837. *The Kinetics of the Solvolysis of t-Butyl Chloride, Bromide, and Iodide in Methanol–Water Solutions.*

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The rates of reaction of t-butyl bromide with water and of t-butyl chloride, bromide, and iodide with methanol–water have been determined conductometrically. It is found that the logarithm of the corrected first-order constant, k_1, governing solvolysis at a given temperature, can be expressed as a quadratic function of the molar fraction, x_m, of methanol in the solvent. The relative rates of hydrolysis of the three t-butyl halides in water stand in the same order as the relative rates of methanolysis in pure methanol. From the variation of the apparent energy of activation with respect to solvent composition, and from the limiting value of the isothermal gradients d ln k_1/dx_m in dilute aqueous solutions, it is concluded that the hydrolysis is a reaction of unit kinetic order with respect to the t-butyl halide and the fifth kinetic order with respect to water. The rate-determining step is regarded as the simultaneous attack of the solute molecule by five water molecules, or as the combined conversion of a cluster of molecules. This conclusion is identical with that reached by Scatchard on the mechanism of inversion of sucrose, and with the conclusion reached, from a different line of approach, in earlier papers of this series.

IN an attempt to gain some insight into the mechanism of hydrolysis, the rates at which the t-butyl halides react with a mixture of water and methanol have been measured over such ranges of concentration and temperature as are feasible with a conductometric method. The solutes, solvents, apparatus, and method have previously been described.[1]

EXPERIMENTAL METHOD AND RESULTS

The Hydrolysis of t-Butyl Bromide in Water.—The chemical change taking place is $Bu^tBr + H_2O \longrightarrow Bu^tOH + H^+ + Br^-$. No olefin or ether is formed.[2] As with the chloride reproducible results could be obtained only for dilute solutions. The rapidity of the reaction made measurements difficult except at 0·09°, where the first-order constant could be reproduced

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[1] Biordi and Moelwyn-Hughes, preceding paper.

[2] Olson and Halford, *J. Amer. Chem. Soc.*, 1937, **59**, 2644; Speith and Olson, *ibid.*, 1955, **77**, 1412.

to within ±0·8% of the mean value. At this temperature the bromide is hydrolysed **34** times as fast as the chloride. The results are summarised in Table 1. Inaccuracies increase as the temperature is raised. Only one run was carried out at 292·90° K; and the value of k_1 given for 298·16° is obtained indirectly as described in a later section. The results are only approximately summarised by eqn. (1):

TABLE 1.

First-order velocity constants of the hydrolysis of t-butyl bromide in water.

T (°K)	273·25	277·62	292·90	298·16
$k_1 \times 10^2$	2·36 ± 0·02	4·46 ± 0·40	42·1 ± 10·6	76·0 ± 8·3

$$k_1(\text{sec.}^{-1}) = 2{\cdot}6 \times 10^{16}e^{-(22,560 \pm 750)/\boldsymbol{R}T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At the mean temperature of 285·7° K, E_A for the chloride is 24,100 ± 90 cal./mole. Hence E_A (chloride) $-$ E_A (bromide) = 1540 ± 840 cal./mole. The difference in rates could thus arise from that in the apparent energies of activation, since $\boldsymbol{R}T \ln (k_{Br}/k_{Cl})$ is 1910 ± 95 cal./mole. The high pre-exponential term can be understood if the energy of activation is shared among classical oscillators.

t-Butyl iodide reacts too rapidly with water to allow of precise velocity measurements by the conductometric method.

Solvolysis in Methanol–Water Mixtures.—The mixed solvents were prepared by weight, and in sufficient quantities to allow numerous experiments to be carried out with each of the three solutes in each of the solvents. The composition of the solvent is expressed as the molar fraction, x_m, of methanol. The kinetic behaviour of the three t-butyl halides in mixtures of methanol and water closely resembles that found for the pure solvents. During a given run, the apparent first-order velocity-coefficient falls by a few per cent., while the true first-order coefficient corrected for the complicated dependence of conductivity on concentration, remains constant. These features become apparent from an analysis of the typical conductivity–time data given in Table 2. For Table 2*a*, for example, the plot of $\log_{10}(\kappa_\infty - \kappa)$ against time for the first 15 min. shows a zero-time error of 17·5 sec., and an apparent first-order constant of $k_0' = 6{\cdot}56 \times 10^{-5}$ sec.$^{-1}$. The complete logarithmic plot gives an inadmissibly larger zero-

TABLE 2.

(*a*) $[\mathrm{Bu^tCl}]_0$ = 14·05 mmoles/l.; x_m = 0·800; T = 316·94° K.

t (min.)	$\kappa \times 10^5$ (ohm^{-1} cm.$^{-1}$)	t (min.)	$\kappa \times 10^5$ (ohm^{-1} cm.$^{-1}$)	t (min.)	$\kappa \times 10^5$ (ohm^{-1} cm.$^{-1}$)
0	(0·2)	15	9·521	385	123·1
6	3·969	40	23·58	410	126·6
8	5·235	65	36·19	480	134·8
10	6·473	340	116·1	680	149·7
				∞	164·0

(*b*) $[\mathrm{Bu^tBr}]_0$ = 12·77 mmoles/l.; x_m = 0·800; T = 298·21° K.

t (min.)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)	t (min.)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)	t (min.)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)
0	(−0·0391)	15	2·267	70	7·171
3·5	0·5218	20	2·903	85	7·958
4	0·6522	25	3·478	100	8·590
5	0·8102	30	4·023	145	9·851
6	0·9610	40	4·989	170	10·28
8	1·243	50	5·830	195	10·58
10	1·581	60	6·551	370	11·08
				∞	11·28

(*c*) $[\mathrm{Bu^tI}]_0$ = 22·06 mmoles/l.; x_m = 0·500; T = 298·21° K.

t (sec.)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)	t (sec.)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)	t (sec.)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)
0	(0·043)	120	1·740	215	2·269
75	1·304	145	1·932	248	2·372
101	1·581	172	2·087	300	2·485
				∞	2·679

time error, and an apparent constant of $5{\cdot}95 \times 10^{-5}$ sec.$^{-1}$. Thus k' falls by 9·3% of its initial value when the extent of reaction is 94%. Table 2*b* gives one set of data for t-butyl bromide in the same solvent at another temperature. The zero-time error is now 13·7 sec.; $k_0' = 2{\cdot}514 \times 10^{-4}$ sec.$^{-1}$, and when the reaction is 94% complete, $k_1' = 2{\cdot}349 \times 10^{-4}$ sec., indicating a relative decline of 6·6%. Table 2*c* is typical of runs that are so fast that the initial rate of solvolysis cannot be measured. Between 50 and 83% of the total change in conductivity, the apparent first-order coefficient is constant at $8{\cdot}70 \times 10^{-4}$ sec.$^{-1}$. The zero-time error is 1·85 sec. The times listed in Tables 2 and 3 were measured on a standardised stop-clock and are regarded as accurate to within ±1 sec.

In converting the apparent first-order constants into their true values, extensive calibrations were not found necessary, as the charts soon made it apparent that the function, *f*, defined in terms of the ionic concentrations and specific conductivities as $\mathrm{d}\ln(c_\infty - c)/\mathrm{d}\ln(\kappa_\infty - \kappa)$, depends primarily on the composition of the solvent and the concentration of the solute, and is only slightly different for the three solutes. The values accepted for the corrected first-order constants governing the production of ions at 298·16° K are summarised in Table 3. They can be reproduced by the empirical equations:

$$\mathrm{Bu^tCl}:\quad \log_{10}k_1 = \bar{2}{\cdot}464 - 5{\cdot}147x_\mathrm{m} + 0{\cdot}626x_\mathrm{m}^2 \qquad (2)$$

$$\mathrm{Bu^tBr}:\quad \log_{10}k_1 = \bar{1}{\cdot}881 - 4{\cdot}806x_\mathrm{m} + 0{\cdot}465x_\mathrm{m}^2 \qquad (3)$$

$$\mathrm{Bu^tI}:\quad \log_{10}k_1 = 0{\cdot}186 - 4{\cdot}938x_\mathrm{m} + 0{\cdot}849x_\mathrm{m}^2 \qquad (4)$$

In aqueous solutions containing but little methanol, log k_1 decreases almost linearly with respect to the mole fraction, x_m, of methanol. A curvature, however, appears in the methanol-rich systems, which can be more clearly seen when relative rates are expressed as a function of x_m, as, for example, in eqn. (5):

$$\log_{10}[k_1(\text{iodide})/k_1(\text{bromide})] = 0{\cdot}305 - 0{\cdot}132x_\mathrm{m} + 0{\cdot}384x_\mathrm{m}^2. \qquad (5)$$

The bracketed values in Table 3 have been interpolated by means of equations (3) and (4). A comparison with the results of other investigations is possible with t-butyl chloride, and is given in Table 4. Having regard to the variety of techniques employed, the agreement between the various sets of observations may be regarded as satisfactory.

TABLE 3.

Corrected first-order constants governing the solvolysis of t-butyl halides in methanol–water mixtures at 298·16° K.

	7 + $\log_{10}k_1$ (sec.$^{-1}$)				7 + $\log_{10}k_1$ (sec.$^{-1}$)		
(x_m)	Chloride	Bromide	Iodide	(x_m)	Chloride	Bromide	Iodide
0	5·464	[6·881]	[7·186]	0·300	4·001	5·476	—
0·075	5·081	—	—	0·400	3·520	5·000	5·326
0·100	4·980	—	—	0·500	3·047	4·594	4·939
0·150	4·725	—	—	0·600	2·605	4·160	4·533
0·200	4·509	—	—	0·800	1·756	3·389	3·848
0·250	4·239	—	—	1·000	0·943	2·540	3·097

TABLE 4.

Rate constants for the solvolysis of t-butyl chloride in methanol–water mixtures at 298·16° K.

		7 + $\log_{10}k_1$ (sec.$^{-1}$)				7 + $\log_{10}k_1$ (sec.$^{-1}$)	
x_m	Ref.	obs.	by eqn. (2)	x_m	Ref.	obs.	by eqn. (2)
0	3	5·431	5·464	0·640	4	2·348	2·325
0·047	4	5·246	5·223	0·640	5	2·326	2·325
0·100	4	4·992	4·956	1·000	4	0·877	0·943
0·228	4	4·358	4·323	1·000	2	0·909	0·943

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[3] Winstein and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.
[4] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.
[5] Bunton and Nayak, *J.*, 1959, 3843.

TABLE 5.

A comparison of the rates of reaction of the t-butyl halides with methanol and water at 298·16° K.

	Chloride	Bromide	Iodide
Relative rates of methanolysis	1	40	143
Relative rates of hydrolysis	1	26	53
k_1 (hydrolysis)/k_1 (methanolysis)	$3·3 \times 10^4$	$2·2 \times 10^4$	$1·2 \times 10^4$

TABLE 6.

Apparent energies of activation for the solvolysis of t-butyl chloride in methanol–water mixtures at 307·52° K.

x_m	0	0·2	0·4	0·6	0·8	1·0
E (cal./mole)	20,130	20,230	20,710	21,870	23,410	25,160

Table 5 is based on the present data and on those of Biordi and Moelwyn-Hughes.[1] If the effect of substituting one halogen atom for another were ascribed entirely to a change in the energy of activation, it would suffice to conclude that, in both media, E_A for the bromide is less than that for the chloride by 2060 ± 130 cal., and that E_A for the iodide is less than that for the bromide by 590 ± 170 cal. While data of sufficient accuracy to test this view are not available, the energy differences closely resemble those found in other halide series.[6] To attribute the effect of changing the solvent entirely to a change in the apparent energies of activation, would require E_A(methanol) − E_A(water) to be 5865 ± 300 cal./mole for the three solutes. The observed value for the chloride is 3750, indicating changes other than those in the energies.

Table 6 shows how E_A for the solvolysis of t-butyl chloride changes with the composition of the solvent. The first additions of methanol to the aqueous solution have but a slight effect, *e.g.*, 100 cal./mole for a change of x_m from zero to 0·2. The term $\boldsymbol{R}T \ln (k_0/k_{0·2})$ at this temperature is 1344 cal./mole.

DISCUSSION

The problem of correlating reaction velocity with solvent composition is well known to be difficult and is still far from being solved, even in systems where only one chemical change is taking place. Definite advances, however, have been made by Olson and Halford [2] in the study of the solvolyses here considered, in terms of the escaping tendency of the solute, and by Winstein and Fainberg [4] in terms of the dielectric constant of the solvent.

The object of the present experiments was to seek information which would yield some insight into the largely unsolved problem of simple hydrolysis. We are not primarily interested in methanolyses or in elimination reactions in solution, and methanol has been used only to bring the reaction rate within the reach of the conductometric method, and to allow an indirect estimate, based on extrapolation, of the rates of hydrolysis of t-butyl bromide and iodide in aqueous solution. In water the chemical change is

$$\mathrm{Bu^tX} + \mathrm{H_2O} \longrightarrow \mathrm{Bu^tOH} + \mathrm{H^+} + \mathrm{X^-}$$

or, since both the ionic products are hydrated,

$$\mathrm{Bu^tX} + (\nu_1 + \nu_2 + 1)\mathrm{H_2O} \longrightarrow \mathrm{Bu^tOH} + [\mathrm{H},\nu_1\mathrm{H_2O}]^+ + [\mathrm{X},\nu_2\mathrm{H_2O}]^-$$

when ν_1 and ν_2 are ionic solvation numbers. If, between the reactants and products as written here, intermediates exist, their concentrations must be so low as to make negligible contribution to the electrical conductivity, and the evidence for their existence is inferential.

The first fact to note is that, with t-butyl chloride, a change in the composition of the solvent from pure water to 8 : 2 water–methanol causes the first-order constant to decrease nine-fold, while the apparent energy of activation is increased by only 100 cal./

[6] Moelwyn-Hughes, *Acta Physicochemica U.R.S.S.*, 1936, **4**, 223.

mole. It is, therefore, possible that the role of the methanol molecules in this region is simply that of a hindrance, reducing the likelihood of water molecules from reaching the solute, without greatly affecting the nature of its reaction with it. In solvents with higher proportions of the alcohol, other reactions are known to occur. We are concerned mainly, as stated, with hydrolysis, and therefore concentrate our attention on solutions where the proportion of methanol is small.

A simple way of interpreting the results is to assume that, in solutions containing relatively little methanol, the rate of change in the concentration, c, of solute consists of the following two components,

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = k_{\mathrm{w}}c_{\mathrm{w}}^{n_{\mathrm{w}}}c + k_{\mathrm{m}}c_{\mathrm{m}}^{n_{\mathrm{m}}}c \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where c_{w} and c_{m} are the concentrations of water and methanol, respectively, and n_{w} and n_{m} are the orders of reaction with respect to molecules of the medium. Concurrent hydrolysis and methanolysis in methanol-rich systems require for their formulation a number of other rate constants and integers lying between n_{w} and n_{m}, which are here omitted. Then,

$$k_1 = k_{\mathrm{w}}c_{\mathrm{w}}^{n_{\mathrm{w}}}\left[1 + \left(\frac{k_{\mathrm{m}}c_{\mathrm{m}}^{n_{\mathrm{m}}}}{k_{\mathrm{w}}c_{\mathrm{w}}^{n_{\mathrm{w}}}}\right)\right]$$

From the two rate constants relating to the pure solvents, the second term is known to be small enough to be ignored so that,

$$\ln k_1 = \ln k_{\mathrm{w}} + n_{\mathrm{w}} \ln c_{\mathrm{w}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

then

$$\mathrm{d}\ln k_1/\mathrm{d}x_{\mathrm{w}} = n_{\mathrm{w}}\,\mathrm{d}\ln c_{\mathrm{w}}/\mathrm{d}x_{\mathrm{w}}$$

and, c_{w} being expressed in moles/l.,

$$c_{\mathrm{w}} = \frac{1000x_{\mathrm{w}}}{V_{\mathrm{m}} - (V_{\mathrm{m}} - V_{\mathrm{w}})x_{\mathrm{w}}}$$

where V_{m} and V_{w} are the partial molar volumes. In the limit, as x_{w} approaches 1, we have

$$\left(\frac{\mathrm{d}\ln c_{\mathrm{w}}}{\mathrm{d}x_{\mathrm{w}}}\right)_{x_{\mathrm{w}}\to 1} = \frac{V_{\mathrm{m}} - (\mathrm{d}V_{\mathrm{w}}/\mathrm{d}x_{\mathrm{w}})_{x_{\mathrm{w}}\to 1}}{V_{\mathrm{w}}}$$

V_{w} is the ordinary molar volume of water, and V_{m} the partial molar volume of methanol in an infinitely dilute aqueous solution. Experiments show the second term in the numerator to be negligible. Hence, since $x_{\mathrm{w}} + x_{\mathrm{m}} = 1$,

$$n_{\mathrm{w}} = -\frac{V_{\mathrm{w}}}{V_{\mathrm{m}}}\left(\frac{\mathrm{d}\ln k_1}{\mathrm{d}x_{\mathrm{m}}}\right)_{x_{\mathrm{m}}\to 0} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

On using the ordinary molar volumes of the two solvents and the average limiting value of $\mathrm{d}\log_{10}k_1/\mathrm{d}x_{\mathrm{m}} = 4{\cdot}96 \pm 0{\cdot}17$ [eqns. (2)—(4)], we find that $n_{\mathrm{w}} = 5{\cdot}06 \pm 0{\cdot}17$. Use of the partial molar volume of methanol in an infinitely dilute aqueous solution would raise n_{w} by about 4%. The results of these experiments can therefore be explained by regarding the hydrolysis of the t-butyl halides in water as reactions which are of the first kinetic order with respect to the solute, and of the fifth kinetic order with respect to the solvent. The rate-determining step would thus be the critical and simultaneous activation of a cluster of six molecules, one of which is the solute.

Scatchard [7] concluded from his study of the inversion of cane sugar that the order of reaction with respect to the water molecules was 6. Kappanna [8] gives the same number for the decomposition of trichloroacetic acid in water. Glew and Moelwyn-Hughes,[9]

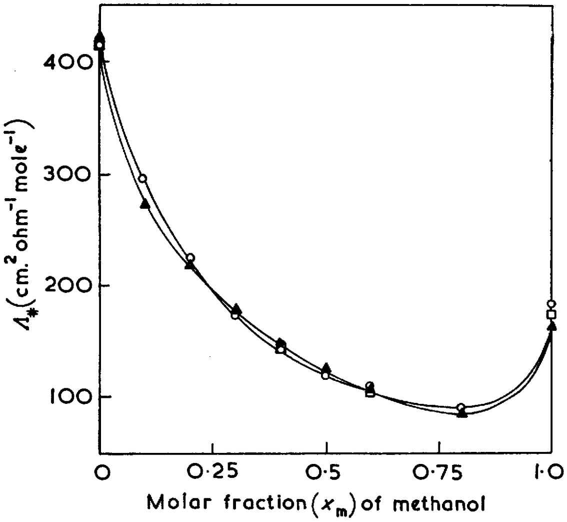
[7] Scatchard, *J. Amer. Chem. Soc.*, 1921, **43**, 2387.

[8] Kappanna, *Z. phys. Chem.*, 1932, **158**, *A*, 355.

[9] Glew and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1953, *A*, **211**, 254.

using a different method, estimated the same order for the hydrolysis of methyl fluoride. Their method is not applicable to pure methanolyses [1] because of the irregular temperature variation of the heat capacity of crystalline methanol near the melting point.[10]

Equivalent Conductances of the Hydrogen Halides in Methanol–Water Mixtures.—The equivalent conductance of each of the three hydrogen halides, at a fixed concentration, varies with the solvent composition as shown in the Figure. The concentrations of a given solute in the series of solvents is accurate only to ±0·5 mmole/l. The curves for hydrogen bromide and hydrogen iodide are almost superimposable and cross the curve for hydrogen chloride at two points. Although the region between $x_m = 0{\cdot}8$ and $x_m = 1{\cdot}0$ has not been explored, it is clear that all the (Λ–x_m) curves pass through a minimum when x_m is about 0·8. A similar behaviour has been found with various salts in ethanol–water mixtures,[11] and for potassium iodide [12] and tetramethylammonium iodide [13] in methanol–water mixtures. The minimum in the fluidity of methanol–water systems at this temperature occurs when $x_m = 0{\cdot}275$. Hence Walden's rule, though seemingly applicable to solutions of the hydrogen halides in methanol, is inapplicable to their solutions in methanol–water mixtures.



The equivalent conductance of, ▲ hydrogen chloride (c = 5 mmoles/l.), ☐ hydrogen bromide (c = 11), and ○ hydrogen iodide (c = 17), in methanol – water mixtures at 298·16° K.

The Rate of Solvolysis of t-Butyl Chloride in an Equimolar Ethanol–Water Solution.—In order to compare our methods and results with those of other workers, one run has been carried out at 25·00° on the rate of solvolysis of t-butyl chloride (c = 10·58 mmoles/l.) in aqueous ethanol in which the mole fraction, x_E, of ethanol was 0·5. The results of analysing extensive readings, taken during 10 days in a Polythene cell, are summarised in Table 7, the entries in the last two columns of which have been found from the intercepts and gradients of the plots of log ($\kappa_\infty - \kappa$) against time. The decline of 14% in k_1' is somewhat greater than that found with similar concentrations of solute in equimolar methanol–water. Calibrations after dilution of the end-solution give the approximate values of f_0 and f_∞ as 0·83 and 1·05, respectively. Within the limits of accuracy claimed we may, therefore, regard k_1 as constant throughout the run, its value being $(1{\cdot}60 \pm 0{\cdot}07) \times 10^{-5}$ sec.$^{-1}$.

[10] Staveley and Gupta, *Trans. Faraday Soc.*, 1949, **45**, 50.

[11] Davies and Thomas, *J.*, 1958, 3660.

[12] Walden, "Das Leitvermögen der Lösungen," Vol. II, Akademische Verlagsgesellschaft, Leipzig, 1924, p. 114.

[13] Kraus, cited by C. W. Davies in "Conductivity of Electrolytes," Chapman and Hall, London, 1933, p. 159.

TABLE 7.

The rate of solvolysis of t-butyl chloride in equimolar ethanol–water at 298·16° K.

Time (min.)	Change in κ (%)	Zero-time error (min.)	$k_1' \times 10^5$ (sec.$^{-1}$)
0—75	0—7·85	0·0	1·83
75—340	7·85—29·34	5·0	1·69
340—3390	29·34—96·14	43·7	1·58

The value of k_1 given by Cooper, Hughes, and Ingold[14] at this temperature in a solvent with $x_E = 0{\cdot}553$ is $8{\cdot}54 \times 10^{-6}$ sec.$^{-1}$. On comparing the two results, we find $d \log_{10}k_1/dx_E = -4{\cdot}95$, indicating that (1) when the effect of the solvent is allowed for, there is complete numerical agreement and (2) an equation of the form of eqns. (2)—(4) probably holds for ethanol–water as for methanol–water systems.

A comparison of our results with those of Shorter and Hinshelwood[15] on the same reaction in the same solvent ($x_E = 0{\cdot}498$) is not so readily made because, for reasons given by them, the sample of t-butyl chloride employed was not purified. Moreover, they assumed ionic concentration to be directly proportional to the specific conductivity and computed their velocity constants by a method which did not involve more than 80% of reaction or require a knowledge of the end-point. Finally, deviations from the first-order law were found during the last 10% of reaction and it proved impossible to reconcile the observed infinity value with that afforded by the intercept of a logarithmic plot. The cause of these effects not being known, it was suggested that they may be connected with some electrode phenomenon. We consider that the effects can now be fully interpreted in terms of the lack of direct proportionality between ionic concentration and specific conductivity. Shorter and Hinshelwood did not measure the rate of solvolysis at 25° but gave an equation of the Arrhenius type from which k_1 at this temperature is found to be within 20% of our value.

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[14] Cooper, Hughes, and Ingold, *J.*, 1937, 1280.
[15] Shorter and Hinshelwood, *J.*, 1949, 2412.