the time of removal of the first tube after attainment of temperature.

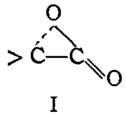
The "infinite" titer of bromide ion agreed well with the expected as indicated by the equivalent weights of the α-bromopropionic acid samples. The "infinite" titer of base was usually unreliable by a few per cent., probably due to reaction of the glass. Soft glass tubes were used in the experiments with methanolic solutions, and Pyrex tubes were employed for the aqueous runs.

In the runs with high base concentration, the reaction was followed chiefly by titration for bromide ion. With the low base concentrations, titration was carried out for both base and bromide ion except where bromide ion was added in large amounts initially. When added sodium perchlorate the rate constants based on the two titrations agreed closely (Table II). With added sodium nitrate, the rate constants from bromide titration were steady but those based on base titration were lower and drifted downward. In run 21 with 0.5 M added sodium nitrate, the base consumed during a run averaged 98.8 ± 0.7% of the bromide ion produced, while the analogous figure was 96.6 ± 1.5% for run 19 with M added sodium nitrate.

Summary

The hydrolysis and methanolysis of sodium α-bromopropionate in the presence of sodium hydroxide or methoxide was investigated in solutions of varying ionic strength at 64.04°. A kinetic analysis reveals that both the bimolecular and unimolecular specific reaction rate constants, k_2 and k_1, respectively, increase with ionic strength.

The variation of k_1 with change in solvent and ionic strength is discussed in terms of a rate-determining ionization either to the zwitterion II (specific rate k_c), or the α-lactone I (specific rate k_Δ). An unambiguous decision regarding the reaction mechanism is not possible from the salt and solvent effects alone.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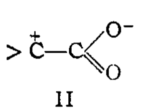
II

However, the sign of these effects and related evidence, particularly the high reactivity of α-bromopropionate ion compared to isopropyl bromide and the contrast with α-bromoisobutyrate ion, are consistent with the rate-determining ionization symbolized by k_Δ.

The ratio of rate constants for reaction of the intermediate in the solvolysis of α-bromopropionate ion with bromide ion and solvent, k_{Br}/k_S, derived from measurements in solutions containing high bromide ion concentrations, is 2.9 in methanol and 0.76 in water.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Correlation of Solvolysis Rates

BY ERNEST GRUNWALD AND S. WINSTEIN

One of the important mechanisms (**A**) for solvolysis[1,2] of alkyl halides involves more than one stage and is at present best formulated as involving a rate-determining ionization (equation 1) to a cationic intermediate. The rate constant k_1

$$RX \xrightarrow{k_1} R^+ + X^- \qquad (1)$$

depends on the so-called ionizing power of the solvent, and it is possible from such rates to arrange solvents in a relative order. For example substitution of the unimolecular type[3] proceeds slightly more rapidly in acetic acid than in absolute ethanol.[4] The rate is increased by addition of water to alcohol or partly aqueous acetone or dioxane.[1,2] Further, substitution is about as rapid in formic acid as in 50% aqueous ethanol.[5]

The question arises whether it is possible to assign to each solvent a definite number **Y** which is a quantitative measure of its ionizing power in determining k_1. In this article is reported a scheme for correlating unimolecular solvolysis rates with the aid of such a set of **Y** values and a simple functional relationship between k_1 and **Y**. Also, the theoretical implications of the method are discussed.

In addition to the solvolysis mechanism **A** there occurs solvolysis in neutral and acidic solvents by a process or processes (**B**, rate constant k_x) for which the nucleophilic character as well as the ionizing power of the solvent is important. The best understood concerted process is the so-called bimolecular substitution in which a solvent molecule plays a role such as that of a pyridine molecule in the Menshutkin reaction. One of the important problems for the proper understanding of such subjects as reactivity, stereochemistry of displacements and rearrangements[1b] is that of sorting out the fractions of solvolysis proceeding by mechanisms **A** and **B**.

The scheme for correlating solvolysis rates allows one to make deductions regarding the rate by process **A** and therefore the fraction of solvolysis by mechanism **A**. This application of the method is being actively pursued and the procedure is illustrated in the present article for isopropyl *p*-bromobenzenesulfonate.

A Quantitative Measure of Ionizing Power. The Y Function.—The specific solvolysis rates k for a number of halides which, the accumulation

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(1) (a) Hughes, *Trans. Far. Soc.*, **37**, 611 (1941); (b) Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 173 (1946).

(2) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 166 ff.

(3) Winstein, Grunwald, Buckles and Hanson, THIS JOURNAL, **70**, 816 (1948).

(4) Winstein, Hanson, and Grunwald, *ibid.*, **70**, 812 (1948).

(5) Dostrovsky and Hughes, *J. Chem. Soc.*, 166, 171 (1946).

TABLE I

SOLVOLYSIS RATES OF SOME HALIDES AND Y VALUES FOR SOLVENTS

Compound	Temp., °C.	Solvent	$E^{\neq}$, kcal.	k(sec.$^{-1}$)	Ref.	Y
$(CH_3)_3CCl$	25.0	Absolute EtOH	25.97	9.70×10^{-8}	Table II	−1.974
		90% EtOH, N_{H_2O} = 0.262		1.73×10^{-6}	6	−0.727
		80% EtOH, N_{H_2O} = 0.448	23.06	9.24×10^{-6}	6	0.000
		70% EtOH, N_{H_2O} = 0.582		4.07×10^{-5}	6	0.644
		60% EtOH, N_{H_2O} = 0.684		1.27×10^{-4}	6	1.139
		50% EtOH, N_{H_2O} = 0.765	22.92	3.67×10^{-4}	6	1.604
		40% EtOH, N_{H_2O} = 0.829		1.29×10^{-3}	6	2.151
		80% $(CH_3)_2CO$	22.6	1.94×10^{-6}	6	
		5% $(CH_3)_2CO$, N_{H_2O} = 0.987		2.57×10^{-2}	7	3.449
		48.61 wt. % H_2O in dioxane	22.8	1.81×10^{-4}	8, 11b	1.292
		H_2O-MeOH, N_{H_2O} = 0.000	25.0	8.20×10^{-7}	8, Table II	−1.052
		H_2O-MeOH, N_{H_2O} = 0.070		1.75×10^{-6}	8	−0.722.
		H_2O-MeOH, N_{H_2O} = 0.175		4.33×10^{-6}	8	−0.329
		H_2O-MeOH, N_{H_2O} = 0.230		7.14×10^{-6}	8	−0.112
		H_2O·MeOH, N_{H_2O} = 0.282		1.13×10^{-5}	8	0.088
		H_2O-MeOH, N_{H_2O} = 0.346		2.12×10^{-5}	8	0.361
		H_2O-MeOH, N_{H_2O} = 0.432		5.28×10^{-5}	8	0.757
		H_2O-MeOH, N_{H_2O} = 0.497		9.75×10^{-5}	8	1.023
		H_2O^{e}		3.3×10^{-2}		3.56
		$HCOOH^{b}$	22.9^{a}	1.1×10^{-3}	9a	2.08
		AcOH, 0.025 M KOAc	26.43	2.13×10^{-7}	Table II	−1.633
		AcOH-Ac_2O, N_{AcOH} = 0.042 0.017 M KOAc	26.4^{a}	4.77×10^{-9}	Table II	−3.287
$(CH_3)_3CBr$	25.0	EtOH	23.0^{a}	5.69×10^{-6}	10c	
		90% EtOH		7.14×10^{-5}	10a	
		80% EtOH	22.8	3.63×10^{-4}	10a	
		76.5% EtOH, N_{H_2O} = 0.501	22.5^{a}	5.22×10^{-4}	10d	
		60% EtOH	21.7	3.76×10^{-3}	10a	
		95% $(CH_3)_2CO$, N_{H_2O} = 0.178	22.7	2.10×10^{-6}	10b	-2.402^{c}
		90% $(CH_3)_2CO$, N_{H_2O} = 0.313	20.8	1.27×10^{-5}	10e	-1.549^{c}
		80% $(CH_3)_2CO$, N_{H_2O} = 0.506	20.8^{a}	1.10×10^{-4}	10a	-0.527^{c}
		70% $(CH_3)_2CO$, N_{H_2O} = 0.637		5.15×10^{-4}	10e	0.205^{c}
$CH_3CHClCH{=}CH_2$	25.0	EtOH	23.5^{a}	8.8×10^{-9}	11a	
		50% EtOH		1.14×10^{-5}	11a	
		H_2O	23.5^{a}	8.1×10^{-4}	11b	
$(CH_3)_3CCH_2Br$	95.0	70% EtOH		1.54×10^{-7}	5	
		50% EtOH	29.0	9.20×10^{-7}	5	
		HCOOH		1.53×10^{-6}	5	
$(C_6H_5)_2CHCl$	25.0	EtOH		5.30×10^{-5}	10f	
		90% EtOH		4.90×10^{-4}	12b	
		80% EtOH		1.72×10^{-3}	12b	
		90% $(CH_3)_2CO$	19.6	4.60×10^{-6}	10e	-3.377^{d}
		80% $(CH_3)_2CO$	21.0	7.24×10^{-5}	10e	-1.797^{d}
		70% $(CH_3)_2CO$		3.20×10^{-4}	10e	-0.945^{d}
$C_6H_5CHClCH_3$	50.0	EtOH	21.9^{a}	5.85×10^{-7}	13	
		80% EtOH	21.4	1.64×10^{-4}	12^{a}	
		MeOH	21.7^{a}	7.06×10^{-6}	13	
		80% $(CH_3)_2CO$	21.8^{a}	1.44×10^{-6}	13	
		60% $(CH_3)_2CO$	21.5^{a}	4.19×10^{-5}	13	
		AcOH, 0.2 M KOAc		3.9×10^{-6}	14	

[a] Value used by the authors. [b] Rate constants have been reported[9a] at 15.0° ranging from 2.0×10^{-4} to 3.9×10^{-4} sec.$^{-1}$. An average value was used. Rate measurements in formic acid are complicated by decomposition of the solvent[9b,c] into carbon monoxide and water. [c] From *t*-butyl bromide. [d] From benzhydryl chloride. [e] Obtained by extrapolation from the plot of log k^{BuCl} *vs.* N_{H_2O} using the data[6,7] in aqueous acetone.

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(6) Hughes, *J. Chem. Soc.*, 255 (1935).

(7) Swain and Ross, THIS JOURNAL, **68**, 658 (1946).

(8) Olson and Halford, *ibid.*, **59**, 2644 (1937).

(9) (a) Bateman and Hughes, *J. Chem. Soc.*, 935 (1940); (b) Bateman and Hughes, *ibid.*, 940 (1940); (c) Weissberger and Proskauer, "Organic Solvents," Clarendon Press, Oxford, 1935, p. 145.

(10) (a) Bateman, Cooper, Hughes and Ingold, *J. Chem. Soc.*, 925 (1940); (b) Cooper and Hughes, *ibid.*, 1183 (1937); (c) Hughes, Ingold, Masterman and McNulty, *ibid.*, 899 (1940); (d) Petrenko-

TABLE II

FIRST-ORDER SOLVOLYSIS RATE CONSTANTS AT 70.0°. FOR *t*-BUTYL CHLORIDE AND PINACOLYL AND ISOPROPYL *p*-BROMOBENZENESULFONATES

Compound	Solvent	(RX) 10^3M	(KOAc) 10^3M	k, sec.$^{-1}$
$(CH_3)_3CCl$	AcOH-97.5% Ac_2O	40.3	19.07	$(1.620 \pm 0.048) \times 10^{-6}$
	$N_{AcOH} = 0.042$	42.3	15.67	$(1.625 \pm 0.048) \times 10^{-6}$
	AcOH-0.1% Ac_2O	12.04	24.63	$(7.12 \pm 0.12) \times 10^{-5}$
		19.25	24.54	$(7.45 \pm 0.10) \times 10^{-5}$
		19.60[a]	24.89	$(8.78 \pm 0.17) \times 10^{-7}$
		18.43[a]	24.91	$(8.91 \pm 0.20) \times 10^{-7}$
	EtOH	52.16	60.2	$(3.19 \pm 0.03) \times 10^{-5}$
		37.25	35.0	$(3.12 \pm 0.03) \times 10^{-5}$
		52.16[b]	60.2	$(3.82 \pm 0.07) \times 10^{-7}$
		37.25[b]	35.0	$(3.69 \pm 0.07) \times 10^{-7}$
	MeOH	19.21	58.5	$(2.07 \pm 0.07) \times 10^{-4}$
		37.40	58.5	$(2.10 \pm 0.03) \times 10^{-4}$
	80% EtOH[c]			1.51×10^{-3}
$(CH_3)_3CCH(OSO_2$ $C_6H_4Br)CH_3$	AcOH-97.5% Ac_2O	33.46	19.91	$(11.49 \pm 0.15) \times 10^{-6}$
	$N_{AcOH} = 0.042$	19.40	8.99	11.66×10^{-6}
	AcOH-80.3% Ac_2O	24.71	. . .	$(7.89 \pm 0.11) \times 10^{-5}$
	$N_{AcOH} = 0.294$			
	AcOH-0.1% Ac_2O	22.61	. .	$(2.734 \pm 0.026) \times 10^{-4}$
		34.29	. . .	$(2.742 \pm 0.033) \times 10^{-4}$
		27.60	24.87	$(2.811 \pm 0.022) \times 10^{-4}$
	EtOH	16.55	. . .	$(7.02 \pm 0.10) \times 10^{-5}$
		12.37	. . .	$(7.01 \pm 0.13) \times 10^{-5}$
		7.16	. . .	$(7.09 \pm 0.09) \times 10^{-5}$
	MeOH	19.82	. . .	$(3.19 \pm 0.06) \times 10^{-4}$
		12.05	. . .	$(3.15 \pm 0.05) \times 10^{-4}$
		5.87	. . .	$(3.29 \pm 0.05) \times 10^{-4}$
	80% EtOH	9.94	. . .	$(1.369 \pm 0.018) \times 10^{-3}$
		12.84	. . .	$(1.386 \pm 0.017) \times 10^{-3}$
$(CH_3)_2CHOSO_2$ C_6H_4Br	AcOH-97.5% Ac_2O	30.65	. . .	1.30×10^{-6}
	$N_{AcOH} = 0.042$	36.72	22.28[d]	1.50×10^{-6}
		21.81	10.25[d]	1.46×10^{-6}
	AcOH-80.3% Ac_2O	28.33	. . .	$(8.48 \pm 0.11) \times 10^{-6}$
	$N_{AcOH} = 0.294$			
	AcOH-0.1% Ac_2O	42.66	. . .	$(6.98 \pm 0.08) \times 10^{-5}$
		26.72	. . .	$(6.90 \pm 0.05) \times 10^{-5}$
		24.10	25.03	$(7.41 \pm 0.07) \times 10^{-5}$
	EtOH	23.16	. . .	$(2.64 \pm 0.04) \times 10^{-4}$
	MeOH	23.31	. . .	$(7.34 \pm 0.08) \times 10^{-4}$
		18.15	. . .	$(7.28 \pm 0.16) \times 10^{-4}$
	80% EtOH	11.35	. . .	1.73×10^{-3}
		11.93	. . .	1.67×10^{-3}

[a] Data at 34.85°; $E^{\neq} = 26.43$ kcal./mole. [b] Data at 34.43°; $E^{\neq} = 25.97$ kcal./mole. [c] From data of Hughes.[6] [d] $k_2 = 3.61 \times 10^{-4}$ sec.$^{-1}$ M^{-1}.

of evidence indicates, react by the unimolecular-type mechanism **A**, are summarized in Table I together with the values of the corresponding Arrhenius activation energies, $E^{\neq}$, wherever available. The solvolysis rates for any one compound have been corrected to one temperature with the aid of available values of $E^{\neq}$ or else on the basis of reasonable estimates of $E^{\neq}$. The values of $E^{\neq}$ for any one compound are fairly insensitive to solvent change and all values of $E^{\neq}$ hover near 22 kcal (Table I). It is therefore possible to estimate $E^{\neq}$ with sufficient accuracy since the corrections made are small. Even an error of 2.0 kcal. in $E^{\neq}$ would cause an error of no more than 0.079 in log k for a 20° correction.

Supplementing the data in Table I are the solvolysis rates k we have measured for *t*-butyl chloride and α-methylneopentyl *p*-bromobenzenesulfonate, $(CH_3)_3CCH(OSO_2C_6H_4Br)CH_3$, in a num-

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Kritschenko, *Ber.*, **61**, 852 (1928); (e) Bateman, Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 979 (1940); (f) Hughes, Ingold and Taher, *ibid.*, 949 (1940).

(11) (a) Young and Andrews, THIS JOURNAL, **66**, 421 (1944); (b) Winstein and Grunwald, *ibid.*, **70**, 828 (1948).

(12) (a) Ward, *J. Chem. Soc.*, 445 (1927); (b) Ward, *ibid.*, 2285 (1927).

(13) Hughes, Ingold and Scott, *ibid.*, 1201 (1937).

(14) Steigman and Hammett, THIS JOURNAL, **59**, 2526 (1937).

ber of solvents. These measurements are summarized in Table II.

Inspection reveals a simple quantitative relationship among the various solvolysis rate constants. Thus, when the values of log k for any one compound in a number of solvents are plotted against log k of some other compound in the same solvents a straight line is obtained. This linear relationship is illustrated for a number of compounds in Fig. 1.

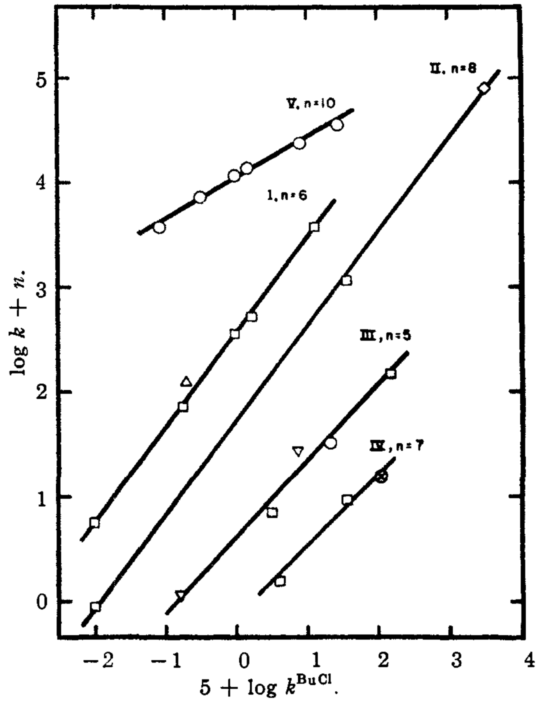

Fig. 1.—Plots of log k *vs.* log k^{BuCl}: I, *t*-butyl bromide 25.0°; II, α-methylallyl chloride, 25.0°; III, α-methylneopentyl *p*-bromobenzenesulfonate, 70.0°; IV and V, neopentyl bromide, 95.0°, and *n*-butyl bromide, 59.4°, both *vs.* *t*-butyl chloride, 25.0°; solvents: ◇, H_2O; □, EtOH–H_2O; ○, MeOH–H_2O; ▽, AcOH–Ac_2O; △, acetone–H_2O; ⊗, HCOOH.

The linear plots illustrated in Fig. 1 indicate that log k^{BuCl} (BuCl = *t*-butyl chloride) satisfies the requirements for a useful quantitative measure of ionizing power of a given solvent. However, log k^{BuCl} varies with temperature and is usually a negative entity of an inconvenient order of magnitude. It is convenient to define Y by equation 2, where k^{BuCl} and k_0^{BuCl} are the rate constants of

$$Y = \log k^{\mathrm{BuCl}} - \log k_0^{\mathrm{BuCl}} \qquad (2)$$

t-butyl chloride at 25.0° in the given solvent and in "80%" ethanol, respectively. By virtue of this definition, Y is zero in "80%" ethanol, a solvent often employed and of intermediate reactivity, and Y varies from *ca.* +4 to −3 for the most common solvolyzing media. Although 25.0° is chosen as the reference temperature for computing values of Y it is clear from the near constancy of $E^{\ddagger}_{\mathrm{BuCl}}$ in various solvents that any other reference temperature would give an almost identical set of Y values.

The linear relationships illustrated in Fig. 1 combined with the defining equation 2 for Y lead to equation 3 for the variation of solvolysis rate constant k with solvent for these compounds. In

$$\log k = mY + \log k_0 \qquad (3)$$

this equation, m and log k_0 are parameters, although physically k_0 is the solvolysis rate constant in "80%" ethanol. Equation 3 is the basis of the quantitative scheme for correlating solvolysis rates.

In Table I are summarized values of Y for an extensive series of solvents. Y values for all solvents except the acetone–water mixtures were calculated from the available data for *t*-butyl chloride at 25.0° (Tables I, II). In order to obtain Y values in the latter solvent mixtures the parameters m and log k_0 were evaluated for *t*-butyl bromide and benzhydryl chloride from data at 25.0° in ethanol–water mixtures, and Y was calculated for various acetone–water mixtures with the aid of equation 3, using the available values of log k for these compounds. Two different sets of Y are obtained in this way, of which one (from *t*-butyl bromide) is used for aliphatic compounds while the other (from benzhydryl chloride) is used with α-phenylethyl chloride. Acetone–water mixtures were the only solvents where it was found necessary to use two different sets of Y in order to correlate all rates of unimolecular-type solvolysis scrutinized by the authors to date.

The functional relationship between Y and the composition of mixed solvents is apparently not

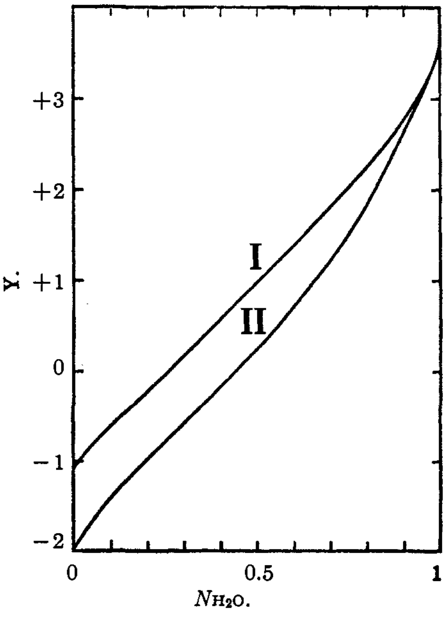

Fig. 2.—Plot of Y *vs.* mole fraction of water (N_{H_2O}) for: I, H_2O–MeOH; II, H_2O–EtOH.

simple. Plots of **Y** *vs.* weight % or volume % of water in aqueous ethanol and methanol have considerable curvature. The plot of **Y** *vs.* mole fraction of water, N_{H_2O}, is more nearly linear for these systems as illustrated in Fig. 2. The latter observation is useful for purposes of interpolation.

The parameters m and log k_0 in equation 3 have been evaluated for a number of compounds by the method of least squares, using the values of k and **Y** in Tables I and II. The results are summarized in Table III together with the probable error of the fit,[15] r. The fit is satisfactory, particularly since the values of k often vary by 3 to 6 powers of ten, the mean value of r for the whole table being less than 0.05. The probable errors in m are of the order of 0.05 or less.

TABLE III

CORRELATION OF SOLVOLYSIS RATES IN VARIOUS SOLVENTS

No.	Compound	Temp., °C.	m	log k_0	
1	*t*-Butyl chloride	25.0	1.000	−5.034	...
2	*t*-Butyl bromide	25.0	0.917	−3.476	0.026
3	Neopentyl bromide	95.0	.712	−7.248	.059
4	α-Methylneopentyl *p*-bromobenzenesulfonate	70.0	.706	−2.837	.096
5	α-Methylallyl chloride	25.0	.894	−6.314	.052
6	Benzhydryl chloride	25.0	.757	−2.779	.004
7	α-Phenylethyl chloride[a]	50.0	1.195	−3.808	.072
8	*n*-Butyl bromide	59.4	0.392	−5.972	.026
		75.1	0.331	−5.419	.034

[a] The value of k for HOAc, 0.2 M KOAc (Table I), was not included since no value of **Y** is available at such high acetate concentration. From the above data k = 1.74×10^{-6} sec.$^{-1}$ at 0.025 M KOAc (Y = −1.633) in reasonable agreement with the value in Table I.

Equation 4 gives the variation of m with temperature T. This is slight since for most solvents the

$$2.303\ \mathrm{Y}\,\frac{\mathrm{d}m}{\mathrm{d}T} = \frac{E^{\ddagger} - E_0^{\ddagger}}{RT^2} \qquad (4)$$

difference between the activation energy $E^{\ddagger}$ and the activation energy $E_0^{\ddagger}$ in "80%" ethanol is small for unimolecular-type solvolysis (Tables I, II).

Theoretical Interpretation. The Activity Postulate.—Application of the Brönsted theory to the variation of k_1 with solvent for unimolecular-

$$k_1 = \kappa\,\frac{f_{\mathrm{A}}}{f_{\mathrm{A}}^{\ddagger}} \qquad (5)$$

type solvolysis leads to equation 5 where κ is the specific rate in the standard state of unit activity and f_{A} and $f_{\mathrm{A}}^{\ddagger}$ are the activity coefficients of reactant and transition-state. In the case of dilute solutions[16] of non-electrolytes it is useful to refer all activity coefficients to the gas phase so that equation 5 reduces to 6. In this equation H_{A} and $H_{\mathrm{A}}^{\ddagger}$ are the Henry's law constants[16] of reactant

$$k_1\,\kappa = (H_{\mathrm{A}}/H_{\mathrm{A}}^{\ddagger}) \qquad (6)$$

and transition-state.

Comparison of equations 6 and 3 leads to 7 which implies a linear relationship, 8, between

$$\log \frac{H_{\mathrm{A}}}{H_{\mathrm{A}}^{\ddagger}} = m\mathrm{Y} + \log \frac{k_0}{\kappa} \qquad (7)$$

log $(H_{\mathrm{A}}/H_{\mathrm{A}}^{\ddagger})$ and log $(H_{\mathrm{B}}/H_{\mathrm{B}}^{\ddagger})$ for any two compounds

$$\log \frac{H_{\mathrm{A}}}{H_{\mathrm{A}}^{\ddagger}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \log \frac{H_{\mathrm{B}}}{H^{\ddagger}} + \left(\frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \log \frac{\kappa_{\mathrm{B}}}{k_{0\mathrm{B}}} - \log \frac{\kappa_{\mathrm{A}}}{k_{0\mathrm{A}}}\right) \qquad (8)$$

A and B solvolyzing by the unimolecular-type mechanism in a series of solvents. This deduction calls to mind the observation[17] that there exists an even simpler linear relationship, shown in equation 9, between log $(f_{\mathrm{B}}/f_{\mathrm{BH^+}})$ for any two

$$\log \frac{f_{\mathrm{B}}}{f_{\mathrm{BH}^+}} = \log \frac{f_{\mathrm{B'}}}{f_{\mathrm{B'H}^+}} \qquad (9)$$

conjugate acid–base systems B and B′ in a series of solvents.

The success of equation 3 for correlating solvolysis rates of the unimolecular type may be due to the validity of a general relationship regarding ratios of activity coefficients. For systems undergoing similar changes of the type AZ → AZ′, BZ → BZ′, etc., the postulated general relationship may be expressed by equation 10, μ and β being parameters.

$$\log \frac{f_{\mathrm{AZ}}}{f_{\mathrm{AZ'}}} = \mu \log \frac{f_{\mathrm{BZ}}}{f_{\mathrm{BZ'}}} + \beta \qquad (10)$$

In the case of solvolysis by mechanism **A** the change AZ → AZ′ is from the dissolved halide or ester to the partly ionized and strongly solvated transition-state molecule. Equation 3 and thus 8 is successful for variations in the ionizing group to include chloride, bromide and bromobenzenesulfonate. Also, the change AZ → AZ′ is not restricted entirely to the A–Z bond. For example, resonance will diffuse any positive charge of the *alpha* carbon atom in the transition state to the *ortho* and *para* positions of an *alpha* phenyl group. Even in aliphatic cases the positive charge will be spread. Now evidently equations 3 and 8 hold for considerable variation in the R part of the solvolyzing molecule RX but further work is necessary to clearly outline the scope and limitations in this respect. The need for two sets of **Y** values for aqueous acetone mixtures is one of the limitations which has already appeared.

Solvolysis of *t*-Butyl Chloride.—The solvolysis rate of *t*-butyl chloride in a range of mixed aqueous solvents has previously been correlated by Olson and Halford[8] with the aid of the fugacity rate equation 11 where p_{w} and p_{a} are vapor

$$k = (k_{\mathrm{w}}\,p_{\mathrm{w}} + k_{\mathrm{a}}\,p_{\mathrm{a}})H_{\mathrm{BuCl}} \qquad (11)$$

pressures of water and alcohol, respectively. This equation, which empirically fits the rates but not

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[15] Margenau and Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p 502.

[16] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, Chapter XX.

[17] Ref. 2, Chapter IX.

the products,[18] is based on assumed bimolecular reactions between halide and water or alcohol but it is set up according to an activity rate formulation, the respective terms not being divided by the activity coefficients of the corresponding transition states. Actually higher order[18] fugacity rate equations fit the rates at least as well as equation 11. Scrutinizing the data with our present approach, seeking generalizations regarding activity coefficients involved, we find that log k is a linear function of log H_{BuCl} for the range of solvents treated by Olson and Halford. Equation 12 fits

$$\log k^{\mathrm{BuCl}} = 1.232 \log H_{\mathrm{BuCl}} - 9.811 \qquad (12)$$

the data at 25.0° for all partly aqueous solvents (including also water and methanol) (Tables I, II, IV, ref. 8) with a probable error of 0.06. Thus, only two parameters are necessary.

The linear relation expressed in equation 12 indicates, according to equation 6, that a linear relation exists between log $H^{\pm}_{\mathrm{BuCl}}$ and log H_{BuCl} in the solvent range involved. This linear relation takes the form shown in equation 13.

$$\log H^{\pm}_{\mathrm{BuCl}} = -0.232 \log H_{\mathrm{BuCl}} + \text{Constant} \qquad (13)$$

TABLE IV

HENRY'S LAW CONSTANTS FOR *t*-BUTYL CHLORIDE AT 25.0°

Solvent	$10^{-3}\ H_{\mathrm{BuCl}}$, mm.
HOH	5×10^{3}
EtOH	1.09 ± 0.09
HOAc, 0.025 M KOAc	1.23 ± 0.05
HOAc – Ac_2O, $N_{\mathrm{AcOH}} = 0.042$	0.786 ± 0.020

While there are indications that linear log–log relationships between the activity coefficients of non-electrolytes are fairly general,[19] the linear log–log relation expressed by equations 12 and 13 for *t*-butyl chloride and its solvolysis transition state breaks down when one proceeds to the more poorly ionizing solvents such as absolute alcohol or acetic acid–acetic anhydride combinations. The plot in Fig. 3 of log k^{BuCl} *vs.* log H_{BuCl} at 25.0° illustrates the linear relation for one range of solvents and the large departure for the slower solvents mentioned. Even with the departure from linearity the curve is smooth. However, a smooth curve is not necessarily to be expected and this feature may be fortuitous.

Further insight into the above-described situation is derived by reference again to equation 6. As shown in equation 14, (log H_{BuCl}–log k^{BuCl}) is a

$$\log H^{\pm}_{\mathrm{BuCl}} - \log \kappa = \log H_{\mathrm{BuCl}} - \log k^{\mathrm{BuCl}} \qquad (14)$$

measure of log $H^{\pm}_{\mathrm{BuCl}}$, and this quantity is plotted against log k^{BuCl} in Fig. 3. It can be seen that in the partly aqueous solvents where equation 12 holds the variation in k^{BuCl} is due largely to changes in H_{BuCl}. On the other hand, in the poorer ionizing media the variation in k^{BuCl} is due largely to changes in $H^{\pm}_{\mathrm{BuCl}}$.

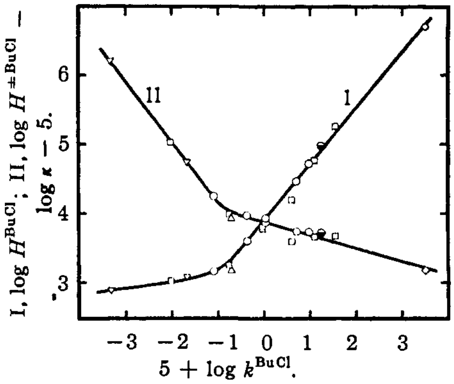

Fig. 3.—Plots of log H^{BuCl} and (log $H^{\pm\mathrm{BuCl}}$ – log κ) against log k^{BuCl}, 25.0°: □, H_2O–EtOH; ○, H_2O–MeOH; ◒, H_2O–dioxane; ▽, AcOH–Ac_2O; △, H_2O–acetone; ◇, H_2O.

Solvolysis of Isopropyl *p*-Bromobenzenesulfonate.—For the simple secondary alkyl compound, isopropyl *p*-bromobenzenesulfonate, without essentially prohibitive steric hindrance to nucleophilic attack on carbon such as evidently obtains in the case of pinacolyl *p*-bromobenzenesulfonate, the nucleophilic character of the solvent is very important. The first-order solvolysis rate constants k for isopropyl *p*-bromobenzenesulfonate are summarized in Table II and inspection reveals the contrast with the other compounds treated successfully by equation 3. For example, the rate constant in ethanol is much greater than in acetic acid although the **Y** value for acetic acid is the higher. This contrast is due to the fact that ionizing power and nucleophilic character of solvents do not go hand in hand. Instead of the rates in all solvents being manageable together it is now necessary to differentiate between basic solvents and others.

Quite a satisfactory understanding of the solvolysis rates of isopropyl *p*-bromobenzenesulfonate may be reached on the assumption that solvolysis proceeds by both mechanism types **A** and **B**, **B** being slight or negligible in the acidic type solvents such as acetic acid or its mixtures with acetic anhydride and serious in the more basic solvents.

In the acetic acid–acetic anhydride solvents the plot of log k for isopropyl *p*-bromobenzenesulfonate against log k' for pinacolyl *p*-bromobenzenesulfonate gives the least squares line shown in equation 15, the probable error[15] being 0.136. The

$$\log k = 1.204 \log k' + 0.031 \qquad (15)$$

straight line fit is not as satisfactory here as in the other cases, possibly because the acetolysis is not cleanly of the unimolecular type ($k = k_1$). It is not out of the question that acetic acid can func-

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[18] (a) Bartlett, THIS JOURNAL, **61**, 1630 (1939); (b) Winstein, *ibid.*, **61**, 1635 (1939); (c) Bateman, Hughes, and Ingold, *ibid.*, **60**, 3080 (1938); (d) Bateman, Hughes and Ingold, *J. Chem. Soc.*, 881 (1938).

[19] Grunwald, Dissertation, University of California at Los Angeles, Calif., 1947, sections 6, 17.

tion in solvolysis by mechanism B. While the addition of 0.025*M* potassium acetate to glacial acetic acid gives no serious change in first-order rate constant the addition of 0.01*M* potassium acetate to the solvent rich in acetic anhydride produces a predominantly bimolecular reaction. However, the slope of the line represented by equation 15 is reasonable for solvolysis largely by mechanism **A**. The value of 1.204 combined with an m value of 0.706 for pinacolyl *p*-bromobenzenesulfonate (Table III) corresponds to 0.850 for m in the case of the isopropyl ester.

Assuming $k = k_1$ in the acidic solvents, equation 15 allows one to estimate k_1 in the nucleophilic alcoholic solvents. These estimates are listed in Table V along with k_x (*i. e.*, $k - k_1$) and the percentage of solvolysis by mechanism **A**, 100 k_1/k.

TABLE V

SOLVOLYSIS OF ISOPROPYL *p*-BROMOBENZENESULFONATE AT 70.0° IN NUCLEOPHILIC SOLVENTS

Solvent	10^4k sec.$^{-1}$	Calcd. 10^4k_1	Calcd. 10^4k_x	Calcd. $100k_1/k$
EtOH	2.64	0.108	2.53	4.1
MeOH	7.31	0.68	6.63	9.3
80% EtOH	17.0	3.86	13.1	22.7

It is interesting that k_x in the small range of comparably nucleophilic alcoholic solvents is fit by a linear equation of the same type as 3, equation 16 fitting the data in Table V with a probable

$$\log k_x = 0.360\ \mathrm{Y} - 2.857 \qquad (16)$$

error of 0.046. In these solvents the rate of solvolysis by mechanism B seems to depend on the same properties of the solvent which control the rate of the **A** type, the slope m, however, being quite small.

It is an especially satisfactory feature of the assumed way of accounting for the solvolysis rates of isopropyl *p*-bromobenzenesulfonate that the slope in equation 16 is so small and so nearly equal to the one which is derivable for *n*-butyl bromide. There is reason to believe that the latter halide solvolyzes exclusively by mechanism B in alcoholic solvents, and Bird, Hughes and Ingold[20] have supplied rates of solvolysis in various aqueous ethanol and methanol solvents.[21] Using their data a plot of log k against log k^{BuCl} is linear as illustrated in Fig. 1 and equation 3 fits the data well as summarized in Table III. The values of m in aqueous methanol at 59.1° and aqueous ethanol at 75.1° are 0.392 and 0.331, respectively. In fact, values of m are also quite similar[22] for other primary halides apparently solvolyzing by mechanism B.

Experimental and Kinetic Part

Materials.—The *t*-butyl chloride was Eastman Kodak Co. "White Label" grade, b. p. 51.2° (752 mm.), $n^{25}\mathrm{D}$ 1.3820.

α-Methylneopentyl alcohol, b. p. 120.0–120.3° (754 mm.), was prepared by Miss Anita Suran from *t*-butyl magnesium chloride[23] and acetaldehyde.

α-Methylneopentyl *p*-bromobenzenesulfonate I and isopropyl *p*-bromobenzenesulfonate II were prepared in *ca.* 50% yield in 0.05 mole batches from the corresponding alcohols and *p*-bromobenzenesulfonyl chloride in pyridine by conventional methods.[24] I crystallized upon pouring the pyridine reaction mixture into ice-cold 6 *N* hydrochloric acid and was recrystallized several times from petroleum ether (b. p. 60–80°); m. p. 53.2–53.5; equivalent weight from quantitative solvolysis: calcd., 321.2; found, 323.2 (in acetic acid), 320.1 (in "80%" ethanol).

Anal. Calcd. for $C_{13}H_{17}O_3SBr$: C, 44.86; H, 5.34. Found: C, 44.99; H, 5.49.

II separated as an oil upon pouring the pyridine reaction mixture into 6 *N* hydrochloric acid. The oil was separated with the aid of *ca.* 40 ml. of carbon tetrachloride and the solution was dried over anhydrous potassium carbonate. After evaporation of the solvent at room temperature the viscous residue was induced to crystallize. The solid was purified by reprecipitation under petroleum ether (b. p. 60–80°); m. p. 32.3–34.1°. Equivalent weight from quantitative solvolysis: calcd. 279.2; found 282.1 (in acetic acid), 278.3 (in methanol). Analysis for carbon and hydrogen was unsuccessful because II decomposed rapidly on heating.

Solvents.—Synthetic methanol, containing less than 0.03% of water by the miscibility temperature with cyclohexane,[25] was used.

Ethanol was dried by the ethyl formate method[26] and contained less than 0.02% of water by Robertson's paraffin oil test.[26]

"80%" ethanol was prepared by adding 317.5 g. of conductivity water to 1000 g. of ethanol.

Acetic acid containing 0.0142 *M* (0.1%) acetic anhydride by Kilpi's anthranilic acid analysis[27] was prepared as described in a previous article.[3]

To 379.0 g. of Baker and Adamson "Reagent Grade" acetic anhydride, equivalent weight 51.20 ± 0.06 by hydrolysis and titration with standard aqueous base to the phenolphthalein endpoint (mole fraction of acetic acid 0.042), was added 80.6 g. of acetic acid containing 0.1 wt. % of acetic anhydride to give a solvent of equivalent weight 52.63 ± 0.06 (mole fraction of acetic acid 0.294).

In order to prepare solvents containing potassium acetate the Baker and Adamson "Reagent Grade" salt was dried to constant weight in a tared glass-stoppered flask at 110° *in vacuo* and dissolved in the desired weight of solvent.

Kinetic Measurements.—Rates were measured by the usual sealed ampoule technique. Titrations were made on 5-ml. aliquots from 5-ml. microburets. For the measurements in ethanol, methanol and "80%" ethanol, titration

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(20) Bird, Hughes and Ingold, *J. Chem. Soc.*, 255 (1943).

(21) In the case of *n*-butyl bromide, the fugacity rate equation 11 has been found by Bird, Hughes and Ingold[20] to fit both rates and products. It must be noted that H may be expressed as the ratio of the vapor pressure of halide to either its mole fraction or its molarity. Olson and Halford[8] have used mole fraction as is also done in the present article, and Bird, Hughes and Ingold[20] have used molarity However, because of differences in molar volumes of various mixed solvents, if the use of molarity furnishes a fit for the product compositions, the use of mole fraction cannot furnish such a fit. A recalculation of the data of Bird, Hughes and Ingold, using mole fraction in evaluating H, shows that equation 11 will fit the rates but not the products.

(22) Winstein and Grunwald, unpublished work.

(23) Puntambeker and Zoellner, "Organic Syntheses," Vol. **23**, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 510.

(24) Winstein, Grunwald and Ingraham, THIS JOURNAL, **70**, 821 (1948).

(25) Jones and Amstell, *J. Chem. Soc.*, 1321 (1930).

(26) Robertson, "Laboratory Practice of Organic Chemistry," Macmillan Co., New York, N. Y., 1943, pp. 178, 296.

(27) Kilpi, *Suomen Kemistilehti*, **13B**, 19 (1940); *C. A.*, **35**, 2445 (1941).

for acid was carried out with 0.05 *N* sodium hydroxide using brom thymol blue as indicator. Titrations in glacial acetic acid and mixtures of acetic acid and acetic anhydride were performed as described previously[3,24] except that 0.05 *N* *p*-toluenesulfonic acid was substituted for perchloric acid in the solvents containing large amounts of acetic anhydride. Reactions were usually followed to *ca.* 75% completion. Reaction mixtures were prepared gravimetrically except for the rate-runs involving *t*-butyl chloride where initial concentrations were obtained from the "infinite" titer of acid and/or from Volhard titration for chloride ion. In order to avoid errors due to the volatility of *t*-butyl chloride, the vapor space above the reaction solutions in the ampoules was kept quite small.

The observed kinetics were first-order within the experimental error of 1–2% in k over the range of concentrations investigated except for the solvolysis of isopropyl *p*-bromobenzenesulfonate (RX) in 4.2 mole % acetic acid in acetic anhydride in the presence of potassium acetate. A representative set of experimental data is shown in Table VI. These data were fitted satisfactorily by equation 17 which assumes a simultaneous first-order solvolysis and second-order reaction with potassium acetate.

$$-\mathrm{d}\ln(\mathrm{RX})/\mathrm{d}t = k_1 + k_2(\mathrm{KOAc}) \qquad (17)$$

Using the data obtained during the latter part of the run where the potassium acetate has been neutralized, k_1 was calculated from the slope (obtained by the method of least squares) of the linear plot of log (RX) *vs.* time, t. The derivative, $-\mathrm{d}\ln(\mathrm{RX})/\mathrm{d}t$, was then obtained at various concentrations of potassium acetate from a large-scale plot of ln (RX) *vs.* t with the aid of a tangent meter. Substitution in equation 17 gave satisfactorily constant values for k_2. The average value of k_2 for this and a duplicate run was $(3.61 \pm 0.07) \times 10^{-4}$ sec.$^{-1}$ M.$^{-1}$

TABLE VI

ACETOLYSIS OF ISOPROPYL *p*-BROMOBENZENESULFONATE (RX) IN 4.2 MOLE % ACETIC ACID IN ACETIC ANHYDRIDE AT 70.0°

Time, hr.	(RX) $10^3 M$	(KOAc) $10^3 M$	$-10^6 \frac{\mathrm{d}\ln(\mathrm{RX})}{\mathrm{d}t}$ (sec.$^{-1}$)
0.0	36.72	22.28	..
11.6	26.89	12.45	5.84
20.7	22.74	8.30	4.47
30.95	19.20	4.76	..
54.1	15.68	1.24	1.94
70.5	14.25	...	..
103.1	12.05	...	..
120.1	11.02	...	..
143.1	9.62	...	..

Equilibrium in the System *t*-Butyl Chloride, *t*-Butyl Acetate, Hydrogen Chloride.—In analogy with the report of Steigman and Hammett[14] for α-phenylethyl chloride, *t*-butyl chloride solvolyzes in initially neutral acetic acid to give an equilibrium mixture according to equation 18. The rate

$$t\text{-BuCl} + \text{HOAc} = t\text{-BuOAc} + \text{HCl} \qquad (18)$$

of establishment of equilibrium is considerably faster than the rate of solvolysis in the presence of potassium acetate. For example, at 40.0° *ca.* 97% of the equilibrium concentration of hydrogen chloride is produced from a solution of *t*-butyl chloride within 28 hours whereas the solvolysis in the presence of potassium acetate is only *ca.* 20% complete within the same period.

The pertinent equilibrium data are summarized in Table VII. The data were obtained by the sealed-ampoule technique described for the kinetic runs. The equilibrium titre of hydrogen chloride was constant within experimental error over a period of several days.

TABLE VII

EQUILIBRIUM IN THE SYSTEM *t*-BUTYL CHLORIDE, *t*-BUTYL ACETATE, HYDROGEN CHLORIDE

Initial *t*-BuCl $10^3 M$	T, °C.	(HCl) at equilibrium $10^3 M$	K^a
81.8	60.2	6.02 ± 0.2	2.1×10^3
158.3	60.2	8.12 ± .2	2.3×10^3
81.8	40.0	4.15 ± .2	4.5×10^3
158.3	40.0	5.65 ± .1	4.8×10^3

[a] $K = (t\text{-BuCl})/(t\text{-BuOAc})(\text{HCl})$.

Measurement of Henry's Law Constants.—Approximate Henry's law constants were determined as follows: A 500-ml. standard-taper round-bottom flask equipped with a graduated dropping funnel and an outlet tube leading by way of a T-joint to a manometer and an oil pump was placed in a thermostat and evacuated until the pressure was below 2 mm. A known volume of standard solution of *t*-butyl chloride in the appropriate solvent was introduced carefully from the dropping funnel and the increase in pressure read. Room temperature was maintained above that of the thermostat to avoid condensation of the vapors. A typical set of experimental data is given in Table VIII. In computing the mole fraction of *t*-butyl chloride, allowance was made for the materials in the known vapor space.

TABLE VIII

HENRY'S LAW CONSTANT OF *t*-BUTYL CHLORIDE IN ACETIC ACID CONTAINING 0.025 *M* POTASSIUM ACETATE, 25.0°

N_{BuCl}	p, mm.^{a}	$10^{-3} H$, mm.
0.0000	16.0	..
.0338	53.6	1.13
.0359	59.1	1.22
.0293	52.3	1.26
.0137	33.5	1.29

[a] p = pressure increase due to the solution.

The Henry's law constant of *t*-butyl chloride in water was estimated from the vapor pressure and a rough determination of the solubility of the halide in water (*ca.* 3×10^{-3} M).

Summary

For compounds which appear to solvolyze by a

rate determining ionization, plots of the logarithm of the first-order rate constant k in various solvents (either from the literature or here reported) against log k for *t*-butyl chloride are linear.

A set of values of the so-called ionizing power, Y, defined by the equation

$$Y = \log k^{\mathrm{BuCl}} - \log k_0^{\mathrm{BuCl}}$$

(k^{BuCl} and $k_0{}^{\mathrm{BuCl}}$ being solvolysis rate-constants for *t*-butyl chloride at 25.0° in the given solvent and in 80% ethanol) has been set up for a number of solvents including water, methanol, ethanol, aqueous alcohols, formic acid and acetic acid. The solvolysis rate constants (varying sometimes by six orders of magnitude) are fitted by the equation

$$\log k = mY + \log k_0$$

with a mean probable error of less than 0.05 in the cases of *t*-butyl bromide, neopentyl bromide, α-methylneopentyl *p*-bromobenzenesulfonate, α-methylallyl chloride, α-phenylethyl chloride and benzhydryl chloride.

The observed linear relationships, interpreted on the basis of the Brönsted equation, lead to the equation

$$\log \frac{f_{\mathrm{A}}}{f_{\mathrm{A}}^{\ddagger}} = \frac{m_{\mathrm{A}}}{m_{\mathrm{B}}} \log \frac{f_{\mathrm{B}}}{f_{\mathrm{B}}^{\ddagger}} + \text{constant}$$

for the relationship among the pertinent activity coefficients (f_{A}, $f_{\mathrm{A}}^{\ddagger}$, *etc.*) for any two compounds A and B. It is postulated that linear logarithmic relationships among ratios of activity coefficients of this type may be quite general.

The solvolysis of *t*-butyl chloride is discussed in terms of the Brönsted equation. It is shown that, to a good approximation, log $f_{\mathrm{BuCl}}^{\ddagger}$ varies linearly with log f_{BuCl} in the partly aqueous solvents and that in these solvents the variation in k is due largely to changes in f_{BuCl}. On the other hand, in the more poorly ionizing solvents changes in k are attributable mainly to changes in $f_{\mathrm{BuCl}}^{\ddagger}$.

The reported method of correlating unimolecular type solvolysis rates is useful in elucidating the nature of the solvolysis of materials the rates of which depend markedly on the nucleophilic character of the solvent. For isopropyl *p*-bromobenzenesulfonate the rates of solvolysis in acetic acid and acetic acid–acetic anhydride mixtures furnish estimates of unimolecular solvolysis rates in ethanol, methanol and aqueous ethanol. The actual solvolysis rates are considerably larger in the latter solvents, the fractions of unimolecular solvolysis being low.

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Hyperconjugation. II. The Competitive Bromination of Benzene and *t*-Butylbenzene

BY ERNST BERLINER AND FRANCES J. BONDHUS

When benzene and *t*-butylbenzene in an equimolecular mixture in 92% acetic acid are allowed to compete for an insufficient amount of bromine, the corresponding brominated hydrocarbons are formed in proportions which show that the ratio of the rates of bromination at 25° is about 115:1 in favor of *t*-butylbenzene. At 45° the ratio is about 72:1. Therefore the bromination of benzene requires a higher energy of activation than the bromination of *t*-butylbenzene.[1] Since under the same conditions toluene is brominated about four times faster than *t*-butylbenzene,[2,3] the rate of bromination of toluene appears to be about 465 times faster than that of benzene. Values for the individual rates of chlorination of toluene and benzene fix the ratio at about 345,[3,4] whereas in nitration with acetyl nitrate toluene reacts twenty-three times faster than benzene.[5]

The difference in the rates of bromination of toluene and *t*-butylbenzene was explained by no-bond resonance of the Baker–Nathan type,[2,3,6] which involves carbon–hydrogen bonds, but the much greater difference between *t*-butylbenzene and benzene clearly cannot be accounted for by such resonance, since no α-hydrogen atoms are available for conjugation.[7] On the other hand, it would be hard to see how the inductive effect, which, on the basis of the Baker–Nathan theory, should be operative in the absence of hydrogen atoms, could alone account for the great activation and strong *ortho–para* directive influence of the *t*-butyl group, particularly since inductive effects of alkyl groups are conceded to operate through a rather feeble relay mechanism. The definitions that make the Baker–Nathan type of resonance

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[1] The bromination of different aromatic compounds is probably another case in which the differences in rate are primarily due to differences in the E term of the Arrhenius equation (Scheffer and Blanksma, *Rec. trav. chim.*, **46**, 522 (1928); Bradfield and Jones, *J. Chem. Soc.*, 1006 (1928)); *i. e.*, the relationship $(\log k_1/k_2)_{T_1} = T_2/T_1 (\log k_1/k_2)_{T_2}$ should hold. In the competitive bromination of toluene and *t*-butylbenzene the calculated ratio at 45° is 3.70 (found, 3.80); in the present bromination the agreement is less satisfactory (calculated ratio at 45°: 85.7, found: 71.5). This may be due to irregularities on account of the greater difference in rate.

[2] Berliner and Bondhus, THIS JOURNAL, **68**, 2355 (1946).

[3] De la Mare and Robertson, *J. Chem. Soc.*, 279 (1943).

[4] This ratio is for 80% acetic acid; the ratio of the rate of chlorination of *t*-butylbenzene and benzene is 110.

[5] Ingold, Lapworth, Rothstein and Ward, *J. Chem. Soc.*, 1959 (1931).

[6] Baker and Nathan, *ibid.*, 1840 (1935).

[7] Baker, *ibid.*, 1150 (1939).