0.08; B = 0.06$	$k_0 AB^2$	23	5.7	-1	(2)

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined Time	Temperature	$k \times 10^n$		Comments	Literature
						k^0	k		
.16	$(C_6H_5)_3SiH + Br_2 \longrightarrow (C_6H_5)_3SiBr + HBr$	CCl_4	A = B = 0.025	Time 60 120 7×10^3 2×10^5	18 18 25 25		% B remaining 60 46 33 33		(¹)
.17	$(C_6H_5)_3SiH + I_2 \longrightarrow (C_6H_5)_3SiI + HI$	CCl_4 $CHCl_3$	A = B = 0.01-0.05	k_{AB}^0	25	3 6.1	-2 0	*	(¹)
.18	$(C_6H_5)_3SiH + AgClO_4 \longrightarrow (C_6H_5)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3CO_2H_6$	A = 0.14; B = 0.43	k_{AB}^0	23	5.8	-4		(²)
.19	$(p-CH_3C_6H_4)_3SiH + I_2 \longrightarrow (p-CH_3C_6H_4)_3SiI + HI$	CCl_4	A = B = 0.01-0.05	k_{AB}^0	25	1.4	-1	*	(²)
.20	$(p-CH_3C_6H_4)_3SiH + AgClO_4 \longrightarrow (p-CH_3C_6H_4)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3CO_2H_6$	A = 0.14; B = 0.43	k_{AB}^0	23	2.2	-3	*	(²)
.21	$(p-ClC_6H_4)_3SiH + I_2 \longrightarrow (p-ClC_6H_4)_3SiI + HI$	$CHCl_3$	A = B = 0.01-0.05	k_{AB}^0	25	1.1	-1	*	(¹)
.22	$(p-ClC_6H_4)_3SiH + AgClO_4 \longrightarrow (p-ClC_6H_4)_3SiClO_4 + Ag + \frac{1}{2}H_2$	$CH_3CO_2H_6$	A = 0.14; B = 0.43	k_{AB}^0	23	1.1	-4	*	(²)

COMMENTS

Reactions. (.1) Good fourth order rate constants observed over course of reaction and with ratio of A/B varied from 0.5-2. At 55° mixed third and fourth order observed. No effect on rate constant of light, O_2 or H_2O . Light does influence reaction products. (.2) Initial rate only. Over the course reaction appears to be slightly less than third order. Rate of hydrogen evolution followed, which was reproducible, although stoichiometry of reaction not always reproducible. Above 0.35 M/l B initial rate appears to be higher than second order with respect to B. (.3) Reaction order assumed identical to (.1). (.4) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve.

COMMENTS

(continued)

(.5) Reaction order assumed identical to (.1). (.6) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. (.7) Reaction order assumed identical to (.1). (.8) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. (.9) Reaction order assumed identical to (.1). (.10) (.11) (.12) (.13) (.14) (.15) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. (.16) Reaction order assumed identical to (.1). (.17) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. (.18) Reaction order assumed identical to (.1). (.19) Reaction order assumed identical to (.1). (.20) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve. (.21) Reaction order assumed identical to (.1). (.22) Initial rate only. Reaction order assumed identical to (.2) on basis of shape of rate curve.

LITERATURE

- (¹) D. R. Deans, C. Eaborn, *CSL* 1954, 3169. (²) C. Eaborn, *CSL* 1955, 2517.

No.	Reaction	Solvent	Amount of reactant	μ	pH	Defined reaction law	Temperature	$k^0 \times 10^n$ k^0 n	$A^0 \times 10^n$ A^0 n	Comments	
.2	$\text{CH}_3\text{NH}_2 + \text{HOCl} \longrightarrow \text{CH}_3\text{NHCl} + \text{H}_2\text{O}$	H_2O	$10^5 A = 2.3, 10^5 B = 1.1$	$[\text{OH}^-] = 0.12$	0.12	k_{AB}	6.5	2.53	+2	13.8	*
				"	"	"	12	3.74	+2		
				"	"	"	16	4.91	+2		
				"	"	"	21	8.00	+2		
				"	"	"	25	1.11	+3		
				.0001	4.33	25	2.52	+2			
				.0001	4.87	25	8.83	+2			
				.0001	5.81	25	7.37	+3			
				.028	12.42	25	3.10	+3			
				.046	12.67	25	1.90	+3			
				.081	12.88	25	1.07	+3			
				$[\text{OH}^-] = 0.12$	"	$k_{A'B'}$	6.5	5.0	+8		
				"	"	"	16	3.3	+8		
				"	"	"	25	5.0	+8	4.5 6 13	
.3	$(\text{CH}_3)_2\text{NH} + \text{HOCl} \longrightarrow (\text{CH}_3)_2\text{NCl} + \text{H}_2\text{O}$	H_2O	$10^5 A = 2.3, 10^5 B = 1.1$	$[\text{OH}^-] = 0.12$	0.12	k_{AB}	6	3.56	+2	10	*
				"	"	"	11	4.84	+2		
				"	"	"	14	5.42	+2		
				"	"	"	21	6.64	+2		
				"	"	"	25	1.05	+3		
				.0001	4.09	25	8.7	+1			
				.0001	4.97	25	8.35	+2			
				.0001	5.80	25	3.50	+3			
				.030	12.45	25	2.54	+3			
				.056	12.74	25	1.37	+3			
				.076	12.87	25	1.08	+3			
				$[\text{OH}^-] = 0.12$	"	$k_{A'B'}$	6	4.3	+8		
				"	"	"	14	4.7	+8	0.8 1 11	
				"	"	"	25	5.0	+8		

COMMENTS

Tabulated values of k are for observed second order rate law in terms of total concentrations of reactants. Specific second order rate constants in terms of calculated concentrations, A', B' , of the specific chemical species are listed as k . The pH dependence is consistent with a reaction mechanism involving NH_3 with $HOCl$ or NH_4^+ with OCl^- .

LITERATURE

1. Weil, J.C. *Mor Is*, *ACS* 1949, 71, 1684.

Homogeneous Reactions

312.571

EXCHANGE
HYDROGEN SUBSTITUTION

Replacement of hydrogen by halogen on nitrogen



Liquid phase

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

No.	Reaction	Solvent	(Medium)	Amount of reactant	Addend (1)	Addend (2)	Amount of addend (2)	Defined mass	pH	Temperature	$k^0 \times 10^n$	n
.1	$CH_3C(ONHCH_3) + H_2O \longrightarrow CH_3C(ONCl)CH_3 + H_2O$	H_2O		$10^{-2}A = 2 \times 10^{-2}B = 5$	CH_3COOH	CH_3COONa	C.035 0.093 0.187 0.280 0.096 0.192 0.365	AB	5.0 5.0 5.0 5.0 6.0 6.0 6.0	25 25 25 25 25 25 25	7.87 1.92 3.58 5.64 3.22 5.02 8.35	-3 -2 -2 -2 -3 -3 -3
					(X) CH_3COOH		0.04-0.3 0.1-0.4	$k = k_0 + k_1[X]$	5.0 6.0 5-6	25 25 25	k_0 8 k_1 1.42 k_2 4.5	-4 -3 -1
					$CH_2ClCOOH$ C_6H_5COOH $o-NO_2C_6H_4COOH$ $(CH_2COOH)_2$					25 25 25 25	k_3 2.50 k_4 1.03 k_5 7.33 k_6 1.02	0 0 0 0
					$HOOC(CF_3)_2COO^-$ $K_2P_2O_7$	$HP_2O_4^-$			6	25	k_7 3.5 k_8 1.2	-1 -3
							0.028 0.0057 0.0114		6 6 6	25 25 25	1.85 2.53 3.85	-3 -3 -3
									7 7	25 25	k_9 5.2 k_{10} 5.90	-3 -3

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1) (Buffer acid)	Amount of addend (1)	Addend (2) (Buffer salt)	Amount of addend (2)	Defined mass fraction	pH	Temperature	$k = k^0 \times 10^n$	
											k^0	n
.1	$\text{CH}_3\text{C}(\text{NH})\text{CH}_3 + \text{HOCl} \longrightarrow$ (continued)	H_2O	$10^2 \text{A} = 2 \times 10^3 \text{B} = 5$	H_2PO_4^-	0.020 0.041	$\text{HPO}_4^{=}$	0.030 0.059	AB	7	25	5.72	-3
				0.0016					7	25	6.37	-3
				0.0032					8	25	k_0 1.20	-2
				0.0064					8	25	1.23	-2
									8	25	1.23	-2
									8	25	1.23	-2
									9	25	1.60	-2
.2	$\text{CH}_3\text{C}(\text{NH})\text{CH}_2\text{COOH} + \text{HOCl} \longrightarrow \text{CH}_3\text{C}(\text{NH})\text{CH}_2\text{COOH} + \text{H}_2\text{O}$	H_2O	$10^2 \text{A} = 2 \times 10^3 \text{B} = 5$	CH_3COOH	0.0038 0.0075	CH_3COONa	0.086 0.192	AB	6	25	5.95	-3
					0.0150		0.385		6	25	6.45	-3
					0.044	$\text{HPO}_4^{=}$	0.0057		6	25	7.70	-3
									6	25	4.67	-3
.3	$\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_4\text{-O-CH}_3 + \text{HOCl} \longrightarrow$ $\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_4\text{-O-CH}_3 + \text{H}_2\text{O}$	H_2O	$10^2 \text{A} = 2 \times 10^3 \text{B} = 5$	CH_3COOH	0.0038 0.0075	CH_3COONa	0.096 0.192	AB	6	25	2.17	-1
									6	25	2.08	-1
.4	$\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_4\text{-p-CH}_3 + \text{HOCl} \longrightarrow$ $\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_4\text{-p-CH}_3 + \text{H}_2\text{O}$	H_2O	$10^2 \text{A} = 2 \times 10^3 \text{B} = 5$	CH_3COOH	0.0075 0.0150		0.192 0.385	AB	6	25	1.80	-1
					0.044	$\text{HPO}_4^{=}$	0.0057		6	25	1.83	-1
									6	25	1.80	-1
.5	$\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_5 + \text{HOCl} \longrightarrow \text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_5 + \text{H}_2\text{O}$	H_2O	$10^2 \text{A} = 2 \times 10^3 \text{B} = 5$	H_2PO_4^-	0.015 0.044	$\text{HPO}_4^{=}$	0.035 0.0057	AB	5	25	2.28	-2
					0.088		0.0114		6	25	2.20	-1
					0.020		0.030		7	25	1.88	-1
					0.0032		0.0468		8	25	1.65	0
									8	25	4.48	0
.6	$\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_4\text{-O-Cl} + \text{HOCl} \longrightarrow$ $\text{CH}_3\text{C}(\text{NH})\text{C}_6\text{H}_4\text{-O-Cl} + \text{H}_2\text{O}$	H_2O	$10^2 \text{A} = 2 \times 10^3 \text{B} = 5$	CH_3COOH	0.0038 0.0075	CH_3COONa	0.096 0.192	AB	6	25	2.58	0
					0.0150		0.385		6	25	2.48	0
					0.044	$\text{HPO}_4^{=}$	0.0057		6	25	2.47	0
									6	25	2.42	0

December, 1956

National Bureau of Standards - National Research Council

COMMENTS

Selected data. Units, seconds converted from original minutes. Rate law followed to about 65% reaction.

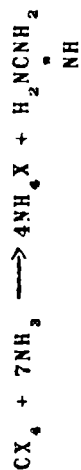
LITERATURE

R.P. Manger, F.O. Soper, *CZ* 1946, 71.

EXCHANGE
Replacement of halogen by NH_3 and NH

Gas phase

Reaction type:



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

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

No.	Reaction	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	Time	% formed	$k =$ $k^0 \times 10^n$	Comments
-1	$\text{CCl}_4 + \text{NH}_3$	$A = 1.5 \times B \sim 10$	I_2	0.05	k_{AL}	150 150 300 300	6.5×10^4 6.5×10^4 6.5×10^4 6.5×10^4	0 ~ 10 10 84	5.3 -4	*
-2	$\text{CBr}_4 + \text{NH}_3$	$A = 0.2 \times B \sim 10$	I KI	0.25		150 150	6.5×10^4 6.5×10^4	62 83		*

COMMENTS

For these reactions below critical temperature of NH_3 , see 332.753. Data gives order of magnitude only. Concentrations estimated at reaction temperatures. Reactions proceed through intermediate which involves about 10% of the reacting carbon for (-2) and less than 5% for (-1). Production of halide ion slightly ahead of guanidine at all stages.

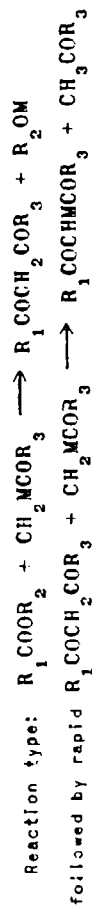
LITERATURE

G.W. Watt, H.T. Hahn, ACS 1955, 77, 312.

Homogeneous Reactions
332.141

EXCHANGE

Alkali metal replaced by C



Liquid phase

Amounts are in M/l.
 Rate constants are
 in M/l and sec.
 Literature and com-
 ments are at end of
 table.

No.	Reaction	Solvent	Amount of reactant	Defined mass- action law	Temperature	$k \times 10^7$ k^0 n	δ	$A \times 10^7$ A^0 n	$\Delta S^\ddagger$	Comments
1.	$CH_3COOC_2H_5 + 2CH_2NaOCH_2CH_2CH_3$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	0 30	7.7 1.10 -3	14.5	3 7	-26.4	
2.	$CH_3COOC_2H_5 + 2CH_2NaOCH(CH_3)_2$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	0 30	9.4 1.09 -3	13.8	1 7	-29.2	
3.	$CH_3COOC_2H_5 + 2CH_2LiOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	30	1.44 -3				
4.	$CH_3COOC_2H_5 + 2CH_2NaOCH_2CH(CH_3)_2$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	0 30	3.85 5.25 -3	14.1	8 7	-24.4	
5.	$CH_3COOC_2H_5 + 2CH_2NaOC(CH_3)_3$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	0 30	3.57 4.03 -4	13.2	1 6	-33.1	
6.	$CH_3COOC_2H_5 + 2CH_2NaOC_6H_5$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	0 30	2.60 3.52 -4	14.2	6 6	-29.5	*
7.	$CH_3COOC_2H_5 + 2CH_2NaOC_6H_4-2,4,6-(CH_3)_3$	$(C_2H_5)_2O$	$10^2A = 4-9; 10B = 1-2$	$-dA/dt = kAB$	30	very slow				*

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k \times 10^n$		$A \times 10^n$		$\Delta S^\ddagger$	Comments
						k°	n	A°	n		
.8	$\text{CH}_3\text{COOCH}(\text{CH}_3)_2 + 2\text{CH}_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	0 30	1.80 7.8	-5 -4	6 20.6	11	-7.4	
.9	$\text{CH}_3\text{COOCH}(\text{CH}_3)_2 + 2\text{CH}_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	30	very slow					*
.10	$(\text{CH}_3)_2\text{CHCOOCH}_2\text{CH}_2 + 2\text{CH}_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	30	2.52	-4				
.11	$(\text{CH}_3)_2\text{CHCH}_2\text{COOCH}_2\text{CH}_2 + 2\text{CH}_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	30	1.53	-4				
.12	$\text{CH}_3\text{COOCH}_2\text{CH}_2 + 2\text{CH}_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	30	2.3	-1				*
.13	$\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_2 + 2\text{CH}_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	0 30	1.07 2.60	-4 -3	1 17.5	1 10	-15.2	
.14	$\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_2 + 2(\text{H}_2)_2\text{NaCOCH}_2\text{CH}(\text{CH}_3)_2$	$(\text{C}_2\text{H}_5)_2\text{O}$	$10^2\text{A}=4-9; 10\text{B}=1-2$	$-dA/dt = kAB$	0 30	7.2 2.2	-2 -1	6	4	-43	*

COMMENTS

General: Reactions studied in presence of excess of alkali metal ketone which was produced by titration with triphenyl methyl sodium or lithium. Diketone first produced reacts rapidly with second molecule of alkali metal ketone to produce sodium, or lithium, diketone so that differential rate equation has the form $dx/dt = k(a-x)(b-2x)$. "a" and "b" are initial concentrations of ester and alkali metal ketone and x is ester reacted at time t. Specific concentrations of reactants not stated in each case. When ester concentration was 0.20 and concentration of sodium ketone only 0.24 the above rate law did not hold. For all data listed concentration of B is greater than twice concentration of A. Authors give units of $\Delta S^\ddagger$ as k cal./deg. the units should be cal./deg. Values of E and $\Delta S^\ddagger$ are based on measurement at only two temperatures so that number after the decimal probably has no significance.

Reaction: (.6) Activation energy and $\Delta S^\ddagger$ recalculated as values given by authors do not agree with the data. (.7)
 (.9) No data given to indicate limiting value of rate constant. (.12) (.14) Value of rate constant in doubt as reaction too fast to measure accurately.

LITERATURE

D.G. Hill, J. Burkus, C.R. Hauser, *ACS* 1959, **61**, 602.

EXCHANGE
Replacement of B by O on aromatic C

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

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Ionic strength	pH	Defined mass action law	Temperature	$k = k_0 \times 10^n$	Comments	Literature
.1	$C_6H_5B(OH)_2 + H_2O \xrightarrow{C_6H_5OH + 3(OH)_3}$	H_2O	$10^2 A = 1-5$ $10^2 B = 5-40$	$HClO_4$	0.0025-0.01	0.2		k_{AB}	25	7.7	*	(1)
					0.20				25	1.58		
					2.5				25	1.80		
					8.2				25	6.05		
					0.2-8				25	$k_0 + k' \alpha_{H_2O}^{-1} \cdot \alpha_{HClO_4}^{-1}$		
									25	k_{AB}		
					0.193				25	1.84		
					1.13				25	9.89		
					3.84				25	9.19		
					6.33				25	5.91		
					8.99				25	3.6		
					0.2-9				25	$k_0 + k' \alpha_{H_2O}^{-1} \cdot \alpha_{H_2SO_4}^{-3/2}$		
									25	k_{AB}		
					0.725				25	1.40		
					2.27				25	1.21		
					5.19				25	2.14		
					9.67				25	$k_0 + k' \alpha_{H_2O}^{-1} \cdot \alpha_{H_3PO_4}^{-1}$		
					0.7-9				25	$k_{AB} + k_2 A^{-2} B$		
						0.2	3.3	$k_{AB} + k_2 A^{-2} B$	25	$k_1 1.05$	*	(2)
						0.2	3.3		25	$k_2 2.40$		
						0.2	4.4		25	$k_3 3.2$		

No.	Reaction	Medium (Solvent)	Amount of reactant	Addend	Amount of addend	Ionic strength	pH	Defined mass action law	Temperature	$k \times 10^2$		Comments	Literature										
										k^0	n												
.1	$\text{C}_6\text{H}_5\text{B(OH)}_2 + \text{H}_2\text{O}_2 \longrightarrow$ $\text{C}_6\text{H}_5\text{OH} + \text{B(OH)}_3$ (continued)	H_2O	$10^2\text{A} = 1-5$ $10^3\text{B} = 5-40$	Na_2IO_4		0.2	4.4	$k_1\text{AB} + k_2\text{A}^2\text{B}$ $k_1' = k_1[\text{H}^+]$ $k_2' = k_2[\text{H}^+]$	25	$k_2^0 5.0$	-2	*	(2)										
														$10^2\text{A} = 2$ 4 2 4 2 4 1 2	$\left. \begin{array}{l} \text{ClCH}_2\text{COOH} \\ \text{ClCH}_2\text{COONa} \end{array} \right\}$ $\left. \begin{array}{l} \text{CH}_3\text{COOH} \\ \text{CH}_3\text{COONa} \end{array} \right\}$ $\text{NaClO}_4 +$ catalyst = X $(\text{HOOCCH}_2)_2\text{C(OH)COOH}$ $(\text{CH}_2)_6\text{C(OH)COOH}$ $(\text{CH}_3)_2\text{C(OH)COOH}$ o-HOC ₆ H ₄ COOH $\text{C}_6\text{H}_5\text{CH(OH)COOH}$ $\text{CH}_3\text{CH(OH)COOH}$ HOCH ₂ COOH HOCH ₂ CH ₂ COOH	0.055 0.22 0.05 0.05	0.2 0.2 0.2 0.2 0.2 0.5 0.5 0.5 0.5 0.5 0.5	~ 2 1.9 2.4 2.3 2.8 2.2 2.4 2.5 2.8	$k = k_0 + k_x X$	$k_0^0 8$ $k_x^0 1.5$ $k_x^0 1.2$ $k_x^0 7.5$ $k_x^0 5.9$ $k_x^0 3.6$ $k_x^0 1.6$ $k_x^0 2.5$ $k_x^0 2$	-4 0 0 -1 -1 -1 -1 -2 -3	*	(3)

(other chelating agents see comments)

COMMENTS

Literature. (1) Selected data. This appears to be a unique case of acid catalysis where each strong acid gives an individual catalytic rate law. With perchloric acid as catalyst linear plot obtained on plotting $\log k_{\text{cor}}$ vs. $\log$ of the product of the activities of the water and the perchloric acid. k_{cor} is observed pseudo second order rate constant corrected for uncatalyzed reaction observed between pH = 2-3. With sulfuric acid no simple linear correlation was found between k_{cor} and the activities of the sulfuric acid and the water but $\log (a_{\text{H}_2\text{O}}^4 \times a^{3/2})$ vs. $\log k_{\text{cor}}$ gave all linear plot over the range studied. Only in the case of phosphoric acid was a linear relationship observed between $\log k_{\text{cor}}$ and H_0 , Hammett's acidity function. (2) Selected data. In absence of buffers initial and integrated course rates obey the rate expression $-dB/dt = k_1 AB + k_2 A^2 B$. In presence of buffer pseudo second order rate law obeyed but calculated constants dependent upon pH with slight dependence upon buffer concentration and initial concentration of A and ionic strength. (3) Selected data. Wide variety of chelating agents tested for catalytic activity. No appreciable catalytic activity observed for the simple dibasic acids used nor for any of the 1,2 or 1,3-diols studied in acetate buffer at pH = 4.7. Concentrations of malonic acid and malonate ion each at 0.5 M/l depressed rate about 35%. All α -hydroxy acids studied showed definite catalytic activity. Detailed studies made using citric acid and α -hydroxy iso-butyric acids as catalysts relating catalytic activity to pH as well as to concentrations of a variety of ions and complexes.

LITERATURE

- (1) H. G. Kuivilla, *ACS* 1955, 77, 4014.
- (2) H. G. Kuivilla, *ACS* 1954, 76, 870.
- (3) H. G. Kuivilla, R. A. Wiles, *ACS* 1955, 77, 4830.

No.	Reaction	Medium (Solvent)	Amount of reactant	Acid (Catalyst)	Amount of addend	μ	Concentration of reagent	Temperature	$k^0 \times 10^7$	n	Comments	Literature
.5	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 \cdot \text{H}_2\text{O} \longrightarrow$	HAcOH^*	$10^3 \text{ A} = 1; 10^3 \text{ B} = 8$	NaBr	0.4	0.4	k_{AB}	25	> 7	+3		(3)*
.6	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{B(OH)}_2 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow$	HMS^*	$10^3 \text{ A} = 2-10;$ $10^3 \text{ B} = 2-18$	$\left. \begin{array}{l} \text{CH}_3\text{COOH} \\ \text{CH}_3\text{COONa} \end{array} \right\}$	$\text{pH} = 4.42$ $[\text{I}^-] = 0.2$ 0.5 0.1-0.5 $[\text{I}^-] = 0.15$ $[\text{CH}_3\text{COONa}] =$ 0.0	0.74	k_{AB}	25	2.48	-2		(5)
				$\left[\begin{array}{l} \text{CH}_3\text{COOH} \\ \text{R}[\text{CH}_3\text{COONa}] \\ \text{R} = \text{H}; \text{pH} = 3.6 \end{array} \right]$	0.05		k_{AB}	25	5.98	-3		
				9	0.10			25	5.27	-3		
				9	0.20			25	3.82	-3		
				9	0.40			25	1.75	-3		
				1.5	0.0			25	3.70	-2		
				1.5	0.10			25	3.50	-2		
				1.5	0.20			25	3.30	-2		
				1.5	0.40			25	2.94	-2		
				1.5	0.58			25	2.58	-2		
				0.43	0.0			25	1.20	-1		
				0.43	0.10			25	1.18	-1		
				0.43	0.20			25	1.15	-1		
				0.43	0.40			25	1.08	-1		
				0.11	0.0			25	4.39	-1		
				0.11	0.10			25	4.27	-1		
				0.11	0.20			25	4.22	-1		
				0.11	0.40			25	4.14	-1		
				$\text{pH} = 4.5-5.6$	0.0	0.74	$k'_{\text{AB}}/[\text{H}^+]$	25	1.2	-6		
				3.5	0.0	0.74		25	1.76	-6		

(Other catalysts see Supplementary Table)

Heterogeneous Reaction Kinetics

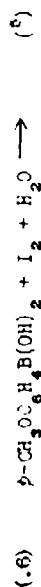
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3

No.	Reaction	Added Salt (g)	Amount of reactant	Aidant (Catalyst)	Amount of aidant	μ	Defined mass action law	Temperature	$k \times 10^3$ k^0 k	Comments	Literature
1	$\text{p-Cl}_2\text{C}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	NaAcO^*	$10^2\text{A} = 1; 10^2\text{B} = 8$	NaBr	0.4		k_{AB}	25	2.10	-4	(²)*
2	$\text{p-Cl}_2\text{C}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	NaAcO^*	$10^2\text{A} = 1; 10^2\text{B} = 8$	NaBr	0.4		k_{AB}	25	5.04	-5	(²)*
3	$\text{p-NO}_2\text{C}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	NaAcO^*	$\text{A} = 0.08$	NaBr	0.4		k_{AB}	25	1.45	-5	(²)*
4	$\text{p-Cl}_2\text{C}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	NaAcO^*	$10^2\text{A} = 1; 10^2\text{B} = 8$	NaBr	0.4		k_{AB}	25	1.87	-4	(¹)
5	$\text{p-Cl}_2\text{C}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	NaAcO^*	$10^2\text{A} = 1; 10^2\text{B} = 8$	NaBr	0.4		k_{AB}	25	1.36	-2	(¹)
6	$\text{p-Cl}_2\text{C}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	C	$10^3\text{A} = 2-10;$ $10^3\text{B} = 2.5-20$ $\text{A} = 0.67$	$[\text{CH}_3\text{COOH}] =$ $3[\text{CH}_3\text{COONa}]$ $\text{pH} = 4.7$	$[\text{Br}^-] = 0.25$ $[\text{CH}_3\text{COOH}] =$ 0	0.70					*
			0.67	4.7	0.15		k_{AB}	25	3.55	-1	
			0.67	4.7	0.30			25	3.60	-1	
			0.67	4.7	0.45			25	3.59	-1	
			1.22	4.4	0			25	3.20	-1	
			1.22	4.4	0.15			25	1.77	-1	
			1.22	4.4	0.30			25	1.60	-1	
			1.22	4.4	0.45			25	1.59	-1	
			2.35	4.1	0			25	1.50	-1	
			2.35	4.1	0.15			25	9.55	-2	
			2.35	4.1	0.30			25	8.76	-2	
			2.35	4.1	0.45			25	7.67	-2	
			5.7	3.7	0			25	6.66	-2	
			5.7	3.7	0.15			25	3.70	-2	
			5.7	3.7	0.30			25	2.75	-2	
			5.7	3.7	0.45			25	2.20	-2	
			5.7	3.7	0			25	1.47	-2	

No.	Reaction	Medium	Amount of reactant	Addend (Catalyst)	Amount of addend	μ	Defined rates	Temperature	$k^o \times 10^7$	Comments	Literature
12	$p\text{-ClC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$ (continued)	C	$10^3\text{A} = 2-10$; $10^3\text{B} = 2.5-20$	CH_2ClCOOH $\text{CH}_2\text{ClCOONa}$ (Other catalysts see Supplementary Table)	$[\text{Br}^-] = 0.25$ $\text{pH} = 2-3$	0.70	$k_{\text{AB}}/[\text{H}^+]$	25	7	-6	(4)
13	$p\text{-ClC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	WAc20*	$10^2\text{A} = 1$; $10^3\text{B} = 8$	NaBr	0.4		k_{AB}	25	2.61	-3	(3)*
14	$p\text{-BrC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	WAc20*	$10^2\text{A} = 1$; $10^3\text{B} = 8$	NaBr	0.4		k_{AB}	25	2.13	-4	(1)
15	$p\text{-BrC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	WAc20*	$10^2\text{A} = 1$; $10^3\text{B} = 8$	NaBr	0.4		k_{AB}	25	2.00	-3	(3)*
16	$p\text{-IC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	WAc20*	$10^2\text{A} = 1$; $10^3\text{B} = 8$	NaBr	0.4		k_{AB}	25	3.46	-4	(1)
17	$p\text{-IC}_6\text{H}_4\text{B(OH)}_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$	WAc20*	$10^2\text{A} = 1$; $10^3\text{B} = 8$	NaBr	0.4		k_{AB}	25	2.41	-3	(1)

SUPPLEMENTARY TABLE



Solvent $\text{H}_2\text{O} + 5 \text{ vol } \% \text{CH}_3\text{OH} \quad 10^3\text{A} = 2-10 \quad 10^3\text{B} = 2-12$

$\mu = 0.70$; $\text{pH} = 4.48$; $\text{NaI} = 0.15$; $\text{CH}_3\text{COOH} = 0.45$; $\text{CH}_3\text{COONa} = 0.30$

$k = 3.20 \times 10^{-2} + k_1[\text{catalyst}]$

(continued on next page)

SUPPLEMENTARY TABLE (continued)

Catalyst	$10^3 \times \text{max. [catalyst]}$	k'
(.6) continued		
H_2SO_4	100	0.048
$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	9.4	0.172
cis-Indane-1,2-diol	1.0	7.0
cis-Indane-1,2-diol	1.0	10.4
H_2SO_4	100	
HOCH_2COOH	2.0	16.1
NaF	2.0	39.4
5- NO_2 -salicylic acid	2.0	39.3
tartaric acid	2.0	80.0
salicylic acid	2.0	184
No catalytic effect with ethylene glycol, pinacol, 2,3-butanediol, or cis-cyclohexane-1,2-diol.		
(.12) $\text{m-ClC}_6\text{H}_4\text{B}(\text{OH})_2 + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow$ ⁽⁴⁾ solvent: H_2O; $10^3 A = 2-10$; $10^3 B = 2.5-20$ $\mu = 0.70$; pH = 2.62; NaBr = 0.25; $\text{CH}_2\text{ClCOOH} = 0.45$; $\text{CH}_2\text{ClCOONa} = 0.45$ $k = 3.79 \times 10^{-3} + k'[\text{catalyst}]$		
Catalyst	$10^3 [\text{catalyst}]$	k'
HOCH_2COOH	1-4	1.8
citric acid	2-4	2.75
$(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$	1-2	16.4
L-tartaric acid	1-2	16.4
NaF	1-2	21.8
cis-cyclohexane-1,2-diol	1-3	<0.1

SOLVENTS

WAc20* (50) $\text{H}_2\text{O} + \text{indicated vol } \% \text{CH}_3\text{COOH}$

WMS* $\text{H}_2\text{O} + 5 \text{ vol } \% \text{CH}_3\text{OH}$

COMMENTS

Literature: (3) Authors stated that rates of replacement of boronic acid and anhydride were identical and did not designate which form was used in rate experiments.

Reactions: (.1) Inhibition by acids but specific base catalysis observed. (.6) Reactive species considered to be I_2 and boronate anion from dependence of rate upon $[\text{I}^-]^{-1}$ and $[\text{H}^+]^{-1}$. In presence of acetate buffer rate constant may be expressed by equation $k = k_0 \{1 - 0.216[\text{CH}_3\text{COOH}] - 0.145[\text{CH}_3\text{COONa}]\}$ where k_0 is a function of pH or buffer ratio and is the tabulated value extrapolated to zero concentration of buffer. For specific catalyst effects see Supplementary Table. (.12) Reactive species considered to be Br_2 and boronate anion as plot of rate constant versus fraction of free Br_2 gives linear plot through origin and rate also proportional to $[\text{H}^+]^{-1}$. Tetra covalent boron in anion probable from specific catalytic activity of F^- and chelating agents. For special catalytic effects see Supplementary Table. In acetate buffer rate constant may be expressed by equation $k = k_0 \{1 - 0.233[\text{CH}_3\text{COOH}] - 0.070[\text{CH}_3\text{COONa}]\}$ where k_0 is a function of pH or buffer ratio and is the tabulated value extrapolated to zero buffer concentration.

LITERATURE

- (1) H.G. Kuivilla, L.E. Benjamin, *ACS* 1955, 77, 4934.
- (2) H.G. Kuivilla, E.E. Easterbrook, *ACS* 1951, 73, 4639.
- (3) H.G. Kuivilla, A.R. Hendrickson, *ACS* 1952, 74, 5068.
- (4) H.G. Kuivilla, E.J. Soboczenski, *ACS* 1954, 76, 2675.
- (5) H.G. Kuivilla, R.M. Williams, *ACS* 1954, 76, 2679.

EXCHANGE

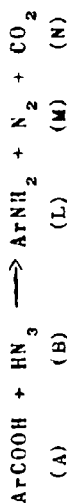
Replacement of C by N on aromatic C

Liquid phase

Amounts are in M/l.

Rate: and rate constants are in M/l and sec.

Reaction type:



No.	Reaction	Solvent (medium)	Amount of reactant	Addend (catalyst)	Amount or added	Defined mass action law	Temperature	Half-time	$k = k_0 \times 10^n$	Comments	Temperature
1	$\text{C}_6\text{H}_5\text{COOH} + \text{HN}_3 \longrightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{N}_2 + \text{CO}_2$	H_2SO_4 95.4 %	A = B = 0.05			k AB	25		1.98	*	(1)
2	$\pi\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow \pi\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	180		*	(2)
3	$p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	120		*	(2)
4	$\pi\text{-HOC}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow \pi\text{-HOC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	H_2SO_4 95.4 %	A = B = 0.05			k AB	25		3.71	*	(1)
5	$o\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow o\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	300		*	(2)
6	$\pi\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow \pi\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	300		*	(2)
7	$p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	240		*	(2)
8	$\pi\text{-C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow \pi\text{-C}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	90		*	(2)
9	$\pi\text{-HOOC}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow \pi\text{-HOOC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	240		*	(2)
10	$\pi\text{-NiOC}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow \pi\text{-NiOC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	ClHC:CCl_2	A = 2.5; B = 0.25	H_2SO_4	1.5		40	1,080		*	(2)

No.	Reaction	Solvent (Medium)	Amount of reactant	Added (Catalyst)	Amount of added	Defined mass action law	Temperature	Half-time	$k^0 \times 10^n$ k^0	Comments	Literature	
11	$o\text{-NO}_2\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow o\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	$\text{ClHC}\cdot\text{CCl}_2$	A = 2.5; B = 0.25	H_2SO_4	1.5		40	120		*	(²)	
12	$m\text{-NO}_2\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow m\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	$\text{ClHC}\cdot\text{CCl}_2$	A = 2.5; B = 0.25	H_2SO_4	1.5		40	6,000		*	(²)	
13	$p\text{-NO}_2\text{C}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	$\text{ClHC}\cdot\text{CCl}_2$	A = 2.5; B = 0.25	H_2SO_4	1.5		40	7,200		*	(²)	
14	$m\text{-ClC}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow m\text{-ClC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	$\text{ClHC}\cdot\text{CCl}_2$	A = 2.5; B = 0.25	H_2SO_4	1.5		40	720		*	(²)	
15	$m\text{-BrC}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow m\text{-BrC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	$\text{ClHC}\cdot\text{CCl}_2$	A = 2.5; B = 0.25	H_2SO_4	1.5		40	600		*	(²)	
16	$m\text{-IC}_6\text{H}_4\text{COOH} + \text{HN}_3 \longrightarrow m\text{-IC}_6\text{H}_4\text{NH}_2 + \text{N}_2 + \text{CO}_2$	$\text{ClHC}\cdot\text{CCl}_2$	A = 2.5; B = 0.25	H_2SO_4	1.5		40	300		*	(²)	
17	$\text{C}_{14}\text{H}_9\text{O}_2 + 2\text{HN}_3 + \text{H}_2\text{O} \longrightarrow \text{C}_{13}\text{H}_9\text{ON} + 2\text{N}_2 + \text{CO}_2 + \text{NH}_3$ (phenanthrenequinone) (phenanthridone)	H_2SO_4 99.5 % 96.8 95.4 92.5 84.3	A $\approx$ 0.02; B = 0.05-0.1		-dA/dt = k'AB		25		4.1 1.14 1.57 3.82 2.32	-2 -1 -1 -1 0	*	(¹)
$-dB/dt = k'AB + k''IB; dI/dt = k'IB; (I = \text{intermediate})$												
		98.5					25		3.58	-3		
		96.8					25		2.1	-3		
		95.4					25		1.6	-3		
		92.5					25		1.02	-3		
		84.3					25		0.76	-3		

COMMENTS

Literature. ⁽²⁾ Units, seconds converted from original minutes.

Reaction. (.1) No appreciable decomposition of B during reaction time but ⁽¹⁾ observed unreliable results with substituted benzoic acid due to decomposition in H_2SO_4 solvent. Aniline sulfate is final product. ⁽²⁾ observed ratio of L/M = 0.70.
(.2) L/M = 0.53. (.3) No appreciable decomposition of B during reaction time. (.4) L/M = 0.88.
(.5) L/M = 0.81. (.6) L/M = 0.87. (.7) L/M = 0.86. (.8) L/M = 0.93. (.9) L/M = 0.71.
(.10) L/M = 0.82. (.11) L/M = 0.71. (.12) L/M = 0.82. (.13) L/M = 0.59. (.14) (.15) (.16) L/M = 0.78.
(.17) Reaction involves consecutive reactions. The first reaction forms an intermediate which reacts with a second molecule of B to form final products. Rate expression broken up into initial k_{AB} and following k'_{IB} rate laws. Where i represents concentration of intermediate.

LITERATURE

- ⁽¹⁾ T. Bak, *Acta. Chem. Scand.* 1954, 8, 1733. ⁽²⁾ L.H. Briggs, J.W. Lyttleton, *CW* 1943, 421.

Homogeneous Reactions

332.464

EXCHANGE

Replacement of C by sulfate on Si

Liquid phase

Amounts are in M/l.

Rate constants are in
M/l and sec.

No.	Reaction	Solvent (Medium)	Amount of reactant	Amount Addend	Amount of addend	Defined base action law	Temperature	$k =$ $k^0 \times 10^n$ k^0 n
1	$\text{HOOCCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3 + 4\text{H}_2\text{SO}_4 \longrightarrow \text{HOOCCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{SO}_3\text{H} + \text{CH}_4$	85-97% $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	A = 0.05; B = 3-22	NaHSO_4	not stated	R AB	20	1.4 -4

COMMENTS

Reaction pseudo first order with respect to A. Second order constant calculated by dividing pseudo first order constant by calculated concentration of molecular H_2SO_4 . This was varied from 2.9 to 22 by adjusting the H_2O concentration. Addition of NaHSO_4 gave a very small salt effect.

LITERATURE

L.H. Sommer, W.P. Barle, J. Gould, ACS 1953, 75, 3765.

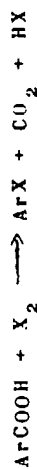
EXCHANGE

Replacement of C by halogen on Aromatic C

Liquid phase

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

Reaction type:



(A)

(B)

(L)

(M)

(N)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1)	Amount of Addend (1)	Addend (2)	Amount of Addend (2)	Defined mass action law	Temperature	$k^0 \times 10^7$	
										k^0	n
.1	$2\text{-OH-3,5-Br}_2\text{C}_6\text{H}_3\text{COOH} + \text{Br}_2 \longrightarrow 1,3,5\text{-Br}_3\text{-2-HOC}_6\text{H}_3 + \text{CO}_2 + \text{HBr}$	AcW 75*	$10^{-3}\text{A} = 5; 10^{-3}\text{B} = 4-8$	HClO ₄	0.10			k AB	20	5.8	-2
			" "		0.30	KClO ₄	0.004		20	2.55	-2
			" "		0.10		0.004		20	5.6	-2
			" "		0.10	KBr	0.004		20	4.7	-2
			" "		0.29	HBr	0.01		20	1.35	-2
			" "		0.25		0.05		20	3.47	-3
			" "		0.20		0.1		20	1.37	-3
			" "		0.10		0.2		20	4.40	-4
			" "		0		0.3		20	2.33	-4
			" "		0.10	LiBr	0.10		20	4.9	-3
			" "	HBr	0.30		0		20	2.33	-4
			" "		0.20		0.10		20	4.28	-4
			" "		0.10		0.20		20	1.15	-3
.2	$4\text{-OH-3,5-Br}_2\text{C}_6\text{H}_3\text{COOH} + \text{Br}_2 \longrightarrow 1,3,5\text{-Br}_3\text{-4-HOC}_6\text{H}_3 + \text{CO}_2 + \text{HBr}$	AcW 70* AcW 80*	$10^{-3}\text{A} = 5; 10^{-3}\text{B} = 6$		0.30		0		20	1.18	-3
			" "		0.30		0		20	2.93	-5
			" "	HClO ₄	0.10			k AB	20	6.3	-1
			" "		0.10	LiBr	0.10		20	1.30	-2
			" "		0.05		0.10		20	3.4	-2
			" "		0.300		0.050		20	3.00	-1
			" "		0.250	HBr	0.050		20	7.6	-3
			" "		0.200		0.100		20	1.82	-3

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend (1)	Amount of addend (1)	Addend (2)	Amount of addend (2)	Defined mass action law	Temperature	$k = k^0 \times 10^n$
.2	4-OH-3,5-Br ₂ C ₆ H ₃ COOH + Br ₂ → 1,3,5-Br ₃ -4-HOC ₆ H ₂ + CO ₂ + HBr (continued)	AcW 75* AcW 70*	10 ³ A = 5; 10 ³ B = 8 " " 8	HClO ₄		HBr	0.300 0.300	k AB	20 20	1.97 1.16 -3 -2

COMMENTS

(.1) Selected data. Rate constant fits the equation

$$k[\text{Br}_2][\text{H}^+]/[\text{Br}_2] = \frac{(0.0103[\text{H}^+] + 0.0042)}{49(\text{H}^+)^2(\text{Br}^-) + 20[\text{H}^+][\text{Br}^-] + 1}$$

where $[\text{Br}_2]$ represents total Br₂ concentration and

(Br_2) represents actual concentration of free Br₂.

(.2) Selected data. Rate constant will fit an equation similar to that for reaction (.1) but it also fits the equation

$$\frac{kK_1[\text{Br}_2][\text{Br}^-]}{[\text{Br}_3^-]} = 2.5 + 0.80[\text{H}^+]^{-1}$$

where $[\text{Br}_2]$ represents the total concentration of Br₂ in all forms.

LITERATURE

Z. Grovenstein, U. V. Henderson, ACS 1956, 78, 569

Homogeneous Reactions

332.473

EXCHANGE

Replacement of Si by halogen on aromatic C

Liquid phase

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

No.	Reaction	Medium (Solvent)	Amount of reactant	Defined basis	Temperature	$k^0 \times 10^n$ k^0 n	Comments
.1	$\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3 + \text{Br}_2 \longrightarrow \text{C}_6\text{H}_4\text{Br} + (\text{CH}_3)_3\text{SiBr}$	CCl_4	A = 0.06-0.4; B = 0.04-0.14	k_{AB}^2	35 40	1.68 -3 2.12 -3	(too rapid to measure)
.2	$o\text{-NO}_2\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_3 + \text{Br}_2 \longrightarrow o\text{-NO}_2\text{C}_6\text{H}_4\text{Br} + (\text{CH}_3)_3\text{SiBr}$	$\text{C}_6\text{H}_5\text{NO}_2$		k_{AB}^2	40	2 -4	*
.3	$m\text{-NO}_2\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_3 + \text{Br}_2 \longrightarrow m\text{-NO}_2\text{C}_6\text{H}_4\text{Br} + (\text{CH}_3)_3\text{SiBr}$	$\text{C}_6\text{H}_5\text{NO}_2$		k_{AB}^2	40	2.5 -3	*
.4	$p\text{-NO}_2\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_3 + \text{Br}_2 \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{Br} + (\text{CH}_3)_3\text{SiBr}$	$\text{C}_6\text{H}_5\text{NO}_2$		k_{AB}^2	40	1 -3	*
.5	$\text{SCBr}:\text{CH}:\text{CH}:\text{CSi}(\text{CH}_3)_3 + \text{Br}_2 \longrightarrow \text{SCBr}:\text{CH}:\text{CH}:\text{CBr} + (\text{CH}_3)_3\text{SiBr}$ (2-bromo-5-trimethylsilylthiophene)	CCl_4		k_{AB}^2	35	4.5 -2	

COMMENTS

Reactions. (.2) (.3) (.4) Order of reaction not definitely established in $\text{C}_6\text{H}_5\text{NO}_2$ as complicated by side reactions and slowness of reaction. Rate constant gives only order of magnitude.

LITERATURE

R. A. Benkeser, A. Torkelson, ACS 1954, 76, 1252.

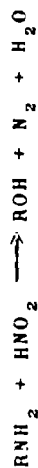
EXCHANGE Replacement of H by C on aliphatic C

Liquid phase

Amounts are in M/l.

Rate constants are in
M/l and sec.

Reaction types:



No.	Reaction	Solvent (Mol/l)	Amount of reactant	Addend	Amount of addend	pH	Defined mass	Temperature	$k =$ $k^0 \times 10^n$ k^0 n	$k =$ $k^0 \times 10^n$ k^0 n	$k =$ $k^0 \times 10^n$ k^0 n	Comments	Literature
.1	$\text{CH}_3\text{NH}_3^+ + \text{HNO}_2 \longrightarrow$ $\text{CH}_3\text{OH} + \text{N}_2 + \text{H}_3\text{O}^+$	H_2O	$A = 0.2-1; B = 0.004-0.2$	$\text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}$	0.50	1.1 1.1 1.12 2.10 2.70 3.70 4.50 1.1	k_{AB}	20 25 30 30 30 30 30 35 25 25	1.91 2.91 4.23 4.02 3.21 1.03 1.87 6.4 1.8 1.1	-4 -4 -4 -4 -4 -4 -5 -4 -2 -2		*	(2)
.2	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ + \text{HNO}_2 \longrightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}, (\text{CH}_3)_2\text{CHOH} + \text{N}_2 + \text{H}_3\text{O}^+$	H_2O	$A = 0.05-0.1; B = 0.05-0.1$ $A = 0.05-0.1; B = 0.05-0.1$	NO_2^- NO_2^-	0.05 0.05		$k_{AB}[\text{NO}_2^-]$ $k_{AB}[\text{NO}_2^-]$	35 25 25	6.4 1.8 1.1	-4 -2 -2	14 9	*	(3) (5)
.3	$\text{HOOCCH}_2\text{NH}_2 + \text{HNO}_2 \longrightarrow$ $\text{HOOCCH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}$	H_2O	$10^2 A = 3-50; 10^2 B = 2-5$	H_2SO_4	0.05-0.1		k_{AB}^2	25	4.0	-1		*	(1) (4)
.4	$\text{HOOCCH}_2\text{CH}_2\text{NH}_2 + \text{HNO}_2 \longrightarrow$ $\text{HOOCCH}_2\text{CH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}$	H_2O	$10^2 A = 2-5; 10^2 B = 2-5$	H_2SO_4	0.05-0.1		k_{AB}^2	25	5.8	-2		*	(4)
.5	$\text{HOOC}(\text{CH}_2)_3\text{CHNH}_2 + \text{HNO}_2 \longrightarrow$ $\text{HOOC}(\text{CH}_2)_3\text{CHOH} + \text{N}_2 + \text{H}_2\text{O}$	H_2O	$10^2 A = 2-5; 10^2 B = 2-5$	H_2SO_4	0.05-0.1		k_{AB}^2	25	2.0	-1		*	(4)

COMMENTS

Reaction. (1) Initial rate measured by (2) and rate constant calculated by dividing initial rate by total concentrations of A and B. Increase in ionic strength from 0.50 to 1.50 depresses rate constant from 5.0×10^{-4} to 3.5×10^{-4} . Change in buffer concentration from 0.25 to 0.75 had no effect on rate. Pseudo second order rate constant over reaction course observed by (3). Third order constant calculated by dividing by concentration of nitrite ion. Units, seconds converted from original minutes. (2) Third order rate law followed up to 30% reaction. Units, seconds converted from original minutes. (3) Reaction found to follow three different rate laws by (4): $k' = 2.0 \times 10^{-4}$ for $k'[\text{HOOCCH}_2\text{NH}_3^+]\text{B}^2$; $k_3 = 4.3$ for $k_3[\text{HOOCCH}_2\text{NH}_3^+][\text{BNO}_2^-]$ and $k_3\text{B}^2$. Each appeared to have some advantage at appropriate conditions, but no one expression was valid over entire range studied by (5). Units, seconds converted from original minutes. Negative salt effect observed by (4) also rate depressed by H_2SO_4 . Rate constant extrapolated to zero time as they decreased with course of reaction. (4) (5) Rate constants extrapolated to zero time as they decreased with course of reaction. Units seconds converted from original minutes.

LITERATURE

- (1) L. Abel, E. Schmid, W. Siedon, *ZAC* 1933, 39, 863. (2) J. H. Dusenbury, R. S. Powell, *ACS* 1951, 73, 3289.
 (3) T. W. J. Taylor, *CSL* 1928, 1099. (4) T. W. J. Taylor, *CSL* 1934, 1897. (5) T. W. J. Taylor, L. S. Price, *CSL* 1929, 5052.

EXCHANGE

Replacement of N= by O= on aromatic C

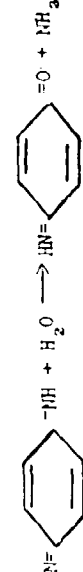
Liquid phase

Amounts are in M/l.

Rate constants are in M/l and sec.

Reaction types:



No.	Reaction	Solvent	Amount of reactant	Allyl	pH	Defined mass action law	Temperature	$k = k^0 \times 10^7$	Comments	Temperature
1	 O=	H_2O	$10^{-4} \text{ A} = 2.5$	$\left. \begin{array}{l} \text{H}_2\text{PO}_4^- \\ \text{HPO}_4^{2-} \\ \text{Fe}(\text{CN})_6^{3-} \end{array} \right\}$	6.1 7.1 8.0 8.7 9.8 11.0 11.9	k_A	25 25 25 25 25 25 25	1.54 5.5 1.92 1.31 1.15 1.54 3.84	* 	(1)
2	 O=	H_2O	$10^{-4} \text{ A} = 2.5$	$\left. \begin{array}{l} \text{H}_2\text{PO}_4^- \\ \text{HPO}_4^{2-} \\ \text{Fe}(\text{CN})_6^{3-} \end{array} \right\}$	6.1 7.1 8.0 8.8 10.0 12.0	k_A	25 25 25 25 25 25	1.62 7.1 1.8 1.2 8 1.8	* 	(1)
3	 O=	H_2O	$10^{-4} \text{ A} = 1.25$	$\left. \begin{array}{l} \text{H}_2\text{PO}_4^- \\ \text{HPO}_4^{2-} \\ \text{Fe}(\text{CN})_6^{3-} \end{array} \right\}$	6.1 7.0 8.0 8.9 10.2-12.0 11.4	k_A	25 25 25 25 25 25	6.34 1.04 4.3 3.5 3.3 2.9	* 	(1)
			$\mu = 0.005-0.08$	OH^-						(2)

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Reaction	Fraction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$K^0 \times 10^3$	Comments	Literature
1.1	 $\xrightarrow{H_2O} (CH_3)_2N^+ + (CH_3)_2N^+ \xrightarrow{OH^-} (CH_3)_2N^+ + (CH_3)_2N^+$	H_2O	$10^{-4} A = 1.69$	$H_2PO_4^-$ HPO_4^{2-} $Fe(OH)_3$	7.1 8.0 10.0 11.1 12.0	$R'A = -dA/dt$ $R = R' + R''[OH^-]$	25 25 25 25 25	2.5 1.63 2.54 3.04 1.96	*	(1)
1.2	 $\xrightarrow{H_2O} (CH_3)_2N^+ + (CH_3)_2N^+ \xrightarrow{OH^-} (CH_3)_2N^+ + (CH_3)_2N^+$	H_2O	(calculated using 1.4 and 1.1)		7.1 8.0	$R'A = dI/dt$	25 25	5 1.8	*	(1)
1.3	 $\xrightarrow{H_2O} (CH_3)_2N^+ + (CH_3)_2N^+ \xrightarrow{OH^-} (CH_3)_2N^+ + (CH_3)_2N^+$	H_2O	(calculated using 1.4 and 1.1)		~12	$R''AB = dI/dt$	25	2.5	*	(1)
1.4	 $\xrightarrow{H_2O} (CH_3)_2N^+ + (CH_3)_2N^+ \xrightarrow{OH^-} (CH_3)_2N^+ + (CH_3)_2N^+$	H_2O	$10^{-4} A = 1.0-1.9$	$H_2PO_4^-$ HPO_4^{2-} $Fe(OH)_3$	6.1 7.1 8.0 9.0 10.1 11.1 12.0	$R'A = -dA/dt$ $R = R' + R''[OH^-]$	25 25 25 25 25 25 25	5.46 1.10 6.46 5.72 1.24 1.11 7.76	*	(1)
1.5	 $\xrightarrow{H_2O} (CH_3)_2N^+ + (CH_3)_2N^+ \xrightarrow{OH^-} (CH_3)_2N^+ + (CH_3)_2N^+$	H_2O	(calculated using 1.5 and 1.1)		7.1 8.0 9.0	$R'A = dI/dt$	25 25 25	3 2 ~10	*	(1)

Reaction	Solvent	Amount of reactant	Added	pH	Defined mass action law	Temperature	$k^0 \times 10^7$	k^0	n	Comments	Uncertainty
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O	(calculated using .5 and .1)		7-9	$k''_{AB} = dI/dt$	25	6.2		+3	*	(1)
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			10.1		25	9		+3		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			11-12		25	8.6		+2		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O	$10^{-4} = 1.2-7.5 \times 10^{-4}$		7.0	$k_A = -dA/dt$	25	3.90		-4	*	(1) (2)
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			8.0	$k = k' + k''[\text{OH}^-]$	25	1.12		-3		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			8.9		25	8.66		-3		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			10.0		25	1.41		-1		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			11.1		25	2.00		0		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			11.9		25	1.32		+1		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O	(calculated using .6 and .2)		7-9	$k'_A = dI/dt$	25	3.9		-4	*	(1)
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			7-12	$k''_{AB} = dI/dt$	25	1.60		-3	*	(1)
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O	$10^{-4} = 1.2$		8.0	$k_A = -dA/dt$	25	9.1		-2	*	(1)
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			8.5		25	1.22		-1		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			10.1		25	1.77		-1		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			11.1		25	4.21		-1		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O			12.0		25	2.16		0		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O					25	$k'/2$		+4		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O					25	$k''/2$		+2		
$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	H ₂ O					25	$k'/2$		-9		
$k = [\text{OH}^-] \left(\frac{k'}{1 + \frac{[\text{OH}^-]}{K_1}} + \frac{k''[\text{OH}^-]}{1 + \frac{[\text{OH}^-]}{K_1} + 10^{-14}} \right)$											

No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k^o \times 10^2$ k^o	Comments	Literature
1	$\text{H}_2\text{O} + \text{N}_2\text{H}_4 \cdot (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$ $\text{H}_2\text{O} \rightarrow (\text{CH}_3\text{SO}_2\text{NH}_2)_2\text{N}^+ + (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$ $\text{OH}^- \rightarrow \text{N}_2 + (\text{CH}_3\text{SO}_2\text{NH}_2)_2\text{N}^+ + (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$	H ₂ O	10 ⁻⁴ A = 1.9	$\left. \begin{array}{l} \text{H}_2\text{PO}_4^- \\ \text{HPO}_4^{2-} \\ \text{Fe}(\text{CN})_6^{4-} \end{array} \right\}$	8.0 8.8 10.1 11.0 11.9	$k_A = -dA/dt$	25 25 25 25 25	2.14 3.19 1.68 5.19 2.86	*	(1)
2	$\text{H}_2\text{O} + \text{N}_2\text{H}_4 \cdot (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$ $\text{OH}^- \rightarrow \text{N}_2 + (\text{CH}_3\text{SO}_2\text{NH}_2)_2\text{N}^+ + (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$	H ₂ O	10 ⁻⁴ A = 1.25	$\left. \begin{array}{l} \text{H}_2\text{PO}_4^- \\ \text{HPO}_4^{2-} \\ \text{Fe}(\text{CN})_6^{4-} \end{array} \right\}$	7.0 8.1 8.9 10.1 11.1 12.0	$k_A = -dA/dt$ $k = k' + k''[\text{OH}^-]$	25 25 25 25 25 25	8.7 5.5 3.3 8.5 7.3 5.6	*	(1) (1) (2)
3	$\text{H}_2\text{O} + \text{N}_2\text{H}_4 \cdot (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$ $\text{OH}^- \rightarrow \text{N}_2 + (\text{CH}_3\text{SO}_2\text{NH}_2)_2\text{N}^+ + (\text{C}_2\text{H}_5)_2\text{N}^+ \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_3$	H ₂ O	(calculated using .9 and .2)		8	$k_A = dL/dt$	25	~5	*	(1)

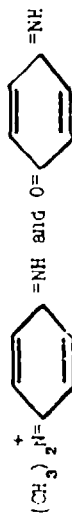
No.	Reaction	Solvent	Amount of reactant	Addend	pH	Defined mass action law	Temperature	$k^o \times 10^{12}$		Comments	Literature
								k^o	n		
150	$ \text{RN} = \text{C}_6\text{H}_5 \text{---} \text{N}(\text{C}_2\text{H}_5)_2 \text{---} \text{SO}_2\text{CH}_3 + \text{CH}^- \longrightarrow $  CH₃ =  CH₃ $ = \text{O} + [\text{CH}_3\text{SO}_2\text{N}(\text{CH}_3)_2] (\text{C}_2\text{H}_5)_2\text{NH} $	H ₂ O	(calculated using .9 and .2)		7-12	$k''_{AB} = dL/dt$	25	6.0	+3	*	(¹)

COMMENTS

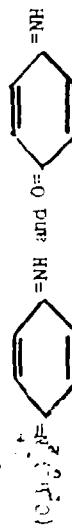
General. All reactions carried out at constant pH in presence of buffer, and in presence of excess $K_2Fe(CN)_6$ used to form A by oxidation of corresponding *p*-phenol amine or *p*-phenyl diamine. At high pH the quinones produced may react further with α -naphthol.

(4) consists of parallel reactions (4.1) and (4.2) with consecutive reaction (1) following (4.2).

(4.4)(4.2) Parallel reactions kinetically separated by following concentrations of the two dyes produced by coupling

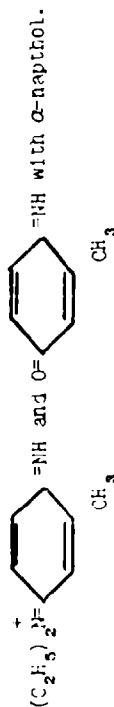


with α -naphthol. This combined with measured rate of (4.1) allowed calculation of rate constant for (4.2). Values for (4.1) were obtained by difference and give only order of magnitude. (5) Consists of parallel reactions (5.1) and (5.2) with consecutive reaction (4.1) following (5.2). Parallel reactions kinetically separated by following the concentrations of the two dyes produced by coupling reactions of:

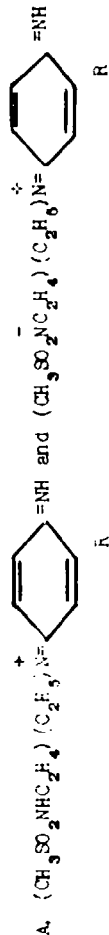


COMMENTS (continued)

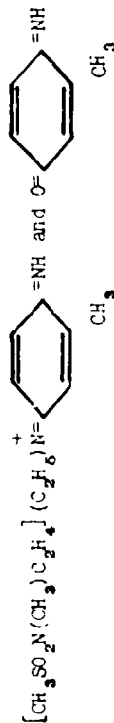
with α -naphthol. This combined with measured rate of (.1) allowed calculation of rate constant for (.5.2). Values for (.5.1) were obtained by difference and give only order of magnitude. (.6) Consists of parallel reactions (.6.1) and (.6.2) with consecutive reactions (.2) following $\log k/k_0$ vs. μ has slope = -1, see (3). (.6.1) (.6.2) Parallel reactions kinetically separated by following the concentrations of the two dyes produced by coupling reactions of



This combined with measured rate of (.2) allowed calculation of rate constant for (.6.2). Values for (.6.1) were obtained by difference and give only order of magnitude. (.7) (.8) Non-linear dependence of $\log k$ with pH accounted for in terms of rapid equilibrium between acid and basic forms of:



with separate rate constants k' and k'' respectively and equilibrium constant K . (.9) Consists of parallel reactions (.9.1) and (.9.2) with consecutive reaction (.2) following (.9.2). Shown by (2) to be independent of ionic strength (.9.1) (.9.2) Parallel reactions kinetically separated by following concentrations of the two dyes produced by coupling reactions of:



with α -naphthol. This combined with measured rate of (.2) allowed calculation of rate constant for (.9.2). Values for (.9.1) were obtained by difference and give only order of magnitude.

LITERATURE

- (1) L.K.J. Tong, *J.P.C.* 1954, 56, 1090.
- (2) L.K.J. Tong, M.C. Glesman, *ACS* 1955, 78, 5627.

Homogeneous Reactions

332.553

EXCHANGE

Replacement of ArSO_3 , (ArSO_2) , (ArSO) by NR_1R_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	$k = k^0 \times 10^n$	k^0	n	B	$A = A^0 \times 10^n$	Comments
1.	$2,4-(\text{HO})_2\text{C}_6\text{H}_3\text{SO}_2\text{C}_6\text{H}_5 + 2\text{CH}_3(\text{CH}_2)_4\text{NH} \longrightarrow$ $2,4-(\text{NO})_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_4\text{CH}_3 + \text{CH}_3(\text{CH}_2)_4\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2^-$	CH_3OH	$A \approx 0.04; 10^3 B \approx 1$	$\text{C}_6\text{H}_5\text{NH}_2^+\text{Cl}^-$	0.02 0.02 0.02	k_{AB}	0 25 46 0 25 46	2.05 1.09 3.20 2.15 1.20 3.94	-3 -2 -2 -3 -2 -2				*
2.	$2,4-(\text{NO})_2\text{C}_6\text{H}_3\text{SO}_2\text{C}_6\text{H}_5 + 2\text{CH}_3(\text{CH}_2)_4\text{NH} \longrightarrow$ $2,4-(\text{NO})_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_4\text{CH}_3 + \text{CH}_3(\text{CH}_2)_4\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2^-$	CH_3OH	$A \approx 0.04; 10^3 B \approx 1$	$\text{C}_6\text{H}_5\text{NH}_2^+\text{Cl}^-$	0.02 0.02	k_{AB}	0 25 0 25	1.43 9.30 1.50 9.56	-3 -3 -3 -3			1.0 6	*
3.	$2,4-(\text{HO})_2\text{C}_6\text{H}_3\text{SO}_2\text{C}_6\text{H}_4-p\text{-CH}_3 + 2\text{CH}_3(\text{CH}_2)_4\text{NH} \longrightarrow$ $2,4-(\text{NO})_2\text{C}_6\text{H}_3\text{N}(\text{CH}_2)_4\text{CH}_3 + \text{CH}_3(\text{CH}_2)_4\text{NH}_2 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$	CH_3OH	$A \approx 0.04; 10^3 B \approx 1$	$\text{C}_6\text{H}_5\text{NH}_2^+\text{Cl}^-$	0.02	k_{AB}	0 0	4.54 4.42	-2 -2			12.0 6	*

COMMENTS

Pseudo first order rate constants observed as A in excess. Second order constant calculated by dividing pseudo first order constant by initial concentration of A and multiplying by ratio of observed to theoretical yield of L. Competing side reactions involving solvent probably responsible for low yields of L. (1) In absence of $\text{CH}_2(\text{CH}_2)_4\text{NH}_2^+\text{Cl}^-$ yield only 25% which increased to 73% in presence of piperidine salt. (2) Yield of L 92% in absence of $\text{CH}_2(\text{CH}_2)_4\text{NH}_2^+\text{Cl}^-$ and 100% in presence of the piperidine salt. (3) Yield of L 53% in absence of piperidine salt and 59% in its presence.

LITERATURE

J. F. Bunnett, E. W. Garblsch, K. M. Pruitt, ACS 1957, 79, 385.

Homogeneous Reactions EXCHANGE Replacement of halogen by C of enolate

332.741

Liquid phase

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



Reaction type:

General comments at
end of Table.

No.	Reaction	Solvent	Amount of reactant	Order of reaction	Temperature	$k^0 \times 10^7$	k^0	n
1	$\text{CH}_3\text{I} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_3 + \text{NaI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.11	k AB	30	4.0		-4
2	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.095	k AB	30	1.0		-6
3	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.14	k AB	30	1.6		-6
4	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.094	k AB	30	1.0		-6
5	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.13	k AB	30	1.0		-6
6	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.14	k AB	30	9		-7
7	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.14	k AB	30	8		-7
8	$\text{C}_2\text{H}_5\text{Br} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.14	k AB	30	8		-7
9	$\text{C}_2\text{H}_5\text{I} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.098	k AB	30	1.3		-5
10	$\text{C}_2\text{H}_5\text{I} + [\text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2]^{-}\text{Na}^{+} \longrightarrow \text{C}_6\text{H}_5\text{C:OC}(\text{CH}_3)_2\text{C}_2\text{H}_5 + \text{NaI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.07	k AB	30	3.7		-6

No.	Reaction	Solvent	Amount of reactant	Defined mass	Temperature	$k = k^0 \times 10^n$
.11	$\text{CH}_3\text{CH}_2\text{CHBr} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)) + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.09	k AB	30	3.4 -7
.12	$(\text{CH}_3)_2\text{CHBr} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{C}_2\text{H}_5)(\text{CH}(\text{CH}_3)_2)) + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.09	k AB	30	1.5 -8
.13	$(\text{CH}_3)_2\text{CHCH}_2\text{Br} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{C}_2\text{H}_5)(\text{CH}_2\text{CH}(\text{CH}_3)_2)) + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.09	k AB	30	4.3 -8
.14	$(\text{CH}_3)_3\text{CBr} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{C}_2\text{H}_5)(\text{C}(\text{CH}_3)_3)) + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.086	k AB	30	7.2 -8
.15	$(\text{CH}_3)_3\text{COCH}_2\text{Br} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{C}_2\text{H}_5)(\text{CH}_2\text{C}(\text{CH}_3)_3)) + \text{NaBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.087	k AB	30	< 1 -10
.16	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5) + \text{NaCl}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.13	k AB	30	2.0 -5
.17	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + [\text{C}_6\text{H}_5\text{C}(\text{OCH}_2\text{H}_6)]^-\text{Na}^+ \longrightarrow \text{C}_6\text{H}_5\text{C}(\text{OCH}(\text{C}_2\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5) + \text{NaCl}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 1.7; B = 0.13	k AB	30	8.8 -6

COMMENTS

Second order rate constants calculated by dividing pseudo first order constant by concentration of A. Pseudo first order constants increased about 50% during second half life except where α -hydrogen of ketone was substituted. Rate law with respect to A not verified.

LITERATURE

H. D. Zook, W. L. Relliehan, *ACS* 1957, **79**, 881.

Homogeneous Reactions

332.744

EXCHANGE

Replacement of halogen on Si by C

Liquid phase

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



Reaction type:

Comments at end of
Table.

No.	Reaction	Solvent	Amount of reactant	Oxidation state	Temperature	$k \times 10^n$		$A \times 10^n$	
						k^0	n	A^0	n
1	$(CH_3)_3SiF + CH_3MgBr \longrightarrow (CH_3)_3Si + MgBrF$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			8.8	3
2	$(CH_3)_3SiF + CH_3MgI \longrightarrow (CH_3)_3Si + MgIF$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			13.5	8
3	$(CH_3)_3SiCl + CH_3MgCl \longrightarrow (CH_3)_3Si + MgCl_2$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			9.0	2
4	$(CH_3)_3SiCl + CH_3MgBr \longrightarrow (CH_3)_3Si + MgBrCl$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			8.1	2
5	$(CH_3)_3SiCl + CH_3MgI \longrightarrow (CH_3)_3Si + MgI_2$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			10.6	5
6	$(CH_3)_3SiBr + CH_3MgBr \longrightarrow (CH_3)_3Si + MgBr_2$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			10.6	5
7	$(CH_3)_3SiBr + CH_3MgI \longrightarrow (CH_3)_3Si + MgIBr$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25				
				k AB	-3	1.43	-3		
					5	2.50	-3		
					20	7.55	-3		
					25	1.12	-2	11.3	2.5
8	$(CH_3)_3SiI + CH_3MgI \longrightarrow (CH_3)_3Si + MgI_2$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			9.2	5
9	$(ClCH_2)(CH_3)_2SiCl + CH_3MgCl \longrightarrow (ClCH_2)(CH_3)_2Si + MgCl_2$	$(C_2H_5)_2O$	$A = B \sim 0.25$	k AB	0-25			8.3	3

Homogeneous Reaction Kinetics

532,744

No.	Reaction	Solvent	Amount of reactant	Defined as	Temperature	$k = k^0 \times 10^n$ k^0 n	E	$A = A^0 \times 10^n$ A^0 n
10	$(\text{ClCH}_2)(\text{CH}_3)_2\text{SiCl} + \text{CH}_3\text{MgBr} \longrightarrow (\text{ClCH}_2)(\text{CH}_3)_3\text{Si} + \text{MgBrCl}$	$(\text{C}_2\text{H}_5)_2\text{O}$	$A = E \sim 0.25$	k_{AB}	0-25		11	~ 8 5
11	$(\text{ClCH}_2)(\text{CH}_3)_2\text{SiCl} + \text{CH}_3\text{MgI} \longrightarrow (\text{ClCH}_2)(\text{CH}_3)_3\text{Si} + \text{MgICl}$	$(\text{C}_2\text{H}_5)_2\text{O}$	$A = E \sim 0.25$	k_{AB}	0-25		9.8	1.6 4

COMMENTS

Rate law with respect to individual reactants not determined as $A=B$ in all experiments. Second order rate law valid until formation of second liquid phase at which point reaction rate observed to increase. At least one half life observed before second phase appeared. Actual rate constants given by authors only for (.7). Values of E and A listed are not known as accurately as given in table. These were not rounded off so that rate constants between 0-25°C may be calculated from them.

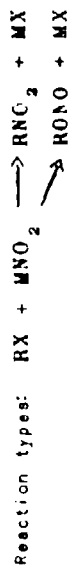
LITERATURE

A. F. Feld, C. J. Wilkins, *Can* 1955, 4079.

EXCHANGE

Replacement of Halogen by NO₂ and/or ONO on aliphatic C

Liquid phase



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

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

No.	Reaction	Solvent	Amount of reactant	Defined mass action class	Temperature	Half-time	$k =$		$A =$		Comments	Literature
							$k^0 \times 10^n$	π	$k^0 \times 10^n$	π		
1	$(\text{CH}_3)_2\text{CHI} + \text{AgNO}_2 \longrightarrow (\text{CH}_3)_2\text{CHONO}_2 + \text{AgI} \quad (135)$ $\longrightarrow (\text{CH}_3)_2\text{CHONO} + \text{AgI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.165; B = saturated		0	480					*	(3)
2	$n\text{-C}_4\text{H}_9\text{Br} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow n\text{-C}_4\text{H}_9\text{NO}_2, n\text{-C}_4\text{H}_9\text{ONO} + \text{AgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.25; B = saturated		0	1,350,000					*	(5)
3	$\text{C}_2\text{H}_5(\text{CH}_3)\text{CHBr} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow \text{C}_2\text{H}_5(\text{CH}_3)\text{CHNO}_2, \text{C}_2\text{H}_5(\text{CH}_3)\text{CHONO} + \text{AgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.25; B = saturated		0	346,000					*	(4)
4	$(\text{CH}_3)_3\text{CBr} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow (\text{CH}_3)_3\text{CNO}_2, (\text{CH}_3)_3\text{CONO} + \text{AgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.25; B = saturated		0	900					*	(4)
4.1	$(\text{CH}_3)_3\text{CBr} + (\text{CH}_3)_4\text{NNO}_2 \longrightarrow$ $\longrightarrow (\text{CH}_3)_3\text{CNO}_2, (\text{CH}_3)_3\text{CONO} + (\text{CH}_3)_4\text{NBr}$	CH_3NO_2	A = 0.0155; B = 0.032	A	25 45 63		5.57 5.24 2.90	-6 -5 -4		7 9	*	(1)

Homogeneous Reaction Kinetics

332,000

2

No.	Reaction	Solvent	Amount of reactant	Defined reaction rate	Temperature	Half-time	$R = 10^n$		$A = 10^n$		Comments	Literature
							R^0	π	A^0	π		
4.4	$(\text{CH}_3)_3\text{COI} + (\text{C}_2\text{H}_5)_4\text{ONO}_2 \longrightarrow (\text{CH}_3)_3\text{COONO} + (\text{C}_2\text{H}_5)_4\text{I}$ $\longrightarrow (\text{CH}_3)_3\text{COONO} + (\text{C}_2\text{H}_5)_4\text{Br}$	CH_3CO_2	A = 0.002; B = 0.0048 0.0006	RA	25 25		3.91 5.56	-8 -6			*	(3)
5	$n\text{-C}_8\text{H}_{17}\text{I} + \text{AzoNO}_2 \longrightarrow n\text{-C}_8\text{H}_{17}\text{ONO} + \text{AzoI}$	$(\text{C}_2\text{H}_5)_2\text{O}$ CH_3CN	A = 0.195; B = saturated 0.16 0.64		0 0	5,700 600					*	(4)
6	$\text{C}_2\text{H}_5(\text{CH}_3)\text{CHI} + \text{AzoNO}_2 \longrightarrow \text{C}_2\text{H}_5(\text{CH}_3)\text{CHNO}_2 + \text{AzoI}$ $\longrightarrow \text{C}_2\text{H}_5(\text{CH}_3)\text{CHONO} + \text{AzoI}$ (154)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.195; B = saturated		0	680					*	(4)
7	$(\text{CH}_3)_3\text{COCHI} + \text{AzoNO}_2 \longrightarrow (\text{CH}_3)_3\text{COCHNO}_2 + \text{AzoI}$ $\longrightarrow (\text{CH}_3)_3\text{COCHONO} + \text{AzoI}$	$(\text{C}_2\text{H}_5)_2\text{O}$ CH_3CN	A = 0.195; B = saturated A = 0.16; B = 0.64		0 27 0 ~25	$(t_{0.1} = 2.5 \times 10^6)$ 940,000 5,800,000 330,000					*	(4)
8	$n\text{-C}_8\text{H}_{17}\text{I} + \text{AzoNO}_2 \longrightarrow n\text{-C}_8\text{H}_{17}\text{ONO} + \text{AzoI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.195; B = saturated		0	6,550					*	(4)
9	$(n\text{-C}_6\text{H}_{13})(\text{CH}_3)\text{CHI} + \text{AzoNO}_2 \longrightarrow (n\text{-C}_6\text{H}_{13})(\text{CH}_3)\text{CHNO}_2 + \text{AzoI}$ $\longrightarrow (n\text{-C}_6\text{H}_{13})(\text{CH}_3)\text{CHONO} + \text{AzoI}$ (224) (184)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.195; B = saturated		0	680					*	(4)
10	$\text{C}_2\text{H}_5\text{OOC}(\text{CH}_3)\text{CHI} + \text{AzoNO}_2 \longrightarrow \text{C}_2\text{H}_5\text{OOC}(\text{CH}_3)\text{CHNO}_2 + \text{AzoI}$ $\longrightarrow \text{C}_2\text{H}_5\text{OOC}(\text{CH}_3)\text{CHONO} + \text{AzoI}$ (804)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.165; B = saturated		0	292,000					*	(3)

No.	Reaction	Solvent	Amount of reactant	Defined mass	Temperature	Half-time	$k^0 \times 10^n$ k^0 n	$A = A^0 \times 10^n$ A^0 n	Comments	Literature
11	$\text{CH}_3(\text{NO}_2)_2\text{HCl} + \text{NaNO}_2 \longrightarrow \text{CH}_3\text{CH}(\text{NO}_2)_2 + \text{NaCl}$	EtOH*	A = 0.0114; B = 0.2-0.8	RAB	30		2.75 -4		*	(2)
12	$\text{CH}_3(\text{NO}_2)_2\text{HCl} + \text{NaNO}_2 \longrightarrow \text{CH}_3\text{CH}(\text{NO}_2)_2 + \text{NaCl}$	EtOH*	A = 0.0114; B = 0.2-0.8	RAB	30		9.5 -5		*	(2)
13	$\text{C}_6\text{H}_5\text{CH}_2\text{Br} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NO}_2 + \text{AgBr}$ (794) $\longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{ONO} + \text{AgBr}$ (794)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.06; B = saturated		0	900			*	(4)
14	$p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NO}_2 + \text{AgBr}$ (524) $\longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{ONO} + \text{AgBr}$ (484)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.06; B = saturated		0	00			*	(4)
15	$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{NO}_2 + \text{AgBr}$ (794) $\longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{ONO} + \text{AgBr}$ (614)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.06; B = saturated		0	Very fast			*	(4)
16	$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{AgNO}_2 \longrightarrow$ $\longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{NO}_2 + \text{AgBr}$ (844) $\longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{ONO} + \text{AgBr}$ (164)	$(\text{C}_2\text{H}_5)_2\text{O}$	A = 0.06; B = saturated		0	10,800			*	(4)

CODER SOLVENTS

EtOH* 50 vol % $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$

COMMENTS

Reactions: (.1) (.2) (.3) (.4) Reaction may be partly or entirely heterogeneous at surface of excess solid AgNO_2 .
 (.4.1) (.4.2) Rate law followed up to 80% reaction. The nitrite ester formed in the reaction reacts further with Fr^- to produce NOEt and $(\text{CH}_3)_3\text{COH}$. Some elimination to form olefin is also observed. At low concentrations of B rate approaches rate of solvolysis, halogen exchange and many other reactions of $(\text{CH}_3)_3\text{COEt}$ in this medium. (.5) (.6) (.7) (.8) In $(\text{C}_2\text{H}_5)_2\text{O}$ reaction may be partly or entirely heterogeneous at surface of AgNO_2 . (.9) When optically active $(\pi\text{-C}_6\text{H}_5)_3(\text{CH}_3)\text{CHI}$ is used both products, $(\pi\text{-C}_6\text{H}_5)_3(\text{CH}_3)\text{CHNO}_2$ and $(\pi\text{-C}_6\text{H}_5)_3(\text{CH}_3)\text{CHONO}$ are obtained with clean inversion of optical configuration and no appreciable racemization. Percent of products based on actual yields. Reaction may be partly or entirely heterogeneous in this medium. (.10) Reaction may be partly or entirely heterogeneous in this medium at surface of excess solid AgNO_2 . (.11) (.12) Pseudo first order up to 80% reaction as B in large excess. Second order constants calculated by dividing pseudo first order constants by concentration of B. Primary isotope effect indicated as ratio is 3.3 showing hydrogen to be involved in rate determining step. Units converted to seconds from original minutes. (.13) (.14) (.15) (.16) Percent of products based on titrations and difference, actual percentage yields somewhat lower. Reactions may be partly or entirely heterogeneous at surface of excess solid AgNO_2 .

LITERATURE

- (¹) P. B. L. de la Mare, E. D. Hughes, C. K. Ingold, Y. Pocker, *OSL* 1954, 2330. (²) M. F. Hawthorne, *ACS* 1955, 78, 4980.
 (³) N. Kornblum, M. E. Chalmers, R. Daniels, *ACS* 1955, 77, 6654. (⁴) N. Kornblum, R. A. Smiley, R. K. Blackwood, D. C. Ireland, *ACS* 1955, 77, 6269.

Homogeneous Reactions

232.751

EXCHANGE

Replacement of halogen by NO_3^-

Liquid phase

Amounts are in M/l.

Rate constants are in
M/l and sec.Reaction type: $\text{RX} + \text{NO}_3^-$

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	Order of reaction	$k \times 10^2$ k^0 n	B	$A =$ $A^0 \times 10^2$ A^0 n	Comments	Reference
.13	$\text{CH}_3\text{Br} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.1; B \approx 0.14$	k_{AB}	64	6.25 -3			*	(1)
.14	$\text{C}_2\text{H}_5\text{Br} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.1; B \approx 0.14$	k_{AB}	34	7.69 -3			*	(1)
.15	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.2; B \approx 0.5$	k_{AB}	95	3.43 -4			*	(1)
.16	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.1; B \approx 0.14$	k_{AB}	34	4.20 -3			*	(1)
.17	$n\text{-C}_4\text{H}_9\text{Cl} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$	$A = B = 1.0$	k_{AB}	50	2.0 -7			*	(2)
.18	$(\text{CH}_3)_2\text{CHCH}_2\text{Cl} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.2; B \approx 0.5$	k_{AB}	55	6.34 -5			*	(1)
.19	$(\text{CH}_3)_2\text{CHCH}_2\text{Br} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.1; B \approx 0.14$	k_{AB}	64	6.44 -4			*	(1)
.20	$(\text{CH}_3)_3\text{COH}_2\text{Cl} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.2; B \approx 0.5$	k_{AB}	95	1.59 -5			*	(1)
.21	$(\text{CH}_3)_3\text{COH}_2\text{Br} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$ 70 vol % + H_2O	$A \approx 0.1; B \approx 0.14$	k_{AB}	64	1.01 -4			*	(1)
Alkenyl halide + nitrate										
.22	$\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{AgNO}_3$	$\text{C}_2\text{H}_5\text{OH}$	$A = 0.5; B = 1.0$	k_{AB}	25 50	1.73 -5 1.74 -4	18	1 8	*	(3)

No.	Reaction	Solvent	Amount of reactant	Defined mass action law	$k \times 10^n$ k^0 η	$k = k^0 \times 10^n$ k^0 η	$A = A^0 \times 10^n$ A^0 η	Comments	Literature
Substituted alkyl halides									
.23	$CH_3CH_2CH_2Cl + AgNO_3$	C_2H_5OH	$A = B = 1.0$	$k AB$	57	1.32	-6		(2)
.24	$CH_3CH_2CH_2CH_2Cl + AgNO_3$	C_2H_5OH	$A = 0.5; B = 1.0$	$k AB$	25	5.56	-3		(3)
.25	$CH_3CH_2CH(CH_3)CH_2Cl + AgNO_3$	C_2H_5OH	$A = 0.5; B = 1.0$	$k AB$	25	3.25	-3		(3)
Di- and Tri-halides									
.26	$CH_3OCH_2Cl + AgNO_3$	C_2H_5OH	$A = B = 1.0$	$k AB$	50	5.2	-8		(2)
.27	$C_6H_5OCH_2Cl + AgNO_3$	C_2H_5OH	$A = B = 1.0$	$k AB$	50	5.3	-8		(2)
.28	$C_6H_5CH_2Cl + AgNO_3$	C_2H_5OH	$A = B = 1.0$	$k AB$	20	1.40	-6		(2)
.29	$C_6H_5OCH_2Cl + AgNO_3$	C_2H_5OH	$A = B = 1.0$	$k AB$	50	1.38	-5	14.4	7
.30	$CH_3CH_2CH_2CH_2Cl + 2AgNO_3$	C_2H_5OH	$A = B = 1.0$	$-dB/dt = k AB$	50	4.3	-5		(2)
.31	<i>cis</i> - $2(CH_3CHCH_2Cl) + AgNO_3$	C_2H_5OH	$A = 0.5; B = 1.0$	$-dB/dt = k AB$	50	2.48	-4		(3)
.32	<i>trans</i> - $2(CH_3CHCH_2Cl) + AgNO_3$	C_2H_5OH	$A = 0.5; B = 1.0$	$-dB/dt = k AB$	50	4.31	-4		(3)
.33	$CH_3CH_2CH_2CH_2Cl + AgNO_3$	C_2H_5OH	$A = 0.5; B = 1.0$	$-dB/dt = k AB$	50	4.22	-4		(3)
.34	$C_6H_5CH_2Cl + 2AgNO_3$	C_2H_5OH	$A = B = 1.0$	$-dB/dt = k AB$	20	2.56	-5		(2)
.35	$C_6H_5OCH_2Cl + 2AgNO_3$	C_2H_5OH	$A = B = 1.0$	$-dB/dt = k AB$	20	5.13	-5		(2)

COMMENTS

By Reference: (1) consider reactions may be partly heterogeneous at surface of precipitated silver halide but observe good second order behavior from 5 to 50% reaction. (2) units converted to seconds from original minutes of authors, who

list values as 10^6 s which have been interpreted to be $10^{-5} \times \text{s}$. (3) carry out reaction in the dark to prevent catalytic action of precipitated silver halide.

Reaction: (.39) Twice authors value, who divided measured value of $-\text{dB}/\text{dt}$ by two. Second halogen considered to react very much more rapidly than first. (.32) (.38) Identical product obtained from both reactions. (.34) Twice value listed by authors. (2) divided measured value of $-\text{dB}/\text{dt}$ by two as second halogen considered to react more rapidly. (.35) Three times value listed by authors. (2) divided measured value of $-\text{dB}/\text{dt}$ by three as second and third halogen considered to react more rapidly.

LITERATURE

- (1) I. Iustrovsky, E. A. Hughes, *CSL* 1946, 169. (2) M. Murakami, S. Gae, S. Takeuchi, *Bull. Chm. Soc. Japan* 1951, 24, 1. (3) S. Gae, C. A. Vander Werf, *ACS* 1953, 75, 2724.

Homogeneous Reactions

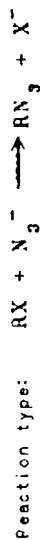
332.753

EXCHANGE

Replacement of halogen by azide

Liquid phase

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



No.	Reaction	Solvent	Amount of reactant	Azide	Amount of addend	Defined mass action law	Temperature	$k = k' \times 10^n$ k^0 n	$A = A' \times 10^n$ A^0 n	Comments	Literature
Aryl-substituted Alkyl halide											
1	$(C_6H_5)_3CCl + (C_6H_5)_2(OH)_2NN_3 \longrightarrow$ $(C_6H_5)_3CN + (C_6H_5)_2(OH)_2NCl$	C_6H_6	$10^2 A \sim 3 \cdot 10^2 B = 1.4$ 3.0 5.4			R AB	50 50 50	4.5 3.3 3.6 -2 -2 -2			(2)
			3.0	C_6H_5OH	$(4-8) \times 10^{-3}$	$kA[B-(C_6H_5OH)] + k_3A[B-(C_6H_5OH)] [C_6H_5OH]$	50 50	$k = 3.3$ $k_3 = 1.6$ -2 +1			
Aryl halide											
2	$2-N_3C_6H_4I + N_3^-$	CH_3OH	$A = B = 0.05$	Na^+	$= B$	R AB	132 150 158 166	9.6 5.35 6.93 1.05 -4 -3 -3 -2			(1)
3	$2-N_3-2-O-CHC_6H_4I + N_3^-$	CH_3OH	$A = B = 0.05$	Na^+	$= B$	R AB	52 64 82	1.68 6.24 3.96 -4 -4 -3			(1)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined as	Temperature	$k \times 10^n$		B	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.4	$2\text{-NO}_2\text{-4-N}(\text{CC}_6\text{H}_4)_2\text{I} + \text{N}_3^-$	CH_3OH	A = B = 0.05	Na^+	= B	k AB	45 50 66 86	1.53 2.59 1.18 7.6	-4 -4 -3 -3				*	(¹)
.5	$2\text{-4-(NO}_2)_2\text{C}_6\text{H}_3\text{I} + \text{N}_3^-$	CH_3OH	A = B = 0.05	Na^+	= B	k AB	20 35 44 59	1.90 9.13 2.26 8.7	-4 -4 -3 -3	21.5	1	11	*	(¹)

COMMENTS

Reaction. (.1) In absence of phenol reaction shows good second order behavior over course. In presence of phenol the concentration of phenol must be subtracted from azide concentration to give second order constant as well as a third order catalytic constant involving total phenol concentration. Variation of rate constant with initial concentration of B assumed to be due to variation in size of salt clusters. (.2)(.3)(.4)(.5) Rate law is total second order but order not determined with respect to A and B independently as A=B in all experiments.

LITERATURE

(¹) J. Miller, A.J. Parker, B. A. Bolto, *ACS* 1957, 79, 93. (²) C.G. Swain, M.M. Kreevoy, *ACS* 1955, 77, 1122.

Homogeneous Reactions

332.754

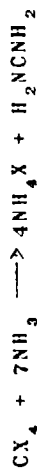
EXCHANGE

Replacement of halogen by NH_2 and :NH

Liquid phase

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

Reaction type:



NH

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

No.	Reaction	Solvent (Mol %)	Amount of reactant	Amount of added solvent	Defined mass action law	Temperature	$k \times 10^7$ k^0 η	Comments	Literature
1	$\text{CCl}_4 + \text{NH}_3$	NH_3	(No appreciable reaction below Tc see 331.754)						
2	$\text{CBr}_4 + 7\text{NH}_3 \longrightarrow 4\text{NH}_2\text{Br} + \text{H}_2\text{NCHNH}_2$ NH	NH_3	A = 0.2	L 0-0.25	$dM/dt = kAL$	125	4.4	-4	*
3	$\text{CI}_4 + 7\text{NH}_3 \longrightarrow (Q) \longrightarrow 4\text{NH}_2\text{I} + \text{H}_2\text{NCHNH}_2$ NH	NH_3	A = 0.07-0.15	L 0-0.29	$dM/dt = kQ$	125	8.0	-4	*

COMMENTS

Reactions carried out under pressure slightly below critical temperature. For reactions above critical temperature of NH_3 see 331.754. (2) Rate law may require alteration after more complete study. Concentrations only estimated at reaction temperature. Formation of Br^- slightly ahead of guanidine formation but results indicate only about 10% of carbon tied up in form of intermediate. Addition of NaBr or KBr at 0.09 M/l increase yield in given time by a factor of about four. BaBr_2 shows no effect. CaBr_2 decreases yield and AlBr_3 or BiBr_3 at 0.03 M/l show only slight increase in yield in given time. (3) All I^- appears in first ten minutes of reaction so that carbon is predominantly in form of intermediate, Q. Concentration of Q = A-L/4. Authors show rate of appearance of guanidine is first order with respect to concentration of Q and first order with respect to effective L. Effective L is NH_4I added + $\frac{1}{2}[\text{NH}_4\text{I}]$ produced by intermediate producing reaction. Rate laws may need to be revised on more complete study. Concentrations only estimated at reaction temperature.

LITERATURE

G.W. Watt, H.T. Hahn, ACS 1955, 77, 312.

EXCHANGE
Replacement of halogen by $S_2O_3^{2-}$

Liquid phase

Reaction type:



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

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

No.	Supplementing 1961 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mechan- ism	Temperature	$k \times 10^7$	n	$A \times 10^7$	Comments	Literature
32	2	$C_2H_5I + S_2O_3^{2-}$ (Na^+)	Me 10* 20* 50*	$A \approx B \approx 0.03$			k AB	25 25 25	3.6 4.3 8.5	-2 -2 -2			(21)
33			Pr 10* 20* 30* 50*	$A \approx B \approx 0.03$			k AB	25 25 25 25	3.9 5.9 6.5 5.0	-2 -2 -2 -2			
35	4	$C_2H_5Br + S_2O_3^{2-}$ (Na^+)	H_2O	$10^2 A \approx 1; 10^2 B \approx 5$			k AB	25 50	1.19 1.92	-3 -2		*	(21)
36			Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k AB	12 25 37	2.93 1.07 3.33	-4 -3 -3		*	(1)
38		$C_2H_5I + S_2O_3^{2-}$ (Na^+)	H_2O	$A = B = 0.01$			k AB	25 35	1.92 6.5	-3 -3		*	(21)

Homogeneous Reaction Kinetics

352.751

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^7$	β	$A =$ $A^0 \times 10^7$	Comments	Literature
37	11	$n\text{-C}_9\text{H}_{17}\text{Br} + \text{Na}_2\text{S}_2\text{O}_3$	Et 49*	A = B = 0.1	CH ₃ COONa	0.01	k AB	12 25 37	1.75 6.31 1.94	-4 -4 -3	1.9 9	*	(1)
			Et 49*	$10^4 A = 4; 10^4 B = 8$ 8 16 19 38 25 60 111 207 443 500 4-400 9-500	CH ₃ COONa	1.25×10^{-4} 2.5×10^{-4} 5.0×10^{-4} 6.1×10^{-4} 8.4×10^{-4} 5.0×10^{-3} $(1-50) \times 10^{-4}$	k AB k A[S ₂ O ₃] ⁻	25 25 25 25 25 25 25	9.44 9.05 9.39 7.73 6.54 5.73 1.02	-4 -4 -4 -4 -4 -4 -3		*	(6)
38	11	$n\text{-C}_9\text{H}_{17}\text{Br} + \text{K}_2\text{S}_2\text{O}_3$	Et 49*	$10^4 A = 5; 10^3 B = 1$ 23 5 443 53 5-400 1-50	CH ₃ COONa	1.0×10^{-4} 4.0×10^{-4} 5.0×10^{-3} $(1-50) \times 10^{-4}$	k AB k A[S ₂ O ₃] ⁻	25 25 25 25	9.12 7.52 5.13 1.02	-4 -4 -4 -4		*	(6)
39	11	$n\text{-C}_9\text{H}_{17}\text{Br} + \text{Na}_2\text{S}_2\text{O}_3$	Et 49*	$10^3 A \approx 2; 10^3 B = 5$	CH ₃ COONa	$\sim 4 \times 10^{-4}$	k AB	15 30 25 30 35	1.57 2.64 4.50 7.39 11.14	-4 -4 -4 -4 -4		*	(6)
				" " " "	"	"	k A[S ₂ O ₃] ⁻	15 30 35 30 35	3.35 5.64 9.62 1.59 2.41	-4 -4 -4 -3 -3	1.5 10		

No.	Supplementing 1961 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	$k \times 10^n$		ρ	$A \times 10^n$		Comments	Literature
								k^0	η		A^0	η		
.40	.11	$n\text{-C}_3\text{H}_7\text{Br} + \text{CaS}_2\text{O}_3$	Et 49*	$10^2 A = 4; 10^2 B = 5.2$	CH_3COONa	5.0×10^{-3}	k_{AB} $k_{A[S_2O_3]}$	25 25	-4 -5				*	(⁶)
.41	.11	$n\text{-C}_3\text{H}_7\text{Br} + \text{SrS}_2\text{O}_3$	Et 49*	$10^4 A = 3; 10^4 B = 6$ 5 3-5 8-10	CH_3COONa	2×10^{-5} 5×10^{-6} $(2-5) \times 10^{-6}$	k_{AB} $k_{A[S_2O_3]}$	25 25 25	-4 -4 -3				*	(⁶)
.42	.12	$(\text{CH}_3)_2\text{CHBr} + \text{Na}_2\text{S}_2\text{O}_3$	Et 49*	$10^5 A = 1; 10^5 B = 2$ 1 0.5 1 1 2 1 1 0.5 1	CH_3COONa	1×10^{-5} 2.5×10^{-5} 2×10^{-6} 1×10^{-5} 2.5×10^{-5} 2×10^{-6}	k_{AB} $k_{A[S_2O_3]}$	25 25 25 25 25 25	-5 -5 -5 -5 -5 -5				*	(⁶) (⁸)
.43	.13	$n\text{-C}_3\text{H}_7\text{I} + \text{S}_2\text{O}_3^{=}$ (Na^+)	EtW 3*	$10^2 A = 1; B > A$			k_{AB}	35	-3				*	(²¹)
.44	.14	$(\text{CH}_3)_2\text{CHI} + \text{S}_2\text{O}_3^{=}$ (Na^+)	EtW 3*	$10^2 A = 1; B > A$			k_{AB}	35	-4				*	(²¹)
.45		$n\text{-C}_4\text{H}_9\text{Br} + \text{S}_2\text{O}_3^{=}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	12 25 37	-4 -4 -3			1.1 1.1 1.1		(¹)
Alkenyl halide														
.46		$\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{S}_2\text{O}_3^{=}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	12 25 37	-4 -3 -3					(¹)
.47	.15	$\text{CH}_2=\text{CHCH}_2\text{I} + \text{S}_2\text{O}_3^{=}$ (Na^+)	EtW 3*	$10^2 A = 1; B > A$			k_{AB}	15 25	-2 -1				*	(²¹)

Homogeneous Reaction Kinetics

352,761

No.	Supplementing Entry No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature, °C.	$k \times 10^3$	k'	k''	$k^0 \times 10^3$	k^0	$k^0 \times 10^3$	Order	Reference
Alkoxy-substituted alkyl halide																
42		$C_2H_5OCH_2CH_2Br + S_2O_8^{2-} (Na^+)$	Et_2SO^*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	37 50 62	3.44 1.12 3.44	-4 -3 -3		19.0	2	9		(1)
43		$C_2H_5OCH_2CH_2CH_2Br + S_2O_8^{2-} (Na^+)$	Et_2SO^*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	25 37 50	1.07 1.36 4.04	-4 -3 -3		17.6	3	9		(1)
43		$C_2H_5OCH_2CH_2CH_2CH_2Br + S_2O_8^{2-} (Na^+)$	Et_2SO^*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	25 37 50	7.26 2.35 6.74	-4 -3 -3		17.0	2	9		(1)
Carbonyl-substituted alkyl halide																
51	53	$CH_3COCH_2Cl + S_2O_8^{2-} (Na^+)$	H_2O	$10^2 A = 1; B > A$			k_{AB}	15 25 25	5.1 1.44 1.45	-3 -2 -2						(21)
			Et_2SO^*					35	4.0	-2						
Carboxy-substituted alkyl halide																
52	57	$C_2H_5OOCCH_2Cl + S_2O_8^{2-} (Na^+)$	Et_2SO^*	$10^2 A \approx 1; B > A$			k_{AB}	35	5.9	-2						(21)
53	58	$(COO^-)CH_2Cl + S_2O_8^{2-} (Na^+)$	H_2O	$10^2 A = 1; B > A$ $A + 2B = 0.02$			k_{AB}	25 50 50 50	1.6 1.36 1.27 1.77	-4 -3 -3 -3						(21) (12) (12) (12, 21)
				$C.04$ $C.08$ 0.15				50	1.96	-3						(12)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	$k = k' + k''[A]$	$k = k' + k''[A]$	$k = k' + k''[A]$	$k = k' + k''[A]$	Study	Reference
56	$(2.5-50) \times 10^{-4}$ (Na ⁺) (continued)	H ₂ O	$\mu = 0.00125$ 0.0050 0.010 0.00125 0.0050 0.010 0.00125 0.0050 0.010	$A = B = (2.5-50) \times 10^{-4}$ NaCl $(2.5-50) \times 10^{-4}$ LaCl ₃ $(2.5-50) \times 10^{-4}$	$(5-1500) \times 10^{-5}$ $(5-5000) \times 10^{-6}$	$k_{AB}; \log k = 10.3 k_0 + 1.62\sqrt{\mu} / (1 + \sqrt{\mu})$ $k_{AB}; \log k = 10.3 k_0 + 1.62\sqrt{\mu} / (1 + \sqrt{\mu})$ $k_{AB}; k = k' + k''[LaCl_3]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	(13) (14) (8) (21) (21) (16) (8) (21)
57	$CH_3COOCH_2Br + S_2O_8^{2-} = (Na^+)$	H ₂ O	$10^2 A \approx 1; B > A$ $A = B = 0.0026$	pressure	1 atm. 340 690 1,280	k_{AB}	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	(21) (21) (16) (8) (21)
58	$CH_3COOCH_2Br + S_2O_8^{2-} = (Na^+)$	H ₂ O	$10^2 A \approx 1; B > A$	pressure	1 atm. 680 1,280	k_{AB}	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	$k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$ $k = k' + k''[A]$	(21) (21) (16) (8) (21)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature $^{\circ}\text{C}$	$k =$ $k^0 \times 10^n$ k^0 n	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
.59	.24	$\text{C}_2\text{H}_5\text{OOCCH}_2\text{I} + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	H ₂ O	$10^3 A \approx 1; B > A$			k_{AB}	15 25	9.8 2.8	-2 -1	*	(21)
.60		$(\text{COO}^-)(\text{CH}_2\text{CH}_2\text{Br}) + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	H ₂ O	$10^3 A = 1-30$; $10^3 B = 2-70$		$\mu = 0.28$ 0.06 0.009 0.006	k_{AB}	25 25 25 25	2.65 3.60 1.4 2.35	-4 -4 -3 -3		(16)
.61		$\text{CH}_3\text{OOCCH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	H ₂ O	$10^3 A = 4.5$ 2.0 1-2.2		$\mu = 0.21$ 0.21 0.005-0.5	k_{AB}	25 25 25	5.0 6.4 5.0	-4 -4 -4		(16)
.62		$(\text{COO}^-)(\text{CH}_3\text{CHBr}) + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	H ₂ O	$10^3 A = 3-30$; $10^3 B = 7-70$		$\mu = 0.008$ 0.03 0.06 0.05	k_{AB}	25 25 25 25	4.40 6.25 7.2 8.5	-5 -5 -5 -5		(16)
.63		$(\text{CH}_3\text{OOC})(\text{CH}_3)\text{CHBr} + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	H ₂ O	$10^3 A = 3$		$\mu = 0.16$ 0.09 0.02 0.005	k_{AB}	25 25 25 25	2.8 3.0 3.7 3.6	-3 -3 -3 -3		(16)
.64	.25	$(\text{C}_2\text{H}_5\text{OOC})(\text{CH}_3)\text{CHBr} + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	EtOH*	$10^2 A \approx 1; B > A$			k_{AB}	25 35	1.4 3.2	-3 -3	*	(21)
.65	.26	$(\text{C}_2\text{H}_5\text{OOC})(\text{C}_2\text{H}_5)\text{CHBr} + \text{S}_2\text{O}_3^{2-}$ (Na ⁺)	EtOH*	$10^2 A \approx 1; B > A$			k_{AB}	35	8.5	-4	*	(21)

[illegible]

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature °C	$k' \times 10^7$	$k'' \times 10^7$	$A^\circ \times 10^7$	Comments	Literature
.69		$\{(\text{COO}^-)(\text{COOCH}_2)\text{CHBr} + \text{S}_2\text{O}_3^{2-}$	H ₂ O	$10^2 A \approx 4; 10^2 B \approx 8$		$\mu = 0.0046$ 0.02 0.05 0.10 0.09 0.15 0.35 0.51 0.04 0.05	$k' AB$	0 0 0 0 25 25 25 25 35 35	6.8 6.5 5.0 2.3 6.04 1.98 9.0 4.7 5.6 5.4	-4 -5 -5 -5 -3 -3 -4 -4 -3 -3		*	(4)
				$10^2 A \approx 1; 10^2 B = 3-6$									(5)
				$10^2 A \approx 4; 10^2 B \approx 8$									(4)
.69		$\{(\text{CH}_3\text{OOC})(\text{CH}_3\text{OOCCH}_2)\text{CHBr} + \text{S}_2\text{O}_3^{2-}$		$10^2 A \approx 1; 10^2 B = 3-6$		$\mu = 0.12$ 0.23 0.50		25 25 25	1.34 1.29 1.24	-3 -3 -3	7 2 15	*	(5)
Aryl-substituted alkyl halide													
.70	.50	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} (\text{Na}^+)$	EtOH* EtOH* DMF*	$10^2 A \approx 1; B > A$ $10^2 A \approx 2; 10^2 B \approx 4$ $10^2 A \approx 2; 10^2 B \approx 4$			$k' AB$	35 30 30	5.5 5.35 7.10	-3 -3 -3		*	(21) (11)
.71		$p\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} (\text{Na}^+)$	EtOH* DMF*	$10^2 A \approx 2; 10^2 B \approx 4$			$k' AB$	30 30	8.35 7.95	-3 -3		*	(11)
.72	.51	$o\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} (\text{Na}^+)$	EtOH*	$10^2 A \approx 1; B > A$			$k' AB$	35	6.5	-3		*	(21)
.73	.50	$m\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} (\text{Na}^+)$	EtOH*	$10^2 A \approx 1; B > A$			$k' AB$	35	7.4	-3		*	(21)
.74	.55	$p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_3^{2-} (\text{Na}^+)$	EtOH* EtOH* DMF*	$10^2 A \approx 1; B > A$ $10^2 A \approx 2; 10^2 B \approx 4$ 2			$k' AB$	35 30 30	1.2 9.6 2.60	-2 -3 -2		*	(21) (11)

Homogeneous Reaction Kinetics

370-761

No.	Supplement 1951	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature		$k \times 10^2$		$A \times 10^2$		Comments	Literature
								k^0	n	k^0	n	A^0	n		
.75		$p\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{Cl} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50* DMF*	$10^{-2} A \approx 2 \times 10^{-2} B \approx 4 \times 10^{-4}$			k_{AB}	30		7.3	-3			*	(11)
.76		$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	37		8.9	-4				(1)
								50		3.24	-3				
								62		8.5	-3	17.9	4		
.77		$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	25		4.17	-4				(1)
								37		1.53	-3				
								50		4.65	-3	17.9	6		
.78		$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	37		1.36	-3				(1)
								50		4.54	-3				
								62		1.28	-2	17.8	5		
Sulfonyl-substituted alkyl (alkenyl) halides															
.79		$\text{C}_2\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	25		7.22	-4				(1)
								37		2.60	-3				
								50		8.1	-3	19.2	8		
.80		$\text{C}_2\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	25		3.38	-3				(1)
								37		1.23	-2				
								50		3.33	-2	17.2	1.4		
.81		$\text{C}_2\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{S}_2\text{O}_8^{2-}$ (Na^+)	Et 50*	$A = B = 0.1$	CH_3COONa	0.01	k_{AB}	12		1.71	-3				(1)
								25		5.36	-3				
								37		1.80	-2	15.8	2		

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 n	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
Halogen-substituted alkyl halide												
.82	.6	$\text{CH}_2\text{ClCH}_2\text{Br} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtSO*	A = B = 0.1	CH ₃ COONa	0.01	k AB	25 37 50 40 50	1.07 3.76 1.26 1.9 5.8	-4 -4 -3 -5 -5	9	(1) *
.83	.7	$\text{CH}_2\text{ClCH}_2\text{I} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtW3*	B > A								(21)
.84	.8	$\text{CH}_2\text{BrCH}_2\text{Br} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtW3*	B > A			k AB	40 50	5.3 1.5	-5 -4		(21)
.85	.9	$\text{CH}_2\text{BrCH}_2\text{I} + 2\text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtW3*	B > A			k AB	40 50	6.4 1.9	-3 -2		(21)
.86	.10	$\text{CH}_2\text{ICH}_2\text{I} + 2\text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtW2*	A ≈ 0.01; B > A			k AB	15 25	8.1 2.1	-3 -2		(21)
.87		$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtSO*	A ≈ 0.01; B > A			k AB	15 25	1.3 3.9	-2 -2		(21)
.88		$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtSO*	A = B = 0.1	CH ₃ COONa	0.01	k AB	25 37 50	4.05 1.35 4.26	-4 -3 -3	2 9	(1)
.89		$\text{cis-ClCH:CHCH}_2\text{Cl} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtSO*	A = B = 0.1	CH ₃ COONa	0.01	k AB	12 25 37	1.97 7.34 2.33	-4 -4 -3	1.1 9	(1)
.90		$\text{cis-ClCH:CHCH}_2\text{Cl} + \text{S}_2\text{O}_3^{=}$ (Na ⁺)	EtSO*	A = B = 0.1	CH ₃ COONa	0.01	k AB	12 25 37	2.59 7.42 2.16	-3 -3 -2	3 8	(1)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^3$	k^0	n	$A = A^0 \times 10^R$	Comments	Literature
.90		$\text{trans-ClCH}_2\text{CH}_2\text{Cl} + \text{S}_2\text{O}_8^{2-} (\text{Na}^+)$	Et 50*	A = B = 0.1	CH ₃ COONa	0.01	k AB	12 25 37	1.60 4.84 1.37	-3 -3 -2				(1)
.91		$\text{O}(\text{CH}_2\text{CH}_2\text{Cl})_2 + 2\text{S}_2\text{O}_8^{2-} (\text{Na}^+)$	H ₂ O	A ≈ 0.02; B = 0.05-0.1			k AB	100	~ 5	-3				(3)

CODED SOLVENTS

Me 10* (20) (30) CH₃OH + H₂O % Indicated of CH₃OH
 Pr 10* (20) (30) (50) (CH₃)₂CHOH + H₂O % Indicated of (CH₃)₂CHOH
 Et 50* (49) (60) H₂O + C₂H₅OH % Indicated of C₂H₅OH
 Et 20* C₂H₅OH + H₂O; C₂H₅OH/H₂O = 5/2 (vol)
 Et 15* C₂H₅OH + H₂O; C₂H₅OH/H₂O = 5/3 (vol)
 M 10 7H* (71) (64) (56) (54) (44) (43) CH₃OH + H₂O in ratio
 necessary to give dielectric constant of value indicated.
 DMF* 60 vol % (CH₃OC₂H₅)₂O + H₂O

COMMENTS

Reaction: (.34) Units converted to K/l , sec. and natural logarithms from ml. of titrating solution, min. and base 10 logarithms respectively. (.35) Rate constant converted to base e logarithms from base 10 logarithms of authors and from values in 1951 Edition of Tables. (.36) Rate constant converted to base e logarithms from base 10 logarithms of authors and from values in 1951 Edition of Tables. Values about 50% higher than values of (.17). (.37) Values of (.1) of rate constants 30 to 40% higher than those of (.17). (.6) determine fraction of total thiosulfate present as $S_2O_3^{=}$ and find rate constant in terms of true $[S_2O_3^{=}]$ is independent of added salt, see (.38) (.39) (.40) (.41). (.39) (.39) (.40) Rate constant calculated on basis of total thiosulfate present decreases both with course of reaction, and with increase in concentration of salts. In terms of calculated $[S_2O_3^{=}]$ the rate constant is independent of cation present. (.42) Data of (.9) converted into terms of calculated concentration of $[S_2O_3^{=}]$ by (.6). (.43) (.44) (.47) (.51) (.52) Converted to base e logarithms from base 10 logarithms of authors and from values in 1951 Edition of Tables. (.53) Converted to base e logarithms from base 10 logarithms of (.21) and from assumed base 10 logarithms of (.13). (.54) (.55) Converted to base e logarithms from base 10 of authors and from values in 1951 Edition of Tables. (.56) Reaction studied by (.8) with regard to pressure dependence from which they concluded the volume of the transition state to be smaller than the volume of the reactants. (.10) determined dependence with respect to ionic strength:

$$\log k = \log k_0 + 2/\sqrt{\mu} \text{ and at } 20^\circ C \quad 10^3 k_0 = 2.54.$$

give plot of data of many previous investigators. (.12) (.13) determine temperature dependence of reaction. (.14) studied reaction over wide range of salt concentrations and observed a specific catalytic effect with $LiCl_3$. Catalytic constant for $LiCl_3$ varied with concentration as did activation energy. (.15) (.16) (.17) studied effect on reaction of a wide variety of salts as well as other addenda. $10^3 (k/k_0)/\sqrt{\mu}$ was not constant but observed to vary from 0.6 at $\sqrt{\mu} = 0.76$ with Li^+ or Na^+ to 5.7 at $\sqrt{\mu} = 0.08$ with Li^{+++} . Other addenda included, urea, sucrose, glycerol and dioxane. (.19) studied reaction with respect to KNO_3 , K_2SO_4 , $K_3Co(CN)_6$ and found rate constant to be nearly the same for 0.03N salts even though μ varied from 0.02 to 0.04. Rate constants of (.21) converted to base e logarithm from base 10 of authors. Reaction also studied by (.23) (.24) whose results agree well with those of later investigators. (.57) Values of (.21) converted to base e loga-

COMMENTS (continued)

ritas from base 10 as in 1951 edition of Tables. ⁽⁸⁾ shows that pressure dependence indicates transition state to have greater volume than volume of reactants. (.38) (.39) (.64) (.65) Converted to base e logarithms from base 10 used by authors and from values in 1951 Edition of Tables. (.66) Values of rate constants of ⁽³⁾ do not apply to initial stages of reaction. Initial rate may be as much as double steady value obtained as reaction proceeds. ⁽⁴⁾ do not give concentrations of reactants used, and reaction followed for only 20%. Values of ⁽⁵⁾ give only order of magnitude as calculated constants show wide variation. (.67) Selected data. Authors attempt to correlate variation of rate constants with dielectric constant of medium by equation of one of the authors. Addition of KNO_3 at constant solvent composition shows very slight negative salt effect. (.68) Selected data. reaction followed to only 20% completion and concentration of reactants and added salts, if any, not stated. (.69) Selected data. Ionic strength as listed is initial value. (.70) Rate constant converted to base e logarithms from base 10 of ⁽²¹⁾ and from value in 1951 edition of Tables. Solvent composition of ⁽¹¹⁾ not exact as no correction for contraction on mixing. (.71) No correction for contraction of solvent on mixing. (.72) (.73) Rate constants converted to base e logarithms from base 10 of authors and from values in 1951 Edition of Tables. (.74) Rate constant converted to base e logarithms from base 10 of ⁽²¹⁾ and from value in 1951 Edition of Tables. No correction made by ⁽¹¹⁾ for solvent contraction on mixing. (.75) No correction made for contraction of solvent on mixing. (.82) (.83) (.84) (.85) (.86) Rate constants converted to base e logarithms from base 10 of ⁽²¹⁾ and from values in 1951 Edition of Tables.

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EXCHANGE

Replacement of halogen by Thio alkyl (aryl)

Liquid phase

Reaction type: $RX + R'S^- \longrightarrow RSR' + X^-$ Amounts are in M/l.
Rate constants are in
M/l an: sec.* Coded solvents at end
of Table.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$		$A =$ $A^0 \times 10^n$		Solvent	Literature
								k^0	n	A^0	n		
1	$C_2H_5Br + C_6H_5S^- (Na^+)$	CH_3OH	$10^2 A = 2-9; 10^2 B = 1-4$			k_{AB}	0 20 35	3.79 3.91 1.82	-4 -3 -2				(⁶)
2	$C_2H_5Br + C_6H_5-N=N-OS^- (Na^+)$ $(sodium\ 3-phenyl-1-thiourazolate)$	Et_5O^*				k_{AB}	25	1.95	-3				(¹) (³)
3	$C_2H_5I + C_6H_5-N=N-OS^- (Na^+)$ $(sodium\ 3-phenyl-1-thiourazolate)$	Et_5O^*				k_{AB}	25	6.0	-3				(¹) (³)
4	$CH_3CH_2CH_2Br + C_6H_5S^- (Na^+)$	CH_3OH	$10^2 A = 2-9; 10^2 B = 2-4$			k_{AB}	0 20 35	2.56 2.58 1.12	-4 -3 -2				(⁶)
5	$CH_3CH_2CH_2Br + C_6H_5-N=N-OS^- (Na^+)$ $(sodium\ 3-phenyl-1-thiourazolate)$	Et_5O^*				k_{AB}	25	1.27	-3				(¹) (³)

No.	Reaction	Solvent	Amount of reactant	Ascorb	Amount of ascorb	Defined mass action law	Temperature	$k \times 10^7$ k^0 n	$A = A^0 \times 10^7$ A^0 n	Comments	Literature
6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A = 1; 10^2 B = 2.4$			k_{AB}	0 20	1.47 1.29 -2	1.0 11		(8)
7	$\text{CH}_3\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{N}^-\text{N}^+\text{CS}^- (\text{Na}^+)$ (sodium 3-phenyl-1,2-thioarazolate)	Et_2SO^*				k_{AB}	25	3.33 -3		*	(1) (3)
8	$n\text{-C}_4\text{H}_9\text{SH} + n\text{-C}_4\text{H}_9\text{S}^- (\text{Na}^+)$	CH_3OH	$A = B = 0.01$			k_{AB}	25 35 42	4.43 1.11 -2 2.00 -2	2 3	*	(8)
9		$\text{C}_2\text{H}_5\text{OH}$	$A = B = 0.05$			k_{AB}	25 25 25 35 35 35 35 35 42 42	2.00 -2 1.81 -2 1.83 -2 5.10 -2 4.84 -2 4.50 -2 4.87 -2 4.78 -2 4.48 -2 4.35 -2 3.0 -2 8.94 -2 8.84 -2 7.58 -2			(9)
			0.1 0.2 0.05 0.1 0.2 0.05 0.05 0.05 0.05 0.05	LICI	0.020 0.033 0.046 0.009 0.084				17 17.5 18	1 9 2 9 3 8	
			0.1 0.2	$\text{C}_6\text{H}_5\text{ONa}$							

No.	Reaction	Solvent	Amount of reactant	Amount of Addend	Amount of Addend	Defined mass action law	Temperature	$k \times 10^n$		δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.9	$n\text{-C}_6\text{H}_5\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A = 2.9; 10^2 B = 2.4$ $A = B = 0.1$ $10^2 A = 2.9; 10^2 B = 2.4$ $A = B = 0.1$			RAB	0	2.77	-4				*	(7)
							20	2.69	-3					
							25	4.43	-3					
							35	1.21	-2	17.2	4	10		
							35	1.11	-2					
							42	2.09	-2					
.10	$n\text{-C}_6\text{H}_5\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	$\text{C}_2\text{H}_5\text{OH}$	$A = B = 0.05$ 0.10 0.20 0.05 0.10 0.20 0.05 0.10 0.10			RAB	25	1.23	-2				*	(9)
							25	1.55	-2					
							25	1.24	-2					
							35	3.40	-2					
							35	3.12	-2					
							35	1.84	-2					
							42	2.57	-2	17.4	9	10		
							42	3.54	-2	15.7	4	9		
							42	4.71	-2	14.1	3	8		
							0	3.14	-4					
Halogen-substituted alkyl halide		CH_3OH	$10^2 A \approx 1; 10^2 B \approx 2.4$			$-dA/dt = kAB$	20	4.48	-6				*	(8)
							40	4.44	-5	22	1.0	11		
							0	1.98	-4					
							40	1.52	-2	18.3	1.3	11		
.10	$n\text{-C}_6\text{H}_5\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \approx 1; 10^2 B \approx 2.4$			$-dA/dt = kAB$	0	2.28	-5				*	(8)
							40	2.51	-3	20.0	2	11		

No.	Reaction	Solvent	Amount of reactant	Added	Amount of added	Defined mass	Temperature	$k \times 10^n$		η	$A = 10^n \times 10^n$		Literature
								k^0	n		A^0	n	
14	$\text{BrCH}_2\text{Br} + 2\text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} \approx 1; 10^2\text{B} \approx 2.4$		$-\text{dA}/\text{dt} = k\text{AB}$	$k\text{AB}$	0 40	7.93 1.00	-8 -3	20.6	2	11	(6)
15	$\text{FCH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} \approx 1; 10^2\text{B} \approx 2.4$		$k\text{AB}$	$k\text{AB}$	0 30	4.79 3.64	-3 -2	12.5	3	10	(6)
16	$\text{ClCH}_2\text{I} + 2\text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} \approx 1; 10^2\text{B} \approx 2.4$		$-\text{dA}/\text{dt} = k\text{AB}$	$k\text{AB}$	0 40	1.33 1.49	-4 -2	13.7	1.8	11	(6)
17	$\text{BrCH}_2\text{I} + 2\text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} \approx 1; 10^2\text{B} \approx 2.4$		$-\text{dA}/\text{dt} = k\text{AB}$	$k\text{AB}$	0 40	8.11 7.93	-5 -3	19.5	3	11	(6)
18	$\text{ICH}_2\text{I} + 2\text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} \approx 1; 10^2\text{B} \approx 2.4$		$-\text{dA}/\text{dt} = k\text{AB}$	$k\text{AB}$	0 40	2.39 2.16	-4 -2	19.2	6	11	(6)
19	$\text{FCH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} = 2-9; 10^2\text{B} = 2-4$		$k\text{AB}$	$k\text{AB}$	0 20 35	4.03 4.95 2.55	-5 -4 -3	20.0	4	11	(7)
20	$\text{ClCH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} = 2-9; 10^2\text{B} = 2-4$		$k\text{AB}$	$k\text{AB}$	0 20 35	4.86 5.61 2.88	-5 -4 -3	19.7	3	11	(7)
21	$\text{FCH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} = 2-9; 10^2\text{B} = 2-4$		$k\text{AB}$	$k\text{AB}$	0 20 35	4.5 5.0 2.43	-5 -4 -3	19.3	1.2	11	(7)
22	$\text{FCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2\text{A} = 1; 10^2\text{B} = 2.4$		$k\text{AB}$	$k\text{AB}$	0 20	1.96 5.20	-4 -3	18.7	2	11	(6)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of added substance	Defined rate action law	Temperature, °C	$k \times 10^7$		B	$A \times 10^{12}$		Concentration	Literature
								k^0	n		A^0	n		
.23	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; 10^2 B \sim 2.4$			k_{AB}	0 23	2.54 7.06	-4 -3	18.6	2	11	*	(8)
.24	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; B \ll A$			k_{AB}	0 20	5.78 5.98	-4 -3	18.7	5	11	*	(8)
.25	$\text{FCH}_2\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; 10^2 B \sim 2.4$			k_{AB}	0 20	1.12 1.04	-3 -2	17.8	2	11	*	(8)
.26	$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; 10^2 B \sim 2.4$			k_{AB}	0 20	1.57 1.36	-3 -2	17.4	1.3	11	*	(8)
.27	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; 10^2 B \sim 2.4$			k_{AB}	0 20	2.18 1.91	-3 -2	17.4	2	11	*	(8)
.28	$\text{ICH}_2\text{CH}_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; B \ll A$			k_{AB}	0 20	4.02 3.62	-3 -2	17.6	5	11	*	(8)
.29	$\text{ClCH}_2(\text{CH}_2)_2\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; 10^2 B \sim 2.4$			k_{AB}	0 20	2.78 2.04	-3 -2	17.2	1.4	11	*	(8)
.30	$\text{ClCH}_2(\text{CH}_2)_3\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{S}^- (\text{Na}^+)$	CH_3OH	$10^2 A \sim 1; 10^2 B \sim 2.4$			k_{AB}	0 20	2.29 1.95	-3 -2	17.1	1.2	11	*	(8)
Halogen-substituted alkenyl halide														
.31	$\text{cis-ClCH=CHCl} + 2p\text{-CH}_3\text{C}_6\text{H}_4\text{S}^- (\text{Na}^+)$	$\text{C}_2\text{H}_5\text{OH}$	$A = 0.13; B = 0.30$	$\text{C}_2\text{H}_5\text{ONa}$	$0.04-0.3$	$-dA/dt = k A [\text{C}_2\text{H}_5\text{ONa}]$	5	1.27	-4	34	4	19	*	(11)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature $k^0 \times 10^n$	$k = k^0 \times 10^n$	R	$A = A^0 \times 10^n$	Comments	Literature
Mono-substituted Aryl halide												
.32	$p\text{-NO}_2\text{C}_6\text{H}_4\text{F} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	CH ₃ OH	$10^2 A = 3; 10^3 B = 6.4$			k AB	35 50 60	5.01 -4 2.17 -3 5.67 -3	19.8	5 10		(2)
.33	$o\text{-NO}_2\text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	D1W 60*	A = B = 0.015			k AB	25	7.7 -5			*	(6)
.34	$p\text{-NO}_2\text{C}_6\text{H}_4\text{Cl} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	D1W 60*	A = B = 0.015			k AB	25	4.5 -4			*	(6)
Di-substituted Aryl halide												
.35	$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{F} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	CH ₃ OH	$10^4 A = 10^4 B = 9$			k AB	0	1.03 +2				(5)
.36	$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Cl} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	CH ₃ OH	$10^3 A = 10^3 B = 4-9$			k AB	0 8 15	3.89 0 6.4 0 1.05 +1				(5)
.37	$2\text{-NO}_2\text{-4-ClC}_6\text{H}_3\text{Cl} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	D1W 60*	A = B = 0.015			k AB	25	3.0 -3			*	(4) (6)
.38	$2\text{-NO}_2\text{-4-FCC}_6\text{H}_3\text{Cl} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	D1W 60*	A = B = 0.015			k AB	0 25	4.37 -2 2.26 -1	10.6	1.4 7		(4)
.39	$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{Br} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	CH ₃ OH	$10^3 A = 10^3 B = 4-9$			k AB	0 8 15	6.7 0 1.1 +1 1.7 +1	9.8	5 8		(5)
.40	$2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{I} + \text{C}_6\text{H}_5\text{S}^-$ (Na ⁺)	CH ₃ OH	$10^3 A = 10^3 B = 4$			k AB	0 8 15	5.2 0 9.3 0 1.4 +1	10.7	2 9		(5)

SOLVENTS

EtSO*

 C_2H_5OH 50 % + H_2O DiH₂SO*60 vol % dioxane + 40 vol % H_2O

COMMENTS

Literature: (7) (6) $\Delta H^\ddagger$ of authors converted to E by adding RT for purpose of comparison.

Reaction: (.2) (.3) (.5) (.7) Structure presented for B is the enolate form favored by (1). (.8) (.9) Reaction followed to about 5%. Parallel solvolysis reaction probably negligible, see 242.471 (.193). Decrease of rate constants with increase in concentration of reactants is of the same order of magnitude as that caused by addition of a neutral salt. Plot of $\log k$ values of (7) (9) versus $1/T$ gave a good straight line from which an average activation energy was determined. (.11) Rate constant calculated on basis of second halogen reacting rapidly after replacement of first halogen. (.12) Rate constant calculated on basis of only Br being replaced. (.13) Rate constant calculated on basis of second halogen reacting rapidly after replacement of first halogen. (.14) Rate constant calculated on basis of second bromine reacting rapidly after replacement of first. Value tabulated is observed rate which is two times the value per halogen of the authors. (.15) Rate constant calculated on basis of only iodine being replaced. (.16) (.17) Rate constant calculated on basis of second halogen reacting rapidly after replacement of first halogen. (.18) Rate constant calculated on basis of second iodine reacting rapidly after replacement of first. Value tabulated is observed rate which is two times the value per halogen listed by the authors. (.19) (.20) Rate constant calculated on the basis of only bromine being replaced. Slight upward drift of rate constant, observed with chloride, eliminated by using excess alkyl halide. (.21) Calculated second order rate constants drift upward due to participation of second bromine. Value tabulated is initial rate obtained by graphical extrapolation to zero time. (.22) (.23) Rate constant calculated on the basis of only bromine being replaced. Second halogen probably contributes very slightly to overall rate constant. (.25) Rate constant calculated on basis of only one bromine reacting as A in large excess. Values tabulated are observed values, or two times the value per halogen listed by authors. (.26) (.27) Rate constant calculated on the basis

COMMENTS

(continued)

of only iodine being replaced. Second halogen probably contributes very slightly to overall rate constant. (.28) Rate constant calculated on basis of only one iodine reacting as A in large excess. Values tabulated are observed values, or two times the value per halogen listed by authors. (.29) (.30) Rate constant calculated on the basis of only iodine being replaced. Second halogen probably contributes very slightly to overall rate constant. (.31) Pseudo first order rate law with respect to A. Second order constant calculated by dividing by the C_2H_5ONa concentration. Authors postulate reaction involves direct elimination of HCl follow by rapid addition to give the dithioalkenylether. High value of "A-factor" probably indicates that this is not the complete rate equation. Reaction deviates from pseudo first order behavior at low concentrations of B. (.33) Spectrophotometric method. "Infinity" samples indicated only 42% of the theoretical amount of sulfide formed. (.34) Value is the average between the spectrophotometric method (higher) and analytical method for following reaction. "Infinity" samples indicated only 69% of the theoretical amount of sulfide formed. (.37) Value is a mean of results of ⁽⁴⁾ ⁽⁹⁾. Spectrophotometric method appears to give higher value.

LITERATURE

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EXCHANGE

Replacement of halogen by thiocyanate

Liquid phase

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



Reaction type:

No.	Reaction	Solvent	Amount of reactant	Defined action law	Temperature	$k = k^0 \times 10^n$		g	$A = A^0 \times 10^n$		Comments	Literature
						k^0	n		A^0	n		
.1	$\text{C}_2\text{H}_5\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.67	-5					(1)
.2	$n\text{-C}_3\text{H}_7\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.15	-5					(1)
.3	$n\text{-C}_4\text{H}_9\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.14	-5					(1)
.4	$(\text{CH}_3)_2\text{CHCH}_2\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	5	-7					(1)
.5	$n\text{-C}_5\text{H}_{11}\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.20	-5					(1)
.6	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	7.3	-6					(1)
.7	$n\text{-C}_6\text{H}_{13}\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.22	-5					(1)
.8	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.23	-5					(1)
.9	$n\text{-C}_7\text{H}_{15}\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.24	-5					(1)
.10	$n\text{-C}_8\text{H}_{17}\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.27	-5					(1)
.11	$n\text{-C}_{10}\text{H}_{21}\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	A = 0.09; B = 0.2	k AB	25	1.23	-5					(1)

No.	Reaction	Solvent	Amount of reactant	Refined base	Temperature	$k \times 10^n$ k^0	$k = 10^n$ k^0	β	$A = 10^n$ A^0	Comments	Literature
.12	$m\text{-C}_6\text{H}_4\text{Br} + \text{NaSCN}$	95% $\text{C}_2\text{H}_5\text{OH}$	$A = 0.03; B = 0.2$	R AB	25	1.20	-5				(1)
Aryl halide											
.13	2-NO ₂ -4-HC(OC ₆ H ₃ I) + KSCN	CH ₃ OH	$A = B = 0.05$	R AB	100 111 132	2.41 5.61 2.38	-4 -4 -3		1.6 21.8	*	(2)
.14	2-NO ₂ -4-CH ₃ C(OC ₆ H ₃ I) + KSCN	CH ₃ OH	$A = B = 0.05$	R AB	111 131 138	2.30 9.06 1.38	-4 -4 -3		3 21.3	*	(2)
.15	2-NO ₂ -4-N(OC ₆ H ₃ I) + KSCN	CH ₃ OH	$A = B = 0.05$	R AB	82 100 131	3.5 3.88 3.70	-5 -4 -3		1.0 21.2	*	(2)
.16	2,4-(NO ₂) ₂ C ₆ H ₃ I + KSCN	CH ₃ OH	$A = B = 0.05$	R AB	60 82 100	1.52 8.42 3.31	-4 -4 -3		2 20.0	*	(2)

COMMENTS

Reactions: (.13) (.14) (.15) (.16) Produce in addition to thiocyanates, diarylsulfides and some disulfides.

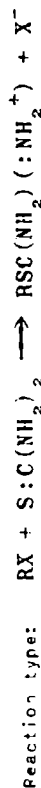
LITERATURE

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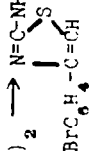
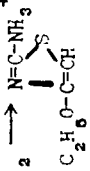
EXCHANGE
Replacement of halogen by S of thiourea

Liquid phase

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



No.	Reaction	Solvent	Amount of reactant	Defined mass	Temperature	$k \times 10^3$	k^0	$k^0 \times 10^3$	R	$A^0 \times 10^3$	Literature
1	$(CH_3)_2C:CHCH_2Cl + S:C(NH_2)_2 \longrightarrow (CH_3)_2C:CHCH_2SC(NH_2)(:NH_2^+) + Cl^-$	$(CH_3)_2CO$	$10^2A=2; 10^2B=7$	k_{AB}	45 75	5.3 3.3	-4 -3	14	1.4	6	(2)
2	$CH_2:CH(CH_3)_2CCl + S:C(NH_2)_2 \longrightarrow CH_2:CH(CH_3)_2CSC(NH_2)(:NH_2^+) + Cl^-$	$(CH_3)_2CO$	$10^3A=3-30; 10^2B=7$	k_{AB}	45 75	2.56 3.22	-5 -4	19	1.8	8	(2)
3	$CH_3CH_2Br + S:C(NH_2)_2 \longrightarrow CH_3CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		k_{AB}	35	7.2	-5				(1)
4	$CH_3CH_2CH_2Br + S:C(NH_2)_2 \longrightarrow CH_3CH_2CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		k_{AB}	35	4.7	-5				(1)
5	$CH_3CH_2CH_2Br + S:C(NH_2)_2 \longrightarrow CH_3CH_2CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		k_{AB}	35	5.5	-3				(1)
6	$C_6H_5CH_2Br + S:C(NH_2)_2 \longrightarrow C_6H_5CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		k_{AB}	35	1.40	-2				(1)
7	$HCOCH_2CH_2Br + S:C(NH_2)_2 \longrightarrow HCOCH_2CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		k_{AB}	35	8.0	-6				(1)
8	$C_6H_5OCH_2CH_2Br + S:C(NH_2)_2 \longrightarrow C_6H_5OCH_2CH_2SC(NH_2)(:NH_2^+) + Br^-$	CH_3OH		k_{AB}	35	8.8	-6				(1)
9	$C_6H_5C:OCH_2CH_2Br + S:C(NH_2)_2 \longrightarrow N=C(NH_2)^+ + H_2O + Br^-$ $C_6H_5-C \equiv CH$	CH_3OH	$10^2A=10^2B=2-5$ $10^3A=8.7; 10^2B=2.6$ 8.5 15 3.5 13.5	k_{AB} k_{AB}	0 0 0 0	4.3 3.5 3.2 2.9	-2 -2 -2 -2			*	(1) (1) (1) (1)

No.	Reaction	Solvent	Amount of reactant	Defined mass-action law	Temperature	$k \times 10^3$		$A \times 10^3$		Literature
						k^0	n	A^0	n	
.10	$2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2\text{C}:\text{OCH}_2\text{Br} + \text{S}=\text{C}(\text{NH}_2)_2 \longrightarrow 2,4,6-(\text{CH}_3)_3\text{C}_6\text{H}_2\text{C}:\text{OCH}_2\text{SC}(\text{NH}_2)_2 + \text{Br}^- + \text{CH}_3\text{OH}$	CH_3OH		k_{AB}	35	6.7	-4			(1)
.11	$\text{BrC}_6\text{H}_4\text{C}:\text{OCH}_2\text{Br} + \text{S}=\text{C}(\text{NH}_2)_2 \longrightarrow \text{N}=\text{C}-\text{NH}_2 + \text{H}_2\text{O} + \text{Br}^-$ 	CH_3OH		k_{AB}	35	7.7	-1			(1)
.12	$\text{C}_2\text{H}_5\text{OOCCH}_2\text{Br} + \text{S}=\text{C}(\text{NH}_2)_2 \longrightarrow \text{N}=\text{C}-\text{NH}_2 + \text{H}_2\text{O} + \text{Br}^-$ 	CH_3OH		k_{AB}	35	3.0	-2			(1)

COMMENTS

No measurable reaction observed with fully substituted thioureas. Reaction (.9) addition of H_2O at 1 M or $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$ at 0.025 M caused no measurable change in rate of reaction. Addition of .007 M KBr may have increased rate slightly.

LITERATURE

- (1) R.G. Pearson, S.H. Langer, F.V. Williams, W.J. McGuire, *ACS* 1952, 74, 5180.
 (2) J.M. Rule, I.J. Wilk, T.I. Wrigley, W.G. Young, *ACS* 1957, 79, 6528.

EXCHANGE

Halogen for halogen on aliphatic carbon

Liquid phase

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

Reaction types:



Coded solvents at end
of table.

No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action la	Temperature	$k \times 10^n$ k^0 n	$k \times 10^n$ k^0 n	$A^0 \times 10^n$ A^0 n	Comments	Literature
.71	$CH_3Br + Cl^{-}$	$(CH_3)_2CO$	$A = 0.12; B = 0.05$	Li^{+}	$= B$	k_{AB}	0.0 12.0 24.8 34.0	5.20 1.75 5.92 1.29	-4 -3 -3 -2			* (26)
.72	$CH_3Br + I^{-}$	$(CH_2OH)_2$	$10^2 A = 4-5; 10^2 B = 3-10$ 4 3-5 4 10 4 4 4 4			k_{AB}	15 25 25 35 45	1.13 3.28 2.90 8.76 2.17	-3 -3 -3 -3 -2	2 9		* (37)
		$(CH_3)_2CO$	$10^2 A = 4; 10^2 B = 2$	Li^{+}	$= B$	k_{AB}	-11 0 10 -20 -11	5.82 2.19 8.15 2.73 7.3	-3 -2 -2 -3 -3	5 10		(18) (13) (38)
				Na^{+} or K^{+}	$= B$		0 10 20	2.66 6.9 2.23	-2 -2 -1	2 3 1.9 11		(16) (28) (18) (16) (28)

No.	Supplementing 1956	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$	δ	$A =$ $A^0 \times 10^n$	Comments	Literature
.73		$\text{CH}_3\text{I} + \text{Cl}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A \sim 6; 10^2 B = 3$	LiClO_4	0.11	k_{AB}	-10 0 14 25 34	1.29 3.79 1.80 4.60 9.64	-4 -4 -3 -3 -3		*	(30)
.74	.2	$\text{CH}_3\text{I} + \text{Br}^-$	H_2O	$A = 0.08; B = 0.1$ $I = 0.08; M = 0.15$			k_{AB}	20 35 51 67	2.69 1.35 6.70 2.41	-5 -4 -4 -3	18.0 2.5 6 9	*	(36)
			$(\text{CH}_2\text{OH})_2$	$10^2 L = 4-5; 10^2 M = 3-10$ 4 4 4			k_{AB}	15 25 25 35 45	6.0 2.13 1.89 6.90 2.05	-5 -4 -4 -4 -3	21.4 1.1 12	*	(37)
			$(\text{CH}_3)_2\text{CO}$	$10^2 A = 4; 10^2 B = 2.3$	Li^+	$= B$	k_{AB}	-11 0 8 16	1.16 3.94 9.60 2.19	-2 -2 -2 -1	16.3 2.5 11	*	(18)
.75	.3	$\text{C}_2\text{H}_5\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; B = 0.04$			k_{AB}	50 60	6.5 1.2	-5 -4		*	(10)
.76		$\text{C}_2\text{H}_5\text{Br} + \text{Cl}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.12; B = 0.07$	Li^+	$= B$	k_{AB}	25 35 45 55 65	9.88 2.43 6.17 1.50 3.14	-5 -4 -4 -3 -3	17.6 6 8 8	*	(28)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^0 η	$A =$ $A^0 \times 10^n$ A^0 η	Comments	Literature
.77		$C_2H_5Br + I^-$	$(CH_3)_2CO$	$10^2 A = 5; 10^2 B = 7$ 4 2 5 7 4 2 " " " "	Li^+	$= B$	k_{AB}	0 17 20 32 40 50	6.1 -5 7.14 -4 6.5 -4 3.52 -3 7.94 -3 2.07 -2	1.0 11	*	(14) (16) (14) (16)
.78		$C_2H_5I + Cl^-$	$(CH_3)_2CO$	$10^2 A = 4-30; 10^2 B = 2-4$ 4 2 " " " " 4 3 " "	$Na^+ \text{ or } K^+$ Na^+ K^+	$= B$ $= B$	k_{AB}	0 20 30 40 64 64	1.4 -4 1.16 -3 3.25 -3 8.90 -3 6.9 -2 4.8 -2	1.6 11	*	(28) (18) (28) (18) (14)
.79		$C_2H_5I + Br^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 3.2$	$LiClO_4$	0.11	k_{AB}	14 25 35 46 54	1.40 -4 4.30 -4 1.13 -2 2.75 -3 5.28 -3	1.3 9	*	(30)
.80	.7	$n-C_3H_7Cl + I^-$	$(CH_3)_2CO$	$A \sim 2; 10^2 B = 1.5-2$ 0.2 4 " " ~2 1.5-2	K^+ K^+	$= B$	k_{AB}	16 25 32 40 50 60 60	6.15 -3 1.49 -2 3.02 -2 5.95 -2 4.8 -6 2.8 -5 4.6 -5 1.03 -4	1.3 11 3 9	*	(10) (10) (16)

No.	Supplement No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined rate action law	Temperature	$k \times 10^n$ k° η	$\bar{k}$	$A \times 10^n$ A° η	Comments	Literature
.81	.8	$(\text{CH}_3)_2\text{CHCl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.25 \cdot 10^2 B = 4$ ~ 2 ~ 2	I^+		k_{AB}	60 60 80	9.4 -7 1.32 -6 1.24 -5	25	6 10	*	(10) (16)
.82		$n\text{-C}_3\text{H}_7\text{Br} + \text{Cl}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.12; 10^2 B = 7$	Li^+	$= B$	k_{AB}	25 35 44 55 65	6.45 -5 1.64 -4 4.10 -4 1.06 -3 2.15 -3	17.5 4 8		*	(28)
.83		$n\text{-C}_3\text{H}_7\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A = 4; 10^2 B = 2$	Li^+	$= B$	k_{AB}	25 35 45 25 35 45	1.37 -3 4.09 -3 1.08 -2 1.45 -3 4.24 -3 1.18 -2	19.0 1.3 11		*	(18)
					Na^+	$= B$		25 35	1.45 -3 4.24 -3				
					K^+	$= B$		25 35 45	1.49 -3 4.10 -3 1.12 -2	19.6 4 11			
.84		$(\text{CH}_3)_2\text{CHCl} + \text{Cl}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.12; 10^2 B = 7$	Li^+	$= B$	k_{AB}	35 45 55 65 80	5.22 -6 1.42 -5 3.49 -5 7.96 -5 2.42 -4	19.5 3 11		*	(29)
.85		$(\text{CH}_3)_2\text{CHBr} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A = 4; 10^2 B = 2$	Li^+	$= B$	k_{AB}	40 50 60	6.70 -5 1.87 -4 4.99 -4	20.5 1.4 10		*	(18)

HOMOGENEOUS REACTION KINETICS

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No.	Indexing No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass	Temperature	$k^0 \times 10^n$	k^0	n	$A^0 \times 10^n$	A^0	n	Comments	Literature
.85		$(CH_3)_2CHBr + I^-$ (continued)	$(CH_3)_2CO$	$10^2 A \sim 300$; $10^2 B \sim 2$ 4	K^+ Na^+ or K^+	B	AB	30 40 50 60 80	2.58 0.8 1.92 3.10 7.3	-5 -5 -4 -4 -4	-5 -5 -4 -4 -4	1.5 10 2 11			*	(16) (18)
.86		$n-C_4H_9I + Cl^-$	$(CH_3)_2CO$	$10^2 A \sim 6$; $10^2 B = 3.2$	K^+ $LiClO_4$	0.11	AB	14 25 35 46 55	7.83 2.46 6.11 1.64 3.47	-5 -4 -4 -3 -2	-5 -4 -4 -3 -2	17.0			*	(16) (20)
.87		$n-C_4H_9I + Br^-$	$(CH_3)_2CO$	$10^2 A = 4$; $10^2 B = 2.3$	Li^+	B	AB	-6 8 26 37	3.07 1.70 1.18 2.44	-4 -3 -2 -2	-4 -3 -2 -2	17.5			*	(19)
.88		$(CH_3)_2CHI + Cl^-$	$(CH_3)_2CO$	$10^2 A \sim 6$; $10^2 B = 3.2$	$LiClO_4$	0.11	AB	25 35 46 55 64	1.26 3.48 3.63 2.03 4.23	-5 -5 -5 -4 -4	-5 -5 -5 -4 -4	18.0			*	(20)
.89		$(CH_3)_2CHI + Br^-$	$(CH_3)_2CO$	$10^2 A = 4$; $10^2 B = 2.3$	Li^+	B	AB	40 50 60 70	1.71 4.33 1.03 2.23	-3 -3 -2 -2	-3 -3 -2 -2	19.5			*	(19)

No.	Supplemental entry No.	Reaction	Solvent	Amount of reactant	Ascend (valence)	Amount of catalyst	Reaction law	Temperature	$k \times 10^n$	k^0	n	$\bar{r}$	$A = A^0 \times 10^n$	Comments	Literature
.90	.12	$n-C_4H_9Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 3$	I^-	B	k_{AB}	20	8.45		-7				(13)
				$0.04-0.07$				30	3.42		-6				
				0.2				40	1.30		-5				
								50	0.12		-5				(15)
								60	0.5		-5				(10), (11), (12)
								60	0.5		-5				
.91		$(CH_3)_2CH_2Cl + Br^-$	Me_2CO^*	$L = M = 0.07$	Li^+	M	k_{AB}	69	1.2		-6				(45)
.92	.23	$CH_3CH_2(CH_2)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	I^-	B	k_{AB}	60	1.4		-6				(10)
.93	.15	$(CH_3)_3COI + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	I^-	B	k_{AB}	60	1.15		-6				(10)
.94		$n-C_4H_9Br + Cl^-$	Me_2CO^*	$A = B = 0.07$	Li^+	B	k_{AB}	40	2.15		-5				(45)
								55	3.70		-5				
								69	3.51		-4	10.0	2.0		
.95		$n-C_4H_9Br + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	I^-	B	k_{AB}	15	4.07		-4				(48)
								25	1.30		-3				
				0.06				25	1.90		-3				(1)
				0.2				25	3.18		-3	16.6	2		(48)
.96		$(CH_3)_2CHCH_2Br + Cl^-$	$(CH_3)_2CO$	$A = 0.12 \times 10^2 B = 7$	Li^+	B	k_{AB}	25	1.53		-5				(20)
								35	4.03		-5				
								44	1.04		-4				
								55	2.97		-4	16.1	2.5		
								40	1.12		-6				(45)
								55	0.31		-6				
								69	2.49		-5	21.7	1.8		

Heterogeneous Reaction Kinetics

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No.	Supplementing Ref. No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass ratio	Temperature	$k^0 \times 10^n$ k^0 n	R $A^0 \times 10^n$ A^0 n	Comments	Literature
37		$(CH_3)_2CHCH_2Br + I^-$	$(CH_3)_2CO$	$10^2 A = 4; 10^2 B = 2$	$Li^+, Na^+ \text{ or } K^+$	= 3	k_{AB}	40 50 60	3.15 8.44 2.18	-4 -4 -3	1.9 10	(18) *
38		$(CH_3)_3CBr + I^-$	SO_2	$10^2 A = 3-8; 10^2 B = 1.1$ 2.1 4.0 6.0 7.4	$(CH_3)_4N^+$	= B	k_{AB}	-15 -15 -15 -15 -15	5.92 6.37 7.52 1.06 1.15	-5 -5 -5 -4 -4		(18) *
39		$(CH_3)_3CBr + Cl^-$	$(CH_3)_2CO$	$A = 0.12; 10^2 B = 7$	Li^+	= B	k_{AB}	44 55 65	2.7 7.6 1.94	-6 -6 -5	8 8	(29) *
40		$(CH_3)_3CBr + I^-$	$(CH_3)_2CO$	$10^2 A = 4; 10^2 B = 2$	K^+	= B	k_{AB}	55 45 52 61	3.6 1.06 2.26 5.63	-6 -5 -5 -5		(18) *
41		$(CH_3)_3CBr + ICl$ $\longrightarrow (CH_3)_3CCl + IBr$ $\longrightarrow$ (mixed dihalides)	CCl_4	$A = 0.34; 10^3 B = 2-10$ 0.17 0.086 0.043 0.032			$-dB/dt = k_B^2$ $-dB/dt = 1.43 \text{ dy/dt}$	25 25 25 25 25	2.3 1.02 1.15 7.85 3.70	-1 -1 -1 -2 -2		(32) *
42		$(CH_3)_2CHCH_2I + Cl^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 3.2$	$LiClO_4$	0.11	k_{AB}	26 35 45 55 64	1.71 4.16 1.04 2.58 5.67	-5 -5 -4 -4 -4	2 8	(30) *

No.	Supplement No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of added	Defined base	Temperature	$k \times 10^2$ k^0 n	k	$A \times 10^2$ A^0 n	Comments	Literature
103		$(CH_3)_2CHCH_2I + Br^-$	$(CH_3)_2CO$	$10^2A = 4; 10^2B = 2.3$	Li^+	$= B$	k_{AB}	37 49 60 75	1.19 3.60 9.62 2.72			*	(19)
104	16	$n-C_8H_{17}Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	50 60	3.5 8.1			*	(10) (10) (11)
105	17	$(CH_3)_2CHCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	60	4.4			*	(10)
106	18	$CH_3CH_2CH_2(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	60	3.1			*	(10)
107		$C_2H_5CH(CH_3)CH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 6; 10^2B = 2$	K^+	$= B$	k_{AB}	25	1.10				(1)
108		$(CH_3)_3CCH_2Br + Cl^-$	$(CH_3)_2CO$	$A = 0.12; 10^2B = 7$	Li^+	$= B$	k_{AB}	100 110 120 130	4.25 8.51 1.74 3.47			*	(28)
109		$(CH_3)_3CCH_2Br + I^-$	$(CH_3)_2CO$	$10^2A = 5; 10^2B = 7$ 4 2	$Li^+, Na^+ \text{ or } K^+$	$= B$	k_{AB}	64 65 73 91 90 98	2.6 4.4 1.02 2.3 5.31 1.14			*	(14) (18)
110		$(CH_3)_3CCH_2I + Cl^-$	$(CH_3)_2CO$	$10^2A = 6; 10^2B = 3.2$	$LiClO_4$	0.11	k_{AB}	80 100 110 120	1.89 1.02 2.17 4.57			*	(30)

Bimolecular Reaction Kinetics

250-771

No.	Reference	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^n$	β	$A = A^0 \times 10^n$	Comments	Temperature	
111	19	$(CH_3)_3COH + Br^-$	$(CH_3)_2CO$	$10^2 A = 4; 10^2 B = 0.5$	Li^+	$= B$	k_{AB}			25.1	1.3	10	*	(19)
112	19	$p-C_6H_4Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50	3.34	-5		*	(10)	
113	30	$C_2H_5CH_2CH_2(CH_3)COCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	8.15	-5	19	*	(10)	
114		$C_2H_5CH_2(C_2H_5)COCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	5.25	-6		*	(10)	
115	101	$C_2H_5CH_2(CH_3)_2COCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	2.91	-6		*	(9)	
116		$(CH_3)_3COH_2C_2Br + I^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 2$	K^+	$= B$	k_{AB}	25	1.84	-6		*	(10)	
117	101	$p-C_6H_4Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50	7.3	-5		*	(1)	
118		$p-C_6H_4Br + I^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 2$	K^+	$= B$	k_{AB}	60	3.2	-5	19	*	(10)	
119		$(CH_3)_3COH_2C_2Br + I^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 2$	K^+	$= B$	k_{AB}	25	2.14	-3			(1)	
120		$p-C_6H_4Br + I^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 2$	K^+	$= B$	k_{AB}	25	1.90	-3			(1)	
121	101	$p-C_6H_4Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50	3.5	-5		*	(10)	
122		$p-C_6H_4Br + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	8.5	-5	19	*	(10)	
123	101	$CH_3(CH_2)_5(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	1.7	-6		*	(10)	
124	101	$p-C_6H_4Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50	3.0	-5		*	(10)	
125	101	$p-C_6H_4Br + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	6.4	-5	17	*	(10)	
126	101	$p-C_6H_4Br + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50	2.5	-5		*	(10)	
127	101	$p-C_6H_4Br + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	6.2	-5	19	*	(10)	

No.	Supplementing Year	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$ k^0 n	β	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
Cyclo alkyl halide													
.104	.28	$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	50	2.3 -5			*	(10)
								60	5.8 -5	19			
.105	.29	$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	50	2.3 -5	19		*	(10)
								60	5.8 -5				
.106		$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.18 \times 10^2 B = 3.4$	K^+	$= B$	k_{AB}	100	(no measurable reaction)				(43)
.107		$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.18 \times 10^2 B = 4$				75	3.08 -5			*	(17)
								80	5.84 -5				
								92	1.86 -4				(17)(43)
								99	3.58 -4				(17)
								110	9.04 -4	24.5	9 10		
.108		$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$L = 0.18 \times 10^2 B = 4$			k_{AB}	75	6.14 -4			*	(17)
								80	1.02 -3				
								92	2.62 -3				
								99	4.62 -3				
								110	9.51 -3	19.9	2.2 9		
.109		$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$		K^+	$= B$	k_{AB}	58	1.95 -6			*	(6)
.110		$\text{C}_6\text{H}_5\text{I} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.18 \times 10^2 B = 4$			k_{AB}	76	7.39 -5			*	(17)
								88	6.22 -4				(17)(43)
								69	1.69 -3				(17)
								76	3.73 -3	20.4	2.6 10		

No.	Supplementing literature	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$ k^n	δ	$A \times 10^n$ A^n	Comments	Literature
131	1951	$\text{CH}_2(\text{CH}_2)_3\text{CH}_2 + \text{Br}^-$	$(\text{CH}_3)_2\text{CO}$	$L = 0.13; 10^2 M = 4$			k_{AB}	36 58 69 78	1.06 7.35 1.82 3.76	-3 -3 -2 -2			(17)
132		$\text{CH}_2(\text{CH}_2)_4\text{CH}_2 + \text{Cl}^-$ $\rightarrow \text{C}_6\text{H}_{11}\text{Cl} + \text{Br}^-$ $\rightarrow \text{C}_6\text{H}_{10} + \text{HBr} + \text{Cl}^-$	An 90*	$A \approx B \approx 0.07$	Li^+	B	$-dA/dt = k_{AB}; k = k_s + k_t$	69 69	2.69 $k_s = 1.3$	-6 -6	18.6	1.4	(45)
133		$\text{CH}_2(\text{CH}_2)_4\text{CH}_2 + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.06; 10^2 B = 2$.13 4	K^+ ...	B	k_{AB}	60 73 89 99 110	2.40 3.21 1.44 3.22 9.08	-5 -5 -4 -4 -4		*	(1) (17) (17) (43) (17)
134		$\text{CH}_2(\text{CH}_2)_4\text{CH}_2 + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$L = 0.13; 10^2 M = 4$			k_{AB}	73 89 99 110	6.98 2.86 8.11 1.45	-4 -3 -3 -2	23.5	2.1	(17)
135		$\text{CH}_2(\text{CH}_2)_4\text{CH}_2 + \text{Br}^- + \text{Cl}^-$	An 90*	$A = B = 0.07$	Li^+	B	k_{AB}	40 55 69	8.86 4.84 1.97	-7 -6 -5	6		(45)
136		$\text{CH}_2(\text{CH}_2)_5\text{CH}_2 + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.13; 10^2 B = 4$			k_{AB}	37 48 58 73	4.71 1.43 3.95 1.53	-5 -4 -4 -3	22.3	3	(17)
											20.4	1.1	20

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No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass	Temperature	$k^0 \times 10^n$	E	$A = A^0 \times 10^n$	Comments	Literature
.137		$\text{CH}_2(\text{CH}_2)_3\text{Br} + \text{Br}^-$	$(\text{CH}_3)_2\text{CO}$	$L = 0.13 \times 10^{-2} M = 4$			k_{AB}	37	7.23	-4		*	(17)
.138		$\text{CH}_2(\text{CH}_2)_4\text{CHCH}_2\text{CH}_2\text{Cl} + \text{Br}^-$	An 90*	$L = M = 0.07$	Li^+	$= M$	k_{AB}	48	1.93	-3			
.139		$\text{H}_2(\text{CH}_2)_4\text{CHCH}_2\text{CH}_2\text{Br} + \text{Cl}^-$	An 90*	$A = B = 0.07$	Li^+	$= B$	k_{AB}	58	4.78	-3			
.140		$\text{CH}_2(\text{CH}_2)_6\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.13 \times 10^{-2} B = 4$		$= B$	k_{AB}	73	1.62	-2	18.2	9	
.141		$\text{CH}_2(\text{CH}_2)_6\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$L = 0.13 \times 10^{-2} M = 4$		$= B$	k_{AB}	55	~ 7	-7		*	(45)
.142		$\text{CH}_2(\text{CH}_2)_6\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.13 \times 10^{-2} B = 4$		$= B$	k_{AB}	40	1.70	-5		*	(45)
.143		$\text{C}_{10}\text{H}_{17}\text{Cl} + \text{I}^-$ (bornyl chloride)	$(\text{CH}_3)_2\text{CO}$	$A \sim 2 \times 10^{-2} B = 1-4$	K^+	$= B$	k_{AB}	56	6.17	-5			
.144		$\text{HOCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$		$= B$	k_{AB}	69	2.21	-4	20.3	2	
.145		$\text{CH}_3\text{OCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$		$= B$	k_{AB}				21.2	1.0	
.146		$\text{HOCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$		$= B$	k_{AB}				19.5		
.147		$\text{CH}_3\text{OCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$		$= B$	k_{AB}	80	< 1	B		*	(16)
Hydroxy substituted alkyl halide													
.148		$\text{HOCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$	K^+	$= B$	k_{AB}	50	4.5	-5		*	(33)
.149		$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$	K^+	$= B$	k_{AB}	60	1.29	-4	22	6	
.150		$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$	K^+	$= B$	k_{AB}	35	1.00	-5		*	(33)
.151		$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$	K^+	$= B$	k_{AB}	45	3.13	-5	22	4	
Alkoxy substituted alkyl halide													
.152		$\text{CH}_3\text{OCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$	K^+	$= B$	k_{AB}	0	~ 1.2	-4		*	(12)
.153		$\text{CH}_3\text{OCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^{-2} B = 4$	K^+	$= B$	k_{AB}	10	~ 3.9	-4			

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k \times 10^7$ k^0 n	β	$A \times 10^7$ A^0 n	Comments	Literature
Keto-substituted alkyl halide													
.136		$\text{CH}_3\text{OCH}_2\text{CH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	15 25	5.47 1.67 -4	19	1 10	*	(48)
.137		$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	35	9.8 -7			*	(48)
.138		$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	25	1.6 -4			*	(48)
.139		$n\text{-C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	15 25 35	4.90 1.46 3.82 -4	18.2	3 9	*	(48)
Carboxy-substituted alkyl halide													
.140	.10	$\text{CH}_3\text{COOCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	0 10	4.8 1.8 -2	20	5 13	*	(12)
.151	.9	$\text{C}_2\text{H}_5\text{OOCCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	25	6.0 -5			(10) (11) (12)	
.152	.11	$\text{C}_2\text{H}_5\text{OOCCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A = 6; 10^2 B = 1.5$ 20 4	K^+	$= B$	k_{AB}	0 20 25 30	3.78 3.55 4.05 6.68 -3	1.9 17.1	10 10	* * (10) (11) (12)	(36)
.153		$\text{C}_2\text{H}_5\text{OOCCH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^3 A = 6; 10^2 B = 5$	K^+	$= B$	k_{AB}	0 20	5.34 2.77 -1	11.5	9 8	*	(36)
.154	.6	$\text{NH}_2\text{COCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	25 30 50	2.3 3.8 2.53 -4	18.3	6 9	*	(12)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined class	Temperature	$k \times 10^2$	ρ	$A = A^0 \times 10^2$	Comments	Literature
.155		$C_2H_5OOCCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	50	4.26	-5		*	(11)
.156		$C_2H_5OOC(CH_3)CHBr + I^-$	$(CH_3)_2CO$	$10^2A = 6; 10^3B = 5$	K^+	$= B$	k_{AB}	0 20	8.22 7.73	-4 -3	1.5	*	(36)
.157		$C_2H_5OOCCH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	50	4.39	-5		*	(11)
.158		$C_2H_5OOCCH_2(CH_2)_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	50	3.60	-5		*	(11)
.159		$l-HOOCCH_2(COOH)CHCl + Br^-$	H_2O	$A = 0.18; B = 2$			k_{AB}	50 62 75 88	7.25 2.76 9.83 3.54	-7 -6 -6 -5	9	* (41) (42)	
.160		$l-HOOCCH_2(COOH)CHBr + Cl^-$	H_2O	$A = 0.18; B = 2$			k_{AB}	50 62 75 88	3.88 1.45 5.50 1.88	-6 -5 -5 -4		* (41) (42)	
.161	.23	$(C_2H_5OOC)_2CHCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	0 10	8.3 1.5	-3 -2		*	(12)
Carboxylate-substituted alkyl halide													
.162	.11	$CH_3OOCCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	20 30	3.7 6.2	-4 -4	1	*	(12)
.163		$C_6H_5OOCCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	25 35	1.1 2.08	-4 -4	12	*	(33)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined base	Temperature	$k = k^0 \times 10^4$	B	$A = A^0 \times 10^4$	Comments	Temperature
									k^0	n	A^0	n	
Nitrile substituted alkyl halide													
.166	.5	$\text{CNCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	10 20	1.42 4.5	-3 -3		*	(12)
Silyl-substituted alkyl halide													
.167		$(\text{CH}_3)_3\text{SiCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 3$	K^+	$= B$	k_{AB}	20 30 40 50	2.22 7.45 2.26 3.33	-5 -5 -4 -4	1.2 11	*	(13)
.168		$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A \approx 4; 10^2 B \approx 2$	K^+	$= B$	k_{AB}	50	1.88	-4	20	*	(15)
.169		$p\text{-CH}_3\text{C}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A \approx 4; 10^2 B \approx 2$	K^+	$= B$	k_{AB}	50	1.47	-4	21	*	(15)
.170		$p\text{-CH}_3\text{OC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A \approx 4; 10^2 B \approx 2$	K^+	$= B$	k_{AB}	50	1.45	-4	22	*	(15)
.171		$p\text{-ClC}_6\text{H}_4(\text{CH}_3)_2\text{SiCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A \approx 4; 10^2 B \approx 2$	K^+	$= B$	k_{AB}	50	4.31	-4	21	*	(15)
.172		$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 3$	K^+	$= B$	k_{AB}	30 30 40	1.05 3.30 1.07	-5 -5 -4	7 10	*	(13)

No.	Supplementing No. 1951	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^3$	k^0	β	$A^0 \times 10^3$	Comments	Literature	
173		$\text{ClSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 3$	K^+	$= B$	k_{AB}	30 30 40	5.86 1.97 6.30	-6 -5 -5	21.5	6	10	*	(13)
Alkyl thio-substituted alkyl halide															
174		$\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	50 60	4.02 1.07	-5 -4	21	5	9	*	(34)
175		$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	50 60	6.68 1.52	-5 -4	17			*	(34)
Halogen-substituted alkyl halide															
176		$\text{ClCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A \sim 0.3 \times 10^2 B \sim 4$	Na^+	$= B$	k_{AB}	50 60	4.22 1.68	-6 -5	29	2	14	*	(28)
177		$\text{ICH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A \sim 0.3 \times 10^2 B \sim 4$	Na^+	$= B$	k_{AB}	50	1.55	-6					(28)
178		$\text{ICH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A \sim 0.3 \times 10^2 B \sim 4$	Na^+	$= B$	k_{AB}	20 50	6.4 1.36	-4 -2	19	1.0	11		(28)
179		$\text{ClCH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A \sim 0.3 \times 10^2 B \sim 4$	Na^+	$= B$	k_{AB}	20 30 50	7.3 4.77 2.18	-5 -4 -3	30.9	2.8	11		(28)
180		$\text{BrCH}_2\text{Br} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A \sim 0.3 \times 10^2 B \sim 4$	Na^+	$= B$	k_{AB}	20 36 50	4.06 3.20 1.38	-5 -4 -3	22	1.1	12	*	(28)

No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass	Temperature	$k =$		ρ	$A =$ $k^0 \times 10^n$	Comments	Literature
								k^0	n				
121	$(CH_3)_2CH_2Br + I^-$	$(CH_3)_2CO$	$A \approx 0.3 \times 10^2 B \approx 4$	Na^+	$= B$	k_{AB}	20 50	5 1.0	-5 -3	18	1 9		(28)
122	$(CH_3)_2CH_2Br + I^-$	CH_3OH	$10^2 A = 9; 10^2 B = 6$	K^+	$= B$	k_{AB}	40	5.5	-4				(27)
123	$BrCH_2CH_2Br + I^- \longrightarrow$ (elimination see 422,477,1)												(27)
124	$(CH_3)_2CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A \approx 0.3 \times 10^2 B = 1-4$	K^+	$= B$	k_{AB}	60 80	1.44 1.00	-6 -5	22	4 8	*	(16)
125	$CH_3CH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A \approx 0.3 \times 10^2 B = 1-4$	K^+	$= B$	k_{AB}	60 80	9.9 5.42	-6 -5	19	3 7	*	(16)
Unsaturated alkenyl halide													
126	$CH_2=CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.3 \times 10^2 B = 3.7$ 0.2 4 0.1 2 0.04 2	K^+	$= B$	k_{AB}	0 20 25 25	2.28 1.41 3.18 2.6	-5 -4 -4 -3	15	1 7	* (22), (47) (44)	(6)
127	$CH_3CH=CHCl + I^-$	$(CH_3)_2CO$	$A = 0.3 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	20	< 1	-6			*	(23)
128	$CH_2=CHCH_2Br + I^-$	$(CH_3)_2CO$	$10^2 A = 1.8; 10^2 B = 1$	K^+	$= B$	k_{AB}	25	1.22	-1				(1)
129	$CH_3CH=CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.3 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	20	3.41	-4			*	(47)
130	$CH_2=CH(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.3 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	20	2.23	-4			* (22), (47)	(22)
131	$CH_3CH(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$		K^+	$= B$	k_{AB}	20 50	1.4 3.1	-6 -5	24	3 11	*	(40)

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Reaction mass	Temperature °C	$k \times 10^n$ k^0 n	δ $A^0 \times 10^n$ n	Comments	Literature
192		$(CH_3)_2C=CHCH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	$k AB$	20	4.6 -3		*	(21)
193		$cis-CH_3CH=CHC(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	$k AB$	20	7.4 -4		*(24); (47)	
194		$trans-CH_3CH=CHC(CH_3)CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	$k AB$	20	5.3 -3			(24)
Unsaturated alkynyl halide												
195		$CH_3CH_2CH_2CH_2C\equiv CH_2Br + I^-$	$(CH_3)_2CO$	$10^2 A = 1.5; 10^2 B = 1$	K^+	$= B$	$k AB$	25	6.9 -2			(1)
196		$(CH_3)_3CC\equiv CH_2Br + I^-$	$(CH_3)_2CO$	$10^2 A = 1.5; 10^2 B = 1$	K^+	$= B$	$k AB$	25	8.7 -2		*	(1)
Aryl-substituted alkyl halide												
197	30	$C_6H_5CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$ ~ 2 2-4 0.2 4 0.16 3-4 0.08 3 0.02 0.4 ~ 2 2-4 0.2 4 " "	K^+	$= B$	$k AB$	0 20 25 25 25 25 30 30 50	3.35 3.39 5.0 5.8 1.0 1.2 9.5 3.4 5.0	-4 -4 -4 -4 -3 -2 -4 -4 -3	* (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12)	(8a) (10) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12) (10) (11) (12)
198		$C_6H_5CH_2Br + I^- \longrightarrow$ $C_6H_5H_2Cl + I^-$	$CHCl_3$	$10 A = 1-4; 10^2 B = 2-4$ B			$k AB^2$	25 25	1.98 2.43	-2 -2	*	(31)
199		$C_6H_5CH_2Br + I^-$	$(CH_3)_2CO$	$A \sim 2; 10^2 B \sim 2-4$	K^+	$= B$	$k AB$	0 20	2.89 2.32	-2 -1		(5) (16)

No.	Supplementing Reaction	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$	$k^0 \times 10^n$	$A^0 \times 10^n$	Comments	Temperature literature
.200		$C_6H_5CH_2I + ICl \longrightarrow$ $C_6H_5CH_2Cl + I_2$	CCl_4	$10^2A = 3-14$ $10^4B = 5-20$			k_{AB}^2	25	1.09	0		*	(23)
.201		$o\text{-CH}_3C_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1; 10^2B = 2$ 0.2 4	K^+	$= B$	k_{AB}	0	3.04	-4			(9a)
.202		$p\text{-CH}_3C_6H_4CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1; 10^2B = 2$ 0.2 4 2 2-4	K^+	$= B$	k_{AB}	0	5.1	-5			(9a)
.203		$p\text{-CH}_3C_6H_4CH_2Br + I^-$	$(CH_3)_2CO$				k_{AB}	0	5.46	-5			(18)
.204		$C_6H_5CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	60	5.00	-4	1 10		(5)
.205		$C_6H_5(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$10^2A = 5; B = 0.1$	Na^+	$= B$	k_{AB}	44	4.23	-2			(12)
.206		$C_6H_5CH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	60	2.93	-5	4 7		(9a)
.207		$2,4\text{-(CH}_3)_2C_6H_3CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2B = 4$	K^+	$= B$	k_{AB}	50	6.91	-3	13		(12)
.208		$2,4\text{-(CH}_3)_2C_6H_3CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1; 10^2B = 2$ 0.2 4	K^+	$= B$	k_{AB}	60	4.52	-5	17 3		(9a)
.209		$2,6\text{-(CH}_3)_2C_6H_3CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1; 10^2B = 2$	K^+	$= B$	k_{AB}	0	1.34	-3			(9a)
.209		$o\text{-CH}_3C_6H_4(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$10^2A = 5; B = 0.1$	Na^+	$= B$	k_{AB}	0	1.52	-3			(9a)
.210		$p\text{-CH}_3C_6H_4(CH_3)CHCl + I^-$	$(CH_3)_2CO$	$10^2A = 5; B = 0.1$	Na^+	$= B$	k_{AB}	44	6.00	-3			(9a)
.210			$(CH_3)_2CO$		Na^+	$= B$	k_{AB}	44	8.04	-4			(9a)
.210			$(CH_3)_2CO$		Na^+	$= B$	k_{AB}	44	6.07	-5			(9a)

No.	Supplement No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Reaction class	Temperature	$k^0 \times 10^n$	k^0	$k^0 \times 10^n$	k^0	Comments	Literature
211		$C_6H_5(CH_2)_3H_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.25 \times 10^2 B = 4$	K^+	$= B$	k_{AB}	50	3.94		-5		*	(11)
212		$C_6H_5(CH_2)_3CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.1; 10^2 B = 2$	K^+	$= B$	k_{AB}	60	3.65		-5			
213		$C_6H_5(CH_2)_2CH_2(CH_2)_2CH_2Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 5; B = 0.1$	Na^+	$= B$	k_{AB}	44	2.47		-3			(9a)
214		$C_6H_5(CH_2)_2CH_2(CH_2)_3CH_2Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 5; B = 0.1$	Na^+	$= B$	k_{AB}	44	2.75		-4			(9a)
215		$C_6H_5(CH_2)_3CH_2CH_2CH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 5; B = 0.1$	Na^+	$= B$	k_{AB}	44	1.73		-3			(9a)
216		$p-CH_3C_6H_4CH_2CH_2Cl + I^-$	$(CH_3)_2CO$				k_{AB}	0	3.92		-2			(5)
217		$C_6H_5(CH_2)_4CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	8.25		5		*	(11)
218		$C_6H_5(CH_2)_6CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	60	9.51		-5		*	(11)
219		$C_6H_5(CH_2)_8CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50	2.12		-5		*	(11)
220		$(C_6H_5)_2CHCl + I^-$	SO_2	$A = 0.12; 10^2 B = 1.5$ 10 $5-10$	$(CH_3)_4N^+$ $(C_2H_5)_4N^+$	$= B$	k_A	-17	8		-4			(2)
221		$(C_6H_5)_3CCl + I^-$	C_6H_6	$10^2 A = 3; 10^2 B = 2-6$	$(C_{10}H_8)_2N^+$	$= B$	k_A	0	9.5		-5		*	(46)
222	233	$(C_6H_5)_3CCl + I^-$	$(CH_3)_2CO$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	0	5.25		-3		*	(12)
223		$p-NO_2C_6H_4CH_2Cl + I^-$	$AcOH$	$10^2 A = 5; 10^2 B = 3-300$	Li^+	$= B$	k_{AB}	0	1.27		-3		*	(7)
								30	7.09		-2	21.5		

No.	Date	Reaction	Solvent	Amount of reactant	Added (salt)	Medium	Defined mass	Temperature	$k \times 10^n$		δ	$A \times 10^{12}$		Comments	Literature
									k^0	n		A^0	n		
1001	1951	$2-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} + \text{I}^-$	ACN^*	$10^{-2}A = 10^{-3}B = 3-300$			RAB	0	1.92	-4	22	8	13	*	(7)
1002	1951	$2-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{Cl}^-$	ACN^*	$10^{-2}A = 10^{-3}B = 3-300$	Li^+	= M	RAB	0	1.8	-3	18	4	11	*	(7)
1003	1951	$2-\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.1-10^{-2}B = 4$	I^+	= B	RAB	25	1.72	-3	18	3	10	*	(10)
1004	1951	$2-\text{ClC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Cl} + \text{I}^-$	SO_2	$10^{-2}A = 10^{-3}B = 2.8$ 8.7 19 25 50 5.7	$(\text{CH}_3)_4\text{N}^+$	= B	RA	-11	2.38	-5				*	(2) (3)
1005	1951	$2-\text{ClC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{CH}_2\text{Cl} + \text{I}^-$	SO_2	$10^{-2}A = 10^{-3}B = 2.8$ 6.6	NH_4^+	= B	RA	-11	4.1	-5				*	(2) (3)
Aryl-substituted alkenyl halide															
1006		$\text{CH}_2=\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.1-10^{-2}B = 4$	K^+	= B	RAB	20	3.16	-4				*	(25)
Arylalkoxy-substituted alkylhalide															
1007		$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.1-10^{-2}B = 4$	K^+	= B	RAB	50	7.94	-6	21	2	9	*	(33)
1008		$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.1-10^{-2}B = 4$	K^+	= B	RAB	60	2.2	-5	21	7	9	*	(33)

No.	Chemical reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass	Temperature	$k \times 10^n$	$A \times 10^n$	Comments	Literature
								k^0	A^0		
1070	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	50	3.66	1	*	(23)
1071	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	60	1.00	2	*	(25)
1072	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	50	8.7	6	*	(25)
1073	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	60	2.54	5	*	(25)
1074	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	50	8.8	5	*	(25)
1075	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	60	2.46	19	*	(25)
1076	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	50	5.34	5	*	(25)
1077	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	60	1.31	5	*	(25)
1078	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	50	5.36	5	*	(25)
1079	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	60	1.36	19	*	(25)
Aryl-oxo-substituted alkyl halide											
1080	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	0	1.0	2	*	(11) (12)
1081	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	-10	3.78	13	*	(10) (11) (12)
1082	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	0	1.45	2	*	(11)
1083	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	40	7.61	2	*	(11)
1084	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	50	2.30	11	*	(11) (12)
1085	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	25	5.41	2	*	(11) (12)
Aryl-carboxy-substituted alkyl halide											
1086	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	25	4.09	1.9	*	(49)
1087	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	45	1.16	1.9	*	(49)
1088	$C_6H_5COCH_2CH_2Cl + I^-$	$(CH_3)_2CO$	$A = 0.2 \times 10^2 B = 4$	K^+	$= B$	$R AB$	49	5.19	1.9	*	(49)

No.	Supplementing entry No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^n$	η	$A^0 \times 10^n$	A^0	n	Comments	Literature
.043		$t\text{-BuOC}(\text{C}_6\text{H}_5)_3\text{SO}_2\text{CH}_2\text{Cl} + \text{I}^- \longrightarrow$ $d\text{-BuOC}(\text{C}_6\text{H}_5)_3\text{SO}_2\text{CH}_2\text{Cl} + \text{Br}^-$	H_2O	$10^2 A = 1.5; B = 1.0$	H^+	$= B$	k_{AB}	25 35 49	2.09 6.02 2.64	-5 -5 -4		7 19.8	9	*	(49)
Aryl-thio-substituted alkyl halide															
.044		$\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50 55 60	1.50 2.53 4.08	-5 -5 -5		5 21	9	*	(34) (4) (35)
.045		$\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	50 55 60	7.3 9.16 1.79	-5 -5 -4		6	8	*	(35) (4) (35)
.046		$o\text{-NO}_2\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	55	5.00	-5					(4)
.047		$p\text{-NO}_2\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	55	5.25	-5					(4)
.048		$p\text{-NO}_2\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	55	7.15	-5					(4)
.049		$p\text{-NO}_2\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	55	2.32	-4					(4)
.050		$p\text{-NO}_2\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2; 10^2 B = 4$	K^+	$= B$	k_{AB}	55	5.98	-5					(4)
Aryl sulfonyl-substituted alkyl(alkenyl)halide															
.051		$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$10^2 A = 2.5; 10^2 B = 3$	K^+	$= B$	k_{AB}	0	< 1	-8				*	(0)
.052		$\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CH}=\text{CH}_2 + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.1; 10^2 B = 3.1$	K^+	$= B$	k_{AB}	0	3.6	-4				*	(6)

No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^n$	k^0	$A^0 \times 10^n$	A^0	Comments	Literature
255	$5\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 3.1$	I^+	$= B$	k_{AB}	0	3.06	-4				(6)
Nitrile substituted alkenyl halide													
256	$\text{N}(\text{CH}_3)_2\text{CH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 3.6$	I^+	$= B$	k_{AB}	0	3.92	-4				(6)
Halogen-substituted alkenyl halide													
257	$\text{F}_2\text{CHCH}_2\text{Cl} + \text{I}^- \longrightarrow \text{CH}_2\text{CHCH}_2\text{Cl} + \text{Cl}^-$	$(\text{CH}_3)_2\text{CO}$		I^+	$= B$	k_{AB}	25	8	-7	25	8	11	(40)
258	$\text{CH}_2\text{COCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$		I^+	$= B$	k_{AB}	50	2.0	-5				(22)
259	$\text{cis-CHClCHCH}_2\text{Cl} + \text{I}^-$ (low boiling isomer)	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	1.1	-4				(22)
260	$\text{trans-CHClCHCH}_2\text{Cl} + \text{I}^-$ (high boiling isomer)	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	1.20	-3				(22)
261	$\text{CH}_2\text{CHCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	4.04	-4				(22)
262	$\text{CH}_2\text{CHCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	1.22	-4				(22)
263	$\text{cis-CHBrCHCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	2.8	-3				(23)
264	$\text{trans-CHBrCHCH}_2\text{Cl} + \text{I}^-$	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	1.6	-1				(23)
265	$\text{trans-CHBrCHCH}_2\text{Cl} + \text{I}^-$ (low boiling isomer)	$(\text{CH}_3)_2\text{CO}$	$A = 0.2 \times 10^2 B = 4$	I^+	$= B$	k_{AB}	20	2.9	-3				(23) (26)

Homogeneous Reaction Kinetics

332.771

25

No.	Supplementing 1951 No.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined mass action law	Temperature	$k \times 10^3$ k^0 n	$A \times 10^3$ A^0 n	Comments	Reference
.262		β -CH ₃ COCl:CH ₂ Cl + I ⁻ (high boiling isomer)	(CH ₃) ₂ CO	A = 0.2; 10 ² B = 4	K ⁺	= B	R AB	20	8.60 -3		* (20) (26)	
.263		CHCl:C(CH ₃)CH ₂ Cl + I ⁻ (low boiling isomer)	(CH ₃) ₂ CO	A = 0.2; 10 ² B = 4	K ⁺	= B	R AB	20	4.6 -3		* (22)	
.264		CHCl:C(CH ₃)CH ₂ Cl + I ⁻ (high boiling isomer)	(CH ₃) ₂ CO	A = 0.2; 10 ² B = 4	K ⁺	= B	R AB	20	1.17 -3		* (22)	
.265		Cl ₂ C:(CH ₃)CH ₂ Cl + I ⁻	(CH ₃) ₂ CO	A = 0.2; 10 ² B = 4	K ⁺	= B	R AB	20	5 -3		* (22)	
Carboxy and halogen substituted alkyl halide												
.266		C ₂ H ₅ OOCCHCl + I ⁻ → C ₂ H ₅ OOCCHCl + Cl ⁻	(CH ₃) ₂ CO	A = 0.1; 10 ² B = 1.5	K ⁺	= B	R AB	20	3.1 -6	1.0	*	(36)
.267		C ₂ H ₅ OOCCHCl ₂ + I ⁻ → C ₂ H ₅ OOCCHCl + Cl ⁻	(CH ₃) ₂ CO	A = 0.1; 10 ² B = 1.5	K ⁺	= B	R AB	40	6.3 -5	1.0	*	(36)
.268		C ₂ H ₅ OOCCHBr + I ⁻ → C ₂ H ₅ OOCCHCl + Br ⁻	(CH ₃) ₂ CO	10 ² A = 6; 10 ³ B = 5	K ⁺	= B	R AB	20	1.89 -5	8	*	(36)
.269		C ₂ H ₅ OOCCHClBr + I ⁻ → C ₂ H ₅ OOCCHCl + Br ⁻	(CH ₃) ₂ CO	10 ² A = 6; 10 ³ B = 5	K ⁺	= B	R AB	40	2.2 -4	11	*	(36)
.270		C ₂ H ₅ OOCCHBr ₂ + I ⁻ → C ₂ H ₅ OOCCHBr + Br ⁻	(CH ₃) ₂ CO	10 ² A = 6; 10 ³ B = 1.5	K ⁺	= B	R AB	0	1.66 -3	4	*	(36)
								20	8.48 -3	7	*	(36)
								0	2.14 -4	1.7	*	(36)
								20	2.22 -3	11	*	(36)
								0	9.22 -5	7	*	(36)
								20	1.12 -3	11	*	(36)

No.	Supplementing 1951 no.	Reaction	Solvent	Amount of reactant	Addend (salt)	Amount of addend	Defined masses action law	Temperature	$k \times 10^n$ k^0 n	β	$A =$ $A^0 \times 10^n$ A^0 n	Comments	Literature
.271		$C_2H_5OCCBr_2 + I^- \longrightarrow$ $C_2H_5OCCBrI^- + Br^-$	$(CH_3)_2CO$	$10^2 A = 6; 10^2 B = 1.5$	K^+	$= B$	k_{AB}	10 40	6.40 5.90	-5 -4	6 10	*	(36)
Benzimidazolyl-substituted alkyl halide													
.272	.39	$NHC_6H_4N^+CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 5; 10^2 B = 2$ 2 1 2.5	K^+	$= B$	k_{AB}	25 25 25 25	1.22 2.54 3.82 4.55	-2 -2 -2 -2		*	(44)
.273	.41	$N(CH_3)_6H_4N^+CH_2Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 2; 10^2 B = 2$ 2.5 1 2	K^+	$= B$	k_{AB}	25 25 25	5.95 2.54 7.11	-2 -1 -1		*	(44)
.274	.42	$N(CH_3)_6H_4N^+CH(CH_3)Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 4; 10^2 B = 2$ 3 2.5 0.5	K^+	$= B$	k_{AB}	25 25 25 25	1.20 1.65 1.50 2.30	-2 -2 -1 -1		*	(44)
.275	.39	$NHC_6H_4N^+CH(C_2H_5)Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 5; 10^2 B = 2$ 1.6 2.5 1	K^+	$= B$	k_{AB}	25 25 25 25	1.26 4.9 5.7 9.3	-2 -2 -2 -2		*	(44)
.276	.40	$NHC_6H_4N^+CCl(CH_3)_2Cl + I^-$	$(CH_3)_2CO$	$10^2 A = 2; 10^2 B = 2$ 2.5 1 2	K^+	$= B$	k_{AB}	25 25 25	6.5 2.42 4.26	-2 -1 -1		*	(44)

SOLVENTS

AN90*	$(\text{CH}_3)_2\text{CO}$ 90 vol % + H_2O (43)
AN75*	$(\text{CH}_3)_2\text{CO}$ + 5 vol % CH_3OH + 0.31% in H_2O (7)

COMMENTS

Classification			
(.71) - (.125)	Saturated alkyl halides	(.197) - (.228)	Aryl-substituted alkyl halide
(.126) - (.142)	Saturated cyclo-alkyl halide	(.229)	Aryl-substituted alkenyl halide
(.143) - (.144)	Hydroxy-substituted alkyl halide	(.240) - (.236)	Arylalkoxy-substituted alkyl halide
(.145) - (.149)	Alkoxy-substituted alkyl halide	(.237) - (.240)	Aryloxy-substituted alkyl halide
(.150)	Keto-substituted alkyl halide	(.241) - (.242)	Aryl-carboxy substituted alkyl halide
(.151) - (.161)	Carboxy-substituted alkyl halide	(.243) - (.249)	Arylthio-substituted alkyl halide
(.162) - (.165)	Carboxylate-substituted alkyl halide	(.250) - (.252)	Arylsulfonyl-substituted alkyl halide
(.166)	Nitrile-substituted alkyl halide	(.253)	Nitrile-substituted alkenyl halide
(.167) - (.173)	Silyl-substituted alkyl halide	(.254) - (.265)	Halogen-substituted alkenyl halide
(.174) - (.175)	Alkylthio-substituted alkyl halide	(.266) - (.271)	Carboxy and halogen-substituted alkyl halide
(.176) - (.195)	Halogen-substituted alkyl halide	(.272) - (.276)	Benzimidazolyl-substituted alkyl halide
(.186) - (.194)	Unsaturated alkenyl halide		
(.195) - (.196)	Unsaturated alkynyl halide		

COMMENTS

(continued)

General. Halogen exchange reactions usually studied in acetone as solvent using lithium, sodium or potassium salts. When sodium or potassium iodide used insoluble chloride or bromide separates and reaction goes to completion. When lithium salts are used reactions proceed to equilibrium and reverse reactions may be studied. Salt effects are observed and vary slightly with different halides.

Comments by Literature References. ⁽⁹⁾(¹⁰)(¹¹)(¹²) Units of rate constants converted to seconds and base e logarithms from original hours and base 10. ⁽¹³⁾(¹⁶) Units converted to seconds from original hours. ⁽²⁰⁾(²¹)(²²) Units converted to seconds and base e logarithm: from original hours and base 10. ⁽²³⁾(²⁴)(²⁵)(²⁶) Units converted to seconds from original hours. ⁽³¹⁾(³²) Units converted to seconds from original minutes. ⁽³³⁾(³⁴)(³⁵) Units converted to seconds and base e logarithms from original hours and base 10. ⁽³⁶⁾(⁴⁰) Units converted to seconds from original hours. ⁽⁴¹⁾(⁴²)(⁴³) Units converted to seconds from original minutes. ⁽⁴⁴⁾ Units converted to seconds from original hours. ⁽⁴⁷⁾(⁴⁸) Units converted to seconds and base e logarithms from original hours and base 10. ⁽⁴⁹⁾ Units converted to seconds from original minutes.

Comments by Reaction. ^(.71) Rate law followed up to 70% reaction with reverse reaction considered negligible. Negative salt effect. ^(.72) Rate of forward reaction only. For simultaneous reverse reaction see ^(.74). ^(.73) Addition of LiClO_4 eliminates drift in rate constants with course of reaction. Reverse reaction considered negligible. ^(.74) In H_2O reaction is in competition with hydrolysis and reverse reaction. In ethylene glycol solvolysis is unimportant below 50°C . Rate constants are for forward reaction only. For competing reverse reaction see ^(.72). In $(\text{CH}_3)_2\text{CO}$ rate constants drift with progress of reaction. This is attributed to greater retarding salt effect of LiI than of the LiBr initially present. ^(.75) Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. ^(.76) Rate law followed up to 70% reaction with reverse reaction considered negligible. Negative salt effect. ^(.77) Rate constant for forward reaction only. For competing reverse reaction see ^(.79). Only about 10% conversion at equilibrium. Negative salt effect. ^(.78) In absence of added LiClO_4 , rate constants drift with course of reaction. Reverse reaction considered negligible, see ^(.75). ^(.79) Rate constant for forward reaction only. For competing reverse reaction

COMMENTS

(continued)

see (.77). Rate constants drift with course of reaction as LiI replaces LiBr. Values are calculated for rate near end of reaction as system approaches equilibrium. (.80) Rate constant for forward reaction only. For competing reverse reaction see (.86). Corrected to base e logarithm from uncorrected values in 1951 edition of Tables. (.81) Rate constant for forward reaction only. For competing reverse reaction see (.86). Corrected to base e logarithm from uncorrected values in 1951 edition of Tables. (.82) Reaction followed to 70% completion and reverse reaction considered negligible. (.83) Selected data. Rate constant for forward reaction only. For competing reverse reaction see (.87). In presence of Li^+ calculated rate constants increase with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. (.84) Reaction followed to 70% completion and reverse reaction considered negligible. Negative salt effect. (.85) Rate constant for forward reaction only. For competing reverse reaction see (.89). In presence of Li^+ calculated rate constants increase with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. (.86) Calculated rate constants drift with course of reaction in absence of added LiClO_4 . For competing re-

verse reaction see (.80). (.87) Rate constant for forward reaction only. For competing reverse reaction see (.83). Calculated rate constants decrease with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. Value used is that calculated for end of reaction as equilibrium is approached. (.88) Calculated rate constants drift with course of reaction in absence of added LiClO_4 . Reverse reaction negligible, see (.81). (.89) Rate constant for forward reaction only. For competing reverse reaction see (.85). Calculated rate constants decrease with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr. Value used is that calculated for end of reaction as equilibrium is approached. (.90) Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. (.91) Approximate value giving order of magnitude only. Determined by getting best fit of data for reverse reaction. See (.96). (.92) (.93) Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. (.94) Rate constant for forward reaction only, but rate constant for reverse reaction not determined with precision. (.96) Reaction followed up to 70% completion in $(\text{CH}_3)_2\text{CO}$, and reverse reaction, (.91), considered negligible by (.29). Negative

COMMENTS

(continued)

salt effect. In $(\text{CH}_3)_2\text{CO}$ and H_2O mixture rate constant for forward reaction only. For competing reverse reaction see (.91). (.97) Selected data. Rate constant for forward reaction only. For competing reverse reaction see (.103). In presence of Li^+ calculated rate constants increase with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr . Values calculated are for initial conditions. (.98) Rate constant for forward reaction only and values are for initial rates. Increase of calculated rate constants with increase in initial concentration of B attributed to a salt effect and at ionic μ

$$\log k_{\mu} = \log k_0 + 9.12 \times 10^{16} \mu \sigma / D^2 \tau^2$$

where $\sigma = 0.93 \text{ \AA}$. Rate determining step involves formation of $(\text{CH}_3)_3\text{C}^+$ and ratio of competition of F^- to Br^- in reacting with $(\text{CH}_3)_3\text{C}^+$ determined to be 0.30. (.99) Reaction followed to only 40% completion as total halide increased with reaction indicating competing elimination reaction. Rate constants determined by graphical extrapolation to time zero. Negative salt effect. (.101) Reaction followed to only 25% completion as I_2 formed in later stages. Some isobutylene dihalide also formed. (.102) Calculated rate constants drift with progress of reaction in absence of added LiClO_4 . Reverse reaction considered

negligible. (.103) Rate constant for forward reaction only. For competing reverse reaction see (.97). Calculated rate constants decrease with progress of reaction. This is attributed to a greater negative salt effect of LiI than of LiBr . Value used is that calculated for end of reaction as system approaches equilibrium. (.104) Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. Calculated rate constants decrease with course of reaction. (.105) (.106) Corrected to base e logarithms from uncorrected values in 1951 edition of Tables. (.108) Reaction followed to 70% completion and reverse reaction considered negligible. Negative salt effect. (.109) Rate constant for forward reaction only. For competing reverse reaction see (.111). Negative salt effect with LiI retarding reaction more than LiBr . (.110) Calculated rate constants drift with progress of reaction in absence of added LiClO_4 . Reverse reaction considered to be negligible. (.111) Rate constant for forward reaction only. For competing reverse reaction see (.109). Calculated rate constants decrease with progress of reaction. This is attributed to greater negative salt effect of LiI than of LiBr . Value used is that calculated at end of reaction as system approaches equilibrium. (.112) (.113) (.115) (.117) (.121) (.122)

COMMENTS

(continued)

(.123) (.124) (.125) Converted to base e logarithms from uncorrected values in 1951 edition of Tables. (.127) Rate constant for forward reaction only. For competing reverse reaction see (.128). (.128) Rate constant for forward reaction only. For competing reverse reaction see (.127). (.129) Reaction followed only to 27% completion as faint iodine coloration appears at this point. Calculated rate constants decrease about 4% in this range. (.130) Rate constant for forward reaction only. For competing reverse reaction see (.131). (.131) Rate constant for forward reaction only. For competing reverse reaction see (.130). (.133) Rate constant for forward reaction only. For competing reverse reaction see (.134). Some parallel elimination reaction noted by ¹. (.134) Rate constant for forward reaction only. For competing reverse reaction see (.133). (.135) Rate constant for forward reaction only. Corrected for reverse reaction but rate constant for reverse reaction not given. (.136) Rate constant for forward reaction only. For competing reverse reaction see (.137). (.137) Rate constant for forward reaction only. For competing reverse reaction see (.136). (.138) Rate constant gives order of magnitude only. Determined by obtaining best fit for data of reverse reaction (.139). (.139) Rate con-

stant for forward reaction only. For competing reverse reaction see (.138). (.140) (.141) Forward and reverse reactions. Actual rate constants not given only activation energies and frequency term for (.140). (.145) (.150) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. (.151) (.152) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. Calculated rate constants decrease with progress of reaction. (.154) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. (.155) Calculated rate constants decrease with course of reaction. (.156) Reaction followed to only 35% completion due to subsequent decomposition of iodoester. (.157) (.158) Calculated rate constants decrease with course of reaction. (.159) Rate constant for forward reaction only. Accompanied by parallel elimination and racemization reactions see 422.471 and 112.470. For reverse reaction see (.160). (.160) Rate constant for forward reaction only. Accompanied by parallel elimination and racemization reactions see 422.471 and 112.470. For reverse reaction see (.159). (.161) (.162) (.166) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. (.169) Slight negative salt effect. (.176) (.180) Actual rate of ex-

COMMENTS

(continued)

change is tabulated rather than half rate, (per halogen), listed by (28). (.184) (.185) Some iodine is also liberated during reaction. (.147) No measurable reaction after six hours. (.192) Rate constants decrease with progress of reaction. Value is average for first 40% reaction rather than average of all values by (21). (.196) Rate constants calculated practically but decrease with course observed as first and last points fell below authors straight line. (.197) Converted to base e logarithms from uncorrected values in 1951 edition of Tables. Addition of H_2O observed by (44) to cause decrease in reaction rate. Values from 0.09 to 21% by weight of water are given. (.198) (.200) Third order rate constant calculated by dividing pseudo second order constant by concentration of A. Reaction performed in the dark to avoid halogenation. At concentrations of A and B > 1 M/l reaction much faster and some halogenation of benzene ring occurs. (.211) (.219) Calculated rate constants decrease with course of reaction. (.221) First order rate law valid for first 40% reaction only. Beyond this rate drops to less than 1% of initial rate when 50% of whichever reactant was in lower concentration is consumed. This is not an equilibrium effect. (.222) Converted to base e logarithms from uncorrected

value in 1951 edition of Tables. (.223) (.224) Rate constants for the forward reaction only. For competing reverse reaction see (.225). Authors consider total reaction to be best expressed as the sum of the parallel reactions (.223) and (.224) involving Hr^- and the ion pair $Hr.H^+$ respectively. (.225) Rate constant for forward reaction only. For competing reverse reaction see (.223) (.224). (.228) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. (.227) (.228) Calculated rate constants decrease with course of reaction. Value tabulated is that extrapolated to zero time. (.237) (.238) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. Calculated rate constants decrease with course of reaction. (.240) Converted to base e logarithms from uncorrected value in 1951 edition of Tables. (.241) (.242) Rate constants of these opposing reactions calculated from analysis of polarimetric data involving simultaneous, exchange racemization and solvolysis reactions. See 112.470 and 212.471. (.250) No measurable reaction in 10 weeks. (.251) Calculated rate constants increase 15% in first 45% reaction. (.253) (.256) (.257) (.258) Only allyl halogen assumed to react, as $CH_3CH:CHCl$ gives no measurable exchange in 8 hr. See

COMMENTS

(continued)

- (.127). (.259) Reaction studied in mixture containing 95% cis- and 5% trans-isomer. Rate constant extrapolated to 100% cis-isomer. (.260) Reaction studied in mixture containing 75% trans-isomer and 25% cis-isomer. Rate constant extrapolated to 100% trans-isomer. (.261) (.262) Only allyl halogen assumed to react, as $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ gives no measurable exchange in 8 hours. See (.187). (.263) (.264) (.265) Calculated rate constants decrease with course of reaction. Only allyl halogen assumed to react. See (.187). (.266) Reaction followed to only about 20% due to subsequent decomposition of iodoester. Negative test for F^- . (.267) Reaction followed to only 35% due to subsequent decomposition
- of iodoester. (.268) Reaction followed to 60%. Subsequent decomposition of iodoester occurs. Negative test for F^- . (.269) (.270) Reaction followed to only 35% due to subsequent decomposition of iodoester. (.271) Reaction followed to only 35% due to subsequent decomposition of iodoester. Negative test for F^- . (.272) Formula corrected from incorrect structure given in 1951 edition of Tables. (.273) Rate constants corrected by power of ten from values listed in 1951 edition of Tables. (.274) (.275) (.276) Formula corrected from incorrect structure given in 1951 edition of Tables.

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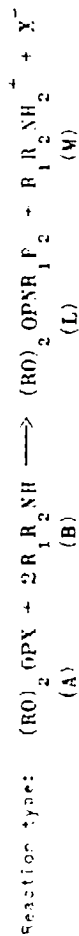
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CHANGE
ON Vth GROUP ELEMENT
Halogen Replaced by Nitrogen on P

Liquid phase

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



No.	Reaction	Solvent	Amount of reactant	Added	Amount of added	Defined law	Temperature	$k^o \times 10^7$	k^o	$k^o \times 10^7$	Contents	Literature
1	$(CH_3)_2OPCl + 2(n-C_4H_9)_2NH \longrightarrow$	C_2H_5OH				$-dA/dt = kAP$	-15	1.9	-2	1	5	
2	$(C_2H_5O)_2OPCl + 2(n-C_4H_9)_2NH \longrightarrow$	C_2H_5OH				$-dA/dt = kAB$	0	3.9	-2	8		
3	$[(CH_3)_2CHO]_2OPCl + 2n-C_4H_9NH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	-15	8	-3	5	4	
4	$[(CH_3)_2CHO]_2OPCl + 2(CH_3)_2CHOH NH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	25	3.0	-2	9		
5	$[(CH_3)_2CH]_2OPCl + 2C_2H_5(CH_3)OCH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	25	6.6	-2			
6	$[(CH_3)_2CH]_2OPCl + 2C_2H_5(CH_3)OCH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	1.20	-2			
7	$[(CH_3)_2CH]_2OPCl + 2(CH_3)_3COH \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	7	-4			
8	$[(CH_3)_2CH]_2OPCl + 2C_2H_5NH_2 \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	7	-6			
9	$[(CH_3)_2CH]_2OPCl + 2(C_2H_5)_2NH \longrightarrow$	C_6H_6				$-dA/dt = kAB$	40	1.1	-3			
10	$[(CH_3)_2CH]_2OPCl + 2(n-C_4H_9)_2NH \longrightarrow$	C_2H_5OH				$-dA/dt = kAB$	-15	7	-4			
							0	1.2	-3			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined law	Temperature	$k \times 10^n$ k^0 n	R	$A \times 10^n$ A^0 n	Comments	Literature
9	$[(CH_3)_2CHO]_2OPCl + 2(n-C_4H_9)_2NH \rightarrow (cont.)$	C_2H_5OH	$10^2 A = 5; B = 0.1$		$-dA/dt = kAB$		25 40	5.5 -3 1.03 -2				
			2 0.05	$NaClO_4$	0.2		25	2 -2				
			2 0.1	NH_4NO_3	0.2		25	7 -2				
			4 0.1	L	0.04		25	8 -3				
			4 0.1	H	0.12		25	1.5 -2				
		C_6H_6	$10^2 A = 1.8; 10^2 B = 8.3$		$-dA/dt = kAB$		25	6 -4				
			0.9 4.4	$(C_2H_5)_3N$	0.18		25	5 -4				
		$n-C_7H_{16}$ Dioxane $(CH_3)_2CO$			0		40	1.1 -3				
					0		64	2.0 -3	8.9	2 4		
		CH_3NO_2 $C_6H_5NO_2$ CH_3CN					25	1.7 -4				
							25	8 -3				
							0	8 -3				
							25	2.5 -2				
							25	4 -2				
							25	2 -2				
							25	7.5 -2				
10	$[(CH_3)_2CHO]_2OPCl + 2[C_2H_5(CH_3)CH]_2NH \rightarrow$	C_6H_6			$-dA/dt = kAB$		40	1 -5				
							64	2 -5				
11	$[(CH_3)_2CHO]_2OPCl + (C_2H_5)_3N \rightarrow$ (products not determined but only one mole of amine consumed.)	C_6H_6			kAB		0	5 -5				

LITERATURE

I. Dostrovsky, M. Halmann, *CSU* 1953, 511.

EXCHANGE
on Vth Group Element
Exchange of halogen for halogen on P

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 rate law	Temperature	$k = k^0 \times 10^2$ k^0 n	β	$A = A^0 \times 10^3$ A^0 n	Comments
1	$(CH_3)_2OPCl + F^- \rightarrow (CH_3)_2OPF + Cl^-$	C_2H_5OH		K^+	$= B$	k_{AB}	0	(too fast to measure)			
2	$(C_2H_5)_2OPCl + F^- \rightarrow (C_2H_5)_2OPF + Cl^-$	C_2H_5OH		K^+	$= B$	k_{AB}	0	2.8 -1			*
3	$[(CH_3)_2CHO]_2OPCl + F^- \rightarrow [(CH_3)_2CHO]_2OPF + Cl^-$	C_2H_5OH	$10^3 A = 5-14$ $10^3 B = 3-23$	K^+	$= B$	k_{AB}	0	3.0 -2			*
		$60\% C_2H_5OH + 40\% H_2O$		K^+	$= B$		25	2.3 -1	13	5	8
				K^+	$= B$		25	3.9 -2			

COMMENTS

Reaction: (.2) Value of rate constant approximate as reaction almost too fast to measure. (.3) Value of rate constant in 60% C_2H_5OH solution corrected for parallel solvolysis reaction see 252.570.

LITERATURE

I. Eestrovsky, M. Halmann, *CSL* 1953, 508.

Homogeneous Reactions

402.450

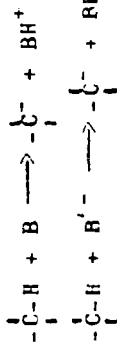
ELIMINATION

Hydrogen ion elimination from CH bond activated
by adjacent CO, (COOR), (ON), NO₂

Liquid phase

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

* Coded solvents at end
of Table.



Reaction type:

No.	Supplementing 1951 No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$k \times 10^n$	k	$A =$ $A^0 \times 10^n$	Comments	Reference
Single activating group NO ₂													
.24	.11	$\text{C}_2\text{H}_5\text{NO}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}:\text{NO}_2^- + \text{H}_3\text{O}^+$	B	A = 0.2-0.3	Br ₂ or I ₂	0-0.02	k A	15	9.0	-9		*	(8)
				~0.001	buffers	pH = 6.1		26	4.05	-8			
						7.0		35	1.25	-7			
						8.0		70	4.4	-6	22.9	9	
						8.9		25	3.22	-8			(5)
						10.0		25	4.27	-8			(6)
						10.9		25	8.33	-8			
								25	1.02	-7			
								25	3.14	-7			
								25	6.60	-7			
.25	.12	$\text{C}_2\text{H}_5\text{NO}_2 + \text{OH}^- \longrightarrow \text{CH}_3\text{CH}:\text{NO}_2^- + \text{H}_2\text{O}$	H ₂ O	A = B = 0.02-0.06	NaCl	0.011	k AB	25	5.8	0	14.2	11	*
						0.02-0.05		25	5.75	0			
						0.06		25	5.55	0			
						0.09		25	5.75	0			
						0.02		25	5.85	0			
						0.04		25	4.8b	0			
						0.06		25	4.5	0			
								25	4.1	0			

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined rate	Temperature	$k = A^0 \times 10^n$ k^0 n	B $A^0 \times 10^n$ A^0 n	Comments	Reference
26	$C_2H_5NO_2 + C_2H_5NH_2 \longrightarrow$ $CH_3CH:NO_2^- + C_2H_5NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	1.42 -2		*	(12)
27	$C_2H_5NO_2 + n-C_4H_9NH_2 \longrightarrow$ $CH_3CH:NO_2^- + n-C_4H_9NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	1.48 -2		*	(12)
28	$C_2H_5NO_2 + (CH_3)_2CHNH_2 \longrightarrow$ $CH_3CH:NO_2^- + (CH_3)_2CHNH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	1.90 -2		*	(12)
29	$C_2H_5NO_2 + n-C_4H_9NH_2 \longrightarrow$ $CH_3CH:NO_2^- + n-C_4H_9NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	1.88 -2		*	(12)
30	$C_2H_5NO_2 + (CH_3)_3CNH_2 \longrightarrow$ $CH_3CH:NO_2^- + (CH_3)_3CNH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	1.88 -2		*	(12)
31	$C_2H_5NO_2 + n-C_6H_{13}NH_2 \longrightarrow$ $CH_3CH:NO_2^- + n-C_6H_{13}NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	1.88 -2		*	(12)
32	$C_2H_5NO_2 + (C_2H_5)_2NH \longrightarrow$ $CH_3CH:NO_2^- + (C_2H_5)_2NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	4.64 -2		*	(12)
33	$C_2H_5NO_2 + [(CH_3)_2CH]_2NH \longrightarrow$ $CH_3CH:NO_2^- + [(CH_3)_2CH]_2NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	4.34 -2		*	(12)
34	$C_2H_5NO_2 + \overbrace{(CH_3)_2CH}^4NH \longrightarrow$ $CH_3CH:NO_2^- + CH_2(CH_2)_4NH_3^+$	H ₂ O	A = B = 0.01-0.03			k AB	0	8.30 -2		*	(12)

No.	Reaction	Solvent (medium)	Amount of reactant	Addend	Amount of addend	Defined rate	Temperature	$k \times 10^n$ k^0 n	B	$A \times 10^n$ A^0 n	Comments	Literature
.35	$C_2H_5NO_2 + (C_2H_5)_3N \longrightarrow$ $CH_3CH_2NO_2^- + (C_2H_5)_3NH^+$	H ₂ O	A = B = 0.1-0.03			k AB	0	5.20 -2			*	(12)
.36	$C_2H_5NO_2 + CH_2CH_2CH_2N \longrightarrow$ $CH_2CH_2CH_2NO_2^- + CH_2CH_2CH_2NH^+$ (quinuclidine)	H ₂ O	A = B = 0.1-0.03			k AB	0	9.8 -2			*	(12)
.37	$C_2H_5NO_2 + C_6H_5N \longrightarrow$ $CH_3CH_2NO_2^- + C_6H_5NH^+$	H ₂ O	A = 0.1-0.2 B = 0.1-0.2	I ₂	0.002-0.004	k AB	17 25 35	6.07 -5 1.49 -4 3.57 -4		2 8	*	(8) (11)
		Et 30*	A = 0.1-0.2 B = 0.1-0.2	I ₂	0.002-0.004	k AB	0 25 35	8.61 -6 1.08 -4 2.32 -4		4 7		
		Et 70*	A = 0.1-0.2 B = 0.1-0.2	I ₂	0.002-0.004	k AB	0 25 35	4.6 -7 5.87 -6 1.62 -5		2 7		
.38	$C_2H_5NO_2 + 2-CH_3C_6H_4N \longrightarrow$ $CH_3CH_2NO_2^- + 2-CH_3C_6H_4NH^+$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I ₂	0.002-0.004	k AB	25	4.1 -4			*	(11)
.39	$C_2H_5NO_2 + 3-CH_3C_6H_4N \longrightarrow$ $CH_3CH_2NO_2^- + 3-CH_3C_6H_4NH^+$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I ₂	0.002-0.004	k AB	25	2.20 -4			*	(11)

Homogeneous Reaction Kinetics

402.430

4

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined base	Temperature	$k = k^0 \times 10^n$	B	$A = A^0 \times 10^n$	Comments	Literature
								k^0	n	A^0	n	
.40	$C_2H_5NO_2 + 4-CH_3C_6H_4N \longrightarrow$ $CH_3CH:NO_2^- + 4-CH_3C_6H_4NH^+$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I_2	0.002-0.004	k AB	25	3.03	-4		*	(11)
.41	$C_2H_5NO_2 + 2,6-(CH_3)_2C_6H_3N \longrightarrow$ $CH_3CH:NO_2^- + 2,6-(CH_3)_2C_6H_3NH^+$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I_2	0.002-0.004	k AB	25	3.47	-4		*	(11)
.42	$C_2H_5NO_2 + \overline{C_6H_4CH:CH:N} \longrightarrow$ (quinoline) $CH_3CH:NO_2^- + \overline{C_6H_4CH:CH:NH^+}$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I_2	0.002-0.004	k AB	25	7.5	-5		*	(11)
.43	$C_2H_5NO_2 + \overline{C_6H_4CH:CH:N} \longrightarrow$ (isoquinoline) $CH_3CH:NO_2^- + \overline{C_6H_4CH:CH:NH^+}$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I_2	0.002-0.004	k AB	25	1.27	-4		*	(11)
.44	$C_2H_5NO_2 + \overline{C_6H_4CH:CH:(CH_3)_2N} \longrightarrow$ (2-methyl quinoline) $CH_3CH:NO_2^- + \overline{C_6H_4CH:CH:(CH_3)_2NH^+}$	Et 30*	A = 0.1-0.2 B = 0.1-0.2	I_2	0.002-0.004	k AB	25	1.28	-4		*	(11)
.45	$CH_3CH:NO_2 + H_2O \longrightarrow$ $CH_3CO:NO_2^- + H_3O^+$	B		Br_2	> A and < A	k A	35 35 48	1.05 1.7 6.2	-6 -6 -6	3 20		(3) (8)
.46	$C_6H_2(NO_2)_3CH_3 + C_2H_5O^- \longrightarrow$ $C_6H_2(NO_2)_3CH_2^- + C_2H_5OH$	M				k AB	-78 -70 -60 -50 -40 -30 19	4.58 2.18 1.00 4.42 1.64 5.61 6.30	-4 -3 -2 -2 -1 -1 +1	13.6 1.0 12		(2)

No.	Reaction	Conc. (mole)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k =$ $k^0 \times 10^n$	δ	$A =$ $A^0 \times 10^n$	Comments	Literature
Two activating groups C:O and NO ₂												
43	$\text{CH}_3\text{COCH}_2\text{CO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COCH}_2\text{CO}_2^- + \text{H}_3\text{O}^+$	B		Br ₂	> A	kA	0 10	2.0 6.4	-3 -3	3 12		(8)
44	$\text{NO}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{NO}_2\text{CH}_2\text{CH}_2\text{CO}_2^- + \text{H}_3\text{O}^+$	B		Br ₂	> A	kA	0 10	5.3 1.52	-4 -3	3 9		(8)
Two NO ₂ activating groups												
49	$\text{CH}_2(\text{NO}_2)_2 + \text{H}_2\text{O} \rightarrow \text{CH}(\text{NO}_2)_2^- + \text{H}_3\text{O}^+$	B		Br ₂	> A	kA	0	4.5	-2			(11)
Two C:O activating groups												
50	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{COCH}_3 + \text{H}_2\text{O} \rightarrow$ $\text{CH}_3\text{COCH}(\text{CH}_3)\text{COCH}_2^- + \text{H}_3\text{O}^+$	B	A = 0.033	Br ₂	0.003	kA	21 25 35	5.4 8.3 2.3	-5 -5 -4	1.2 9		(9)
51	$\text{CH}_3\text{COCH}_2\text{COCH}_3 + \text{H}_2\text{O} \rightarrow$ $\text{CH}_3\text{COCHCOCH}_2^- + \text{H}_3\text{O}^+$	Et 12*	K ₂ A = 4-8 M = 0.1-0.5	3Br ₂	0.04-0.08	kA	0 14 25 25 25 25 25 25 25	8.99 4.65 1.57 1.48 1.49 1.37 1.37 1.26 9.27 6.44	-4 -3 -2 -2 -2 -2 -2 -2 -3 -3	4 13		(15)
52	$(\text{CH}_3)_2\text{CHCOCH}_2\text{COCH}_3 + \text{H}_2\text{O} \rightarrow$ $(\text{CH}_3)_2\text{CHCOCHCOCH}_2^- + \text{H}_3\text{O}^+$	Et 16* Et 33* Et 30* Et 67* Et 95* Et 95*	A = 0.01	Br ₂	0.014	kA	14 25	3.42 1.18	-3 -2	1 12		(13)

Heterogeneous Reaction Kinetics

402.456

8

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Reaction class	Temperature	$k \times 10^n$		$k \times 10^n$		Comments	Literature
								k^0	n	k^0	n		
1.53	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	EtOH	A ≈ 0.01	Br ₂	0.009	kA	14	3.70	-3	3	7	(13)	
1.54	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	EtOH	A ≈ 0.01	Br ₂	~ 0.01	kA	25	8.55	-3	13		(13)	
1.55	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B	$10^3 A = 3$	Br ₂	0.001	kA	14	2.96	-3	7	11	(9)	
1.56	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B	$10^3 A = 5-25$	Br ₂	0.001-0.003	kA	25	1.01	-2	19		(9)	
1.57	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B	$10^3 A = 1-4$	Br ₂	0.0001-0.003	kA	25	4.8	-6	15.5	1.6	(9)	
1.58	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂		kA	25	7.6	-6			(9)	
1.59	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂		kA	25	1.73	-5			(9)	
1.60	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂		kA	25	3.0	-5			(9)	
1.61	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂		kA	25	1.4	-4			(9)	
Activating groups C:O and C:N													
1.62	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂	>A	kA	0	7.1	-5	2	9	(8)	
1.63	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂	>A	kA	10	2.3	-4	17		(8)	
1.64	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂	>A	kA	0	0	-2			(8)	
Two C:N activating groups													
1.65	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B	$10^3 A = 2-3$	Br ₂	0.005-0.02	kA	0	1.00	-3	2	11	(8)	
1.66	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂	>A	kA	10	2.9	-3	18		(8)	
1.67	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B		Br ₂	>A	kA	0	>> 2	-1			(8)	
Two Aryl and a C:O activating groups													
1.68	$(C_2H_5)_2O + H_2O \longrightarrow (C_2H_5)_2OH^+ + H_3O^+$	B	A = 0.24 B = 0.2	D ₂ O	3M	kA	100	6.4	-6			(4)	

CODED SOLVENTS

Et 30*(70) C₂H₅OH vol % indicated + H₂O

COMMENTS

General. Ionization assumed to be rate controlling step in halogenation and enolization reactions. For additional reactions under these categories see 312.471 and 112.440. For reverse reactions see 622.450.

Methods: Polarography (4)

Hydrogen-deuterium exchange (3)

Substitution (halogenation) (7) (8) (10) (11) (12)

Conductometric (7) (8) (10) (11)

Thermal Maximum (1)

Steady State, while introducing "B" at controlled rate (9)

Spectrophotometric (2)

Reactions: (.24) Values of (4) Include reaction with base of buffer but actual concentration of buffer not stated. (.25) Selected data of (1) who use reaction rates to calculate dissociation constants

of such bases as CaOH⁺, BaOH⁺ and TlOH based on the assumption that OH⁻ is the only base reacting. (.26) - (.46) Simultaneous reaction with OH⁻, (.25) corrected for. Integrated form of rate equation

used was:

$$t = \frac{k_3 k_b}{(ak + k_b k_3)^2} \ln \frac{a-x}{kx + k_3 k_b} + \frac{a}{(ak + k_3 k_b)(ak + k_3 k_b)(a-x)} + C$$

Where, k_3 = independently determined rate constant for (.25). k_b = ionization constant of amine, "a" = initial concentration of A and x = amount of A reacted at time t . (.37) - (.44) Simultaneous reaction, (.26), with OH⁻ eliminated by addition of drop of strong acid. Amount shown to be not critical.

LITERATURE

- (¹) R.P. Bell, M.H. Panchhurst, *CSL* 1956, 2836. (²) E.F. Caldin, G. Long, F.W. Trowse, *Nature* 1953, 171, 1124. (³) M.F. Hawthorne, R.D. Strain, *ACS* 1957, 79, 7471. (⁴) D.J.G. Ives, G.C. Wilks, *CSL* 1938, 1455. (⁵) Junell, *Arkiv. Kemi. Mineral. Geol.* 1934, 11B, 30. (⁶) E.W. Miller, A.P. Arnold, M.J. Astle, *ACS* 1948, 70, 3971. (⁷) R.G. Pearson, *J.C.P.* 1952, 30, 1478. (⁸) R.G. Pearson, R.L. Dillon, *ACS* 1953, 75, 2439. (⁹) R.G. Pearson, J.M. Mills, *ACS* 1950, 72, 1892. (¹⁰) R.G. Pearson, L.H. Plette, *ACS* 1954, 76, 3087. (¹¹) R.G. Pearson, F.V. Williams, *ACS* 1953, 75, 3073. (¹²) R.G. Pearson, F.V. Williams, *ACS* 1954, 76, 258. (¹³) J.C. Reid, M. Calvin, *ACS* 1950, 72, 2948.

ELIMINATION

Bond Unsaturation

Liquid phase

Elimination of C_8H_8N and H^+ to form $C:C$

Reaction type:

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

Rate measured:

-d[OH]⁻/dt

No.	Reaction	Solvent	Amount of reactant:	Defined mass action law	Temperature	$k = k^0 \times 10^n$	Comments
1	$\text{C}_8\text{H}_8\text{N}(\text{C}_5\text{H}_5)_2\text{CH}_2\text{SO}_3^- + \text{OH}^- \rightarrow \text{C}_8\text{H}_8\text{N}(\text{C}_5\text{H}_5)_2\text{CH} + \text{H}_2\text{O}$ [2,2'-bis(1-pyridyl)-1-benzenesulfonate]	H_2O	A = 0.022 B = 0.00-0.04	k AB	65	1.22 -5	
2	$\text{C}_8\text{H}_8\text{N}(\text{C}_5\text{H}_5)_2\text{CH}_2\text{SO}_3^- + \text{OH}^- \rightarrow \text{C}_8\text{H}_8\text{N}(\text{C}_5\text{H}_5)_2\text{CH} + \text{H}_2\text{O}$ (2-methoxy-2-(1-pyridyl)-1-benzenesulfonate)	H_2O	A = B = 0.02	k AB	20	1.0 -3	
3	$\text{C}_8\text{H}_8\text{N}(\text{C}_5\text{H}_5)_2\text{CH}_2\text{SO}_3^- + \text{OH}^- \rightarrow \text{C}_8\text{H}_8\text{N}(\text{C}_5\text{H}_5)_2\text{CH} + \text{H}_2\text{O}$ (2-methoxy-2-(2-pyridyl)-1-benzenesulfonate)	H_2O	A = B = 0.02	k A ²	99	0.0 -2	†

COMMENTS

Reaction. (1) 1st law with respect to each reactant not determined as A & B. Calculated third order constant gave best fit for the single determination. The cyclooctene reacted very slowly except in presence of Be^{++} where a slight autocatalysis was observed leading to a steady state order rate, possibly due to catalysis at surface of precipitating Barium sulfonate.

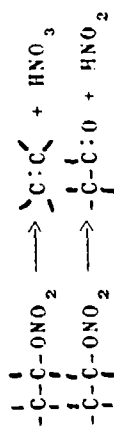
LITERATURE

F.G. Bordwell, M.L. Peterson, JCS 1955, 77, 1145.

ELIMINATION

Double bond formation by elimination from nitrate ester

liquid phase



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

Reaction types:

Coded solvents at end of table.

No.	Reaction	Solvent (Medium)	Amount of reactant	Amount of Addend	Diluent	Coded solvents	Temperature	$k \times 10^{12}$		$A =$ $A^0 \times 10^7$	Comments	Temperature
								k^0	n			
1	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*	$10^2 A = 3; 10^2 B = 9$			Et 90*	50	6	-8		*	(1)
2	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}=\text{O} + \text{HNO}_2$	Et 60*				Et 60*	50	8	-7		*	(1)
3	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*	$10^2 A = 3; 10^2 B = 9$			Et 90*	50	3	-3		*	(1)
4	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}=\text{O} + \text{HNO}_2$	Et 60*				Et 60*	45	2.1	-6		*	(1)
5	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*	$10^2 A = 3$			Et 90*	60	4	-8		*	(1)
6	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*	$10^2 A = 3; 10^2 B = 9$			Et 90*	75	2.4	-7		*	(1)
7	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*				Et 90*	59	3	-9		*	(1)
8	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*	$10^2 A = 3; 10^2 B = 9$			Et 90*	80	9	-7		*	(1)
9	$\begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}-\text{C}-\text{ONO}_2 + \left\{ \begin{array}{c} \text{H}_2\text{O} \\ \text{H}_2\text{OH} \end{array} \right\} \longrightarrow \begin{array}{c} \text{I} \\ \\ \text{I} \end{array} \text{C}=\text{C} + \text{HNO}_3$	Et 90*				Et 90*		7.2	-6		*	(1)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^2$		δ	$A \times 10^2$		Comments	Literature
								k^0	n		A^0	n		
.5	$(\text{CH}_3)_2\text{CHNO}_2 + \text{OH}^- \longrightarrow$ $(\text{CH}_3)_2\text{CHO}^- + \begin{cases} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{cases} + \text{NO}_2^-$	Et 90*	$10^2 A = 3$ $10^2 B = 9$			k AB	50	9	-7				*	(1)
		Et 80*					80	5.5	-8					
							60	3	-7					
.6	$(\text{CH}_3)_3\text{CONO}_2 \longrightarrow (\text{CH}_3)_2\text{C}(\text{OH})_2 + \text{H}^+ + \text{NO}_3^-$	Et 90*	$10^2 A = 2-5$			k A	0	3.3	-7				*	(1)
							20	5.6	-6					
							30	2.38	-5					
		Et 90*	$10^2 A = 2-4$	NaOH	0.083	k A	0	6	-7					
							20	1.54	-5					
							30	5.5	-5					
		Et 80*	$10^2 A = 3-4$			k A	0	8.0	-6					
							10	3.9	-5					
							30	5.19	-4					
				NaOH	0.057		0	1.1	-5					
					0.10		9	4.95	-5					
					0.11		30	2.94	-4					
(6)		DW 95*	$10^2 A = 6-14$			k A	25	6	-7				*	(6)
		DW 85*					25	5.1	-6					
		DW 75*					25	1.7	-5					
		DW 90*					0	2.2	-6					
							10	1.0	-5					
				NaClO ₄	0.1		0	2.5	-6					
				NaOH	0.1		10	1.2	-5					
					0.1		10	1.1	-5					

Thermodynamic Properties of Chemical Compounds

622.1-1

No.	Reaction	Solvent (Medium)	Amount of reactant	Acid	Amount of added	Defined mass action law	Temperature	$k \times 10^n$		δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
1	$C_6H_5CH_2NO_2 \xrightarrow{C_6H_5OH} C_6H_5CH_2OH + HNO_2$	C_6H_5OH DMF	$10^2 A = 13$ 11 15 8	C_6H_5OH	C 1.0	KA	60	1.27	-8				*	(4)
2	$C_6H_5CH_2NO_2 + C_6H_5O^- \rightarrow C_6H_5CH_2O^- + C_6H_5OH + NO_2^-$	C_6H_5OH	$10^2 A = 4$; B = 0.10	$NaClO_4$	0.11 0.11	KAB	60	1.37	-7	24.2			*	(4)
3	$C_6H_5CH_2NO_2 + OH^- \rightarrow C_6H_5CH_2O^- + H_2O + NO_2^-$	EtOH	$10^2 A = 3-9$ $10^2 B = 3-10$			KAB	20 30 45 60	9.24 3.16 1.75 8.47	-5 -4 -3 -3				*	(2)
4	$C_6H_5CH_2NO_2 + C_6H_5O^- \rightarrow C_6H_5CH_2O^- + C_6H_5OH + NO_2^-$	EtOH				KAB	20 30 45 60	2.45 7.90 4.10 1.90	-5 -5 -4 -3	21.6	1.9	12		(2) (4)
5	$C_6H_5CH_2NO_2 + C_6H_5O^- \rightarrow C_6H_5CH_2O^- + C_6H_5OH + NO_2^-$	EtOH	$10^2 A = 4$; B = 0.1	CO_2 $C_6H_5O^-$	.03 .03	KAE	60 60 60	9.9 7 9	-5 -5 -5	20.9	1	11		(2) (4) (4) (5) (5) (5)
6	$C_6H_5CH_2NO_2 + C_6H_5O^- \rightarrow C_6H_5CH_2O^- + C_6H_5OH + NO_2^-$	C_6H_5OH	$10^2 A = 3-9$ $10^2 B = 3-11$	C_6H_5OH	.030 .046 .090 .21 ∞	KAE	45 45 45 45 45 60 60	3.8-3.4 2.72 1.77 1.08 7 4.9-3.6 2.7-2.2	-5 -5 -5 -5 -6 -4 -4				*	(2) (4)

Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of product	Defined mass	Temperature	$R \times 10^3$	R	$A = A^0 \times 10^3$	Comments	Literature
1. $C_6H_5OH + C_6H_5OH \rightarrow C_{12}H_{10}O_2$	C_6H_5OH	$10^2 A = 5-9$ $10^2 B = 7-11$	C_6H_5OH	0.001 0.10 0.05 0.70 ∞	RAB	60	1.28 9.9 6.3 2.97 3.80			*	(3) (4)
2. $C_6H_5OH + C_6H_5OH \rightarrow C_{12}H_{10}O_2$	C_6H_5OH	$10^2 A = 5-9$ $B = 0.10$	N	0.001 0.032 0.032 0.097 0.30 0.50 ∞	RAB	60	9.9-7.4 3.4-3.2 2.75 1.77 1.11 6.38 5.23			*	(4)
3. $C_6H_5OH + C_6H_5OH \rightarrow C_{12}H_{10}O_2$	C_6H_5OH	$10^2 A = 5$ $10^2 B = 9-10$	N	0.001 0.16 0.08 0.41 1.00 ∞	RAD	60	0.4-1.6 5.84 4.40 3.60 1.43 2.2			*	(4)
4. $C_6H_5OH + C_6H_5OH \rightarrow C_{12}H_{10}O_2$	C_6H_5OH	$10^2 A = 5-8$ $B = 0.1$	N	C 0.083 0.090 0.15 39 ∞	R/B	60	2.0-1.5 1.22 1.08 1.00 7.6 9.5			*	(4) (5)

No.	Reaction	Solvent (Medium)	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		Δ	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
.12	$\text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{ONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$ $\text{p-NO}_2\text{C}_6\text{H}_4\text{CHO} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90* Et 60*	$10^2\text{A} \sim 3; 10^2\text{B} \sim 5$			k AB	-10 0 10 0	1.01 3.48 1.08 7.4	-1 -1 0 -2	17.9	8 13	*	(2)	
.19	$\text{p-BrC}_6\text{H}_4\text{CH}_2\text{ONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$ $\text{p-BrC}_6\text{H}_4\text{CHO} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90* Et 60*	$10^2\text{A} \sim 3; 10^2\text{B} \sim 5$			k AB	20 20	8.54 2.04	-4 -4			*	(2)	
.20	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{ONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$ $\text{C}_6\text{H}_5\text{CH}_2\text{CHO} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90*	$10^2\text{A} \sim 3; 10^2\text{B} \sim 5$			k AB	60	8.1	-5			*	(2)	
.21	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{ONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$ $\text{C}_6\text{H}_5\text{CH}_2\text{CHO} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90*	$10^2\text{A} \sim 3; 10^2\text{B} \sim 5$			k AB	60	3.3	-8			*	(2)	

No.	Reaction	Solvent (Medium)	Amount of reactant	Defined species	Temperature, °C.	k = k ⁰ × 10 ¹⁷ r ⁰ n	B	A = A ⁰ × 10 ¹⁷ A ⁰ n	Comments	Literature
.22	$\text{C}_6\text{H}_5(\text{CH}_3)\text{CHONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{OH} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90*	10 ² A ~ 3; 10 ² B ~ 5	k AB	30	1.6 -7			*	(2)
.23	$\text{C}_6\text{H}_5(\text{CH}_3)\text{CHONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow \text{C}_6\text{H}_5(\text{CH}_3)\text{C}(\text{O})\text{OH} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90*	10 ² A ~ 3; 10 ² B ~ 5	k AB	20	1.27 -6			*	(2)
.24	$(\text{C}_6\text{H}_5)_2\text{CHONO}_2 + \text{C}_2\text{H}_5\text{O}^- \longrightarrow (\text{C}_6\text{H}_5)_2\text{C}(\text{O})\text{OH} + \text{C}_2\text{H}_5\text{OH} + \text{NO}_2^-$	C ₂ H ₅ OH	10 ² A ~ 3; 10 ² B ~ 5	k AB	10 20 30	1.61 5.25 1.59 -4 -4 -3	19.5	2 11	*	(2)
.25	$(\text{C}_6\text{H}_5)_2\text{CHONO}_2 + \left\{ \begin{array}{l} \text{OH}^- \\ \text{C}_2\text{H}_5\text{O}^- \end{array} \right\} \longrightarrow (\text{C}_6\text{H}_5)_2\text{C}(\text{O})\text{OH} + \left\{ \begin{array}{l} \text{H}_2\text{O} \\ \text{C}_2\text{H}_5\text{OH} \end{array} \right\} + \text{NO}_2^-$	Et 90*	10 ² A ~ 3; 10 ² B ~ 5	k AB	0 10 20	2.98 1.07 3.17 -5 -4 -4	19.0	5 10		(2)

SOLVENTS

Et 90* (60) (45) C₂H₅OH vol. & indicated + H₂O (1) (2) (4) (5)

DW 95* (85) (75) (60) Dioxane wt. & indicated + H₂O (6)

COMMENTS

General. In aqueous and alcoholic solutions elimination reactions occur simultaneously with solvolysis reactions which lead to the formation of corresponding alcohols and ethers. For these reactions see 212,451. Elimination may simultaneously lead to two types of products, (a) formation of olefin by loss of H^+ and NO_2^- , (b) the formation of aldehyde, ketone by elimination of H^+ and NO_2^- . The total reaction involving solvolysis and elimination has been broken up into the individual reactions by determination of the amount of olefin, nitrite and the total base consumed.

Reactions. (1) (2) Reactions occur simultaneously and are assumed to be of the same order. (3) Extent of olefin formation is indicated. (4) (5) Reactions occur simultaneously and are assumed to be of the same order.

(6) First order rate law observed in even addition of strong base. OH^- did not appear to increase more than observed with salts. Values given by (6) are for initial rate since calculated first order constants tended to increase with the source of reaction in dioxane solutions. (7) In absence of strong base first order rate law valid. Values listed by (6) in dioxane solutions are initial rates as calculated constants increased slightly with course of reaction.

(8) No observable solvolysis observed. (9) Elimination reaction observed by (2) to make up 87% of total reaction. (10) (11) (12) Total rate observed is composite of reaction due to $C_6H_5O^-$ and $C_2H_5O^-$. Addition of C_2H_5OH shifted the equilibrium from $C_2H_5O^-$ to $C_6H_5O^-$ and C_2H_5OH . Value listed under C_6H_5OH obtained by extrapolation to value of k for $C_2H_5O^-$ at 10^{-2} M. (13) Phenol concentrations abnormally large decreases in k were observed which were neglected in making the extrapolations. (14) Elimination observed to represent 54% of total reaction. (15) Reaction is predominantly solvolysis and elimination accounts for only 0.2% of total reaction. (16) No observable solvolysis.

(17) (18) (19) Elimination accounts for 90% of total reaction. (20) (21) Reactions occur simultaneously and are assumed to be of the same order. (22) (23) Reactions occur simultaneously and are assumed to be of the same order. (24) Elimination accounts for only 17% of total reaction.

LITERATURE

- (1) J. W. Baker, A. J. Neale, *CSZ* 1952, 1208.
- (2) J. W. Baker, T. G. Hedges, *CSZ* 1955, 616.
- (3) J. W. Baker, A. J. Neale, *MT* 1953, 172, 563.
- (4) J. W. Baker, A. J. Neale, *CSZ* 1954, 5225.
- (5) J. W. Baker, A. J. Neale, *CSZ* 1955, 208.
- (6) G. N. Lucas, L. P. Hammett, *ACS* 1942, 64, 1928.

ELIMINATION

Bond-unsaturation elimination

Thio ether and H⁺ from alkyl sulfonium ion

Liquid phase

Amounts are in M/l.

Rate constants are in M/l and sec.

* Coded solvents at end of table.

For simultaneous solvolysis reactions see 742.461. Reaction measured +dL/dt unless stated otherwise.

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k \times 10^n$		δ	$A \times 10^{11}$		Successes	Literature
								k^0	n		A^0	n		
.1	$(CH_3)_2SCH_2CH_2CH_3 + C_2H_5O^- \rightarrow CH_2=CH_2 + (CH_3)_2S + C_2H_5OH$ $\rightarrow$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = kAB$	45 64	5.0 6.0	-5 -4	28	9	14	*	(⁵)
.2	$(CH_3)_2SCH_2CH_2CH_3 + C_2H_5O^- \rightarrow CH_2=CHCH_3 + (CH_3)_2S + C_2H_5OH$ $\rightarrow$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = kAB$	64	2.7	-4				*	(⁵)
.3	$(CH_3)_2SCH_2CH_2CH_3 + C_2H_5O^- \rightarrow CH_2=CHCH_2 + (CH_3)_2S + C_2H_5OH$ $\rightarrow$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = kAB$	45 64	1.14 1.04	-3 -2	25	2	14	*	(⁶)
.4	$(CH_3)_2SCH_2CH_2CH_2CH_3 + C_2H_5O^- \rightarrow$ $\rightarrow CH_2=CHCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ $\rightarrow$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = kAB$	64	1.7	-4				*	(⁵)
.5	$(CH_3)_2SCH_2CH_2CH_2CH_3 + C_2H_5O^- \rightarrow$ $\rightarrow CH_2=C(CH_3)_2 + (CH_3)_2S + C_2H_5OH$ $\rightarrow$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = kAB$	64	1.4	-4				*	(⁵)
.6	$(CH_3)_2SCH_2CH_2CH_2CH_3 + C_2H_5O^- \rightarrow \left\{ CH_2=CHCH_2CH_3 + (CH_3)_2S + C_2H_5OH \right\}$ $\rightarrow$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	= A = B	$dL/dt = kAB$	64	6.9	-3				*	(⁶)

No.	Reaction	Solvent	Amount of reactant	Added	Amount of added	Defined mass action law	Temperature	$k \times 10^n$		$\bar{r}$	$A \times 10^n$		Comments	Literature
								k^0	n		A^0	n		
7	$(CH_3)_2S(CH_3)_3^+ + CH_3OH \rightarrow (CH_3)_2S + CH_3OH$ (solvolysis)	Et 97*	A = 0.02-0.03	I ⁻	A	$dL/dt = kA$	50	9.0	-8				*	(7)
8	$(CH_3)_2S(CH_3)_3^+ + CH_3OH \rightarrow (CH_3)_2S + CH_3OH$ (solvolysis)	C ₂ H ₅ OH	A = 0.02; B = 0.1	I ⁻	A	k AB	20	1.14	-3	24	8	14	*	(2)
		Et 97*	A = 0.02-0.05; B = 0.3-0.5	I ⁻	A		45	2.94	-2					(7)
		Et 97*	A = 0.02-0.05; B = 0.3-0.5	Na ⁺	B		24	7-9	-2					
9	$(CH_3)_2S(CH_3)_3^+ + CH_3OH \rightarrow (CH_3)_2S + CH_3OH$ (solvolysis)	Et 97*	A = 0.02-0.12	I ⁻	A	k A	50	9.7	-5				* (1) (2) (7)	(1) (2)
		Et 90*					50	3.18	-5					(1) (2)
		Et 50*					65	3.05	-4					
							93	3.29	-3	32.1	1.7	17		
							65	1.82	-4					
10	$(CH_3)_2S(CH_3)_3^+ + CH_3OH \rightarrow (CH_3)_2S + CH_3OH$ (solvolysis)	Et 97*	A = 0.05-0.09; B = 0.3-0.4	I ⁻	A	k AB	24	5-6	-4				*	(7)
				Na ⁺	B									
11	$(CH_3)_2S(CH_3)_3^+ + CH_3OH \rightarrow (CH_3)_2S + CH_3OH$ (solvolysis)	H ₂ O	A = B = 0.1	Et ⁻	A	$-dB/dt = kAB$	41	1.30	-5				*	(4)
				Na ⁺	B		59	1.14	-4	24.9	2	12		
							71	4.32	-4					
12	$(CH_3)_2S(CH_3)_3^+ + CH_3OH \rightarrow (CH_3)_2S + CH_3OH$ (solvolysis)	C ₂ H ₅ OH	A = 0.06; B = 0.1	I ⁻	A	$-dE/dt = kAB$	30	3.79	-3				*	(3)
			0.05 0.1	Na ⁺	B		35	1.05	-2	24	1.6	15	*	(5)
							46	3.94	-2					

HOMOGENEOUS REACTION KINETICS

422-463

3

No.	Reaction	Solvent	Amount of reactant	Catalyst	Pressure	Concentration	Temperature	$k^o \times 10^2$	Comments	Literature
17	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	A = B	DL/dt = R AB	64	5.72	-2	(6)
18	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	A = B	DL/dt = R AB	80	9.17	-4	(3)
19	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	C_2H_5OH	A = 0.05; B = 0.1	I^- Na^+	A = B	DL/dt = R AB	80	8.12	-2	(3)
20	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	H_2O	A = 0.2-0.4; B = 0.2-0.7	Na^+	A = B	DL/dt = R AB	100	2.4	-5	(4)
21	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	Et_2O^*	A = 0.2-0.7	Na^+	A = B	DL/dt = R AB	100	2.05	-2	
22	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	Et_2O^*	A = 0.2	Na^+	A = B	DL/dt = R AB	100	2.10	-3	
23	$(CH_3)_2SCH(CH_3)_2 + C_2H_5O^- \rightarrow CH_3CH_2SCH_2CH_3 + (CH_3)_2S + C_2H_5OH$ (solvolysis)	Et_2O^*	A = 0.2-0.4	Na^+	A = B	DL/dt = R AB	100	1.89	-3	(4)

CODED SOLVENTS

Et 97*	$C_2H_5OH + 2.9 vol. \% H_2O$ (97 vol. % C_2H_5OH)
Et 80*	C_2H_5OH 80 vol. % + H_2O 20 vol. %
Et 60*	C_2H_5OH 60 vol. % + H_2O 40 vol. %
Et 50*	C_2H_5OH 50 vol. % + H_2O 50 vol. %

COMMENTS

General. Reactants are listed in the order of increasing complexity. First are dimethyl sulfonium salts in the order of increasing numbers of C atoms of the third alkyl group. Straight chain isomers precede the branched-chain isomers. The dimethyl sulfonium salts are followed by diethyl, etc. In almost all cases the elimination is accompanied by a parallel solvolysis reaction which in some cases may be the predominant reaction. Both reactions appear to be of the same order. These are listed together with a rate constant $k = k_E + k_S$ in table 242.461. In this table the derived rate constant for the elimination reaction only is listed. This constant has been calculated from the overall constant by multiplying k by the fraction of olefin found in the reaction products.

Reaction. (.1) Elimination accounts for 12% and 15.4% of the total reaction at 45 and 64°C respectively. (.2) Elimination accounts for 7.1% of total reaction. (.3) Elimination accounts for 61 and 65.7% of the total reaction at 45 and 64°C respectively. (.4) Elimination accounts for 4.7% of the total reaction. (.5) Elimination accounts for 2.4% of the total reaction. (.6) Elimination accounts for 57.7% of total reaction with 74% of olefin as $\text{CH}_2=\text{CHC}_2\text{H}_5$ and 26% as $\text{CH}_3\text{CH}=\text{CH}_2$. (.7) Elimination accounts for 50.5% of the total reaction. (.8) Parallel solvolysis reaction negligible and amounts to less than 1% of total reaction. (.9) Elimination accounts for 84.4% and 39.9% of total reaction in the 97 vol % and 50 vol % ethanol respectively. In 80 vol % ethanol elimination accounts for 47.8%, 49.4% and 53.7% of the total reaction at 50°, 65°, and 85°C respectively. A slight decrease in olefin % with course of reaction is probably due to a consecutive solvolysis of the olefin. (.10) Elimination accounts for 96-98% of total reaction. Olefin consists of 86% of $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$ and 14% of $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$. Second order rate law followed for 90% of reaction course but calculated constants showed slight decrease with increase in B. (.11) Extent of parallel solvolysis reaction not stated. At 59°C isotope effect S^{32}/S^{34} is + 0.15%. (.12) At 64°C elimination accounts for 89.4% of total reaction. (.13) Elimination accounts for 53.1% of total reaction at 64°C. Rate constant extrapolated to 64°C from 50° and 45°. (.14) (.15) Extent of parallel solvolysis reaction not determined and rate constant given is for total reaction, elimination and solvolysis. (.16) Elimination accounts for 86% of total reaction in H_2O and 100% in the ethanol water mixtures. (.17) No appreciable solvolysis reaction in contrast to this reaction in H_2O where no appreciable olefin formation is observed and reaction obeys first order kinetics.

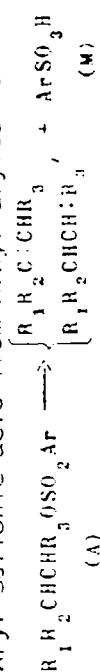
LITERATURE

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(⁴) J. L. Glavin, E. D. Hughes, C. K. Ingold, *CSL* 1935, 236. (⁵) E. D. Hughes, C. K. Ingold, G. A. Maw, *CSL* 1948, 2072.
(⁶) E. D. Hughes, C. K. Ingold, G. A. Maw, L. I. Woolf, *CSL* 1948, 2077. (⁷) E. D. Hughes, C. K. Ingold, L. I. Woolf, *CSL* 1948, 2084. (⁸) W. H. Saunders, S. Asperger, *ACS* 1957, 79, 1612.

ELIMINATION

Bond-unsaturation elimination

Aryl sulfonic acid from alkyl arylsulfonate



Liquid phase
Amounts are in M/l.
Rate constants are in
M⁻¹ and sec.
Codes solvent and/or
cat. Table.

Rate measured M/d² unless otherwise indicated

For data on ester exchange see 422.467

No.	Reaction	Solvent	Amount of reactant	Amount added	Notes (M, M ⁻¹ , sec.)	Temperature, °C.	Rate M/d ²	Code
1	$(R_1R_2CH_2)_3OSO_2R_3 \xrightarrow{H^+} R_1R_2C=CH_2 + R_3SO_3H$ $\left\{ \begin{array}{l} (R_1R_2CH_2)_3OSO_2R_3 \\ (R_1R_2CH_2)_3OSO_2R_3 \end{array} \right\} \xrightarrow{H^+} R_1R_2C=CH_2 + R_3SO_3H$ (ester exchange)	CH ₃ COOH	A ~ 0.6	cat.	cat. = 0.1A	60 65	0 0	(7)
2	$(R_1R_2CH_2)_3OSO_2R_3 \xrightarrow{H^+} R_1R_2C=CH_2 + R_3SO_3H$ $\left\{ \begin{array}{l} (R_1R_2CH_2)_3OSO_2R_3 \\ (R_1R_2CH_2)_3OSO_2R_3 \end{array} \right\} \xrightarrow{H^+} R_1R_2C=CH_2 + R_3SO_3H$ (ester exchange)	Ac ⁺	A ~ 0.03	-1A, 2A = R' + 0.7A		70	1.20 -4	(4)
3	$(R_1R_2CH_2)_3OSO_2R_3 \xrightarrow{H^+} R_1R_2C=CH_2 + R_3SO_3H$ $\left\{ \begin{array}{l} (R_1R_2CH_2)_3OSO_2R_3 \\ (R_1R_2CH_2)_3OSO_2R_3 \end{array} \right\} \xrightarrow{H^+} R_1R_2C=CH_2 + R_3SO_3H$ (ester exchange)	Ac ⁺	A ~ 0.03	-1A, 2A = R' + 0.7A		70	3.0 1.20 -4	(4)

National Bureau of Standards - National Research Council

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^3$	n	Comments	Literature	
Aryl-substituted-alkyl-arylsulfonates												
8	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3 + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$ $\longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + \text{C}_2\text{H}_5\text{OH} \quad (\text{elim.}) \quad k'$ $\longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- \quad (\text{exchange}) \quad k''$	$\text{C}_2\text{H}_5\text{OH}$	A = 0.06; B = 0.12			$-\frac{dA}{dt} = (k' + k'')AB$	30 30	3.92 1.16	-5 -4			(⁷)
9	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3 + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$ $\longrightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + \text{C}_2\text{H}_5\text{OH} \quad (\text{elim.}) \quad k'$ $\longrightarrow p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- \quad (\text{exchange}) \quad k''$	$\text{C}_2\text{H}_5\text{OH}$	A = 0.06; B = 0.12			$-\frac{dA}{dt} = (k' + k'')AB$	30 30	1.69 8.61	-5 -5			(⁸)
10	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3 + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$ $\longrightarrow p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}_2 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + \text{C}_2\text{H}_5\text{OH} \quad (\text{elim.}) \quad k'$ $\longrightarrow p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- \quad (\text{exchange}) \quad k''$	$\text{C}_2\text{H}_5\text{OH}$	A = 0.06; B = 0.12			$-\frac{dA}{dt} = (k' + k'')AB$	30 30	1.36 2.93	-4 -4			(⁸)
11	$p\text{-BrC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3 + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$ $\longrightarrow p\text{-BrC}_6\text{H}_4\text{CH}_2\text{CH}_2 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + \text{C}_2\text{H}_5\text{OH} \quad (\text{elim.}) \quad k'$ $\longrightarrow p\text{-BrC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OC}_2\text{H}_5 + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- \quad (\text{exchange}) \quad k''$	$\text{C}_2\text{H}_5\text{OH}$	A = 0.06; B = 0.12			$-\frac{dA}{dt} = (k' + k'')AB$	30 30	3.69 5.53	-4 -4			(⁸)
Sulfone-substituted Alkyl arylsulfonates												
12	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3 + \text{OH}^- \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3) + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + \text{H}_2\text{O}$	D_2SO_4	$10^3 A = 4-5$; $10^3 B = 4-5$	Na^+ KCl	B 0.1	$k \text{ AB}$	25	1.84	+2	*		(⁹) (¹⁰)

No.	Reaction	Solvent	Amount of reactant	Addend	Amount of addend	Defined mass action law	Temperature	$k^0 \times 10^7$	ρ	$A = A^0 \times 10^n$	Comments	Literature	
146	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3 + p\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + (\text{CH}_3)_3\text{NH}^+$	CH_3OH^*	$10^2 A = 1$; $10^2 B = 2-9$	M + N	.003-.007	R AB	25	1.30	-1		*	(9) (11)	
147	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3 + p\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + (\text{C}_2\text{H}_5)_3\text{NH}^+$	CH_3OH^* CHCl_3 $\text{CH}_3\text{COOC}_2\text{H}_5$ CH_3CN Diox^* C_6H_6 $\text{C}_6\text{H}_5\text{Cl}$	$10^2 A = 1$; $10^2 B = 6-10$	M + N $(\text{C}_2\text{H}_5)_3\text{NH}^+$ Cl^- M + N	.003-.008	R AB	25	5.93	-2		*	(8) (11)	
148	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3 + p\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + (\text{C}_2\text{H}_5)_3\text{NH}^+$	CH_3OH CHCl_3 $\text{CH}_3\text{COOC}_2\text{H}_5$ CH_3CN Diox^* C_6H_6 $\text{C}_6\text{H}_5\text{Cl}$	$10^4 A = 2$; $10^2 B = 2-6$	$\text{C}_2\text{H}_5\text{OH}$	0.5		25	9.31 1.46 7.69 7.55 9.36 9.83 8.64 1.76	-3 -3 -4 -3 -4 -4 -4 -3				(2)
149	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3 + p\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + (\text{CH}_3)_3\text{NH}^+$	CH_3OH^*	$10^4 A = 2$; $10^2 B = 2-6$			R AB	25	3.29 1.06 2.30	-3 -2 -2	14.5	1.1		(2)
150	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3 + p\text{-CH}_3\text{C}_6\text{H}_4\text{N}^+ \longrightarrow$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH} + p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3^- + (\text{CH}_3)_3\text{NH}^+$	CH_3OH^* CHCl_3 $\text{CH}_3\text{COOC}_2\text{H}_5$ CH_3CN Diox^* C_6H_6 $\text{C}_6\text{H}_5\text{Cl}$	$10^4 A = 2$; $10^2 B = 2-6$			R AB	25	7.62 2.17 4.10	-3 -1 -2	12.9	2.0		(2)

[illegible]

No.	Reaction	Solvent	Amount of reactant	Added amount	Refined mass	Adjusted k^0	$k^0 \times 10^7$	$\bar{z}$	$A^0 \times 10^5$	Comments	Reference
17	$\text{cis-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + (\text{CH}_3)_3\text{N} \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + (\text{CH}_3)_3\text{NH}^+$	DW 50*	$10^3 A = 1$ $10^3 B = 6-10$		R 45	25	2.97	-3		*	(⁰) (11)
18	$\text{cis-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + (\text{C}_2\text{H}_5)_3\text{N} \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + (\text{C}_2\text{H}_5)_3\text{NH}^+$	DW 50*	$10^3 A = 1$ $10^3 B = 6-19$		R 48	25	9.5	-4		*	(⁰) (11)
19	$\text{trans-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + \text{OH}^- \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + \text{H}_2\text{O}$	DW 50* DW 55*	$10^3 A = 4-5$ $10^3 B = 4-5$ $10^3 A = 5-17$ $10^3 B = 6-33$	0.1	R 49	25	3.30	-2	17.4		(⁰) (10) (1)
20	$\text{trans-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + \text{OH}^- \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + \text{H}_2\text{O}$	DW 60*	$10^3 A = 6-17$ $10^3 B = 6-33$			30	1.07	-2	17.6		
21	$\text{cis-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + (\text{CH}_3)_3\text{N} \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + (\text{CH}_3)_3\text{NH}^+$	DW 70*	$10^3 A = 6-17$ $10^3 B = 6-33$			40	1.28	-1	17.6		
22	$\text{cis-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + (\text{C}_2\text{H}_5)_3\text{N} \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + (\text{C}_2\text{H}_5)_3\text{NH}^+$	DW 70.5*	$10^3 A = 6-17$ $10^3 B = 6-33$			40	1.28	-1	17.6		
23	$\text{cis-} \phi\text{-CH}_3\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} \xrightarrow{\text{H}_2\text{O}} \text{HOOC-(CH}_2\text{)}_6\text{CO}_2\text{H} + (\text{C}_2\text{H}_5)_3\text{N} \longrightarrow$ $\phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2\text{H} + \phi\text{-CH}_2\text{-(CH}_2\text{)}_6\text{CO}_2^- + (\text{C}_2\text{H}_5)_3\text{NH}^+$	DW 55*	$10^3 A = 6-17$ $10^3 B = 6-33$			40	1.28	-1	17.6		

COMMENTS.

General. Reactants are listed in the order of increasing complexity of the alkyl group. Primary precede secondary precede tertiary except that cyclic follow tertiary. Aryl substituted alkyl follow allyl and allyl substituted alkyl follow allyl-substituted. Parallel ester exchange to varying extent occurs in acid catalysis, base catalysis. Parallel solvolysis occurs in aqueous and alcoholic solvents. See 312.461.

Reaction. (1) Rate constant for elimination reaction only, which accounts for about one third of total reaction. Olefin distribution is 40.37 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$; 29.04 $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ with 43.27 cis and 46.37 trans-isomer. (2) extent of parallel ester exchange not determined. Rate constant is for total reaction, elimination and solvolysis. (3) Products determined were 50% ester exchange and 71.5% olefin made up of 15.7% $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, 35% cis- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ and 49% trans- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$. (4) Products determined were 35% ester exchange and 45% olefin made up of 10.7% $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, 35% cis- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ and 49% trans- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$. (5) Products determined were 10% ester exchange and 15% olefin made up of 12% $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, 17% cis- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$ and 73% trans- $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$. (6) Elimination accounts for only 39% of reaction with ester exchange accounting for 37%, see 302.461. (7) Elimination accounts for 55% and ester exchange for only 17% of reaction. (12) Extent of any parallel solvolysis reaction not indicated. (13) (.16) (.17) Rate constant corrected for simultaneous (.12), elimination catalyzed by OH^- . (21) (.22) Rate constant corrected for simultaneous (.20) elimination catalyzed by OH^- . (24) (.25) Rate constant corrected for simultaneous (.23) elimination catalyzed by OH^- . (27) (.28) Rate constant corrected for simultaneous (.26) elimination catalyzed by OH^- . (30) (.31) (.32) Rate constant corrected for simultaneous (.29) elimination catalyzed by OH^- .

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422.487

Bond Unsaturation

Elimination of ArSO_3^- and halide ion to form C:C



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W. J. L. G. B. C.

[illegible]

LITERATURE

1. *What is the purpose of this study?*

C. I. 1993b: 56. *Wageningen*, 175, 2009, 78, 199.

SECRET

Chemical and Biological Abstracts

1958, 1959

No.	Reaction	Solvent	Amount of reactant	Yield, %	Elemental analysis	λ_{max} , μ	ϵ		$A^{254} \times 10^3$	η_{inh}	Literature
							ϵ^0	ϵ^0			
101	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	0.3	-7			(21)
102	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	4.5	-5			(32)
103	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	3.39	-7			(41)
104	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	3.5	-1			(22)
105	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	1.7	-7			(104)
106	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	0.3	-5			(30)
107	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	1.91	-7			(30)
108	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	2.27	-5			(30)
109	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	1.55	-7			(41)
110	$\text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO} \xrightarrow{\text{C}_6\text{H}_5\text{MgBr}} \text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$	$\text{C}_6\text{H}_5\text{OH}$	$\text{A} = 1.0; \text{B} = 1.0$	100	84.3	20	1.29	-5			(104)

Continued on p. 3

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1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.

| Reaction | Position | Solvent | Amount of reactant | Radical | Escape probability | Rate constant $k \times 10^4$ | $R = k \times 10^4$ | $A = A^0 \times 10^4$ | Stoichiometry | Comments |
|----------|--|------------|--------------------|---------|--------------------|-------------------------------|---------------------|-----------------------|---------------|----------|
| 1 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.15; B = 0.84 | Na^+ | 0.1 | 44 | 4.3 | -6 | * | (26) |
| 2 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 45 | 4.37 | -5 | * | (26) |
| 3 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 45 | 4.10 | -5 | * | (26) |
| 4 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 58 | 2.00 | -4 | * | (26) |
| 5 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 65 | 6.00 | -4 | * | (26) |
| 6 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 51 | 9.5 | -9 | * | (40) |
| 7 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 50 | 2.44 | -6 | * | (40) |
| 8 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 26 | 9.0 | -7 | * | (31) |
| 9 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 1.35 | -6 | * | (31) |
| 10 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 2.04 | -6 | * | (31) |
| 11 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 3.00 | -5 | * | (31) |
| 12 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 4.0 | -5 | * | (31) |
| 13 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 4.5 | -6 | * | (31) |
| 14 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 5.3 | -6 | * | (31) |
| 15 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 7.4 | -6 | * | (31) |
| 16 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 8.9 | -6 | * | (31) |
| 17 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 1.10 | -5 | * | (31) |
| 18 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 1.43 | -5 | * | (31) |
| 19 | $(C_2H_5)_3COH + C_2H_5OH \rightarrow (C_2H_5)_3COH + C_2H_5OH + Cl^-$ | C_2H_5OH | A = 0.35; B = 0.2 | Na^+ | 0.1 | 25 | 2.4 | -6 | * | (31) |

| Reaction | Solvent | Amount of reactant | Reagent | Reagent concn | Temperature, °C | $k \times 10^3$ | $k_0 \times 10^3$ | k_0 | k_0 | k_0 | Comments |
|---|---------------------------------|----------------------------|---------|---------------|--|--|--|--|--|--|----------|
| $(\text{C}_2\text{H}_5)_3\text{C} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{COH} + \text{C}_2\text{H}_5\text{OH}$ | E | $10^2 A = 5.4$
C.9 | | | 25
40
51
61
61
61
61
61
61
61 | 1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5 | 1.5
1.5
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1.5 | 1.5
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1.5
1.5 | 1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5 | * (49) |
| $(\text{C}_2\text{H}_5)_3\text{C} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{COH} + \text{C}_2\text{H}_5\text{OH}$ | E | $10^2 A = 1.4$
10-20 | | | 25
39
51
51
51
51
51
51
51
51 | 1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5 | 1.5
1.5
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1.5
1.5 | 1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5
1.5 | * (49) |
| $(\text{C}_2\text{H}_5)_3\text{C} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{COH} + \text{C}_2\text{H}_5\text{OH}$ | SO_2 | $10^2 A = 2.5$
10-20 | | | 15
15
15 | 1.5
1.5
1.5 | 1.5
1.5
1.5 | 1.5
1.5
1.5 | 1.5
1.5
1.5 | 1.5
1.5
1.5 | * (10) |
| $(\text{C}_2\text{H}_5)_3\text{C} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{COH} + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A = 0.4-0.9$
B = 0.5-1 | | | 30 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | * (10) |
| $(\text{C}_2\text{H}_5)_3\text{C} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{COH} + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A = B = 0.1$ | | | 35 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | * (32) |
| $(\text{C}_2\text{H}_5)_3\text{C} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{C}_2\text{H}_5\text{OH}} (\text{C}_2\text{H}_5)_3\text{COH} + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A = 0.6$
B = 1 | | | 19 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | * (10) |

| Reaction | Reaction | Solvent | Amount of reactant | Assayed | Amount of product | Reaction time, min. | Temperature, °C. | $k \times 10^3$ | $k \times 10^3$ | $k \times 10^3$ | $k \times 10^3$ | Concentration |
|----------|---|------------|----------------------|----------|-------------------|---------------------|------------------|-----------------|-----------------|-----------------|-----------------|---------------|
| 1 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.8; B = 1 | | | | 101 | 4 | | | | (10%) |
| 2 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.2; B = 0.15 | NO_3^- | | | 91 | 1.15 | | | | (1%) |
| 3 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.8; B = 1 | | | | 109 | 4.15 | | | | (10%) |
| 4 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.15 | | | | 91 | 3.0 | | | | (30%) |
| 5 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.2; B = 4.0 | K^+ | | | 90 | 1.1 | | | | (30%) |
| 6 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.15 | Na^+ | | | 90 | 3.9 | | | | (30%) |
| 7 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.15 | | | | 90 | 1.29 | | | | (30%) |
| 8 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.15 | | | | 95 | 2.0 | | | | (30%) |
| 9 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.15 | | | | 90 | 9.0 | | | | (30%) |
| 10 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.2; B = 4.0 | Cl^- | | | 80 | 4.04 | | | | (30%) |
| 11 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 0.1-0.15 | Na^+ | | | 95 | 4.00 | | | | (30%) |
| 12 | $(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^-$ | C_2H_5OH | A = 1.15; B = 1.0 | | | | 130 | 1.21 | | | | (10%) |
| | | | | | | | 140 | 5.2 | | | | |

| No. | Ref. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Refined Mass | Temperature | $k^0 \times 10^2$ | k^0 | $k^0 \times 10^2$ | k^0 | $A^0 \times 10^2$ | Units | Temperature |
|-----|--------------------|---|---------|----------------------------|---------|-----------------|--------------|-------------|-------------------|-------|-------------------|-------|--------------------------------|-------|-------------|
| 89 | 19, 20, 21, 22, 23 | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | A = 0.05 | | | RA | 25 | 5.2 | -6 | 5.2 | -6 | (3), (4), (5), (52), (53), (7) | * | |
| 90 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | A = 0.04 | | | RA | 25 | 2.7 | -6 | 2.7 | -6 | (52) | * | |
| 91 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | A = 0.04 | | | RA | 25 | 3.3 | -6 | 3.3 | -6 | (52) | * | |
| 92 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | A = 0.04 | | | RA | 25 | 1.7 | -6 | 1.7 | -6 | (52) | * | |
| 93 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | $10^2 A = 7.3, 10^2 B = 0$ | N_2^+ | B | RA | 25 | 4.3 | -6 | 4.3 | -6 | (31) | * | |
| 94 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | 1.6 | 2.7 | | RA | 25 | 5.4 | -6 | 5.4 | -6 | | | |
| 95 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | 6.4 | 8.5 | | RA | 25 | 8.8 | -6 | 8.8 | -6 | | | |
| 96 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | 3.9 | 102 | | RA | 25 | 7.12 | -6 | 7.12 | -6 | | | |
| 97 | | $(CH_3)_2CH_2CO_2 + H_2 \longrightarrow$
$C_5H_{10} + H_3O^+ + Cl^-$ | EtOH* | 3.4 | 301 | | RA | 25 | 7.02 | -5 | 7.02 | -5 | | | |

HOMOGENEOUS REACTION KINETICS

422-491

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| No. | Reaction | Solvent | Amount of reactant | Added | Concentration of reagent | Temperature | $k \times 10^n$ | | δ | $A \times 10^{11}$ | | Comments | Literature |
|-----|--|---------------------------------|--------------------|---------------|--------------------------|-------------|---|----------------|----------|--------------------|-----|----------|------------------|
| | | | | | | | k^0 | n | | A^0 | n | | |
| 92 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow$
$\text{C}_6\text{H}_{12} + \text{C}_2\text{H}_5\text{OH} + \text{Et}^+$ (E)
$\longrightarrow (\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{Et}^+$ (S) | $\text{C}_2\text{H}_5\text{OH}$ | B = 1.0 | Na^+ | B | 25 | $k = 1.60$
$k_E = 1.42$
$k_S = 2.7$ | -6
-6
-7 | | | | * | (54) |
| 93 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.06 | | | 25 | 4.9 | -6 | | | | * | (3) (4) |
| 94 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow$
$\text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Et}^+$ (E)
$\longrightarrow (\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} + \text{Et}^+$ (S) | BCl_3^* | | | | 25 | $k = 8.25$
$k_E = 2.6$
$k_S = 5.6$ | -5
-5
-5 | | | | * | (8) |
| 95 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 25 | 6.0 | -6 | | | | * | (5) (6) (37) |
| 96 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 35 | 2.45 | -5 | | | | | |
| 97 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 45 | 7.0 | -5 | | | | | |
| 98 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 55 | 2.1 | -4 | 23 | 5 | 11 | | |
| 99 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow$
$\text{C}_6\text{H}_{12} + \text{C}_2\text{H}_5\text{OH} + \text{Et}^+$ (E)
$\longrightarrow (\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{Et}^+$ (S) | BCl_3^* | | | | 25 | 4.26 | -6 | | | | * | (53) |
| 100 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow$
$\text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Et}^+$ (E)
$\longrightarrow (\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{Et}^+$ (S) | BCl_3^* | | | | 35 | 1.82 | -5 | | | | | |
| 101 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 45 | 5.45 | -5 | | | | * | (7) |
| 102 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 55 | 1.66 | -4 | | | | | |
| 103 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | BCl_3^* | | | | 25 | $k = 5.47$
$k_E = 3.2$
$k_S = 0.3$ | -5
-5
-5 | | | | * | (2) (3) (4) (47) |
| 104 | $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_{12} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et_2SO^* | A = 0.05 | | | 25 | 1.00 | -5 | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Added | Product | Definite reaction | Temperature, °C | $\rho^0 \times 10^3$ | ρ^0 | η | $A = A^0 \times 10^3$ | Notes |
|-----|---|------------|--------------------|--------|---------|-----------------------------|-----------------|--|----------------|--------|-----------------------|--------------|
| 102 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | 90.85* | | | | R_A
$R = R_E + R_S$ | 25 | $R = 1.14$
$R_E = 4.6$
$R_S = 0.6$ | -4
-5
-5 | | | (7) |
| 103 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | C_2H_5OH | B = 1.0 | Na^+ | | R_{AB}
$R = R_E + R_S$ | 25 | $R = 4.72$
$R_E = 1.58$
$R_S = 4.00$ | -6
-5
-5 | | | (54) |
| 104 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | Et 90* | | | | R_A | 25 | $R = 4.19$
$R_E = 6.1$
$R_S = 1.7$ | -5
-7
-6 | 1.2 | 1.7 | (3) (4) |
| 105 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | 90.85* | | | | R_A
$R = R_E + R_S$ | 25 | $R = 1.94$
$R_E = 8.9$
$R_S = 1.0$ | -4
-5
-4 | | | (8) |
| 106 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | Et 90* | A = 0.05 | | | R_A | 25 | $R = 6.5$ | -6 | | | (3) (4) (57) |
| 107 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | B | $10^2 A = 1-9$ | | | R_A | 25 | $R = 1.4$ | -7 | | | (40) |
| 108 | $(CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O \longrightarrow (CH_3)_2CHCH_2COH + H_2O$
(E) (S) | B | $10^2 A = 1-9$ | | | R_A | 25 | $R = 4.4$ | -7 | | | (40) |

Heterogeneous Reaction Kinetics

192,671

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| No. | Reaction | Solvent | Amount of reactant | Defined rate | Temperature | $k^0 \times 10^3$ | k^0 | δ | $A = A^0 \times 10^3$ | Comments | Literature |
|-----|---|--------------------|--------------------|---|-------------|---|-------|----------|-----------------------|----------|--------------|
| 109 | $(\text{CH}_3)_3\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_2\text{COHCH}_3 + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et ₂ O* | A = 0.06 | k _A | 25 | 1.10 | -5 | | | * | (3) (4) |
| 110 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et ₂ O* | | k _A | 0 | 3.9 | -6 | | | * | (2) |
| | | | | | 15 | 3.4 | -5 | | | | |
| | | | | | 25 | 1.02 | -4 | 22.9 | 1 | | (2) (4) (40) |
| | | | | | 25 | 1.19 | -5 | | | | (7) |
| 111 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Br}^-$
$\searrow$
$(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O}$ | Et ₂ O* | | k _A
k = k _A + k _S | 25 | k _A = 1.21
k _S = 0.5 | -3 | | | * | (7) (8) |
| | | | | | 25 | k _A = 0.5
k _S = 0.6 | -4 | | | | |
| | | | | | 25 | k _S = 0.6 | -4 | | | | |
| 112 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et ₂ O* | | k _A | 25 | 2.9 | -5 | | | * | (9) |
| 113 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et ₂ O* | A = 0.06 | k _A | 25 | 1.4 | -5 | | | * | (3) (4) |
| 114 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Cl}^-$ | Et ₂ O* | | k _A | 25 | 1.05 | -4 | | | * | (4) (5) |
| 115 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(1-100000) | Et ₂ O* | A = 0.06 | k _A | 25 | 4.0 | -4 | | | * | (3) (4) |
| 116 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(1-100000) | Et ₂ O* | A = 0.06 | k _A | 25 | 1.0 | -4 | | | * | (3) (4) |
| 117 | $(\text{CH}_3)_3\text{COH}(\text{CH}_3)_2\text{COH} \longrightarrow (\text{CH}_3)_6\text{COH} + \text{H}_2\text{O}$ | A | | k _A | 25 | 5 | -0 | | | * | (2) |

| No. | Reaction | Solvent | Amount of reactant | Refined rates | Order of reaction | $k \times 10^3$
k^0 η | β | $\delta = A^0 \times 10^3$
A^0 η | Comments | Temperature |
|-----|---|------------|--------------------|--------------------------|-------------------|---|----------------------------------|--|----------|-------------|
| 118 | $[(CH_3)_3CCH_2]_2(C_2H_5)Cl + H_2O \longrightarrow C_{12}H_{24} + H_3O^+ + Cl^-$ | Et 50* | | k_A | 0 | 2.51
1.01
5.25
0
4.84
4.69
23 | -4
-3
-3
-3
-4
-3 | 15.6
1.2
12 | * | (2) |
| 119 | $[(CH_3)_2CCH_2]_2(C_2H_5)Cl + C_2H_5OH \longrightarrow C_{12}H_{24} + C_2H_5OH_2^+ + Cl^-$ | C_2H_5OH | | k_A | 15
25
30 | 2.61
1.95
6.65 | -5
-4
-4 | 21.0
1.0
12 | * | (2) |
| 120 | $cyclo-C_4H_9Cl + H_2O \longrightarrow$ | Et 50* | $A = 0.5-1$ | k_A
$k = k_E + k_S$ | 95
100 | 1
1.3 | -7
-5 | | * | (46) |
| 121 | $cyclo-C_4H_9Cl + H_2O \longrightarrow$ | Et 50* | $A = 0.5-1$ | k_A
$k = k_E + k_S$ | 95 | 3.8 | -4 | | * | (48) |
| 122 | $cyclo-C_4H_9Cl + H_2O \longrightarrow$
$\swarrow$
$cyclo-C_4H_8 + H_3O^+ + Cl^-$ (F)
$\searrow$
$C_4H_9OH, C_4H_9O^+H_2 + HCl$ (8) | Et 50* | $A = 0.5-1$ | k_A
$k = k_E + k_S$ | 95
95
95 | $k = 1.35$
$k = 4.3$
$k_S = 0.5$ | -4
-5
-5 | | | (49) |

| Yr. | Reaction | Solvent | Amount of reactant | Group | Group for transfer | Calcd. rate law | Temp. (°C) | $k \times 10^3$
k_0 | n | Reference |
|------|---|--------------------|--|----------------|--------------------|-----------------|----------------------|--------------------------|----------------------|-----------|
| 1950 | $\text{Cyclo-1,4-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(1) | Et ₂ O* | | | | | 25 | 25.67 | -6 | (6) |
| 1954 | $\text{Cyclo-1,4-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(2) | Et ₂ O* | $10^2 A \approx 4; 10^2 B = 0$
0.345
0.52 | N ⁺ | -3 | $k = k_1 + k_2$ | 25
25
25 | 5.0
1.08
2.43 | -6
-5
-5 | (14) |
| 1954 | $\text{Cyclo-trans-1,2-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(3) | Et ₂ O* | $10^2 A \approx 4; 10^2 B = 0$
3.95
7.90
34.5
52.0 | N ⁺ | -3 | | 25
25
25
25 | 6.0
1.0
2.7
9.7 | -6
-5
-5
-4 | (14) |
| 1957 | $\text{Cyclo-trans-1,2-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(4) | CH ₃ OH | $10^2 A \approx 4; 10^2 B = 0$
1.51
3.08
6.05
1.58 | N ⁺ | -3 | | 25
25
25
25 | 2.0
7.0
7.7
9.0 | -5
-5
-5
-4 | (14) |
| 1957 | $\text{Cyclo-1,4-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(5) | Et ₂ O* | | | | | 25 | 2.72 | -6 | (6) |
| 1957 | $\text{Cyclo-1,4-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(6) | Et ₂ O* | | | | | 25 | 2.97 | -6 | (6) |
| 1957 | $\text{Cyclo-1,4-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(7) | Et ₂ O* | $A = 0.12$ | | | | 105
160 | 2
6.4 | -6
-6 | (30a) |
| 1957 | $\text{Cyclo-1,4-(CH}_2\text{)}_2\text{C}_6\text{H}_9\text{O} + \text{H}_2\text{O} \xrightarrow{\text{Et}_2\text{O}} \text{C}_6\text{H}_{18} + \text{H}_3\text{O}^+ + \text{Cl}^-$
(8) | Et ₂ O* | $10^2 A = 9$ | | | | 125 | 1.57 | -4 | (30a) |

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Substituted cyclo-alkyl halides

| H_2O | $10^3 A = 0$ | μ_A | μ_B | μ_C | μ_D | μ | $\Delta G^\circ = -RT \ln K$ |
|----------------------|--------------|---------|---------|---------|---------|-------|------------------------------|
| H_2O | $10^3 A = 0$ | μ_A | μ_B | μ_C | μ_D | μ | $\Delta G^\circ = -RT \ln K$ |
| H_2O | $10^3 A = 0$ | μ_A | μ_B | μ_C | μ_D | μ | $\Delta G^\circ = -RT \ln K$ |
| H_2O | $10^3 A = 0$ | μ_A | μ_B | μ_C | μ_D | μ | $\Delta G^\circ = -RT \ln K$ |
| H_2O | $10^3 A = 0$ | μ_A | μ_B | μ_C | μ_D | μ | $\Delta G^\circ = -RT \ln K$ |

| Reaction | Solvent | Amount of reactant | Added to solution | Calculated rate law | Temp., °C. | $k \times 10^3$
k_0 | δ | $A = A_0 \times 10^3$
A_0 | Comments | Reference |
|---|--------------------|----------------------------|-------------------|---------------------|------------|--------------------------|----------|--------------------------------|----------------------------|-----------|
| 1. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 100 | <1 | -6 | | * | (33) |
| 2. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 1.5-3; B = 0.11$ | Na^+ | | 80 | 8.15 | -4 | | $\Delta S^\ddagger = -4$ | (33) |
| 3. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 100 | 1.93 | -8 | | $\Delta S^\ddagger = -10$ | (33) |
| 4. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 80 | 1.07 | -6 | | * | (33) |
| 5. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 100 | 7.59 | -5 | | $\Delta S^\ddagger = -10$ | (33) |
| 6. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 1.5-3; B = 0.11$ | Na^+ | | 80 | 1.76 | -6 | | $\Delta H^\ddagger = 22.3$ | (33) |
| 7. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 80 | 1.84 | -4 | | $\Delta S^\ddagger = -7$ | (33) |
| 8. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 80 | 2.69 | -3 | | $\Delta S^\ddagger = -7$ | (33) |
| 9. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 80 | 6.7 | -5 | | * | (33) |
| 10. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 100 | 7.9 | -7 | | $\Delta S^\ddagger = -1$ | (33) |
| 11. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 1.5-3; B = 0.11$ | Na^+ | | 80 | 9.50 | -4 | | $\Delta S^\ddagger = -7$ | (33) |
| 12. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 80 | 2.61 | -3 | | $\Delta S^\ddagger = -15$ | (33) |
| 13. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 80 | 1.34 | -7 | | $\Delta S^\ddagger = -15$ | (33) |
| 14. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 100 | 1.02 | -6 | | $\Delta S^\ddagger = -15$ | (33) |
| 15. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 2-5$ | | | 100 | 1.1 | -7 | | $\Delta S^\ddagger = -15$ | (33) |
| 16. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 1.5-3; B = 0.11$ | Na^+ | | 80 | 5.27 | -5 | | $\Delta S^\ddagger = -15$ | (33) |
| 17. $2\text{C}_2\text{H}_5\text{I} + 2\text{C}_2\text{H}_5\text{MgBr} \xrightarrow{10^{-2}\text{M}} 2\text{C}_2\text{H}_5\text{MgI} + \text{H}_2$ | Et ₂ O* | $10^2 A = 1.5-3; B = 0.11$ | Na^+ | | 80 | 1.52 | -3 | | $\Delta S^\ddagger = -15$ | (33) |

| No. | Reaction | Amount of reactant | Addend | Amount of addend | Defined mass | Temperature | $k^0 \times 10^n$ | β | $A^0 \times 10^n$ | Comments | Temperature |
|----------------------------|--|----------------------|-----------------|------------------|--------------|-------------|-------------------|---------|---------------------------|----------|-------------|
| | | | | | | | | | | | |
| Unsaturated-Alkenyl halide | | | | | | | | | | | |
| 173 | $\text{CH}_2=\text{CHBr} + \text{OH}^- \longrightarrow$ | H_2O | Na^+ | $\mu = 3$ | R AB | 70 | 1.4 | 21.5 | $\Delta S^\ddagger = -11$ | | (38) |
| | | | | | | 75 | 2.7 | | | | |
| 174 | $\text{cis-(COO)}^-\text{CH}_2\text{CH(COO)}^-\text{Cl} + \text{OH}^- \longrightarrow$ | H_2O | NaNO_3 | $\mu = 0.1$ | R AB | 70 | 3.09 | 24.9 | $\Delta S^\ddagger = -9$ | * | (17), (36) |
| | (chloromaleate) | | | 0 | | 70 | 2.79 | | | | (36) |
| | | | | $\mu = 0.1$ | | 70 | 3.72 | 24.0 | $\Delta S^\ddagger = -14$ | | (17), (36) |
| | | | | 0 | | 70 | 6.9 | | | | (36) |
| 175 | $\text{trans-(COO)}^-\text{CH}_2\text{CH(COO)}^-\text{Cl} + \text{OH}^- \longrightarrow$ | H_2O | NaNO_3 | $\mu = 0.1$ | R AB | 70 | 3.15 | 21.0 | $\Delta S^\ddagger = -16$ | * | (17), (36) |
| | (chlorofumarate) | | | 0 | | 70 | 2.54 | | | | (36) |
| | | | | $\mu = 0.1$ | | 70 | 3.96 | 23.1 | $\Delta S^\ddagger = -12$ | | (17), (36) |
| | | | | 0 | | 70 | 5.45 | | | | (36) |
| 176 | $\text{cis-(COO)}^-\text{CH}_2\text{CH(COO)}^-\text{Br} + \text{OH}^- \longrightarrow$ | H_2O | NaNO_3 | $\mu = 0.1$ | R AB | 70 | 1.13 | 22.6 | $\Delta S^\ddagger = -11$ | * | (17), (36) |
| | (bromomaleate) | | | 0 | | 70 | 3.94 | | | | (36) |
| | | | | $\mu = 0.1$ | | 70 | 1.23 | 22.5 | $\Delta S^\ddagger = -12$ | | (17), (36) |
| | | | | 0 | | 70 | 1.70 | | | | (36) |
| 177 | $\text{trans-(COO)}^-\text{CH}_2\text{CH(COO)}^-\text{Br} + \text{OH}^- \longrightarrow$ | H_2O | NaNO_3 | $\mu = 0.24$ | R AB | 45 | 1.09 | | | * | (17) |
| | (bromofumarate) | | | 0.10 | | 45 | 7.9 | | | | |
| | | | | 0.055 | | 45 | 6.6 | | | | |
| | | | | 0.10 | | 70 | 1.39 | 17.9 | $\Delta S^\ddagger = -10$ | | (17), (36) |
| | | | | 0 | | 70 | 4.55 | | | | (36) |
| | | | | $\mu = 0.10$ | | 70 | 2.04 | 19.7 | $\Delta S^\ddagger = -16$ | | (17), (36) |
| | | | | 0 | | 70 | 1.92 | | | | (36) |
| 178 | $\text{cis-(COO)}^-\text{CH}_2\text{CH(COO)}^-\text{Cl} + \text{OH}^- \longrightarrow$ | H_2O | K^+ | $\mu = 3$ | R AB | 50 | 1.7 | | | * | (42) |
| | | | | | | 75 | 6.3 | 31 | | | |
| | | | | | | 95 | 6.9 | 1.8 | | | |

Heterogeneous Reaction Kinetics

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| No. | Reaction | Substance | Amount of reactant | Added | Added to surface | Temperature | $k \times 10^2$
k^0 n | β | $A \times 10^7$
A^0 n | Comments | Source |
|-----|--|---------------------------------|--|---------------|------------------------|-------------------------|--|---------|-----------------------------------|---------------------------|--------|
| 120 | $\text{cis-2-CH}_3\text{CH=CHCl} + \text{CH}_3\text{O}^- \longrightarrow \text{HClOCH} + \text{CH}_3\text{OH} + \text{Cl}^-$ | CH_3OH | $10^3\text{A} = 6-100; 10^2\text{B} = 4-12; \text{Na}^+$ | Na^+ | $\text{B} = \text{AB}$ | 58
72
85 | 9.13 -6
8.00 -5
5.17 -4 | 35.1 | 1.5 16 | | (43) |
| 121 | $\text{trans-2-CH}_3\text{CH=CHCl} + \text{OH}^- \longrightarrow \text{HClOCH} + \text{H}_2\text{O} + \text{Cl}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10\text{A} = 1-2; 10\text{B} = 1$ | K^+ | $\text{B} = \text{AB}$ | 60
65
75
85 | 3.0 -9
1.1 -8
3.4 -8
6.6 -8 | 20 | 1.1 5 | * | (42) |
| 122 | $\text{trans-2-CH}_3\text{CH=CHCl} + \text{CH}_3\text{O}^- \longrightarrow \text{HClOCH} + \text{CH}_3\text{OH} + \text{Cl}^-$ | CH_3OH | $10\text{A} = 2-16; 10\text{B} = 1-16$ | Na^+ | $\text{B} = \text{AB}$ | 96
109
122
133 | 3.5 -7
1.44 -6
6.0 -6
1.60 -5 | | $\Delta S^\ddagger = -12$
6 10 | * | (43) |
| 123 | $\text{cis-2-CH}_3\text{CH=CHBr} + \text{CH}_3\text{O}^- \longrightarrow \text{HClOCH} + \text{CH}_3\text{OH} + \text{Br}^-$ | CH_3OH | $10^3\text{A} = 8-30; 10^2\text{B} = 1-39$ | Na^+ | $\text{B} = \text{AB}$ | 24
35
45 | 1.18 -4
6.03 -4
2.55 -3 | 28 | 5 16 | $\Delta S^\ddagger = +16$ | (43) |
| 124 | $\text{trans-2-CH}_3\text{CH=CHBr} + \text{CH}_3\text{O}^- \longrightarrow \text{HClOCH} + \text{CH}_3\text{OH} + \text{Br}^-$ | CH_3OH | $10^2\text{A} = 2-24; 10\text{B} = 1.5-6$ | Na^+ | $\text{B} = \text{AB}$ | 79
94
109 | 5.3 -7
4.2 -6
2.55 -5 | 33.4 | 3 14 | $\Delta S^\ddagger = +5$ | (43) |
| 125 | $\text{CH}_3\text{COBr} + \text{OH}^- \longrightarrow \text{HClOCH} + \text{H}_2\text{O} + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | | Na^+ | $\text{B} = \text{AB}$ | 55 | 3.9 -4 | | | * | (50) |
| 126 | $\text{trans-2-CH}_3\text{CH=CHBr} + \text{OH}^- \longrightarrow \text{HClOCH} + \text{H}_2\text{O} + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2\text{A} = 4; \text{B} = 0.24$ | Na^+ | $\text{B} = \text{AB}$ | 25 | 2.6 -3 | | | * | (50) |
| 127 | $\text{cis-1-CH}_3\text{CH=CHCl} + \text{CH}_3\text{O}^- \longrightarrow \text{HClOCH} + \text{CH}_3\text{OH} + \text{I}^-$ | CH_3OH | $10^2\text{A} = 1-3; 10^2\text{B} = 1-3$ | Na^+ | $\text{B} = \text{AB}$ | 0
25 | 3.90 -4
1.78 -2 | 24.7 | 2 15 | $\Delta S^\ddagger = +14$ | (43) |

| No. | Reaction | Solvent | Amount of reactant | Anion | Amount of added base | Reaction time, sec | Temperature | | $k^0 \times 10^n$ | | $\bar{r}$ | $A \times 10^3$ | | Literature |
|-----------------------------------|---|---------------------------------|-------------------------------|---------------|----------------------|--------------------|--------------------|--------------------|-------------------|------|-----------|----------------------------|-----------|------------|
| | | | | | | | $^{\circ}\text{C}$ | $^{\circ}\text{F}$ | k^0 | n | | A^0 | n | |
| 197 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{O}^- + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 9.55; 10^3 B = 4.2$ | Na^+ | B | 60 | 58 | 9 | -6 | | | $\Delta H^\ddagger = +21$ | (43) | |
| | | | | | | 60 | 59 | 5.1 | -5 | | | | | |
| | | | | | | 60 | 63 | 4.0 | -4 | 20 | 5 | 18 | | |
| Aryl-substituted aliphatic halide | | | | | | | | | | | | | | |
| 198 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{O}^- + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 5; B = 0.10$ | Na^+ | B | 30 | 40 | 4.17 | -4 | | | $\Delta H^\ddagger = 19.6$ | (29) (50) | |
| | | | | | | 41 | 41 | 1.35 | -5 | | | $\Delta S^\ddagger = -9.7$ | (50) | |
| | | | | | | 50 | 50 | 3.47 | -5 | | | | | |
| | | | | | | 59 | 59 | 8.14 | -3 | 20.2 | 1.5 | 11 | | |
| 199 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{I} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{O}^- + \text{I}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 6; B = 0.12$ | Na^+ | B | 30 | 30 | 2.06 | -3 | | | | (29) | |
| 200 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 5; B = 0.10$ | Na^+ | B | 41 | 41 | 7.50 | -4 | | | $\Delta H^\ddagger = 20.3$ | (50) | |
| | | | | | | 50 | 50 | 2.00 | -3 | | | $\Delta S^\ddagger = -5.2$ | | |
| | | | | | | 59 | 59 | 4.04 | -3 | 20.9 | 3 | 11 | | |
| 201 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 6; B = 0.12$ | Na^+ | B | 30 | 30 | 1.73 | -4 | | | $\Delta H^\ddagger = 20.9$ | (29) (50) | |
| | | | | | | 41 | 41 | 5.58 | -4 | | | $\Delta S^\ddagger = -7.5$ | (50) | |
| | | | | | | 50 | 50 | 1.61 | -3 | | | | | |
| | | | | | | 59 | 59 | 8.03 | -3 | 21.4 | 5 | 11 | | |
| 202 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{I} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{I}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 6; B = 0.12$ | Na^+ | B | 30 | 30 | 9.56 | -4 | | | | (20) | |
| 203 | $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 5; B = 0.10$ | Na^+ | B | 0 | 0 | 1.35 | -3 | | | $\Delta H^\ddagger = 17.6$ | (50) | |
| | | | | | | 10 | 10 | 4.64 | -5 | | | $\Delta S^\ddagger = -7.0$ | | |
| | | | | | | 30 | 30 | 1.54 | -2 | 19.2 | 5 | 11 | | |

Aryl-substituted aliphatic halide

| No. | Reaction | Solvent | Amount of reactant | Legend | Amount of added | Defined mass | Temperature | $k \times 10^3$ | | R | $A^\circ \times 10^3$ | | Comments | Literature |
|--------------------------------------|--|---------------------------------|--|---------------|-----------------|--------------|----------------|----------------------|----------------|-----|--|--------|----------|-------------------|
| | | | | | | | | k° | η | | A° | η | | |
| 194 | $5\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$5\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 5; B = 0.10$ | Na^+ | B | k_{AB} | 0
10 | 2.66
9.14 | -2
-2 | 12 | $\Delta S^\ddagger = -0.8$ | | | (50) |
| 195 | $2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 6; B = 0.12$
3 0.10 | Na^+ | B | k_{AB} | 70
41
50 | 1.22
4.83
1.41 | -3
-3
-2 | | $\Delta H^\ddagger = 16.7$
$\Delta S^\ddagger = -9.1$ | | | (29) (50)
(50) |
| 196 | $2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{I} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{I}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 9; B = 0.12$ | Na^+ | B | k_{AB} | 30 | 1.05 | -2 | | | | | (29) |
| 197 | $2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 6; B = 0.12$ | Na^+ | B | k_{AB} | 30 | 3.71 | -3 | | | | | (29) |
| 198 | $2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{I} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$2\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{I}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 6; B = 0.12$ | Na^+ | B | k_{AB} | 30 | 2.03 | -2 | | | | | (29) |
| Di-aryl-substituted aliphatic halide | | | | | | | | | | | | | | |
| 199 | $4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 4-8; B = 1-2$ | Na^+ | B | k_{AB} | 50 | 5.29 | -6 | | | | * | (11) |
| 200 | $4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | $(\text{CH}_3)_3\text{COH}$ | 7 0.9 | K^+ | B | | 75 | 4.48 | -5 | | | | | |
| 201 | $4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | $(\text{CH}_3)_3\text{COH}$ | $10^2 A = 5-7; B = 0.80$
0.86
0.80 | K^+ | B | k_{AB} | 75 | 2.93
4.80
3.76 | -6
-5
-5 | | | | * | (11) |
| 202 | $4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow$
$4\text{-N}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$ | M | $10^2 A = 7; B = 0.7$ | K^+ | B | k_{AB} | 75 | 4.95 | -5 | | | | * | (11) |

Homogeneous Reaction Kinetics

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| No. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Definite position | Temperature | $k \times 10^n$ | k^0 | n | $A = A^0 \times 10^n$ | Comments | (11) |
|-----|--|---|---|-----------------------------------|-----------------|-------------------|-------------|-----------------|----------|-----|-----------------------|----------|------|
| 202 | threo-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + π -C ₆ H ₅ O ⁻ $\longrightarrow$ (trans) | M | 10 ² A = 7; B = 0.93
0.85
0.50 | Na ⁺ | = B | k AB | 75 | 1.14 | -6 | | | * | (11) |
| 203 | threo-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + π -C ₆ H ₅ O ⁻ $\longrightarrow$ (trans) | C ₆ H ₆ | 10 ² A = 7.5; B = 1.08
7 0.12 | K ⁺ | = B | k AB | 75 | 1.90 | -5 | | | * | (11) |
| 204 | erythro-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + C ₂ H ₅ O ⁻ $\longrightarrow$
cis-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + C ₂ H ₅ OH + Cl ⁻ | C ₂ H ₅ OH
(CH ₃) ₂ COH | 10 ² A = 3-7; B = 1-2
7 1.1 | Na ⁺
K ⁺ | = B | k AB | 50
75 | 1.90
4.30 | -6
-5 | | | * | (11) |
| 205 | erythro-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + (CH ₃) ₂ CO ⁻ $\longrightarrow$ (cis) | (CH ₃) ₂ COH | 10 ² A = 7; B = 0.77
.92
1.28
.92
1.28 | K ⁺ | = B | k AB | 75 | 4.04 | -6 | | | * | (11) |
| 206 | erythro-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + C ₂ H ₅ (CH ₃) ₂ CO ⁻ $\longrightarrow$ (cis) | M | 10 ² A = 7; B = 0.70 | K ⁺ | = B | k AB | 75 | 4.60 | -6 | | | * | (11) |
| 207 | erythro-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + π -C ₆ H ₅ O ⁻ $\longrightarrow$ (cis) | M | 10 ² A = 4; B = 0.93
7 0.85 | Na ⁺ | = B | k AB | 75 | 1.25 | -6 | | | * | (11) |
| 208 | erythro-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHCl + π -C ₆ H ₅ (CH ₃)CHO ⁻ $\longrightarrow$ (cis) | C ₆ H ₆ | 10 ² A = 7.5; B = 1.08
7 0.12 | Na ⁺
K ⁺ | = B | k AB | 75 | 5.10 | -6 | | | * | (11) |
| 209 | threo-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHBr + C ₂ H ₅ O ⁻ $\longrightarrow$ (trans) | EtOH | 10 ² A = 3.7; B = 0.61 | Na ⁺ | = B | k AB | 50 | 2.10 | -4 | | | * | (11) |
| 210 | threo-CH ₃ (C ₆ H ₅)CH(C ₆ H ₅)CHBr + (CH ₃) ₂ CO ⁻ $\longrightarrow$ (trans) | (CH ₃) ₂ COH | 10 ² A = 3.7; B = 0.57 | K ⁺ | = B | k AB | 50 | 6.6 | -5 | | | * | (11) |

| No. | Supplementing 1951 No. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Defined mass-action law | Temperature | $k^o \times 10^n$ | | E | $A^o \times 10^n$ | | Comments | Literature |
|------|------------------------|---|-----------------------------|---|---------------|-----------------|-------------------------|----------------|----------------------|----------------|-----|-------------------|-------|----------------------------------|------------|
| | | | | | | | | | k^o | π | | A^o | π | | |
| .211 | | $\alpha\gamma\text{thio-CH}_3(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBr} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow (\text{cis})\text{CH}_3(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBr} + \text{C}_2\text{H}_5\text{O}^- \longrightarrow (\text{cis})\text{CH}_3(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBr} + \text{C}_2\text{H}_5\text{O}^-$ | EtB* | $10^2\text{A} = 3.7\%$
$\text{B} = 0.61$ | Na^+ | B | k_{AB} | 50 | 3.0 | -4 | | | | * | (11) |
| .212 | | $\alpha\gamma\text{thio-CH}_3(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBr} + (\text{CH}_3)_3\text{CO}^- \longrightarrow (\text{cis})\text{CH}_3(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBr} + (\text{CH}_3)_3\text{CO}^- \longrightarrow (\text{cis})\text{CH}_3(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBr} + (\text{CH}_3)_3\text{CO}^-$ | $(\text{CH}_3)_3\text{COH}$ | $10^2\text{A} = 3.7\%$
$\text{B} = 0.57$ | K^+ | B | k_{AB} | 50 | 1.22 | -5 | | | | * | (11) |
| .213 | .207 | $(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{OH}^- \longrightarrow$
$(p\text{-ClC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} + \text{Cl}^-$ | Et92.6 wt* | $10^3\text{A} = 5.10$
$10^2\text{B} = 5.6$ | Na^+ | B | k_{AB} | 20
30
40 | 9.1
2.82
8.49 | -4
-3
-3 | | | | $\Delta S^\ddagger = -5.8$
12 | (12) (22) |
| .214 | | $(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{OH}^- \longrightarrow$
$(p\text{-BrC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} + \text{Cl}^-$ | Et92.6 wt* | $10^3\text{A} = 5.10$
$10^2\text{B} = 5.6$ | Na^+ | B | k_{AB} | 20
30
40 | 1.26
4.06
1.17 | -3
-3
-3 | | | | $\Delta S^\ddagger = -5.0$
12 | (12) (22) |
| .215 | | $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{Cl} + \text{OH}^- \longrightarrow (\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} + \text{Cl}^-$ | Et92.6 wt* | $10^2\text{A} = 1$
$10^2\text{B} = 5.3$ | Na^+ | B | k_{AB} | 20
30
40 | 1.43
5.11
1.62 | -4
-4
-3 | | | | $\Delta S^\ddagger = -3.4$
12 | (12) (22) |
| .216 | | $(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{OH}^- \longrightarrow$
$(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} + \text{Cl}^-$ | Et92.6 wt* | $10^2\text{A} = 1$
$10^2\text{B} = 5.3$ | Na^+ | B | k_{AB} | 20
30
40 | 4.33
1.57
5.10 | -5
-4
-4 | | | | $\Delta S^\ddagger = -4.4$
12 | (12) (22) |
| .217 | | $(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{OH}^- \longrightarrow$
$(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} + \text{Cl}^-$ | Et92.6 wt* | $10^2\text{A} = 1$
$10^2\text{B} = 5.3$ | Na^+ | B | k_{AB} | 20
30
40 | 3.36
1.26
4.27 | -5
-4
-4 | | | | $\Delta S^\ddagger = -0.5$
12 | (12) (22) |
| .218 | | $(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{OH}^- \longrightarrow$
$(p\text{-HOC}_6\text{H}_4)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} + \text{Cl}^-$ | Et92.6 wt* | $10^2\text{A} = 1$
$10^2\text{B} = 5.3$ | Na^+ | B | k_{AB} | 20
30
40 | 7.10
2.35
7.74 | -4
-3
-3 | | | | $\Delta S^\ddagger = -1.3$
12 | (12) (22) |

| No. | Supplementing (95-100) | Reaction | Solvent | Amount of reactant | Assumed | Amount of added | Refined mass | Temperature | $\log k$ | $\log k$ | $\log k$ | $\Delta \log k$ | Comments | Temperature |
|-----|------------------------|--|-------------|-----------------------------------|-----------------|-----------------|--------------|-------------|----------|----------|----------|----------------------|-----------|-------------|
| 200 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 200 | | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 201 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 202 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 203 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 204 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 205 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 206 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 207 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |
| 208 | .25 | $(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \longrightarrow$
$(p\text{-CH}_3)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{O}^- + \text{H}_2\text{O} + \text{Cl}^-$ | Et 92.6 wt. | $10^3 A = 4-10$
$10^2 B = 2-5$ | Na ⁺ | = B | kAB | 30 | 0.69 | -3 | 0.69 | $\Delta \log = -2.2$ | (12) (22) | |

| No. | Supplementing
1951 No. | Reaction | Solvent | Amount of
reactant | Added | Amount of
addend | Defined mass-
action law | Temperature | $k \times 10^n$ | | R | $A^\circ \times 10^n$ | | Comments | Literature |
|---|---------------------------|--|-----------------|---|-----------------|---------------------|-----------------------------|--------------------------------------|--|----------------------------------|------|-----------------------|-----|----------------------------|------------|
| | | | | | | | | | k° | n | | A° | n | | |
| .227 | .36 | $C_6H_5(p-ClC_6H_4)CHCl_3 + OH^- \rightarrow$
$C_6H_5(p-ClC_6H_4)C:OCl_2 + H_2O + Cl^-$ | Et 92.6 wt. * | $10^2 A = 1$;
$10^2 B = 4.7$ | Na ⁺ | = B | kAB | 20.1
30.4 | 3.01
9.04 | -3
-3 | 19 | 5 | 11 | | (12) (22) |
| .228 | | $(o-ClC_6H_4)(p-ClC_6H_4)CHCl_3 + OH^- \rightarrow$
$(o-ClC_6H_4)(p-ClC_6H_4)C:OCl_2 + H_2O + Cl^-$ | Et 92.6 wt. * | $10^2 A = 1$;
$10^2 B = 4.7$ | Na ⁺ | = B | kAB | 20.1
30.4 | 3.71
1.21 | -4
-3 | 20 | 6 | 11 | | (12) (22) |
| .229 | .37 | $(p-BrC_6H_4)_2CHCl_3 + OH^- \rightarrow$
$(p-BrC_6H_4)_2C:OCl_2 + H_2O + Cl^-$ | Et 92.6 wt. * | $10^3 A = 2-5$;
$10^2 B = 1-2$ | Na ⁺ | = B | kAB | 20
30
35 | 3.47
1.03
1.70 | -2
-1
-1 | 18.8 | 4 | 12 | $\Delta S^\ddagger = -3$ | (12) (22) |
| Aryl-substituted unsaturated alkenyl halide | | | | | | | | | | | | | | | |
| .230 | | $cis-C_6H_5CH:CHBr + OH^- \rightarrow C_6H_5C:CH + H_2O + Br^-$ | $(CH_3)_2CHOH$ | $10^2 A = 1$;
$10^2 B = 10$
10
6.7
12 | Na ⁺ | = B | kAB | 22
32
43
43 | 2.84
9.22
3.16
2.84 | -4
-4
-3
-3 | | | | $\Delta S^\ddagger = -5.6$ | (25) |
| .231 | | $cis-C_6H_5CH:CHBr + 2C_6H_5Li \rightarrow$
$C_6H_5C:CH + 2C_6H_5 + LiBr$ | $(n-C_4H_9)_2O$ | $10^2 A = 3$;
$10B = 1-2$ | | | kAB | 2 | 3.81 | -3 | 21.1 | 1.2 | 12 | * | (23) |
| .232 | | $trans-C_6H_5CH:CHBr + OH^- \rightarrow$
$C_6H_5C:CH + Br^- + H_2O$ | $(CH_3)_2CHOH$ | $10B = 3.4$
1.7
1.7
3.8
1.9
3.8
1.9 | Na ⁺ | = B | kAB | 98
98
107
107
118
118 | 2.38
2.43
6.64
7.61
2.11
2.55 | -5
-5
-5
-5
-4
-4 | | | | $\Delta S^\ddagger = +4$ | (25) |

| No. | Supplementing
1952 No. | Reaction | Solvent | Amount of
reactant | Addend | Defined mass-
action law | Temperature | $k^0 \times 10^7$
k^0 n | R | $A^0 \times 10^7$
A^0 n | Comments | Reference |
|---------------|---------------------------|--|--|--|---------------|-----------------------------|--|--|------------------------------------|---|----------|-----------------------------|
| 233 | | $\text{trans-C}_6\text{H}_5\text{CH:CHBr} + 2\text{C}_6\text{H}_5\text{Li} \longrightarrow$
$\text{C}_6\text{H}_5\text{C:ClLi} + 2\text{C}_6\text{H}_5 + \text{LiBr}$ | $(n\text{-C}_4\text{H}_9)_2\text{O}$ | $10^2\text{A}=3; 10^2\text{B}=6-12$ | | k_{AB} | 2 | 2.11 -2 | | | * | (23) |
| 234 | | $\text{cis-}p\text{-NO}_2\text{C}_6\text{H}_4\text{CH:CHBr} + \text{OH}^- \longrightarrow$
$p\text{-NO}_2\text{C}_6\text{H}_4\text{C:CH} + \text{H}_2\text{O} + \text{Br}^-$ | $(\text{CH}_3)_2\text{CHOH}$
Et92.6 wt. * | $10^2\text{A}=3; 10^2\text{B}=13$
7.7
7.7
7.6 | Na^+ | k_{AB} | 2
10
22
11
20
25
30 | 6.07 -2
6.29 -2
1.73 -1
5.24 -1
2.62 -3
9.77 -3
1.88 -2
3.69 -2 | 17.1 2 | $\Delta S^\ddagger = -4.0$
12 | | (25) |
| 235 | | $\text{trans-}p\text{-NO}_2\text{C}_6\text{H}_4\text{CH:CHBr} + \text{OH}^- \longrightarrow$
$p\text{-NO}_2\text{C}_6\text{H}_4\text{C:CH} + \text{H}_2\text{O} + \text{Br}^-$ | $(\text{CH}_3)_2\text{CHOH}$
Et92.6 wt. * | $10^2\text{A}=1; 10^2\text{B}=1-2$
2
1
1.8 | Na^+ | k_{AB} | 43
56
61
71
75
40 | 2.46 -4
4.58 -4
1.63 -3
1.53 -3
1.70 -5
3.09 -5
5.77 -5 | 23.9 6
21.3 1.1
23.8 2 | $\Delta S^\ddagger = -12$
15
$\Delta S^\ddagger = -10$
10
$\Delta S^\ddagger = -4$
12 | * | (25)
(18) |
| Aromatization | | | | | | | | | | | | |
| 236 | 138 | $\alpha\text{-C}_6\text{H}_6\text{Cl} + 3\text{OH}^- \longrightarrow$
(taeece configuration)
$\text{C}_6\text{H}_5\text{Cl} + 3\text{H}_2\text{O} + 3\text{Cl}^-$
products 1,2,3-17%
1,2,4-76%
1,3,5-7% | Et76.1 wt. *
Et92.6 wt. *
Et97.6 wt. * | $10^4\text{A}=4-10$;
$10^3\text{B}=3-10$;
$10^4\text{A}=4-10$;
$10^3\text{B}=3-10$;
$10^4\text{A}=4-10$;
$10^3\text{B}=3-10$ | Na^+ | $k_{AB} =$
$-dA/dt$ | 1.1
20.1
-0.3
16.2
7.1
14.4
22.5 | 1.9 -2
1.70 -1
2.43 -2
1.77 -1
7.7 -2
1.67 -1
4.95 -1 | 18.5 1
18.6 2
20.0 3 | $\Delta S^\ddagger = -1.0$
13 *
$\Delta S^\ddagger = 0$
15 *
$\Delta S^\ddagger = +6$
14 | | (15) (21) (37)
(15) (21) |

| No. | Supplementing
1951 No. | Reaction | Solvent | Amount of
reactant | Added | Amount of
added | Defined rate
law | Temperature | $k \times 10^n$ | | E | $A \times 10^n$ | | Comments | Literature |
|------|---------------------------|---|---|--------------------------------------|---------------|--------------------|---------------------|---|--|--|--|----------------------------------|---|----------------|----------------|
| | | | | | | | | | k^0 | n | | A^0 | n | | |
| .236 | .38 | $\alpha\text{-C}_6\text{H}_4\text{Cl} + 3\text{OH}^- \longrightarrow$ (continued) | Et80*
Et90* | $10^3 A \approx 2; 10^2 B \approx 1$ | Na^+ | $= B$ | $k_{AB} = -dA/dt$ | 0
-15
-9
0
14
20
0 | 1.50
2.3
7.05
2.00
1.09
2.28
3.12 | -2
-3
-3
-2
-1
-1
-2 | 19.0 | 3
13 | * | (38) | |
| .277 | .39 | $\alpha\text{-C}_6\text{H}_4\text{Cl} + \text{OH}^- \longrightarrow$
$\text{C}_6\text{H}_4\text{Cl}_2 + \text{H}_2\text{O} + \text{Cl}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | | Na^+ | $= B$ | | | | | | | | * | (15) (21) (39) |
| .238 | .41 | $\beta\text{-C}_6\text{H}_4\text{Cl}_2 + 3\text{OH}^- \longrightarrow$
(see configuration)
$\text{C}_6\text{H}_3\text{Cl}_3 + 3\text{H}_2\text{O} + 3\text{Cl}^-$
products 1,2,3-4.6%
1,2,4-86%
1,3,5-9% | Et76.1 wt.*
Et81.5 wt.*
Et89.0 wt.*
Et91.2 wt.*
Et92.6 wt.*
Et94.1 wt.*
Et97.6 wt.* | $10^4 A = 4-40$;
$10^2 B = 2-9$ | Na^+ | $= B$ | $k_{AB} = -dA/dt$ | 30.6
50.0
30-50
30-50
30-50
30.6
50.0
30-50
30.6
50.0
30-50 | 2.30
4.71

2.23
6.16
1.97
4.67
2.38
1.21
1.37
3.19
8.70
3.01
1.49 | -5
-4

-5
-4
-5
-4
-2
-1
-3
-3
-2
-1 | 30.9
30.6
31.4
31.1

33.1
32.1
31.7
32.3 | 4

2

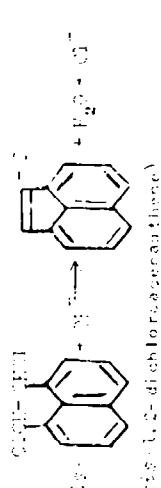
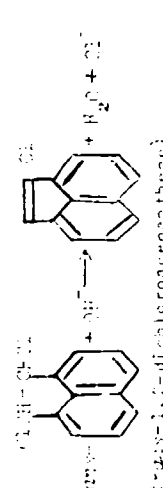
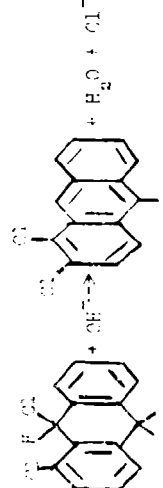
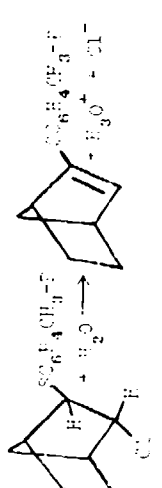
1
3 | $\Delta S^\ddagger = +20$
17
$\Delta S^\ddagger = +19$

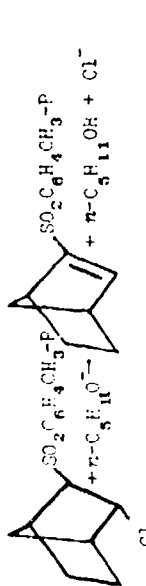
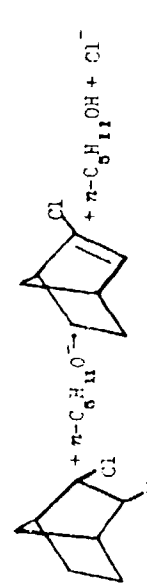
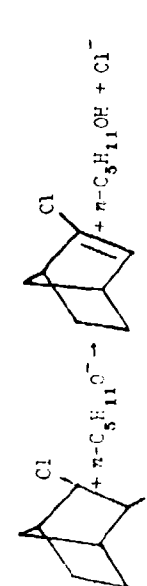
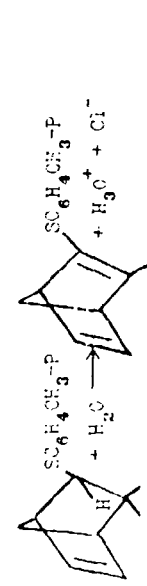
$\Delta S^\ddagger = +27$
19
$\Delta S^\ddagger = +24$
$\Delta S^\ddagger = +22$ | (15) (21) (57) | |
| | | | Et80*
Et90* | $10^3 A \approx 2; 10^2 B \approx 1$ | | | $k_{AB} = -dA/dt$ | 77
90
55
61
68
77
90 | | | | 18
18 | | | (39) |

| No. | Supplement No. | Reaction | Solvent | Amount of reactant | Amount added | Defined rate - action law | Temperature | $k \times 10^2$ | $k^0 \times 10^2$ | E | $A^0 \times 10^2$ | Comments | Literature |
|------|----------------|--|-----------------------------------|---|---------------|---------------------------|---|---|--|------|-------------------|---------------------------------|------------------------|
| .238 | .41 | $\beta\text{-C}_6\text{H}_5\text{Cl}_6 + 3\text{OH}^- \longrightarrow$ (continued) | $\text{C}_2\text{H}_5\text{OH}$ | $10^3\text{A} \sim 2; 10^2\text{B} \sim 1$ | Na^+ | $k_{AB} = -dA/dt$ | 77
90 | 2.73
1.36 | -2
-1 | 73 | 1 | * | (39) |
| .239 | .42 | $\beta\text{-C}_6\text{H}_5\text{Cl}_6 + \text{OH}^- \longrightarrow$
$\beta\text{-C}_6\text{H}_4\text{Cl}_6 + \text{H}_2\text{O} + \text{Cl}^-$ | See reaction (.238) | | Na^+ | $k_{AB} = -dA/dt$ | | | | | | * | (15) (21) (39) |
| .240 | .43 | $\gamma\text{-C}_6\text{H}_5\text{Cl}_6 + 3\text{OH}^- \longrightarrow$
(same configuration)
$\text{C}_6\text{H}_3\text{Cl}_3 + 3\text{H}_2\text{O} + 3\text{Cl}^-$
products 1,2,3-4.6%
1,2,4-61%
1,3,5-14% | Et 76.1 wt. %
Et 80*
Et 90* | $10^4\text{A} = 5-10$;
$10^3\text{B} = 4-10$
$10^3\text{A} \sim 2; 10^2\text{B} \sim 1$
$-dA/dt = k_{AB}$
$-dB/dt = k_{AB} + 2k'A'B$
for k' see reaction (.252) | Na^+ | $k_{AB} = -dA/dt$ | 10.1
20.1
29.7
14
-8.5 | 1.44
4.5
1.51
5.27
3.12 | -2
-2
-1
-2
-3 | 20.6 | 1.1
14 | $\Delta S^\ddagger = +3.8$
* | (15) (21) (57)
(39) |
| .241 | .44 | $\gamma\text{-C}_6\text{H}_5\text{Cl}_6 + \text{OH}^- \longrightarrow$
$\text{C}_6\text{H}_5\text{Cl}_6 + \text{H}_2\text{O} + \text{Cl}^-$ | $\text{C}_2\text{H}_5\text{OH}$ | | Na^+ | $k_{AB} = -dA/dt$ | 0
7
14
20
14 | 1.12
2.74
6.85
1.46
3.87 | -2
-2
-2
-1
-2 | 20.4 | 2.5
14 | * | (15) (21) (39) |
| .242 | .40 | $\beta\text{-C}_6\text{H}_5\text{Cl}_6 + 3\text{OH}^- \longrightarrow$
(same configuration)
$\text{C}_6\text{H}_3\text{Cl}_3 + 3\text{H}_2\text{O} + 3\text{Cl}^-$
products 1,2,3-5%
1,2,4-86%
1,3,5-9% | Et 76.1 wt. %
Et 80*
Et 90* | $10^4\text{A} = 3-10$;
$10^3\text{B} = 3-5$
$10^3\text{A} \sim 2; 10^2\text{B} \sim 1$
$-dA/dt = k_{AB}$
$-dB/dt = k_{AB} + 2k'A'B$
for k' see reaction (.252) | Na^+ | $k_{AB} = -dA/dt$ | 20
-15
-27
-21
-15
-8
-15 | 1.1
1.10
1.86
5.08
1.48
4.51
1.20 | -1
-2
-3
-3
-2
-2
-2 | 21.6 | 2.5
16 | * | (13)
(39) |

| No. | Concentration
mole/l. | Reaction | Solvent | Amount of
reactant | Added
substance | Amount of
added
substance | Defined mass-
action law | Temperature | $k \times 10^2$ | | $k \times 10^2$ | $\Delta A = 10^2$ | Comments | Literature |
|-----|--------------------------|--|---------------------|------------------------------------|--------------------|---------------------------------|-----------------------------|-------------|-----------------|-----|-----------------|-------------------|-----------------------------|------------|
| | | | | | | | | | k^0 | n | k^0 | n | | |
| 243 | 0.07 | $2-C_6H_4Cl + OH^- \longrightarrow C_6H_4O + H_2O + Cl^-$ | See reaction (.242) | | Na^+ | $= B$ | | | | | | | | (13) (38) |
| 244 | 0.01 | $2-C_6H_4Cl + 3OH^- \longrightarrow$
(neat configuration)
$C_6H_4O + 2H_2O + 3Cl^-$
products 1,2,3-5%
1,2,4-95%
1,3,5-C | Et 76.1 wt.* | $10^4 A = 5-20$
$10^3 B = 5-18$ | Na^+ | $= B$
$-dA/dt = kAB$ | | 10.1 | 1.42 | -2 | | | * | (16) (21) |
| | | | | | | | | 20.3 | 5.65 | -2 | | | | |
| | | | | | | | | 29.7 | 1.70 | -1 | 21.4 | 5 | | |
| | | | | | | | | 10.4 | 1.47 | -2 | | | | |
| 245 | 0.01 | $2-C_6H_4Cl + OH^- \longrightarrow C_6H_4O + H_2O + Cl^-$ | Et 92.6 wt.* | | Na^+ | $= B$ | | 22.5 | 9.07 | -2 | | | * $\Delta S^\ddagger = -10$ | (15) (21) |
| | | | | | | | | 30.6 | 2.63 | -1 | 22.3 | 2 | | |
| 246 | 0.01 | $2-C_6H_4Cl + OH^- \longrightarrow C_6H_4O + H_2O + Cl^-$ | See reaction (.244) | | Na^+ | $= B$ | | | | | | | * | (15) (21) |
| 247 | 0.01 | $2-C_6H_4Cl + OH^- \longrightarrow$
(neat configuration)
$C_6H_4O + 2H_2O + 2Cl^-$
47.8% O-, 50.4% T-, 1.9% P- | Et 60* | $10^2 A = 1$; $10^3 B = 2$ | Na^+ | $-dA/dt = kAB$ | | 29 | 7.13 | -3 | | | * | (47) |
| | | | | | | | | | | | | | * | (47) |
| 248 | 0.01 | $2-C_6H_4Cl + OH^- \longrightarrow$
(neat configuration)
$C_6H_4O + 2H_2O + 2Cl^-$
5.9% O-, 51.1% T-, 66% P- | Et 60* | $10^2 A = 1$; $10^3 B = 2$ | Na^+ | $-dA/dt = kAB$ | | 29 | 0 | | | | * | (47) |
| | | | | | | | | 29 | 6.07 | -2 | | | * | (47) |

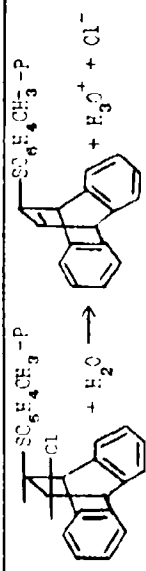
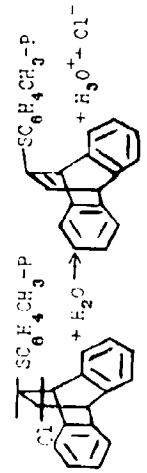
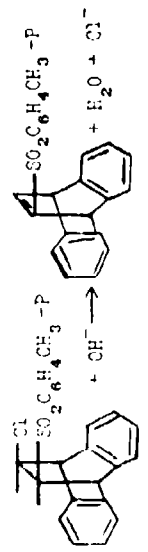
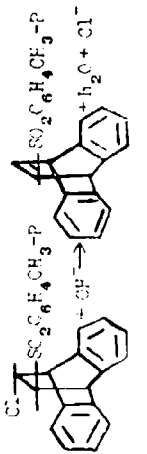
| No. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Defined mass | Temperature | $k^0 \times 10^2$ | | $k^0 \times 10^2$ | $k^0 \times 10^2$ | | Contents | Literature |
|-----|---|----------------|--|---------------|-----------------|--------------|--------------------------------------|--|--|-------------------|-------------------|-----|----------|----------------------|
| | | | | | | | | k^0 | n | | k^0 | n | | |
| 180 | $\gamma\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) 28.4% o-, 42.7% p-, 28.9% b- | Et80* | $10^3\text{A}=1; 10^3\text{B}=2$ | Na^+ | -dA/dt=kAB | | 29 | 2.77 | -1 | | | | * | (47) |
| 181 | $\delta\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) 15.8% o-, 53.7% p-, 60.5% b- | Et80* | $10^3\text{A}=1; 10^3\text{B}=2$ | Na^+ | -dA/dt=kAB | | 29 | 1.90 | -3 | | | | * | (47) |
| 182 | $\alpha\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) 7.5% o-, 25% p-, 67.5% b- | Et80* | $10^3\text{A}=2; 10^3\text{B}=4$ | Na^+ | -dA/dt=kAB | | 29 | 8.37 | 0 | | | | * | (47) |
| 183 | $\beta\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) 7.5% o-, 25% p-, 67.5% b- | Et80* | $10^3\text{A}=2; 10^3\text{B}=4$ | Na^+ | -dA/dt=kAB | | 29 | 5.72 | 0 | | | | | (47) |
| 184 | $\gamma\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) 1.2, 3.5-5%
1.2, 4-8%
1.5, 5-9% | Et80*
Et90* | $10^3\text{A}=0-1; 10^3\text{B}=1$ | Na^+ | -dA/dt=kAB | | 14
0
7
14
20
29
14 | 2.79
5.92
1.53
4.00
7.70
1.92
5.18 | -2
-3
-2
-2
-2
-1
-2 | | 27.1 | 1.7 | * | (39)
(47)
(39) |
| 185 | $\gamma\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) products 1.2, 3.5-5%
1.2, 4-8%
1.5, 5-9% | Et80*
Et90* | $10^3\text{A}=0-1; 10^3\text{B}=1$
0-1
0-1 | Na^+ | -dA/dt=kAB | | 0
29
-8
0
14
10
0 | 9.59
3.20
3.50
1.13
7.79
1.93
1.93 | -3
-1
-3
-2
-2
-1
-2 | | 20.3 | 1.7 | * | (39)
(47)
(39) |
| 186 | $\gamma\text{-C}_6\text{H}_4\text{Cl}_2 + \text{COF}^- \rightarrow \text{C}_6\text{H}_4\text{Cl}_2 + \text{CF}_2\text{O} + \text{COI}^-$
(near configuration) products 1.2, 3.5-5%
1.2, 4-8%
1.5, 5-9% | Et80*
Et90* | $10^3\text{A}=2; 10^3\text{B}=4$ | Na^+ | -dA/dt=kAB | | 29 | 5.00 | 0 | | | | | (47) |

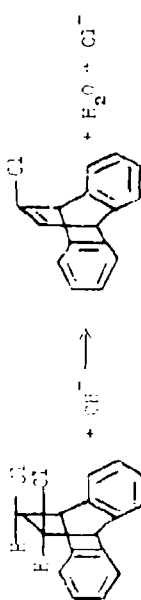
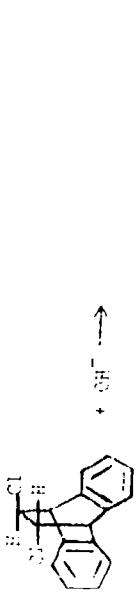
| No. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Defined mass-action law | Temperature | $k^0 \times 10^2$ | n | $\bar{A}$ | $A^0 \times 10^2$ | $\Delta S^\ddagger$ | Comments | Literature |
|----------------------|---|--------------|-----------------------------------|---------------|-----------------|-------------------------|----------------------|----------------------|----------------|-----------|-------------------|---------------------|---------------------------|------------|
| 295 | 
(cis-1,2-dichloronaphthalene) | EtO2.6 wt. * | $10^3 A = 11$
$10^3 B = 2.7$ | Na^+ | = B | kAB | 2.2
10.5
22.1 | 1.77
5.52
1.09 | -2
-2
-1 | 20.8 | 6 | 14 | $\Delta S^\ddagger = 6.0$ | (26) |
| 296 | 
(trans-1,2-dichloronaphthalene) | EtO2.6 wt. * | $10^3 A = 11$
$10^3 B = 2.7$ | Na^+ | = B | kAB | 20.5
26.4
45.1 | 7.65
1.89
3.93 | -4
-3
-3 | 24.8 | 6 | 14 | $\Delta S^\ddagger = 6.0$ | (26) |
| 297 | 
(trans-1,8,9,10-tetrachloro-9,10-dihydroanthracene) | DMS* | $10^3 A = 1.25$
$10^3 B = 2.9$ | Na^+ | = B | kAB | 6.4
10.5
19.1 | 1.47
2.64
5.50 | -1
-1
-1 | 15.3 | 2 | 11 | $\Delta S^\ddagger = -9$ | (16) |
| Bridged-ring systems | | | | | | | | | | | | | | |
| 298 |  | Et85 wt. * | $10^3 A = 4.9$ | | | kA | 116 | 2.6 | -5 | | | | * | (14) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k \times 10^n$ | k^0 | n | $A^0 \times 10^n$ | Comments | Literature |
|------|--|-----------------------------------|---|-----------------|------------------|-------------------------|-------------|-----------------|----------|-----|-------------------|----------|-------------------|
| .261 | 
(<i>endo</i> -2-(<i>p</i> -toluenesulfonyl)- <i>endo</i> -3-chloronorbornane) | C ₆ H ₁₁ OH | 10 ³ A=7-15;
10 ³ B=9-24 | Na ⁺ | = B | k _{AB} | 0
12 | 4.91
2.15 | -3
-2 | | 8
12 | | (²⁴) |
| .262 | 
(<i>endo</i> - <i>cis</i> -2,3-dichloronorbornane) | C ₆ H ₁₁ OH | 10 ² A=2-3;
10B=2-4 | Na ⁺ | = B | k _{AB} | 101
116 | 1.01
5.0 | -6
-6 | | 1
12 | | (²⁴) |
| .267 | 
(<i>trans</i> -2,3-dichloronorbornane) | C ₆ H ₁₁ OH | 10 ² A=1-3;
10B=7-23 | Na ⁺ | = B | k _{AB} | 101
116 | 6.5
3.4 | -5
-4 | | 6
14 | * | (²⁴) |
| .264 | 
(<i>endo</i> -2,3-dichloronorbornane) | Et85 wt. * | 10 ³ A=4 | | | k _A | 116 | 6.6 | -6 | | | * | (¹⁴) |

HOMOGENEOUS REACTION KINETICS
450.471

33

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined reaction law | Temperature | $k \times 10^n$ | | E | $A = A^0 \times 10^n$ | | Comments | Literature |
|------|---|----------|--------------------------------|--------|------------------|----------------------|-------------|-----------------|---------|------|-----------------------|-----|----------|------------|
| | | | | | | | | k^0 | n | | A^0 | n | | |
| .255 |  | EDS wt.* | $10^3 A=3$ | | | k_A | 116 | 1.1 | -6 | | | | * | (14) |
| .256 |  | EDS wt.* | $10^3 A=1-2$ | | | k_A | 116 | 5.8 | -6 | | | | * | (14) |
| .257 |  | DE* | $10^3 A=2$
$10^3 B=2-2.5$ | Na^+ | $=B$ | k_{AB} | 0
12 | 2.65
9.65 | 0
0 | 16 | 3 | 13 | | (24) |
| .258 |  | DE* | $10^3 A=2-6$
$10^3 B=2.5-4$ | Na^+ | $=B$ | k_{AB} | 0
12 | 9.20
3.10 | -1
0 | 15.6 | 3 | 12 | | (14) |

| No. | Reaction | Solvent | Amount of reactant | Additive | Amount of added | Defined reaction law | Temperature | $k^0 \times 10^7$
k^0 η | $k^0 \times 10^7$
k^0 η | Δ | $A = A^0 \times 10^7$
A^0 η | Concentration | Unit |
|------|--|---------|---------------------------------|-----------------|-----------------|----------------------|--------------------------|-----------------------------------|-----------------------------------|----------|---------------------------------------|---------------|------|
| 1003 | 
(11,11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene) | DEW* | 10 ³ A=9;
10B=2-4 | Na ⁺ | = H | kAB | 102
110
120
129 | 3.01
6.42
1.45
3.43 | -5
-5
-4
-4 | 26.5 | 8 10 | * | (20) |
| 1004 | 
(trans-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene) | DEW* | 10 ³ A=9;
10B=2-4 | Na ⁺ | = B | kAB | 91
102
110
120 | 5.70
2.18
4.59
1.34 | -5
-4
-4
-3 | 30.6 | 1.5 14 | * | (20) |

CODED SOLVENTS

1:50* (5, 25, 60, 70, 75, 80, 85, 90)

C_2H_5OH (vol. % as indicated) + H_2O
 π -butyl cellosolve 85 volumes + 15 vol. H_2O

1,4-dioxane (vol. % as indicated) + H₂O
$$O^3H + \frac{1}{2}M^{3/2}HO^{3/2}$$
$$C_2H_5OH + X \text{ wt. } H_2O$$
$$2 \text{ C}_2\text{H}_5\text{OH} + \text{C}_6\text{H}_6 \rightarrow 2 \text{ C}_2\text{H}_5\text{OC}_6\text{H}_5$$

Equal volumes of dioxane and C_2H_5OH 92.6% by weight

vol. % dioxane in 92.6 wt.-% $\text{C}_2\text{H}_5\text{OH}$

C_2H_5OH 40.5 wt. %, Dioxane 55.0 wt. %, H_2O 4.3 wt. %

COMMENTS

General: Elimination reaction frequently accompanied by parallel solvolysis reaction leading to substitution of hydrogen or alkyl group for halogen. See 212,471. Both reactions may occur through same intermediate by removal of H^+ by base forming carbanion intermediate with either elimination or substitution of halogen following. For detailed discussion of mechanism of elimination and substitution reactions see (319).

Classification: The aliphatic halides undergoing elimination are grouped under the headings: Saturated alkyl halide (52)-(119); Cyclo alkyl halide (120)-(140); Hydroxy-substituted alkyl halide (141)-(142); Di-carboxy substituted alkyl halide (143)-(145); Halogen substituted alkyl halide (146)-(151); Substituted cycloalkyl halide (152)-(172); Unsaturated alkenyl halide (173)-(187); Aryl-substituted alkyl halide (188)-(198); Di-aryl substituted alkyl halide (199)-(229); Aryl-substituted unsaturated alkenyl halide (230)-(235); Aromatization (236)-(259); Bridged ring systems (260)-(270).

Reaction: (52) See 212,471, 183 for important parallel solvolysis reaction. (53) See 212,471, 184 for important parallel solvolysis reaction. (54) See 212,471, 185 for parallel solvolysis reaction. (55) See 212,471, 186 for parallel solvolysis reaction. (56) See 212,471, 187 for parallel solvolysis reaction. (57) See 212,471, 188 for important parallel solvolysis reaction. (58) See 212,471, 193 for important parallel solvolysis reaction. (59) Products of reaction not determined. Reaction followed by formation of I^- . (60) See 212,471, 194 for parallel solvolysis reaction. (61) See 212,471, 195

for parallel solvolysis reaction. (62) See 212,471, 196 for important parallel solvolysis reaction. (63) See 212,471, 197 for parallel solvolysis reaction. (64) See 212,471, 198 for parallel solvolysis reaction. (65) Products of reaction not determined. Reaction followed by formation of I^- . (66) See 212,471, 200 for parallel solvolysis reaction. (67) Ratio of elimination to solvolysis not stated. Total rate measured. (68) Rate constant corrected for thioether formation amounting to 7% of total reaction. (69) Products of reaction not determined. (70) See 212,471, 206 for important parallel solvolysis reaction. (71) Initial rate only as reverse reaction important. In absence of $(C_2H_5)_4NCl$ no elimination observed. (72) Products not identified except for 46% yield of isobutylene. (73)-(74) Products not determined except yield if isobutylene varied between 85 and 100%. (75) Rate law over course of reaction given by:

$$-dA/dt = k_1AB/(aM + B)$$

where a was found to have an average value of 25. The initial rate giving value of rate constant k_1 in absence of added Br^- . (76) See 212,471, 208 for important parallel solvolysis reaction. (77) See 212,471, 210 for important parallel solvolysis reaction. (78) See 212,471, 211 for important parallel solvolysis reaction. (79) See 212,471, 213 for important parallel solvolysis reaction. (80) Relative amount of parallel solvolysis and elimination reactions not determined. (81) See 212,471, 215 for parallel solvolysis reaction. (82) See 212,471, 216 for important parallel solvolysis reaction. (83) See 212,471, 217 for parallel solvolysis reaction. (84)

COMMENTS

(continued)

See 212.471, .218 for parallel solvolysis reaction. Olefin analysis gave 71% $\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_3$ and 29% $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$. (.85) See 212.471, .219 for important parallel solvolysis reaction. (.86) See 212.471, .220 for parallel solvolysis reaction. (.87) See 212.471, .221 for parallel solvolysis reaction. (.88) See 212.471, .223 for parallel solvolysis reaction. (.89) See 212.471, .224 for important parallel solvolysis reaction. Rate constant reported for (7) in 85% *n*-butyl cellosolve is total rate constant for both the elimination and solvolysis reactions. (.90) See 212.471, .225 for important parallel solvolysis reaction. (.91) See 212.471, .226 for important parallel solvolysis reaction. (.92) See 212.471, .227 for important parallel solvolysis reaction. (.93) Elimination reaction yields 80% 2-methyl-2-butene and 20% 2-methyl-1-butene. (.94) See 212.471, .232 for important parallel solvolysis reaction. At low $[\text{C}_2\text{H}_5\text{O}^-]$ 81.6% of 2-methyl-1-butene and 18.4% of 2-methyl-2-butene produced. At $[\text{C}_2\text{H}_5\text{O}^-] = 2.0$ the % 2-methyl-1-butene is 71.9% with 28.1% of 2-methyl-2-butene. (.95) Elimination reaction yields 19% $(\text{CH}_3)_2\text{CHCH}=\text{CHCH}_3$ and 78% *trans*- $(\text{CH}_3)_2\text{CHCH}=\text{CHCH}_3$ and 3% *cis*- $(\text{CH}_3)_2\text{CHCH}=\text{CHCH}_3$. (.96) See 212.471, .238 for important parallel solvolysis reaction. (.97) Elimination reaction yields 71% 2-methyl-2-pentene and 29% 2-methyl-1-pentene. (.98) See 212.471, .239 for parallel solvolysis reaction. (.99) See 212.471, .240 for parallel solvolysis reaction. (.100) Elimination reaction yields 82% 2,3-dimethyl-2-butene and 18% 2,3-dimethyl-1-butene. (.101) See 212.471, .241 for important parallel solvolysis reaction. (.102) Elimination yields 96.5% of 3-methyl-2-pentene, 38.5% *cis*,

58.0% *trans* and 3.5% of 2-ethyl-1-butene. (.103) Elimination reaction yields 21% 4,4-dimethyl-1-pentene, 77% *trans*-4,4-dimethyl-2-pentene and 2% *cis*-4,4-dimethyl-2-pentene. (.104) See 212.471, .242 for important parallel solvolysis reaction. (.105) Elimination reaction yields 59% 2,4-dimethyl-2-pentene and 41% 2,4-dimethyl-1-pentene. (.106) See 212.471, .244 for rate constant for total solvolysis and elimination reaction. (.107)(.108) Products of reaction not determined. Reaction followed was rate of production of chloride ion. (.109) See 212.471, .244 for rate constant for total solvolysis and elimination reaction. (.110) See 212.471, .245 for parallel solvolysis reaction. In *n*-butyl cellosolve (7) finds rate constant for total solvolysis and elimination reaction to be 2.09×10^{-6} . In this solvent elimination yields 81% 2,4,4-trimethyl-1-pentene and 19% of 2,4,4-trimethyl-2-pentene. (.111) Elimination reaction yields 81% 2,4,4-trimethyl-1-pentene and 19% 2,4,4-trimethyl-2-pentene. (.112) See 212.471, .248 for rate constant for total solvolysis and elimination reaction. (.113) See 212.471, .250 for rate constant for total solvolysis and elimination reaction. (.114) See 212.471, .251 for rate constant for total solvolysis and elimination reaction. (.115)(.116) See 212.471, .253 for rate constants for total solvolysis and elimination reactions. (.117) First order rate law assumed from behavior in ethanol-water solvent. Pure chloride decomposes at room temperature. Prepared by saturating olefin at -40 °C. (.118)(.119) Only olefins produced no solvolysis to give alcohol or ether. (.120) (.121) Extent of olefin production not stated. (.123) See 212.471, .257 for parallel solvolysis reaction. (.124)

COMMENTS

(continued)

(.125)(.126)(.127) Extent of elimination and parallel solvolysis not stated. (.128) See 332.771, 132 for parallel exchange reaction. (.132) Extent of elimination and parallel solvolysis not stated. (.133) Pseudo first order rate law followed after rapid reaction of trans-isomer in mixture, see .134. Extrapolation to zero time used to determine relative amounts of isomers present. In mixture starting with 63% cis-isomer products were 50% 1,2-dimethylcyclohexene and 50% 2-methylene-methylcyclohexane. (.134)(.135) Pure trans-isomer yields exclusively 1,2-dimethylcyclohexene. (.136) Relative extent of elimination and solvolysis reactions not stated. (.137) Relative extent of elimination and solvolysis reactions not stated. No appreciable difference in rate for cis-rich or trans-rich isomer mixtures. (.138) See 212.471, 264 for parallel solvolysis reaction. (.139) See 212.471, 256 for parallel solvolysis reaction. (.140) See 212.471, 267 for parallel solvolysis reaction. (.141)(.142) Alcohol and ester yield same product L involving rearrangement. (.143)(.144) Values reported by (.49) corrected by (.49). (.145) Reaction followed was rate of formation of Br⁻. Calculated first or second order constants for rate of disappearance of B decrease with progress of reaction. (.146) Elimination represents only about 9% of total reaction. Remaining 91% is parallel solvolysis. (.147) Rate constant for elimination reaction calculated from rate law for parallel reactions with different stoichiometry as solvolysis reaction consumes second mole of B for production of ethylene oxide. (.148) Rate constants of (.69) include parallel solvolysis reaction in 18.5% yield compared to 79.5% of CH₂:CHBr. (.36) calculated

ated rate constant of elimination reaction separately by means of the difference in stoichiometry since solvolysis consumes two moles of B for each mole A reacting. Rate constants listed are actual rate constants not constant per halogen of (.36). (.149) Rate constants are extrapolated to zero time since calculated constants decrease with progress of reaction. (.151) Reaction yields sodium acetate as final product but acetyl bromide considered to be product of rate determining step. (.152) Products of reaction are 84% cyclohexene-ol and 16% of a 1,4 oxide bridged cyclohexane. (.153) Products of reaction are less than 30% cyclohexene-ol and more than 70% of the 1,4 oxide bridged cyclohexane. (.158) Products of reaction not determined. Reaction probably complex involving elimination and solvolysis. Rate given is for production of HCl. Calculated constants drift with course of reaction. Values given should not be considered accurate. (.161) Reaction was so slow that alkali in glass was thought to complicate measurements. Value tabulated is for initial rate. (.163)(.165) Rate constant listed only approximate as calculated constants drifted seriously. Products of reaction not determined. (.167) Calculated rate constants drifted except in presence of LiClO₄. Products of reaction not determined. (.169) Products of reaction not determined. (.173) Elimination of first Cl⁻ considered to be rate determining step followed by rapid elimination of second and third Cl⁻. (.174)(.175)(.176)(.177) Dependence upon ionic strength given by:

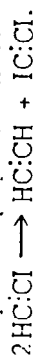
$$\log k = \log k_0 + 4S\sqrt{\mu}/(1 + A\alpha\sqrt{\mu}) \text{ where}$$

$$S = 1.825 \times 10^9 (DT)^{-3/2} \quad A = 50.30 \times 10^8 (DT)^{-1/2} \quad \alpha = 5.0 \text{\AA}$$

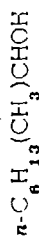
COMMENTS

(continued)

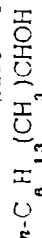
for cis-isomers and $4.0 \text{ \AA}$ for trans-isomers. Values: at $\mu = 0$ are extrapolated values. (.178)(.180) Authors observed that rate based upon consumption of B was always lower than when based upon M produced. Attributed this to acidity of L. (.181) Calculated second order constant increased with progress of reaction. Rate constants extrapolated to zero ionic strength. (.182)(.183) Values extrapolated to zero ionic strength. (.184) Calculated second order constants drift with course of reaction. Negative salt effect apparent. (.185) Calculated second order constants decrease with course of reaction, (one third at $n/2$). Negative salt effect observed. (.186) Values extrapolated to zero ionic strength. (.187) Calculated second order constants increase with progress of reaction. HCl:Cl observed to undergo a subsequent disproportionation reaction:



(.199)(.202) Second order rate constant calculated by dividing pseudo first order constant by concentration of B which was in excess. (.203) For reaction in:



as solvent second order constant calculated from pseudo first order constant by dividing by concentration of B. In C_6H_6 as solvent true second order equation used and calculated constants decreased with progress of reaction. (.204)(.207) Second order rate constant calculated by dividing pseudo first order constant by concentration of B which was in excess. (.208) For reaction in:



as solvent second order constant calculated from pseudo first order constant by dividing by concentration of B. In

C_6H_6 as solvent true second order equation used and calculated second order constants decreased with progress of reaction. (.209)(.212) Second order rate constant calculated by dividing pseudo first order constant by concentration of B. (.231) Calculated second order rate constants fall rapidly beyond 40-60% reaction and were not reproducible. (.232) Good second order rate constants for first 75% reaction with only slight downward drift above 75% reaction. Addition of NaClO_4 had no effect showing negligible salt effect. (.233) Calculated second order rate constants fall rapidly beyond 40-60% reaction and were not reproducible. (.235) Final product in $(\text{CH}_3)_2\text{CHOH}$ is the diisopropyl acetal but authors consider elimination with formation of acetylene as rate determining step. In ethanol-water solvent the product is the diethyl acetal. Total reaction involves 3 moles of base per mole of halide. (.236) Reaction considered to involve three consecutive reactions with (.237) as the rate determining step followed by much more rapid elimination of second and third HCl . (.237) Considered to be rate determining step for (.236). (.238) Reaction considered to involve three consecutive reactions with (.239) as the rate determining step followed by much more rapid elimination of second and third HCl , see reaction (.253). (.239) Considered to be rate determining step for (.238). (.240) Reaction considered to involve three consecutive steps with (.241) and (.254) considered by (.38) to be rate controlling. Rate constant for first step evaluated from initial rates. Composite rate data used to evaluate k' for second step as well as reaction of isolated intermediate see reaction (.254). (.241) Con-

COMMENTS

(continued)

sidered to be one of two rate controlling steps for reaction (.240). See also (.254). (.242) Considered to involve three consecutive steps with rate being controlled by (.243) and (.255). Rate constant for first step evaluated from initial rates. Rate constant for second step evaluated from reaction of isolated intermediate as well as from composite rate data, see (.255). (.244) Reaction considered to involve three consecutive steps with (.245) as the rate determining step followed by much more rapid elimination of second and third HCl. (.245) Considered to be the rate determining step for reaction (.244). (.246)-(.252) Authors show that elimination proceeds in four possible ways, trans 1-2, trans 1-4, cis 1-2 and cis 1-4 arranged in order of decreasing ease. Elimination of second HCl considered to be rapid with first step being rate determining. Importance of base illustrated by reactions (.247) and (.248). (.247) Value only approximate for comparison with rate using stronger base NaOH see (.246). (.248) No measurable reaction

in 2 hrs. (.254) One of the rate controlling steps in the aromatization of γ -C₆H₄Cl₃ see (.240). Rate constant calculated from composite data for consecutive reactions as well as by direct measurement. (.255) One of the rate controlling steps in the aromatization of δ -C₆H₄Cl₃ see (.247). Rate constant calculated from composite data for consecutive reactions as well as by direct measurement. (.260) Initial rate, as calculated first order rate constants decreased with progress of reaction. (.263) Calculated second order constants decreased with progress of reaction. Behavior consistent with an assumed mixture of 71% trans and 29% cis-isomer which reacted 1/85th as fast, see (.262). (.264)(.265)(.266) Calculated first order rate constants decreased with progress of reaction. (.269) (.270) Second order rate constants calculated by dividing pseudo first order constants by concentration of B which was in large excess.

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ELIMINATION

of halogen molecule by halogen ion

Reaction type:



Liquid phase

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

* Coded solvents at end
of table.

Rate law is for $-dA/dt$ unless stated otherwise.

| No. | Supplementing
1951 No. | Reaction | Solvent | Amount of
reactant | Addend | Amount of
addend | Defined mass-
action law | Temperature | $k \times 10^2$ | g | $A =$
$A^0 \times 10^2$ | Comments | Literature |
|-----|---------------------------|---|-------------------------------|----------------------------------|---------------|---------------------|-----------------------------|-------------|-----------------|-----|----------------------------|----------|------------|
| .19 | .1 | $\text{CH}_2\text{BrCH}_2\text{Br} + 3\text{I}^- \longrightarrow \text{CH}_2\text{:CH}_2 + \text{I}_3^- + 2\text{Br}^-$ | H_2O
M 99* | $10^2 A = 7-14$;
$B = 1$ | K^+ | $= B$ | k_{AB} | 25 | 2.63 | -6 | | * | (10) |
| | | | | $10^2 A \sim 2$;
$10B = 1-2$ | K^+ | $= B$ | | 30 | 2.82 | -6 | | | (5) |
| | | | | | | | | 60 | 8.34 | -5 | | | (5) (7a) |
| | | | | | | | | 75 | 3.72 | -4 | 22.7 | | (5) (7a) |
| | | | | $10^2 A \sim 2$;
$10B = 1-2$ | K^+ | $= B$ | | 60 | 1.13 | -4 | | | (5) |
| | | | | | | | | 30 | 4.31 | -6 | | | |
| | | | | | | | $\mu = 0.22$ | 40 | 2.22 | -5 | | | |
| | | | | | HCl | | $\mu = 0.33$ | 40 | 2.16 | -5 | | | |
| | | | | | KBr | | $\mu = 0.44$ | 40 | 2.01 | -5 | | | (4) |
| | | | | $10^2 A = 1.5$;
$B = 0.5$ | Na^+ | $= B$ | | 25 | 3.40 | -6 | | | |
| | | | | | | | | 37 | 1.28 | -5 | | | (10) |
| | | | | | | | | 56 | 9.42 | -5 | 8 | | |
| .20 | | $\text{CH}_2\text{BrCH}_2\text{I} + 2\text{I}^- \longrightarrow \text{CH}_2\text{:CH}_2 + \text{I}_3^- + \text{Br}^-$ | Et_5^* | $10^2 A = 2.5-5$;
$B = 0.10$ | K^+ | $= B$ | k_{AB} | 25 | 8.1 | -4 | | * | (2) |
| | | | | 0.05 | | | | 35 | 1.65 | -3 | | | |
| | | | | 0.10 | | | | 35 | 1.57 | -3 | | | |
| | | | | 0.15 | | | | 35 | 1.50 | -3 | | | |

Homogeneous Reaction Kinetics

422.477

2

| No. | Supplementing
1951 No. | Reaction | Solvent | Amount of
reactant | Addend | Amount of
addend | Reaction
order | Temperature | $k = k^0 \times 10^n$ | β | $A = A^0 \times 10^n$ | Comments | Literature |
|-----|---------------------------|---|--|---|---|---------------------|-------------------|----------------------------|--------------------------------------|----------------------------|-----------------------|----------|------------|
| .21 | | $\text{CH}_2\text{I} \cdot \text{CH}_2\text{I} + \text{I}^- \longrightarrow \text{CH}_2\text{I} \cdot \text{CH}_2\text{I} + \text{I}_3^-$ | Et_2S^* | $10^2 A = 2-3.5$
$B = 0.025$
0.054
0.10
0.075
0.10 | K^+ or NH_4^+
or Na^+ | B | k_{AB} | 25
25
25
35
35 | 2.26
2.08
1.94
5.35
4.88 | -3
-3
-3
-3
-3 | | * | (9) |
| .22 | | $\text{trans-ICH} \cdot \text{CHI} + \text{I}^- \longrightarrow \text{HC} \cdot \text{CH} + \text{I}_3^-$ | CH_3OH | $10^2 A = 2-6$
$10B = 1-3.5$ | | | k_{AB} | 79
94.5
109 | 1.83
1.18
5.07 | -6
-5
-5 | 4
12 | * | (7) |
| .23 | | $\text{cis-ICH} \cdot \text{CHI} + \text{I}^- \longrightarrow$ | CH_3OH | $10^2 A = 4$
$B = 0.1$ | | | | 140 | 0 | | | * | (7) |
| .24 | .2 | $\text{CH}_3\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow \text{CH}_3\text{CH} \cdot \text{CH}_2 + 2\text{Br}^- + \text{I}_3^-$ | M 99*
M 72*
E 68.3*
$\text{C}_2\text{H}_5\text{OH}$ | $10^2 A \sim 2$
$10B = 1-2.5$ | K^+ | B | k_{AB} | 80
75
80
80 | 3.11
1.61
4.67
7.25 | -6
-5
-6
-6 | 9
10 | (7) (7*) | (7) |
| .25 | .10 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow \text{C}_3\text{H}_7\text{CH} \cdot \text{CH}_2 + 2\text{Br}^- + \text{I}_3^-$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 1.5$
$10B = 3$ | Na^+ | B | k_{AB} | 25
37
58 | 3.55
2.48
2.67 | -7
-6
-5 | 3
11 | * | (4) |
| .26 | .12 | $\text{dl-threo-CH}_3\text{CH}_2\text{CHBrCHBrCH}_3 + 3\text{I}^- \longrightarrow$ | M 99* | $10^2 A \sim 2$
$10B \sim 2$ | K^+ | B | k_{AB} | 60
75 | 1.86
9.95 | -6
-6 | 1
11 | * | (14) |

Supplement 1958

| No. | Supplementing literature | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass | Temperature | $k \times 10^2$ | k^0 | η | $A = A^0 \times 10^2$ | Comments | Literature |
|-----|--------------------------|--|---------------------------------|---------------------------------|---|------------------|--------------|----------------------|------------------------------|----------------------|--------|-----------------------|----------|------------------------------|
| .27 | .12 | dl-erythro- $\text{CH}_3\text{CH}_2\text{CHBrCHBrCH}_3 + 3\text{I}^- \longrightarrow$ | M 99* | $10^2 A \sim 2$
$10B \sim 2$ | K^+ | B | k AB | 60
75 | 4.98
2.63 | -8
-5 | | 4
11 | * | (14) |
| .28 | | meso- $\text{C}_2\text{H}_6\text{CHBrCHBrC}_2\text{H}_6 + 3\text{I}^- \longrightarrow$ | M 99* | $10^2 A \sim 2$
$10B \sim 2$ | K^+ | B | k AB | 60
75 | 8.35
4.29 | -8
-5 | | 2
11 | * | (14) |
| .29 | | dl- $\text{C}_2\text{H}_6\text{CHBrCHBrC}_2\text{H}_6 + 3\text{I}^- \longrightarrow$ | M 99* | $10^2 A \sim 2$
$10B \sim 2$ | K^+ | B | k AB | 60
75 | 2.18
1.23 | -6
-5 | | 6
11 | * | (14) |
| .30 | .15 | meso- $\text{C}_3\text{H}_7\text{CHBrCHBrC}_3\text{H}_7 + 3\text{I}^- \longrightarrow$ | M 99* | $10^2 A \sim 2$
$10B \sim 2$ | K^+ | B | k AB | 60
60
75
75 | 7.68
9.61
3.78
5.11 | -6
-6
-5
-5 | | | * | (16)
(14)
(16)
(14) |
| .31 | .16 | dl- $\text{C}_3\text{H}_7\text{CHBrCHBrC}_3\text{H}_7 + 3\text{I}^- \longrightarrow$ | M 99* | $10^2 A \sim 2$
$10B \sim 2$ | K^+ | B | k AB | 60
60
75
75 | 5.70
3.43
2.99
1.68 | -6
-6
-5
-5 | | 4
10 | * | (16)
(14)
(16)
(14) |
| .32 | .3 | HC(CH ₃) ₂ CHBrCH ₂ Br + $3\text{I}^- \longrightarrow$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 1.5$
$10B = 3$ | Na^+ | B | k AB | 25
37
56 | 1.55
9.1
8.52 | -7
-7
-6 | | 5
12 | | (4) |
| .33 | .4 | $\text{HOOCCH}_2\text{CHBrCH}_2\text{Br} + \text{KI} \longrightarrow$ | H_2O | $10^2 A = 2.5$
B = 1.0 | $\left\{ \begin{array}{l} \text{K}^+ \\ \text{HCl} \end{array} \right.$ | B
0.25 | k AB | 25 | 5.52 | -6 | | | * | (10) |
| | | | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 1.5$
B = 0.7 | Na^+ | B | | 25
37
56
0 | 5.80
5.93
2.40
1.33 | -6
-6
-5
-4 | | 1.4
9 | | (4) |
| | | | $(\text{CH}_3)_2\text{CO}$ | $10^2 A = 1.5$
B = 0.3 | Na^+ | B | | 25 | 8.1
1.73 | -5
-3 | | 7
11 | | |

Homogeneous Reaction Kinetics

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| No. | Reference | Reaction | Solvent | Amount of reactant | Addend | Amount of added | Det. method | Temperature | | $k = k^0 \times 10^n$ | | k | $A = A^0 \times 10^n$ | | Comments | Literature |
|-----------------------------------|-----------|--|---------------------------------|------------------------------|-----------------|-----------------|-------------|-------------|-----|-----------------------|-----|------|-----------------------|-----|----------|------------|
| | | | | | | | | k^0 | n | k^0 | n | | A^0 | n | | |
| 34 | | $\text{NaOOCCH}_2\text{CH}_2\text{P}_2 + 3\text{I}^- \longrightarrow$ | H_2O | $10^2 A = 2.5$
$B = 1.0$ | K^+ | $= B$ | k_{AB} | 25 | -7 | 7.39 | -7 | | | | * | (10) |
| | | | | 2.0 | " | " | | 25 | -6 | 1.16 | -6 | | | | | |
| | | | | 1.0 | KBr | 1.0 | | 25 | -6 | 1.21 | -6 | | | | | |
| | | | | 1.0 | KCl | 1.0 | | 25 | -6 | 1.25 | -6 | | | | | |
| | | | | 1.0 | CuCl_2 | 0.5 | | 25 | -6 | 1.27 | -6 | | | | | |
| | | | | 1.0 | Na^+ | $= B$ | | 25 | -7 | 7.59 | -7 | | | | | |
| | | | | 2.0 | " | " | | 25 | -7 | 8.43 | -7 | | | | | |
| | | | | 1.0 | NaBr | 1.0 | | 25 | -6 | 1.02 | -6 | | | | | |
| | | | | 1.0 | NaCl | 1.0 | | 25 | -6 | 1.04 | -6 | | | | | |
| 35 | | $\text{HOOCCH}_2\text{CH}_2\text{CH}_2 + 3\text{I}^- \longrightarrow$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 1.5$
$B = 0.3$ | Na^+ | $= B$ | k_{AB} | 37 | -6 | 6.75 | -6 | | | | | (4) |
| | | | | | | | | 56 | -5 | 3.27 | -5 | 18 | 3 | 7 | | |
| 36 | 9 | $\text{meso-HOOCCH}_2\text{CH}_2\text{COOH} + 3\text{I}^- \longrightarrow$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 1.5$
$B = 0.3$ | Na^+ | $= B$ | k_{AB} | 25 | -5 | 1.80 | -5 | | | | | (4) |
| | | | | | | | | 37 | -5 | 5.96 | -5 | | | | | |
| | | | | | | | | 56 | -4 | 3.72 | -4 | 19.2 | 4 | 9 | | |
| 37 | | $\text{C}_2\text{H}_5\text{OOCCH}_2\text{CH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | $\text{C}_2\text{H}_5\text{OH}$ | $10^2 A = 1.5$
$B = 0.3$ | Na^+ | $= B$ | k_{AB} | 25 | -5 | 1.92 | -5 | | | | | (4) |
| | | | | | | | | 37 | -5 | 6.88 | -5 | | | | | |
| | | | | | | | | 56 | -4 | 3.43 | -4 | 18.2 | 3 | 8 | | |
| Aryl-substituted alkyl di-halides | | | | | | | | | | | | | | | | |
| 38 | 17 | $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br} + \text{KI}^- \longrightarrow$ | M 99* | $10^2 A = 2.5$
$B = 0.25$ | K^+ | $= B$ | k_{AB} | 40 | -5 | 1.61 | -5 | 21.7 | 2 | 10 | | (8) |
| 39 | | $2\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br} + \text{KI}^- \longrightarrow$ | M 99* | $10^2 A = 2.5$
$B = 0.25$ | K^+ | $= B$ | k_{AB} | 40 | -4 | 4.83 | -4 | | | | | (8) |

| No. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Defined mass-action law | Temperature | $k \times 10^n$ | | ρ | $A \times 10^n$ | | Comments | Literature |
|-----|---|-------------------------------------|--|------------------------------|----------------------|-------------------------|--------------|----------------------|----------------|--------|-----------------|-----|----------|------------|
| | | | | | | | | k^0 | n | | A^0 | n | | |
| .40 | $3\text{-CH}_3\text{C}_6\text{H}_4\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | N_2O^* | $10^{-2}\text{A} = 2.5; \text{B} = 0.25$ | K^+ | $= \text{B}$ | k_{AB} | 40 | 2.42 | -5 | | | | | (8) |
| .41 | $4\text{-CH}_3\text{C}_6\text{H}_4\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | N_2O^* | $10^{-2}\text{A} = 2.5; \text{B} = 0.25$ | K^+ | $= \text{B}$ | k_{AB} | 40 | 8.31 | -5 | | | | | (8) |
| .42 | $2,4\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | N_2O^* | $10^{-2}\text{A} = 2.5; \text{B} = 0.25$ | K^+ | $= \text{B}$ | k_{AB} | 40 | 2.12 | -3 | | | | | (8) |
| .43 | $2,5\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | N_2O^* | $10^{-2}\text{A} = 2.5; \text{B} = 0.25$ | K^+ | $= \text{B}$ | k_{AB} | 40 | 6.55 | -4 | | | | | (8) |
| .44 | $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | N_2O^* | $10^{-2}\text{A} = 2.5; \text{B} = 0.25$ | K^+ | $= \text{B}$ | k_{AB} | 40 | 4.07 | -4 | | | | | (8) |
| .45 | $3,5\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CHBrCH}_2\text{Br} + 3\text{I}^- \longrightarrow$ | N_2O^* | $10^{-2}\text{A} = 2.5; \text{B} = 0.25$ | K^+ | $= \text{B}$ | k_{AB} | 40 | 3.39 | -5 | | | | | (8) |
| .46 | $\text{C}_6\text{H}_5\text{CHBrCHBrC(CH}_3)_3 + 3\text{I}^- \longrightarrow$ | $(\text{C}_2\text{H}_5)_2\text{CO}$ | $10^{-2}\text{A} = 1.5; \text{B} = 0.3$ | Na^+ | $= \text{B}$ | k_{AB} | 25 | 2.07 | -3 | | | | | (4) |
| .47 | $2\text{-H}_3\text{CHBrCHBrC(CH}_3)_3 + 3\text{I}^- \longrightarrow$ | $(\text{C}_2\text{H}_5)_2\text{CO}$ | $10^{-2}\text{A} = 1.5; \text{B} = 0.3$ | Na^+ | $= \text{B}$ | k_{AB} | 0
9
14 | 1.95
5.32
9.9 | -4
-4
-4 | | 2 | 11 | | (4) |
| .48 | $4\text{-NO}_2\text{C}_6\text{H}_4\text{CHBrCHBrC(CH}_3)_3 + 3\text{I}^- \longrightarrow$ | $(\text{CH}_3)_2\text{CO}$ | $10^{-2}\text{A} = 1.5; \text{B} = 0.3$ | Na^+ | $= \text{B}$ | k_{AB} | 0
9
14 | 2.91
8.52
1.68 | -4
-4
-3 | | | 6 | 12 | (4) |
| .49 | $3\text{-ClC}_6\text{H}_4\text{CHBrCHBrC(CH}_3)_3 + 3\text{I}^- \longrightarrow$ | $(\text{CH}_3)_2\text{CO}$ | $10^{-2}\text{A} = 1.5; \text{B} = 0.3$ | Na^+ | $= \text{B}$ | k_{AB} | 14 | 1.52 | -3 | | | | | (4) |
| .50 | $4\text{-NaOOC}_6\text{H}_4\text{CHBrCHBrCOOH} + 3\text{I}^- \longrightarrow$ | H_2O | $10^{-2}\text{A} = 2.5; \text{B} = 1.0$
2.0 | K^+
HCl | $= \text{B}$
0.25 | k_{AB} | 25
25 | 9.12
9.82 | -5
-5 | | | | * | (10) |

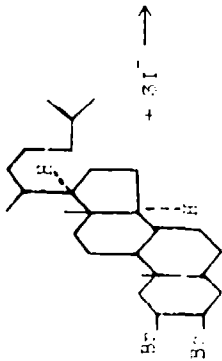
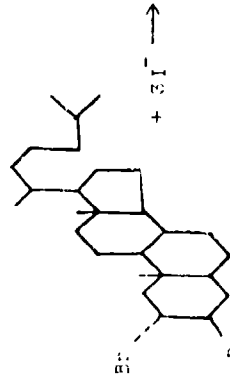
Homogeneous Reaction Kinetics

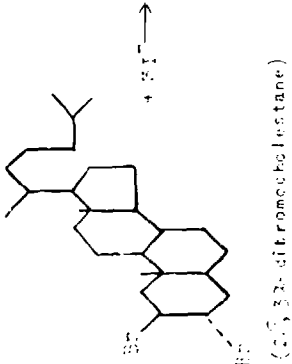
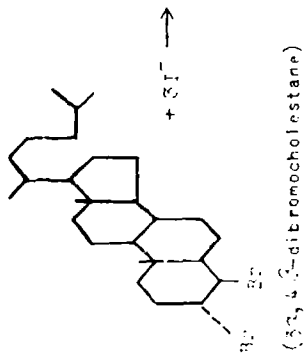
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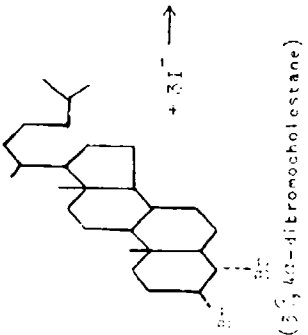
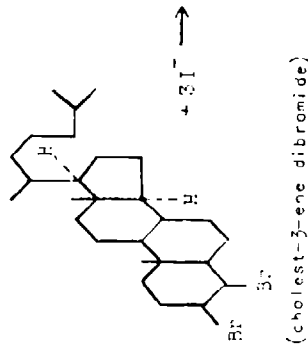
6

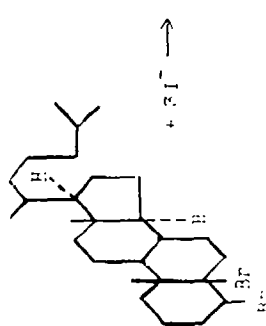
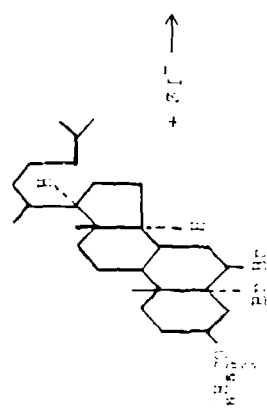
| No. | Reaction | Solvent | Amount of reactant | Addend | Amount added to run | Defined reaction law | Temperature | $k \times 10^n$ | | β | $A \times 10^n$ | | Comments | Literature |
|------------------------|---|------------------------|---|--|--|----------------------|--|--|--|---------|-----------------|-----|----------------------|------------|
| | | | | | | | | k^0 | n | | A^0 | n | | |
| .51 | $4\text{-NaSO}_3\text{C}_6\text{H}_4\text{CHBrCHBrCOONa} + 3\text{I}^- \longrightarrow$ | H_2O | $10^2 A = 2.5; B = 1.0$
2.0
1.0
1.0
1.0
1.0
1.0
2.0
1.0 | I^+
"
+ KBr
+ KCl
+ CaCl_2
Na^+
"
+ NaBr | $= B$
"
1.0
1.0
0.5
$= B$
"
1.0 | k_{AB} | 25
25
25
25
25
25
25
25
25 | 1.83
2.45
2.52
2.58
2.84
1.71
2.24
2.31 | -5
-5
-5
-5
-5
-5
-5
-5 | | | * | (10) | |
| Cyclo-alkyl di-halides | | | | | | | | | | | | | | |
| .52 | $\text{trans-CH}_2(\text{CH}_2)_3\text{CHBrCHBr} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A = 2.5; B = 0.25$ | K^+ | $= B$ | k_{AB} | 110 | 4.5 | -7 | | | | * | (11) |
| .53 | $\text{trans-CH}_2(\text{CH}_2)_3\text{CHBrCHBr} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A = 2.5; B = 0.25$ | K^+ | $= B$ | k_{AB} | 75
95
110 | 2.88
1.97
7.13 | -5
-4
-4 | | 1.2 | 10 | (11)
(12)
(11) | |
| .54 | $\text{cis-CH}_2(\text{CH}_2)_3\text{CHClCHCl} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A \sim 3; B = 0.26$ | K^+ | $= B$ | k_{AB} | 100 | <2 | -7 | | | | * | (6) |
| .55 | $\text{trans-CH}_2(\text{CH}_2)_3\text{CHClCHCl} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A \sim 3; B = 0.26$ | K^+ | $= B$ | k_{AB} | 100 | <2 | -7 | | | | * | (6) |
| .56 | $\text{cis-CH}_2(\text{CH}_2)_3\text{CHClCHBr} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A = 2.5-3.3; B = 0.26$ | K^+ | $= B$ | k_{AB} | 80
100 | 3.80
2.75 | -7
-6 | | 2 | 9 | * | (6) |
| .57 | $\text{trans-CH}_2(\text{CH}_2)_3\text{CHClCHBr} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A = 2.5-3.3; B = 0.26$ | K^+ | $= B$ | k_{AB} | 80
100 | 3.05
2.48 | -7
-6 | | 1.4 | 10 | * | (6) |
| .58 | $\text{cis-CH}_2(\text{CH}_2)_3\text{CHBrCHBr} + 3\text{I}^- \longrightarrow$ | H_9O^+ | $10^2 A = 2.5-3.3; B = 0.26$ | K^+ | $= B$ | k_{AB} | 80
100 | 9.51
6.85 | -7
-6 | | 5 | 9 | * | (6) |

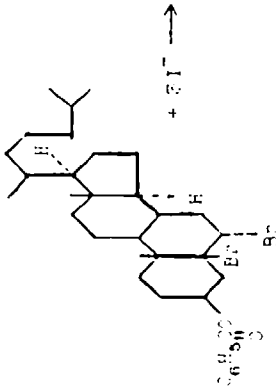
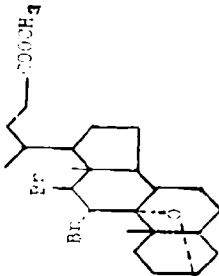
| No. | Reaction | Solvent | Amount of reactant | Addend: Amount of | Reaction law | Temperature | $k \times 10^n$ | | β | $A = 10^n \times 10^n$ | | Comments | Literature |
|-----|--|--|-----------------------------|-------------------|--------------|-------------|-----------------|-----|---------|------------------------|-----|----------------|------------|
| | | | | | | | k^0 | n | | A^0 | n | | |
| .59 | $\text{trans-CH}_2(\text{CH}_2)_3\text{CHBrCHBr} + 3\text{I}^- \longrightarrow$ | M99* | $10^2 A = 2.5; B = 0.25$ | K^+ | k AB | 75 | 6.27 | -6 | | | | (11) (12) (13) | |
| | | | " | | | 80 | 1.10 | -5 | | | | (6) | |
| | | | " | | | 95 | 4.32 | -5 | | | | (11) | |
| | | | " | | | 100 | 8.16 | -5 | | | | (6) | |
| | | | 0.15 | | | 100 | 8.5 | -5 | | | | (11) | |
| | | | 0.25 | | | 110 | 1.86 | -4 | | | | (6) | |
| | | | " | | | 100 | 7.77 | -5 | | | | | |
| | | CH ₃ OH | " | | | 100 | 7.90 | -5 | | | | | |
| | | M99.5* | " | | | 100 | 8.56 | -5 | | | | | |
| | | M98* | " | | | 100 | 1.48 | -8 | | | | * | (3) |
| | | n-C ₃ H ₇ OH | $10^2 A = 2.5; B = 0.2-0.5$ | Na^+ | k AB | 62 | 5.93 | -6 | | | | | |
| | | | " | | | 74 | 2.34 | -5 | | | | | |
| | | | " | | | 85 | 1.2 | -5 | | | | | |
| .60 | $\text{trans-CH}_2(\text{CH}_2)_4\text{CHBrCHBr} + 3\text{I}^- \longrightarrow$ | M99* | $10^2 A = 2.5; B = 0.25$ | | k AB | 75 | 1.35 | -4 | | | | * | (11) |
| | | | " | | | 95 | 7.79 | -4 | | | | | |
| | | | " | | | 110 | 2.88 | -3 | | | | | |
| .61 | $\text{trans-CH}_2(\text{CH}_2)_3\text{CHBrCHBr} + 3\text{I}^- \longrightarrow$ | M99* | $10^2 A = 2.5; B = 0.25$ | | k AB | 75 | 2.53 | -5 | | | | * | (11) |
| | | | " | | | 110 | 5.25 | -4 | | | | | |
| .62 | $\text{cis-CH}_2\text{CHCH}_2\text{CH}_2\text{CHBr} + 3\text{I}^- \longrightarrow$ | CH ₃ COOC ₂ H ₅ | $10^2 A = 6; 10^2 B = 10$ | Na^+ | k AB | 24 | 8.89 | -3 | | | | | (15) |
| | | | 9.7 | | | 24 | 9.58 | -3 | | | | | |
| | | | 6.9 | | | 24 | 1.04 | -2 | | | | | |
| | | | 5.0 | | | 24 | 1.30 | -2 | | | | | |
| .63 | $\text{trans-CH}_2\text{CH}_2\text{CH}_2\text{CHBr} + 3\text{I}^- \longrightarrow$ | CH ₃ COOC ₂ H ₅ | $10^2 A = 6; 10^2 B = 1$ | Na^+ | k AB | 24 | 7.38 | -3 | | | | | (15) |
| | | | " | | | | | | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k = k^0 \times 10^n$ | $A = A^0 \times 10^n$ | Comments | Literature |
|-------------------------|--|--------------|-----------------------------|--------|------------------|-------------------------|-------------|----------------------------------|--|----------|------------------|
| Poly-cyclic di-bromides | | | | | | | | | | | |
| .64 | 
(cholest-2-one dibromide) | $(CH_3)_2CO$ | $10^3 A = 3; 10^3 B = 6.7$ | K^+ | $= B$ | | ~20 | % reacted
3.4
22.5
46.6 | Time (secs)
5.4×10^6
1.0×10^7
1.9×10^7 | * | (²) |
| .65 | 
(2,6-dibromocholestane) | $(CH_3)_2CO$ | $10^3 A = 5; 10^3 B \sim 7$ | Na^+ | $= B$ | | ~20 | 0 | 5.1×10^6 | * | (¹) |

| No. | Reaction | Solvent | Amount of reactant | Added | Amount of added | Temperature | $k = k^0 \times 10^n$
k^0 n | $A = A^0 \times 10^2$
A^0 n | Literature |
|-----|--|--------------|-----------------------------|--------|-----------------|--------------------------|--------------------------------------|---|------------|
| .66 | 
(27,28-dibromocholestane) | $(CH_3)_2CO$ | $10^3 A = 5; 10^2 B \sim 7$ | Na^+ | $= B$ | ~ 20
"
"
" | % reacted
7
14
43
77 | Time (secs)
2.8×10^6
8.6×10^6
2.2×10^6
5.1×10^6 | $*$
(1) |
| .67 | 
(33,34-dibromocholestane) | $(CH_3)_2CO$ | $10^3 A = 5; 10^2 B \sim 7$ | Na^+ | $= B$ | ~ 20
"
" | 10
21
91 | 1.7×10^6
3.4×10^6
1.2×10^6 | $*$
(1) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Temperature | $k = \frac{k^0 \times 10^n}{k^0}$ | | $A = \frac{A^0 \times 10^n}{A^0}$ | | Literature |
|-----|---|--------------|-----------------------------|--------|------------------|-------------|-----------------------------------|-----|-----------------------------------|-------------------|------------|
| | | | | | | | k^0 | n | A^0 | n | |
| .68 |  <p>(3,4-dibromocholestan-3-ene)</p> | $(CH_3)_2CO$ | $10^3 A = 5; 10^3 B \sim 7$ | Na^+ | B | ~ 20 | g reacted | 1 | time (secs) | 1.2×10^6 | (1) |
| .69 |  <p>(cholest-3-ene dibromide)</p> | $(CH_3)_2CO$ | $10^3 A = 3; 10^3 B = 6.7$ | K^+ | B | ~ 20 | 0.1 | | 1.9×10^7 | * | (2) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Temperature | $k \times 10^7$ | | k | $A \times 10^{12}$ | | Literature |
|-----|---|--------------|----------------------------|--------|------------------|-------------|-----------------|---|-----|--------------------|-----|------------------|
| | | | | | | | k^0 | k | | A^0 | A | |
| .70 | 
(cholest-6-ene dibromide) | $(CH_3)_2CO$ | $10^3 A = 3; 10^2 B = 6.7$ | K^+ | $= B$ | ~ 20 | 79.7
100 | time (secs)
900
5.4×10^4 | * | | | (²) |
| .71 | 
(5,2,6,2-dibromocholest-3-ene) | $(CH_3)_2CO$ | $10^3 A = 3; 10^2 B = 6.7$ | K^+ | $= B$ | ~ 20 | 30.1
69.8 | 900
1.35×10^4 | * | | | (²) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Temperature | $k = k^0 \times 10^n$ | | δ | $A = A^0 \times 10^n$ | | Literature |
|-----|---|--------------|----------------------------|--------|------------------|-------------|-----------------------|-----|-------------------|-----------------------|-----|------------------|
| | | | | | | | k^0 | n | | A^0 | n | |
| 72 |  <p>(5,6-dibromocholestan-3-one + $2I^- \rightarrow$)</p> | $(CH_3)_2CO$ | $10^3 A = 7; 10^2 B = 6.7$ | K^+ | B | ~ 20 | % reacted | | time (secs) | | * | (²) |
| 73 |  <p>(methyl 11a,12a-dibromo-3a,9a-epoxy cholanate)</p> | $(CH_3)_2CO$ | $10^3 A = 5; 10^2 B = 6.7$ | K^+ | B | ~ 20 | 0 | | 1.9×10^7 | | * | (²) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Temperature | $k = k^0 \times 10^n$ | | $A = A^0 \times 10^n$ | | Literature |
|-----|---|------------------------------------|----------------------------|----------------|------------------|-------------|-----------------------|-----|-----------------------|-----|------------------|
| | | | | | | | k^0 | n | A^0 | n | |
| .74 |
(methyl 11β, 12α-dibromo-3α, 9α-epoxycholate) | (CH ₃) ₂ CO | $10^3 A = 3; 10^2 B = 0.7$ | K ⁺ | B | ~20 | % reacted | | time (secs) | | (²) |
| | | | | | | | 12.6 | | 1.35×10^4 | * | |
| | | | | | | " | 53.1 | | 1.91×10^5 | | |
| | | | | | | " | 93.7 | | 1.04×10^7 | | |

CODED SOLVENTS

M93* (99.5) (98) (72) (68.3) (63) (60)

Methanol wt. % indicated with H₂O.

E60* (68.3)

Ethanol wt. % indicated with H₂O.

E55*

Ethanol 5 volumes + H₂O 2 volumes.

COMMENTS

Reaction: (.19) Rate constant calculated by (.10) based on assumed rate law kAB^2 but converted to kAB which was shown to be rate law by (.7). (.20)(.21) Rate constants converted to seconds from original minutes and base e from base 10 logarithms. Second order constants calculated by dividing pseudo first order constants by concentration of B. (.22) Values of rate constant extrapolated to zero ionic strength. For reverse reaction see 522,477,85. (.23) No measurable reaction in 22 hours. (.24) By variation of initial concentration (.7) confirmed reaction order as second order and the stoichiometry involving 3 molecules of B for 1 of A. Recalculated earlier work of (.19). Second order rate constants of (.4) observed to decrease with course of reaction. (.25) Calculated second order rate constants observed to decrease with course of reaction. (.26)(.27)(.28)(.29) Rate constants corrected for solvent expansion and empirically determined salt effect. (.30)(.31) Rate constants of both authors corrected for solvent expansion and empirically determined salt effect. Reason for difference between values not apparent. (.33)(.34)(.50)(.51) Data of (.19) recalculated to stoichiometry involving $3I^-$ and second order rate law by editor. (.52) Rate constant not corrected for thermal expansion of solvent. (.54)(.55) Rate constant limit based upon 1% reaction. (.56) Rate constant calculated for first 30% reaction as calculated

values decrease with progress of reaction. Attributed partly to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.11. (.57) Rate constants calculated for first 30% reaction since calculated values decrease with progress of reaction. Attributed partly to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.22. (.58) Rate constants calculated for first 30% reaction since calculated values decrease with progress of reaction. Attributed partly to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.08. (.59) Rate constants calculated for first 30% reaction by (.9) and up to 20-60% by (.3) as both found calculated values decreased with progress of reaction. (.9) found his initial rates to be independent of variation in initial concentrations of both A and B. (.9) attributed decrease in rate constant to be partially due to parallel solvolysis reaction. Ratio of rate constants of solvolysis to elimination reaction is 0.006. (.60) $\Delta H^\ddagger = 22.5$ of authors converted to F. by adding RT. (.61) Rate constant at 110° not corrected for solvent expansion. (.64)(.65)(.66)(.67)(.68)(.69)(.70)(.71)(.72)(.73)(.74) Data gives only order of magnitude of reaction velocity at room temperature. Probably second order rate law but accuracy not sufficient to warrant calculation.

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- (¹¹) J. Weinstock, G.M. Lewis, F.G. Bordwell, *ACS* 1956, 78, 8072. (¹²) J. Weinstock, F.G. Pearson, F.G. Bordwell, *ACS* 1954, 76, 4748. (¹³) S. Winstein, *ACS* 1942, 64, 2792. (¹⁴) W.G. Young, S.J. Cristol, T. Skel, *ACS* 1943, 65, 2039. (¹⁵) W.G. Young, H.K. Hall, S. Winstein, *ACS* 1956, 78, 4333. (¹⁶) W.G. Young, D. Pressman, C.D. Coryell, *ACS* 1939, 61, 1540.

ELIMINATION
Ring closure by elimination of CO₂

Liquid phase

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

| No. | Reaction | Medium | Addend | Amount of
addend | Defined reaction law | Temperature | $k \times 10^n$ | | δ | $A \times 10^n$ | | Comments |
|-----|--|------------|-------------|---------------------|--------------------------|--------------------------|---|----------------------|----------|-----------------|-----|----------|
| | | | | | | | k^0 | n | | A^0 | n | |
| .1 | $\text{NaOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa} \longrightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O} + \text{Na}_2\text{CO}_3$ | softened A | M | 0-10% | k_A
$k = k_0 + k_c$ | 430
440
449
464 | $k = 2.7$
$k^0 = 2.2$
$k^0 = 6.5$
$k^0 = 1.16$ | -5
-4
-4
-3 | | | | |
| .2 | $\text{NaOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa} \longrightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O} + \text{Na}_2\text{CO}_3$ | Molten A | | | k_A | 440
449
464 | $k = 6.5$
$k^c = 1.38$
$k^c = 2.5$ | -4
-3
-3 | 59 | 1 | 15 | * |
| .3 | $\text{NaOOCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa} \longrightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{O} + \text{Na}_2\text{CO}_3$ | Molten A | M
carbon | 0-10%
11% | k_A | 405
410
415
419 | 1.87
2.78
3.93
5.25 | -4
-4
-4
-4 | 89 | 2 | 18 | |
| | | | | | | 395
410
427
437 | 1.77
4.82
1.38
2.1 | -4
-4
-3
-3 | 59 | 4 | 15 | * |

COMMENTS

Reaction: (.1) Reaction autocatalytic and could be expressed as the sum of two first order rate constants one uncatalyzed and the other catalyzed by carbon. In presence of excess carbon simple first order behavior with rate constant k_c . Reaction rate could be independent of surface of vessel. Materials tried were silicon, platinum and pyrex. (.3) Reaction shows only slight catalysis by carbon compared to reaction (.1).

LITERATURE

R.T. Reed, N.B. Thornley, *CSL* 1957, 3714.

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined reaction law | Temperature | $k^0 \times 10^n$ | n | E | $A^0 \times 10^n$ | Comments | Literature |
|-----|--|--|--|---------------------------------|---|--------------------------------|--|---|--|------------|-------------------|---|------------------------|
| 1 | $\text{cis-CH}_3\text{COOH} \xrightarrow{\text{CH}_3\text{COOH}} \text{(continued)}$

$(\text{CH}_3)_2\text{C}(\text{CH}_2\text{COOH})_2 \rightarrow (\text{CH}_3)_2\text{C}(\text{CH}_2\text{CO})_2 + \text{H}_2\text{O}$ | $\text{A}10^*$

H_2O |

$10^2 A \approx 2$ |

H_2SO_4 |

wt. %
50.6
50.6
50.6
50.6
59.0
64.6
72.3
72.3
72.3
72.3
86.4
91.6 | $k_1 A + k_2 A^2$

k_A | 20
20
20
100
111
117
129
100
100
100
111
117
129
100
100 | $k_1 = 3.8$
$k_2 = 1.77$
6.52

3.97
2.18
3.86
1.52
2.25
4.92
9.13
2.20
3.76
1.01
1.46
2.23 | -5
-3
-4

-6
-5
-5
-4
-5
-5
-5
-4
-4
-3
-4
-4 |

24 |

1
9 |

* | (2)

(1) |
| 2 | CH_3COOH | CH_3COOH |

wt. % $M = .22$
.0
.22
.72
.22 |

H_2SO_4 |

8.94
8.94
8.94
10.05
10.05
10.05
10.05
10.05
44.8
44.8
44.8 |

k_A | 87
100
110
87
100
100
100
100
88
101
110 | 9.86
2.32
4.62
1.22
2.47
2.96
2.71
5.92
6.30
1.86
3.78 | -6
-5
-5
-5
-5
-5
-5
-5
-5
-4
-4 | 23 | 5
9 |

$\Delta S^\ddagger = -18.6$
1.7
9 |

(4)

(4) |

| No. | Reaction | Solvent | Amount of reactant | Amount of added | Defined Pass-
*a. 1000 Pass-
1000 Pass- | Temperature | $k \times 10^3$ | | Σ | $A \times 10^3$ | | Comments | Literature |
|-----|---|------------|--------------------|-----------------|---|-------------|-----------------|-----|----------|-----------------|-----|-----------------------------|------------|
| | | | | | | | k^0 | n | | A^0 | n | | |
| 1 | $C_2H_5COOH + H_2O \rightarrow$ (continued) | H_2O | H_2O | 50.7 | RA | 89 | 1.20 | -4 | | | | $\Delta S^\ddagger = -19.4$ | (4) |
| | | | | 50.7 | | 100 | 3.14 | -4 | | | | | |
| | | | | 50.7 | | 110 | 6.65 | -4 | 21.6 | 1.4 | 9 | | |
| | | | | 61.0 | | 79 | 2.06 | -4 | | | | | |
| | | | | 61.0 | | 87 | 3.82 | -4 | | | | | |
| | | CH_3COOH | H_2O | 61.0 | | 100 | 1.05 | -3 | 20.0 | 5 | 8 | $\Delta S^\ddagger = -20.6$ | |
| | | | | 5.47 | | 81 | 5.50 | -5 | | | | | |
| | | | | 5.47 | | 98 | 7.91 | -5 | | | | | |
| | | | | 5.47 | | 100 | 1.79 | -4 | | | | | |
| | | | | 4.92 | wt. % $H_2O = 0.13$ | 81 | 4.96 | -5 | | | | | |
| 2 | $C_2H_5COOH + H_2O \rightarrow$ (continued) | H_2O | H_2O | 4.92 | | 87 | 7.33 | -5 | | | | $\Delta S^\ddagger = -19.8$ | (4) |
| | | | | 4.92 | 0.13 | 100 | 9.0 | -5 | | | | | |
| | | | | 4.92 | 0.0 | 100 | 1.50 | -4 | | | | | |
| | | | | 4.92 | 0.13 | 100 | 1.59 | -4 | | | | | |
| | | | | 4.92 | 0.40 | 100 | 1.42 | -4 | | | | | |
| | | H_2O | H_2O | 4.92 | | 88 | 1.33 | -5 | | | | $\Delta S^\ddagger = -20.3$ | |
| | | | | 42.8 | | 100 | 3.88 | -5 | | | | | |
| | | | | 42.8 | | 109 | 8.31 | -5 | 22.8 | 9 | 8 | | |
| | | | | 50.7 | | 87 | 3.60 | -5 | | | | | |
| | | | | 50.7 | | 101 | 1.10 | -4 | | | | | |
| 3 | $C_2H_5COOH + H_2O \rightarrow$ (continued) | H_2O | H_2O | 50.7 | | 117 | 3.70 | -4 | 22.0 | 8 | 8 | $\Delta S^\ddagger = -20.6$ | |
| | | | | 61.0 | | 80 | 9.34 | -5 | | | | | |
| | | | | 61.0 | | 87 | 1.38 | -4 | | | | | |
| | | | | 61.0 | | 100 | 3.90 | -4 | 20.7 | 5 | 8 | | |
| | | | | 65.4 | | 79 | 1.35 | -4 | | | | | |
| | | H_2O | H_2O | 65.4 | | 86 | 2.46 | -4 | | | | | |
| | | | | 65.4 | | 99 | 6.72 | -4 | 20.9 | 1.3 | 9 | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k^o \times 10^n$
k^o n | δ | $A^o \times 10^n$
A^o n | Comments | Literature |
|-----|---|----------------------------------|--|-----------------------------------|---|-------------------------|---|--|----------|--------------------------------|---|------------|
| 4 | $\pi\text{-C}_5\text{H}_7\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{COOH} \longrightarrow$ (continued) | H ₂ O | | H ₂ SO ₄ | wt. %
72.5
72.5
72.5
79.5
79.5
79.5 | kA | 21
86
99
84
80
86 | -4
-4
-3
-4
-4
-4 | 19.9 | 7
8 | $\Delta S^\ddagger = -20.5$ | (4) |
| 5 | $\pi\text{-C}_5\text{H}_7\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{COOH} \longrightarrow$
$\pi\text{-C}_5\text{H}_7\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{COOH} \longrightarrow \text{C}_5\text{H}_7\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{CO} + \text{H}_2\text{O}$ | H ₂ O | | H ₂ SO ₄ | wt. %
50.7
50.7
50.7
65.4
65.4
65.4
72.1
72.1
72.1 | kA | 86
100
109
80
87
100
80
86
97 | -5
-4
-4
-4
-4
-4
-4
-4
-3 | 21.4 | 5
8
8 | $\Delta S^\ddagger = -21.5$
$\Delta S^\ddagger = -21.7$
$\Delta S^\ddagger = -20.9$ | (4) |
| 6 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{COOH} \longrightarrow$
$(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{CO} + \text{H}_2\text{O}$ | H ₂ O | | H ₂ SO ₄ | wt. %
61.0
61.0
61.0 | kA | 100
110
117 | -5
-5
-5 | | | $\Delta S^\ddagger = -35$ | (4) |
| 7 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{COOH} \longrightarrow$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{CH}_3)_2\text{CO} + \text{C}_2\text{H}_5\text{OH}$ | C ₂ H ₅ OH | A = 0.10
0.11
0.20
0.1
0.1 | C ₂ H ₅ ONa | 2.85
2.85
2.85
2.85
2.85 | kA | 35
40
40
45
50 | -5
-5
-5
-4
-4 | 17.3 | 4
5 | * | (2) |

| No. | Reaction | Solvent | Amount of reactant | Addend | Amount of addend | Defined mass-action law | Temperature | $k \times 10^7$ | | $A^0 = 10^7$ | Comments | Literature |
|-----|--|---------------------------------|--------------------|----------------------------------|------------------|-------------------------|----------------------|------------------------------|----------------------|--------------|----------|------------------|
| | | | | | | | | k^0 | η | A^0 | | |
| 1.5 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A \approx 0.1$ | $\text{C}_2\text{H}_5\text{ONa}$ | 2.85 | k_A | 45 | 2.82 | -5 | | * | (³) |
| 1.6 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A \approx 0.1$ | $\text{C}_2\text{H}_5\text{ONa}$ | 2.85 | k_A | 25
40
45 | 2.68
3.93
6.36 | -5
-5
-5 | 1
9 | * | (³) |
| 1.7 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A \approx 0.1$ | $\text{C}_2\text{H}_5\text{ONa}$ | 2.85 | k_A | 25
40
45
50 | 2.00
4.20
7.92
1.17 | -5
-5
-5
-4 | 3
14 | * | (³) |
| 1.8 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{C}_2\text{H}_5\text{OH}$ | $\text{C}_2\text{H}_5\text{OH}$ | $A \approx 0.1$ | $\text{C}_2\text{H}_5\text{ONa}$ | 2.85 | k_A | 45 | 2.10 | -5 | | * | (³) |

CODED SOLVENTS

- F x B* $(\text{C}_2\text{H}_5)_2\text{O}$ (100-x) vol + C_2H_5 x vol
 C 99 B* Dioxane 2 vol + C_2H_5 98 vol
 A x W* $(\text{CH}_3)_2\text{CO}$ (100-x) vol + H_2O x vol

COMMENTS

Reaction. (.1) In non-aqueous solvents is second order with respect to A. In aqueous solvent reaction is first order with respect to A and reverse reaction is important, see 632.441. In mixed solvent 90% $(\text{CH}_3)_2\text{CO}$ and H_2O combined first and second order equation followed. Authors observe that in non-aqueous solutions the second order rate constant varies inversely with the square of the concentration of the oxygen containing solvent component. (.2) Selected data. Plot of $\log k$ vs. $\log [\text{H}_2\text{SO}_4]$ is linear with slope of 4.6. Rate constants do not correlate with H_0 function. (.7)-(11) Rate constants calculated from combined rate constants $k_1 + k_{-1}$ for forward and reverse reaction and equilibrium constants. Units converted to seconds from original minutes.

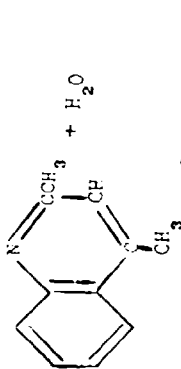
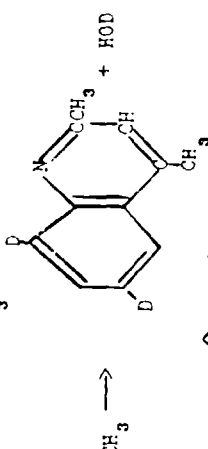
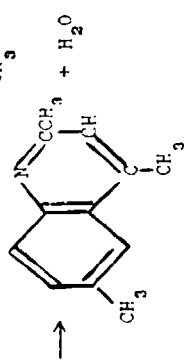
LITERATURE

- (¹) T. Henshall, W.E. Silbermann, J.B. Webster, *ACS* 1955, 77, 6858. (²) J. Koskikallio, *Acta. Chem. Scand.* 1956, 10, 892. (³) R.I. Reed, M.B. Thornley, *CSL* 1954, 2148. (⁴) W.E. Silbermann, T. Henshall, *ACS* 1957, 79, 4107.

ELIMINATION
Elimination of H_2O with formation of aromatic ring

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 | Order of
reaction | Temperature | $k \times 10^n$
k^0 η | Comments | Literature | |
|-----|---|---|-----------------------|-------------|---------------------------------|----------------------|--|--|--|------------|-----------------------------------|
| .1 |  | $H_2O + H_2SO_4$
97.3%
95.7
93.3
91.2
89.2
88.8 | $A=0.1$ | | | | 25
25
25
25
25
25 | 3.50
2.05
1.03
5.70
3.52
2.75 | -4
-4
-4
-5
-5
-5 | * | (¹) (²) |
| .2 |  | $H_2O + H_2SO_4$
95.7%
89.2 | $A=0.1$ | | | | 25
25 | 1.35
2.68 | -4
-5 | * | (²) |
| .3 |  | $H_2O + H_2SO_4$
95.5%
93.1
91.1
89.2
87.6
86.3
84.5
$H_2O + [H_2SO_4] =$
14.42
10.14
7.97
5.80
1.36 | $A=0.1$ | NH_4HSO_4 | 2.0
4.0
5.0
6.0
8.0 | | 25
25
25
25
25
25
25
25
25
25
25
25
25 | 1.41
7.15
3.53
2.05
1.23
6.45
3.98
2.18
9.23
5.23
2.37
4.97 | -3
-4
-4
-4
-4
-5
-5
-3
-4
-4
-4
-5 | * | (¹) |

COMMENTS

Reaction: (.1) Selected data, units converted to seconds from original minutes. Plot of log of rate constant vs. H_0 is linear. (.2) Units converted to seconds from original minutes. (.3) Selected data, units converted to seconds from original minutes. Plot of log of rate constant vs. H_0 is linear for $H_2O-H_2SO_4$ medium and plot of log of rate constant vs. $\log ([H_2SO_4], [HSO_4^-])$ is linear in both media.

LITERATURE

- (¹) T. G. Bonner, M. P. Thorne, J. M. Wilkins, *CSL* 1955, 2351. (²) T. G. Bonner, J. M. Wilkins, *CSL* 1955, 2358.

Homogeneous Reactions
432.455

ELIMINATION

 Elimination of NO_3^- with ring closure

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 t | $k = 10^n$ | | $A = 10^n$ | | $\Delta S^\ddagger$ |
|-----|---|----------------------|----------------------------|-------------------------|-----------------|----------------------|----------------|------------|----------|---------------------|
| | | | | | | k' | n | A' | n | |
| 1 | $\text{NO}_2\text{N}(\text{CH}_2)_2\text{NHCH}_2\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{H}_2\text{O}} \text{NO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}(\text{CH}_3)_2 + \text{NO}_3^-$ | H_2O | $10^{-4} \text{ A} = 5-14$ | k_A | 30
40
50 | 1.77
5.43
1.94 | -6
-6
-5 | | | |
| 2 | $\text{NO}_2\text{N}(\text{CH}_2)_2\text{NHCH}_2\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{H}_2\text{O}} \text{NO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}(\text{CH}_3)_2 + \text{NO}_3^-$ | H_2O | $10^{-4} \text{ A} = 5-14$ | k_A | 40
50 | 3.14
1.11 | -6
-5 | 3
2 | 12
12 | -5 |
| 3 | $\text{NO}_2\text{N}(\text{CH}_2)_2\text{NHCH}_2\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{H}_2\text{O}} \text{NO}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}(\text{CH}_3)_2 + \text{NO}_3^-$ | H_2O | $10^{-4} \text{ A} = 5-14$ | k_A | 30
40
50 | 2.69
1.22
4.99 | -7
-6
-6 | 1.3
1.3 | 14
14 | +4 |

COMMENTS

Reactions followed by conductimetric method as well as analytically for 1. Conductimetric method indicated slightly higher extent of reaction after about 75%. This was attributed to hydrolysis of product and rate constants were corrected for 15.

LITERATURE

C. Boyars, W. F. Sager, S. Skolnik, ACS 1957, 78, 4590.

Homogeneous Reactions
432.476

 ELIMINATION
with Ring Closure

Elimination of halogen from halo thio ether

Coded solvents at end of Table.

 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 | Unfitted mass-
action law | Temperature | $k \times 10^n$ | | $A^\circ \times 10^n$ | Comments | Literature |
|-----|--|---------|-----------------------|--------|---------------------|------------------------------|----------------|----------------------|----------------|-----------------------|----------|------------|
| | | | | | | | | k^0 | n | | | |
| .1 | $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{SCH}_2\text{CH}_2 + \text{Cl}^-$ | An 50* | $10^2 A = 1$ | | | k A | 80 | 2.67 | -4 | | * | (2) |
| .2 | $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2 + \text{Cl}^-$ | An 50* | $10^2 A = 1$ | | | k A | 70
60
90 | 1.08
1.07
2.68 | -4
-3
-3 | | * | (2) |
| .3 | $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2 + \text{Cl}^-$ | An 50* | $10^2 A = 1$ | | | k A | 80
90 | 1.40
3.58 | -5
-5 | | * | (2) |
| .4 | $\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2 + \text{Cl}^-$ | An 5* | | | | k A | 25 | 1.2 | -2 | | * | (1) |

CODED SOLVENTS

 An 50* (5) $(\text{CH}_3)_3\text{C}^+\text{O}^-$ % indicated and H_2O (wt. or vol. % not indicated)

COMMENTS

 Reaction: (.1) (.2) (.3) Reverse reaction negligible. Units converted to seconds from original minutes. (.4) Value of rate constant derived from first stage hydrolytic reaction, 212.471(.421), of "mustard", $\text{S}(\text{CH}_2\text{CH}_2)_2$, with added thio-phosphate. Units converted to seconds from original minutes.

LITERATURE

 (1) P.D. Bartlett, C.G. Swain, *ACS* 1949, 71, 1406. (2) G.M. Bennett, F. Heathcoat, A.N. Moses, *CSL* 1929, 2567.

ELIMINATION
Vth Group Element
Elimination of Carbonium ion from Quaternary ammonium salt

liquid phase

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

| No. | Reaction | Solvent | Amount of
reactant | Added
Amount of | Defined Mass | Temperature | $k \times 10^n$ | | $k^0 \times 10^n$ | | E | $A^0 \times 10^n$ | |
|-----|---|--------------------|--|-------------------------|--------------|--|--|----------------------------------|-------------------|-----|------|-------------------|-----|
| | | | | | | | k^0 | n | k^0 | n | | A^0 | n |
| 1. | $C_6H_5N(CH_3)_3^+ + CH_3O^- \longrightarrow C_6H_5N(CH_3)_2 + (CH_3)_2O$ | CH ₃ OH | $10^2 A \sim 2; 10^2 B \sim 4$ | $I^- = A$
$Na^+ = B$ | k_{AB} | 89.8
80.9
95.3 | 9.71
4.39
2.89 | -5
-4
-3 | | | | 7 | 16 |
| 2. | $p-CH_3C_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow p-CH_3C_6H_4N(CH_3)_2 + (CH_3)_2O$ | CH ₃ OH | $10^2 A \sim 2; 10^2 B \sim 4$ | $I^- = A$
$Na^+ = B$ | k_{AB} | 89.7
80.9
95.2 | 5.88
2.87
1.88 | -5
-4
-3 | | | 33.3 | 1.0 | 17 |
| 3. | $o-FC_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow o-FC_6H_4N(CH_3)_2 + (CH_3)_2O$ | CH ₃ OH | $10^2 A \sim 2; 10^2 B \sim 4$ | $I^- = A$
$Na^+ = B$ | k_{AB} | 58.4
69.6
80.6
90.8 | 2.77
1.28
5.14
1.72 | -4
-3
-3
-2 | | | 30.5 | 4 | 16 |
| 4. | $m-FC_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow m-FC_6H_4N(CH_3)_2 + (CH_3)_2O$ | CH ₃ OH | $10^2 A \sim 2; 10^2 B \sim 4$
2
4
4.1
3.7
~2 | $I^- = A$
$Na^+ = B$ | k_{AB} | 58.3
69.2
80.9
80.9
80.9
91.4 | 7.80
7.59
1.71
1.39
1.25
6.22 | -5
-4
-3
-3
-3
-3 | | | | | |
| 5. | $p-FC_6H_4N(CH_3)_3^+ + CH_3O^- \longrightarrow p-FC_6H_4N(CH_3)_2 + (CH_3)_2O$ | CH ₃ OH | $10^2 A \sim 2; 10^2 B \sim 4$ | $I^- = A$
$Na^+ = B$ | k_{AB} | 58.6
69.9
80.7
91.9 | 3.44
1.52
7.50
3.13 | -5
-4
-4
-3 | | | 32.8 | 9 | 16 |

LITERATURE

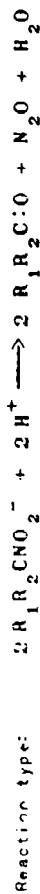
M.L. Bevan, G.C. Bye, *CSL* 1957, 3194.

Homogeneous Reactions
452.451

ELIMINATION FROM FUNCTIONAL GROUP

N₂O from aci form of nitro alkane

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 | Order of reaction | $k = k^0 \times 10^n$
k^0 n | Source |
|-----|--|--|---------------------------------------|-------------------------|-------------------|------------------------------------|--------|
| 1 | $2(CH_3)_2CNO_2^- + 2H^+ \longrightarrow 2(CH_3)_2C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 7$; $10^{-2}B = 2-10$ | $-dA/dt = kAB$ | 0 | 1.30 -2 | |
| 2 | $2CH_2(CH_2)_2CNO_2^- + 2H^+ \longrightarrow 2CH_2(CH_2)_2C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 7$; $10^{-2}B = 3-20$ | $-dA/dt = kAB$ | 0 | 1.3 -1 | |
| 3 | $2CH_2(CH_2)_3CNO_2^- + 2H^+ \longrightarrow 2CH_2(CH_2)_3C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 6$; $10^{-2}B = 4-10$ | $-dA/dt = kAB$ | 0 | 5.3 -3 | |
| 4 | $2CH_2CH_2CH(CH_3)CNO_2^- + 2H^+ \longrightarrow 2CH_2CH_2CH(CH_3)C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 6$; $10B = 1-5$ | $-dA/dt = kAB$ | 0 | 4.5 -3 | |
| 5 | $2CH_2(CH_2)_4CNO_2^- + 2H^+ \longrightarrow 2CH_2(CH_2)_4C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 5$; $10^{-2}B = 3-40$ | $-dA/dt = kAB$ | 0 | 1.48 -1 | |
| 6 | $2CH_2(CH_2)_6CNO_2^- + 2H^+ \longrightarrow 2CH_2(CH_2)_6C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 5$; $10^{-2}B = 5-20$ | $-dA/dt = kAB$ | 0 | 2.3 -3 | |
| 7 | $2[CH_2CH_2CH_2CNO_2^- + 2H^+ \longrightarrow 2[CH_2CH_2CH_2]C:O + N_2O + H_2O$ | 80 vol % CH ₃ OH + H ₂ O | $10^{-4}A \sim 5$; $10B = 1-3$ | $-dA/dt = kAB$ | 0 | 3.0 -3 | * |

COMMENTS

General. Aci form of nitro alkane produced by addition of alkali prior to reaction. Pseudo first order rate constants converted to second order constants by dividing by concentration of excess acid added at start of reaction.

Reaction. (2) In doubt as products other than cyclobutane observed.

LITERATURE

M. F. Hawthorne, ACS 1957, 79, 2510.