The Influence of Electrolytic Dissociation upon Rates of Reactions. Part I. The Common-ion Effect in the Hydrolysis of tert.*-Butyl Bromide.*

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The hydrolysis of *tert.*-butyl bromide in aqueous acetone in the presence of added bromides has been studied. The dissociation constants of hydrobromic acid and the salts used in the kinetic work have been calculated from conductivity measurements, so that the true ionic strengths could be assessed in the hydrolysis studies. In this way a critical examination of Hughes and Ingold's treatment of ionic-strength effects in S_N1 reactions, and of an ion-dipole equation due to Moelwyn-Hughes, has been possible. Both of these approaches account fairly satisfactorily for the observed increasing hydrolysis rates with increasing ionic strengths.

THE dependence of the rates of many chemical reactions upon electrolyte concentrations is expressed satisfactorily by Brønsted's relation. There are, however, a number of examples which cannot be thus accommodated. These include reactions between ions and polar molecules, and for these the theoretical effect of concentration upon the reaction rates is founded upon the polarity of the molecular species, the ion charge, and the ionic strength of the solution. This is dealt with in detail later. Even when both the reacting species are ions, apparent exceptions to Brønsted's equation have been found, and one reason for this may be that all the electrolytes present are assumed to be completely dissociated. For example, Davies and Wyatt (*Trans. Faraday Soc.*, 1949, **45**, 744) have shown that the anomalous rates of reaction between the thiosulphate and bromoacetate ions when calcium and barium salts are added can be attributed to ion-pair formation. Such effects can be important in ion–dipole reactions. Evans and Sugden, for example (*J.*, 1949, 270), showed that the apparently decreasing value of the bimolecular rate constant for the exchange reaction $RBr + Br^{*-} \rightleftharpoons RBr^{*} + Br^{-}$ (where Br^{*} is radioactive and R is an alkyl group) in acetone in presence of increasing concentrations of lithium bromide is accounted for by incomplete dissociation. When lithium bromide ion-pairs are allowed for, the rate constant is independent of the salt concentration.

As a continuation to such aspects of reaction rates we have studied the hydrolysis of *tert.*-butyl bromide in aqueous acetone, both in the absence and in the presence of added bromide electrolytes. In such solvents, if the proportion of water is small, ion-association can be extensive. Olson and Konecny (*J. Amer. Chem. Soc.*, 1953, **75**, 5801) have given data illustrating this for lithium bromide. This salt was used by Bateman, Hughes, and Ingold (*J.*, 1940, **960**) in their studies of the hydrolysis of *tert.*-butyl bromide in aqueous acetone. They found that the first-order rate of hydrolysis in the absence of this salt increases as the reaction proceeds, and the rate constant is much higher when lithium bromide is present. These increases are attributed to an ionic-strength effect, and in the quantitative treatment of this, Bateman, Church, Hughes, Ingold, and Taher (*J.*, 1940, 979) assumed that the inorganic constituents were completely dissociated. Since this appeared doubtful, we have measured the conductivities of hydrobromic acid and of several bromides in aqueous acetone, and from these we have calculated the relevant dissociation constants. These have been used to follow the ionic-strength changes during the hydrolysis of *tert.*-butyl bromide.

Conductivity Measurements.—Dissociation constants in 90% acetone (by vol.) were calculated by Fuoss's method (*J. Amer. Chem. Soc.*, 1935, **57**, 488). The figures are given in Table 1, where $F(z) = 1 - z\{1 - z[1 - z(1 \ldots)^{-\frac{1}{2}}]^{-\frac{1}{2}}\}^{-\frac{1}{2}}$, and $z = \alpha\Lambda_0^{-\frac{3}{2}}(c\Lambda)^{\frac{1}{2}}$, where α is one of the terms of Onsager's conductivity equation

TABLE 1. *Conductivity of hydrobromic acid in aqueous acetone.*

90% Acetone

10^4c	Λ	$10^3F(z)/\Lambda$	$10^2c\Delta f^2/F(z)$	10^3K	10^4c	Λ	$10^3F(z)/\Lambda$	$10^2c\Lambda f^2/F(z)$	10^3K
				25°, $\Lambda^\circ = 117{\cdot}1$					
1·971	109·5	8·75	1·89	6·5	3·356	106·6	8·88	3·01	6·5
1·975	109·7	8·74	1·89	(7·3)	5·145	103·3	9·04	4·29	6·3
2·940	107·2	8·86	2·68	6·2	6·143	101·8	8·99	4·96	5·9
				30°, $\Lambda^\circ = 125{\cdot}6$					
2·873	115·2	8·25	2·80	6·3	8·490	105·9	8·65	6·82	6·3
3·265	114·3	8·28	3·13	6·25	9·598	104·65	8·70	7·50	6·45
5·252	110·4	8·45	4·65	6·1	10·88	103·2	8·78	8·23	6·5
				35°, $\Lambda^\circ = 134{\cdot}8$ (134·4, Davies's method)					
3·249	122·4	7·72	3·31	6·1	8·821	112·9	8·06	7·34	6·2
3·739	121·15	7·79	3·71	5·9	10·46	110·7	8·16	8·30	6·1
5·459	117·9	7·88	5·14	6·0	10·64	110·5	8·16	8·41	6·1

70% Acetone, 25°, $\Lambda^\circ = 133{\cdot}1$

10^4c	Λ	$\Lambda^{\circ\prime}$	10^4c	Λ	$\Lambda^{\circ\prime}$	10^4c	Λ	$\Lambda^{\circ\prime}$	10^4c	Λ	$\Lambda^{\circ\prime}$
3·191	130·1	133·1	5·278	129·2	133·0	6·725	128·9	133·2	8·765	128·1	133·1
3·709	129·9	133·1	5·755	129·1	133·1	7·553	128·6	133·2	9·672	128·1	133·3

$$\Lambda = \Lambda^\circ - (\alpha\Lambda^\circ + \beta)I^{\frac{1}{2}} = \Lambda^\circ - BI^{\frac{1}{2}}$$

in which I is the ionic strength. Fuoss has tabulated values of $F(z)$ for various values of z. For comparative purposes, Davies's method (*Trans. Faraday Soc.*, 1927, **23**, 351) was also used to calculate the dissociation constants, and these are listed under 10^3K.

In Onsager's equation, $B = 355\cdot5$, $379\cdot8$, and $401\cdot3$ at 25°, 30°, and 35° respectively in 90% acetone, and is $169\cdot4$ in 70% acetone. The values of $\Lambda^{\circ\prime}$ in Table 1 were obtained by the addition of $BI^{\frac{1}{2}}$ to Λ; the constancy of $\Lambda^{\circ\prime}$ indicates that dissociation is complete in 70% acetone.

The dissociation data and other calculations were obtained with the help of the following physical constants :

Acetone						Acetone					
vol. %	wt. %	Temp.	D	$10^3\eta$	A	vol. %	wt. %	Temp.	D	$10^3\eta$	A
90	87·5	25°	25·3	4·57	2·787	90	87·5	50°	22·5	—	2·943
90	,,	30	24·6	4·36	2·836	70	64·7	25	38·25	9·40	1·500
90	,,	35	24·1	4·08	2·925						

The dielectric constants D were interpolated from those of Akerlöf (*J. Amer. Chem. Soc.*, 1932, **54**, 4132), and the viscosities (η) from those given in the International Critical Tables (Vol. V, p. 22) and by Olson and Konecny (*loc. cit.*). The factor A refers to the limiting form of the Debye–Hückel activity coefficient expression, $-\log f_i = 1\cdot8246 \times 10^6 z^2 I^{\frac{1}{2}}(DT)^{-\frac{3}{2}} = -Az^2I^{\frac{1}{2}}$.

Lithium and Potassium Bromides.—Table 2 contains the measurements and dissociation constants (calculated by Davies's method, *loc. cit.*).

TABLE 2. *Conductivities of lithium and potassium bromides in* 90% *acetone at* 25°.

LiBr. $\Lambda^\circ = 101\cdot1$, $B = 335\cdot5$

10^4c ...	3·486	5·126	5·904	9·248	13·70	21·61	26·41	38·77
Λ	94·89	90·83	89·95	87·29	83·81	78·72	76·59	71·97
10^3K ...	1·35	1·2	1·25	1·25	1·3	1·15	1·21	1·21

KBr. $\Lambda^\circ = 115\cdot4$, $B = 353\cdot5$

10^4c ...	3·176	4·486	5·144	6·508	6·748	9·218	9·611	11·52	12·43
Λ	107·10	105·30	104·28	102·75	102·40	100·20	99·81	98·40	97·59
10^3k ...	1·3	1·3	1·2	1·25	1·2	1·3	1·25	1·3	1·3

Magnesium Bromide.—On plotting Λ against $c^{\frac{1}{2}}$, a curve was obtained from which a rough estimate of $\Lambda^\circ = 105$ was obtained. On using this in Onsager's equation for a 2 : 1-valent salt, it became apparent that ion-association is considerable in this system and that both of the equilibria (*a*) $MgBr^+ \rightleftharpoons Mg^{2+} + Br^-$ and (*b*) $MgBr_2 \rightleftharpoons MgBr^+ + Br^-$ need considering. By trial and error, $\Lambda^\circ = 108$ gave K' values [where K' is the apparent dissociation constant for process (*a*), it being assumed that process (*b*) can be ignored] which varied linearly with the salt concentration, so this value was used for the final calculations. Assumptions are involved to obtain the limiting ion mobilities. Since Λ° (water) $= 131\cdot36 = 53\cdot06$ for Mg^{2+} + $78\cdot3$ for Br^- (Harned and Owen, " Physical Chemistry of Electrolytic Solutions," Reinhold, 1943, p. 172), λ° (Mg^{2+}, 90% acetone) was taken as $53\cdot06 \times 108/131\cdot4 = 43\cdot6$, and similarly $64\cdot4$ was taken for the bromide ion. The ion-pair $MgBr^+$ was assigned the value of $43\cdot6/2$ on the assumption that its mobility is proportional to that of the ion of like charge. The consequent treatment is as follows. Let α = fraction of $MgBr_2$ dissociated into $MgBr^+$ and Br^-, β = fraction of $MgBr^+$ dissociated into Mg^{2+} and Br^-; then if m is the stoicheiometric molarity,

$$\Lambda\,(\text{obs.}) = (\alpha/2)(1-\beta)\{\lambda_{MgBr^+} + \lambda_{Br^-}\} + \alpha\beta\{\lambda_{Mg^{2+}} + \lambda_{Br^-}\} \quad . \quad . \quad . \quad (1)$$

and

$$I = \alpha m\,(1 + 2\beta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the more dilute solutions, $\alpha = 1$ can be taken as a first approximation, whence, by using the appropriate Onsager equations,

$$\lambda_{MgBr} + \lambda_{Br^-} = 86\cdot2 - 317I^{\frac{1}{2}},\ \text{and}\ \lambda_{Mg^{2+}} + \lambda_{Br^-} = 108\cdot0 - 546I^{\frac{1}{2}}$$

Values of β which will be termed β' can be established, and K_1' calculated where

$$\log K_1' = \log\,(a_{Mg^{2+}}a_{Br^-})/a_{MgBr^+} = \log\,\{\beta'\,(1+\beta')m/(1-\beta')\} - 4AI^{\frac{1}{2}}$$

The values of K_1' are given in Table 3, and extrapolation of K_1' against m gave $K_1 = 3{\cdot}1 \times 10^{-4}$. To obtain K_2 for process (*b*), where

$$\log K_2 = \log (a_{\mathrm{MgBr}^+}\, a_{\mathrm{Br}^-})/a_{\mathrm{MgBr}_2} = \log \{\alpha^2(1 + \beta)(1 - \beta)m/(1 - \alpha)\} - 2AI^{\frac{1}{2}}$$

values of α and β were calculated by approximations using the correct expression for K_1, *i.e.*,

$$\log 3{\cdot}1 \times 10^{-4} = \log \{\alpha\beta\,(1 + \beta)m/(1 - \beta)\} - 4AI^{\frac{1}{2}} \quad . \quad . \quad . \quad (3)$$

and (1) and (2) above. To do this, $\alpha = 1$ was taken, and values of β and I calculated from (1) and (2). Substitution of these in (3) gave a first value of α. This was used in (1) and (2) to give truer values of β and I, and so on until constant α and β values were established. The results are given in Tables 3 and 4.

TABLE 3. *Conductivity of magnesium bromide in* 90% *acetone at* 25°.

10^4c	Λ	$10\beta'$	$10^4K_1'$	10^4c	Λ	$10\beta'$	$10^4K_1'$	10^4c	Λ	$10\beta'$	$10^4K_1'$
4·561	72·08	5·77	2·78	7·486	64·61	4·59	2·38	13·36	55·95	3·50	2·05
4·875	70·86	5·58	2·68	8·023	63·56	4·59	2·44	14·15	55·30	3·43	2·04
6·224	67·29	5·10	2·57	10·37	59·55	4·01	2·22	17·55	52·55	3·06	1·92
7·443	64·69	4·75	2·48	11·02	58·85	3·93	2·22	18·58	51·55	2·90	1·84

TABLE 4. *Calculation of K_2 for magnesium bromide.*

10^4c	11·02	13·36	14·15	17·55	18·58
10α	9·30	9·13	9·14	9·03	8·92
10β	4·80	4·56	4·47	4·23	4·20
10^3K_2	3·5	3·3	3·5	3·7	3·4

Hydrolysis Measurements.—Bateman, Hughes, and Ingold's procedure (*loc. cit.*) was used to follow the rate of hydrolysis of *tert.*-butyl bromide in 90% acetone at 25°, *i.e.*, by measuring the acid liberated. These workers found that the reversibility of the reaction was below the limit of measurement, the proportion of acid formed being at least 99·8%. As a check, we measured the conductivity of a mixture of *tert.*-butyl alcohol and hydrobromic acid in the solvent. No change of the bridge reading over a period of 24 hr. was observed, confirming that the back reaction is negligible. The usual integrated form of the first-order velocity constant expression was used to calculate k_1, $k_1t = 2{\cdot}303 \log (a - a_0)/(a_0 - x)$, where a_0 = initial titre, a = titre for complete hydrolysis, x = titre at time t. In Table 5, m = stoicheiometric molarity of acid at time t, and k_1 is related to the time in secs. Only a few specimen runs are given. Others are given in the graph, and the average slopes and values of $k_1°$ (k_1 at zero ionic strength) are given in Table 7.

TABLE 5. *Hydrolysis of* tert.*-butyl bromide in* 90% *acetone at* 25°.

Initial $\mathrm{Bu^tBr}$ = 0·1039 (data of Bateman, Hughes, and Ingold, *loc. cit.*).

Hrs.	3·15	4·10	6·20	8·20	10·0	13·5	18·3	26·0	30·8	37·3	43·8
10^2m	1·42	1·81	2·63	3·38	4·00	5·10	6·86	7·69	8·32	8·97	9·38
10^2I	0·95	1·17	1·62	2·02	2·33	2·89	3·77	4·18	4·50	4·85	5·03
10^5k_1	1·30	1·30	1·31	1·34	1·36	1·40	1·44	1·45	1·47	1·49	1·50

Initial $\mathrm{Bu^tBr}$ = 0·1105, initial HBr = 0·0533

Hrs.	6·26	8·25	10·33	12·25	14·17	23·17	26·17	28·33	30·67
10^2m	8·61	9·47	10·23	10·85	11·49	13·57	14·04	14·36	14·63
10^2I	4·65	5·08	5·48	5·76	6·07	7·11	7·34	7·50	7·63
10^5k_1	1·56	1·58	1·57	1·57	1·60	1·64	1·65	1·67	1·67

Initial $\mathrm{Bu^tBr}$ = 0·1103, initial LiBr = 0·0463

Hrs.	4·00	6·00	8·00	10·0	12·0	14·0	26·0	30·0
10^2m	2·20	3·23	4·07	4·83	5·55	6·20	8·72	9·24
10^2I	4·40	4·89	5·34	5·73	6·09	6·42	7·68	7·80
10^5k_1	1·54	1·60	1·60	1·60	1·62	1·64	1·67	1·68

Initial $\mathrm{Bu^tBr}$ = 0·1000, initial $\mathrm{MgBr_2}$ = 0·0152

Hrs.	4·00	6·00	8·0	10·25	12·0	14·0	23·4	28·25	30·25
10^2m	1·91	2·74	3·51	4·28	4·81	5·37	7·40	8·07	8·29
10^2I	2·4	2·9	3·3	3·7	4·1	4·2	5·4	5·6	5·9
10^5k_1	1·47	1·48	1·50	1·51	1·52	1·53	1·60	1·62	1·62

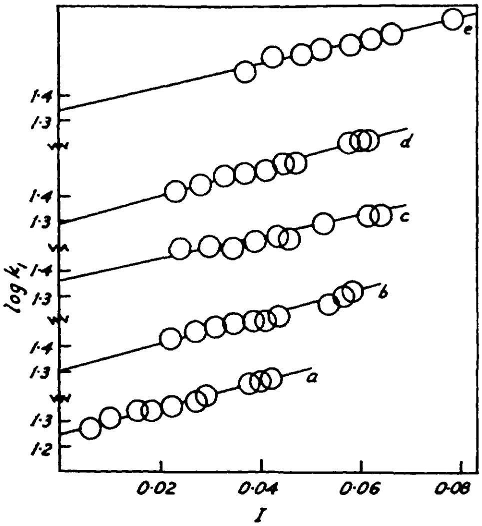
The ionic strengths I in Table 5 were calculated after making allowance for the ion-pair concentrations. These were obtained by approximations from the relevant expressions such as

$$\log [\mathrm{MBr}] = \log [\mathrm{M}^+][\mathrm{Br}^-] - \log K - 2\mathrm{F}(I)$$

where $\mathrm{M}^+ = \mathrm{H}^+, \mathrm{K}^+$, or Li^+, $I = [\mathrm{Br}^-]$, and

$$\mathrm{F}(I) = -\log f_i = Az_i^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I\}$$

The activity coefficient expression is based on that of Davies (*J.*, 1938, 2093), which is satisfactory in aqueous solutions up to $I = 0{\cdot}1$. The values of A have been given on p. 1901.

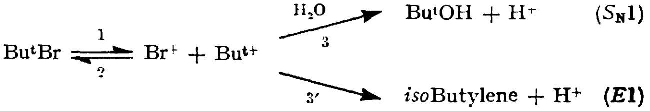


(*a*) 0·1056M-Bu^{t}Br.
(*b*) 0·0991M-Bu^{t}Br, 0·0271M-HBr.
(*c*) 0·1150M-Bu^{t}Br, 0·0240M-LiBr.
(*d*) 0·1070M-Bu^{t}Br, 0·0231M-KBr.
(*e*) 0·1278M-Bu^{t}Br, 0·0404M-KBr.

DISCUSSION

The average dissociation constants obtained from the conductivity data are collected together in Table 6. Olson and Konecny (*loc. cit.*) obtained 0·0095 and 0·0091 for lithium bromide in 90% acetone at 25° and 35° respectively, by using Fuoss's method (*loc. cit.*).

According to Hughes, Ingold, and their collaborators the mechanism of hydrolysis may be represented as follows :



The quantitative treatment developed by Bateman, Church, Hughes, Ingold, and Taher (*loc. cit.*) to account for the changing rates of unimolecular hydrolysis rate constants as the reaction proceeds, or in the presence of added electrolytes, is founded upon the assumption that the measured rate constant is the rate constant for ionisation (designated as 1 above), and the ionic strength influences the extent of Bu^{t}Br ionisation. The Bu^{t}Br

TABLE 6. *Average dissociation constants* (× 10^3).

Temp.	HBr	LiBr	KBr	MgBr$_2$
25°	6·3	12·0	13·0	0·31 (K_1), 3·5 (K_2)
30	6·2	—	—	—
35	6·1	—	—	—
50	6·0 *	10·0$_5$ *	—	

* Estimated.

molecule is assumed to pass through a transition state where it consists, in effect, of two point charges $\pm z\varepsilon$ separated by a fixed distance d. The developed equation is

$$\log k_1 = \log k_1^\circ + 0{\cdot}912 \times 10^{16} z^2 dI/(D^2T^2) = \log k_1^\circ + \phi I \quad . \quad . \quad (4)$$

where k_1° is the rate constant at $I = 0$. The magnitude of the parameter $\sigma = z^2d$ is not known exactly. It is assumed that in the transition state half an electron is transferred from the alkyl group to the bromine atom, *i.e.*, $z^2 = 0{\cdot}25$. It was estimated from the Morse potential-energy function that d is about 2·59 Å, the energy of activation used being that found from the solvolysis rates in 80% ethanol. Franklin (*Trans. Faraday Soc.*, 1952, **48**, 441) calculated the radius of the $\mathrm{Bu^{t+}}$ ion to be 2·8 Å. The crystallographic radius of the $\mathrm{Br^-}$ ion is 1·95 Å, and from Stokes's law and the estimated limiting ion mobility of the $\mathrm{Br^-}$ ion in 90% acetone given previously, the hydrated $\mathrm{Br^-}$ radius is 2·8 Å. These figures give d as between $0{\cdot}5(2{\cdot}8 + 1{\cdot}95) = 2{\cdot}4$ Å, and $0{\cdot}5(2{\cdot}8 + 2{\cdot}8) = 2{\cdot}8$ Å. The mean of 2·6 Å agrees with the estimate of 2·59 Å given above, but is subject to an uncertainty of nearly 10%. In Table 7 the extrapolated values of k_1°, the experimental slopes, and the theoretical slopes ϕ calculated from (4) are given. Some data from other sources are included.

Bateman *et al.* considered that reaction occurs through collapse of the highly solvated $\mathrm{Bu^{t+}}$ ion, when this cation reacts with a water molecule. If, instead, we consider that reaction occurs through the collision of a water molecule of sufficient energy with the $\mathrm{Bu^{t+}}$ ion, an expression derived by Moelwyn-Hughes ("Kinetics of Reactions in Solutions," Oxford Univ. Press, 1947, 985) can be used. This expression, which relates rate constants for reactions between ions and polar molecules with the ionic strength, is

$$\log k_1 = \log k_1^\circ + (8\pi N\varepsilon^3\mu z \cos\theta)/2303(DkT)^2 = \log k_1^\circ + \delta I$$

where μ is the dipole moment of the water molecule (1·85 D), z the valency of the $\mathrm{Bu^{t+}}$ ion, and θ the angle of approach of the ion to the polar axis of the molecule. In Table 7, the value of δ have been calculated with $\cos\theta = 1$.

TABLE 7. *Comparison of experimental and calculated slopes.*

Solute	Solvent	Temp.	$10^5k_1^\circ$	Electrolyte added (m)	Exptl. slope	ϕ	δ	Ref.
$\mathrm{Bu^tBr}$	90% Acetone	25°	1·25 ± 0·02	—	1·65 ± 0·15	1·04	1·26	Table 5
,,	,,	,,	1·24 ± 0·02	—	1·65 ± 0·15	,,	,,	,,
,,	,,	,,	1·30 ± 0·03	0·027 HBr	1·65 ± 0·2	,,	,,	,,
,,	,,	,,	1·39 ± 0·03	0·053 HBr	1·05 ± 0·2	,,	,,	,,
,,	,,	,,	1·36 ± 0·03	0·024 LiBr	1·2 ± 0·2	,,	,,	,,
,,	,,	,,	1·42 ± 0·04	0·046 LiBr	0·9 ± 0·1	,,	,,	,,
,,	,,	,,	1·29 ± 0·02	0·023 KBr	1·7 ± 0·15	,,	,,	,,
,,	,,	,,	1·34 ± 0·03	0·040 KBr	1·3 ± 0·1	,,	,,	,,
,,	,,	,,	1·35 ± 0·02	0·015 $\mathrm{MgBr_2}$	1·4 ± 0·15	,,	,,	,,
,,	,,	50	18·2 ± 0·4	—	1·85 ± 0·15	1·12	1·36	Table 6
,,	,,	,,	~25	0·106 LiBr	~0·6	,,	,,	,,
,,	70% Acetone	,,	51·1 ± 0·4	—	0·39 ± 0·02	0·41	0·54	*a*
,,	80% Ethanol	25	35·6 ± 0·2	—	0·33 ± 0·03	0·52	0·63	*b*
$\mathrm{Am^tCl}$	,,	,,	1·50	—	nil	0·29	0·35	*c*
$\mathrm{Am^tBr}$	,,	,,	55·5 ± 1·0	—	0·6 ± 0·1	,,	,,	*c*
$\mathrm{Am^tI}$	,,	,,	157 ± 3	—	0·8 ± 0·1	,,	,,	*c*
$\mathrm{Bu^tBr}$	60% Dioxan	10	29·0 ± 0·3	—	(0·55)	0·90	1·1	*b*
$\mathrm{Bu^tNO_3}$	85% ,,	25	3·34	—	(1·0)	10·4	12·6	*d*

References : (*a*) Bateman, Hughes, and Ingold, *loc. cit.* (*b*) Benfey, Hughes, and Ingold, *J.*, 1952, 2494. (*c*) Hughes and MacNulty, *J.*, 1937, 1283. (*d*) Lucas and Hammett, *J. Amer. Chem. Soc.*, 1942, **64**, 1928.

Taking the results as a whole, there is broad agreement between the experimental slopes and those calculated by both of the above treatments. For the results in 90% acetone at 25°, which has been studied in the most detail, Moelwyn-Hughes's treatment is in better agreement with experiment than is that of Hughes and Ingold. On the other hand, we have taken $\cos\theta = 1$, which gives the highest values of δ, and we have no means of deciding if this value of θ is justified. Again, with Hughes and Ingold's expression, a slightly higher value of d would effect closer agreement with the average experimental slope.

There is an experimental factor which makes too rigid a comparison difficult. This originates in what may be called the zero-time error. A small period of time is allowed for temperature equilibrium to be reached, and although the corresponding titration is subtracted from those obtained during an actual run, any resulting error has a considerable influence upon the initial values of k_1, and hence upon the evaluated slopes of log k_1 against I.

A more critical evaluation of ion–dipole interactions could be obtained by using solvents of very low dielectric constants such as we have with the last example in Table 7, where ϕ and δ are large. Unfortunately, the experimental results for this cannot yet be analysed since the dissociation constant of nitric acid in 85% dioxan is unknown. It is undoubtedly small, since, *e.g.*, hydrochloric acid has a dissociation constant of 0·0002 in 82% dioxan at 25° (Owen and Waters, *J. Amer. Chem. Soc.*, 1938, **60**, 2371).

EXPERIMENTAL

The conductivity equipment has been described by Davies and Monk (*J.*, 1949, 413). The hydrolyses were carried out in a Pyrex flask fitted with a tightly fitting ground-glass stopper, kept at 25° ± 0·01°. The solvent was introduced at least 30 min. before introduction of the *tert.*-butyl bromide, which was meanwhile distilled from a bulk sample, and the amount added to the hydrolysis flask was found by weight. Two min. after addition, a sample was withdrawn for an "initial" titre, and this was regarded as zero time. For the "infinity" titres, four samples were sealed in tubes and kept at 80—90° for a day. For each titration, a 10 ml. sample was pipetted into 100 ml. of ice-cold acetone, and titrated against sodium hydroxide, with lacmoid as indicator (Bateman, Hughes, and Ingold, *loc. cit.*). The infinity titres agreed with those calculated from the amount of *tert.*-butyl bromide weighed out to within ±0·2%.

Lithium bromide was twice recrystallised from absolute alcohol, then dried to constant weight by heating at 300°. "AnalaR" potassium bromide was dried similarly. A stock solution of magnesium bromide was made by refluxing a solution of "AnalaR" hydrobromic acid and excess of magnesium oxide. The concentration of this, and of a stock solution of hydrobromic acid, was found (±0·02%) by gravimetric determination of bromide.

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