# **836.** *The Kinetics of the Methanolysis of t-Butyl Chloride, Bromide, and Iodide.*

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The kinetics of the reaction between the t-butyl halides and methanol have been studied by the method of electrical conductivity at temperatures between 276° and 326°K. The chemical changes consist of the effectively irreversible methanolysis

$$\mathrm{Bu^tX + MeOH \longrightarrow Bu^tOMe + H^+ + X^-},$$

unattended by the formation of isobutene or t-butyl alcohol. The apparent first-order constants, calculated on the assumption that the equivalent conductance is independent of the concentration of acid, fall during the course of each run, and are greater in concentrated than in weak solutions. When allowance is made for the exact relationship between specific conductivity and concentration, first-order velocity coefficients are obtained which are constant during the complete course of methanolysis and are unaffected by a 200-fold change in the initial concentration.

The rate of solvolysis is increased by the presence of small amounts of water, but not to as great an extent as the equivalent conductance is decreased. The temperature variation of the unimolecular constants (sec.$^{-1}$) obtained with solutions containing 1 mmole/l. of t-butyl halide is summarised by the empirical equations:

$$\mathrm{Bu^tCl}:\quad \log_{10}k_1 = 76{\cdot}402 - 21{\cdot}905 \log_{10}T - 8424{\cdot}73/T$$

$$\mathrm{Bu^tBr}:\quad \log_{10}k_1 = 69{\cdot}927 - 19{\cdot}354 \log_{10}T - 7899{\cdot}79/T$$

$$\mathrm{Bu^tI}:\quad \log_{10}k_1 = 64{\cdot}998 - 17{\cdot}981 \log_{10}T - 7277{\cdot}58/T.$$

The apparent energies of activation decrease as the temperature is raised, as with the hydrolysis of the methyl halides.

The order of the relative rates of reaction of the t-butyl halides with methanol at 25° (Cl : Br : I : : 1 : 40 : 143) differs from that of the relative rates of reaction of the methyl halides with water at the same temperature (Cl : Br : I : : 1 : 18 : 3).

The mechanism, energy, and entropy of activation are briefly discussed.

The presence of 1 mmole/l. of methyl t-butyl ether in methanol slightly reduces the equivalent conductance of hydrogen chloride and hydrogen bromide in this solvent. The equivalent conductance of hydrogen iodide in methanol at infinite dilution is slightly higher than the sum of the ionic mobilities given in the literature. Walden's proportionality between the conductance of an electrolyte and the fluidity of the solvent is established for the hydrogen halides in methanol.

The object of this work is to extend the slender information at present available on the rates of reaction of alkyl halides in pure media.[1,2] After the dissolution of the t-butyl halides in dry methanol, the following changes can in principle occur:

$$\mathrm{Bu^tX + MeOH \longrightarrow Bu^tOMe + H^+ + X^-} \qquad (1)$$

$$\mathrm{Bu^tX \longrightarrow Me_2C{:}CH_2 + H^+ + X^-} \qquad (2)$$

$$\mathrm{Bu^tX + MeOH \longrightarrow Bu^tOH + MeX} \qquad (3)$$

$$\mathrm{MeX + MeOH \longrightarrow Me{\cdot}O{\cdot}Me + H^+ + X^-} \qquad (4)$$

Because of the rapidity with which the t-butyl halides react with water, the rates of change cannot be accurately measured by the conventional methods of analysis. Methods

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[1] Winstein and Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

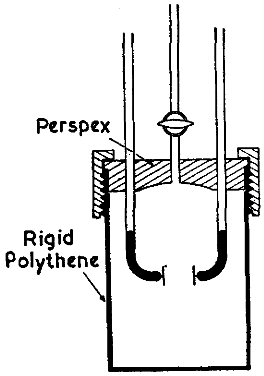
[2] Moelwyn-Hughes, *J.*, 1961, 1517.

based on chemical analysis must be used. They can lead to reliable results for the velocity of chemical change provided that the somewhat laborious steps are taken to correlate the chemical composition of the solution with the magnitude of the physicochemical property measured. Of the many methods available, that of electrical conductivity is used here, as it seemed to be, despite its shortcomings, the most direct.

Most of the kinetic experiments were carried out at concentrations of t-butyl halide of about 1 mmole/l. of solution. The rate of production of ions from the three halides was found to be, at all temperatures, approximately unimolecular with respect to the organic halide. Runs carried out with the object of analysing the products of reaction were made by using approximately 1M-solutions. They indicated the complete absence of isobutene. The elimination reaction (2) does not therefore take place, and the production of ions must consequently be due to reaction (1) or reaction (4). Experiments with the methyl halides in pure methanol indicate that reaction (4) is slower by a factor of about $10^{-3}$ than the rates of increase in conductivity of the t-butyl halide solutions in the same solvent at the same temperature. Reaction (4) can thus be dismissed, as contributing insignificantly to the rate-determining process. The chemical changes taking place are consequently the simple methanolyses represented by reaction (1). They have been found to go to completion.

## EXPERIMENTAL METHOD AND RESULTS

*Methanol.*—Commercial methanol was dried and purified as in an earlier work.[3] A typical b. p. is 64·15°/752 mm. Occasionally however, despite very slow distillation under a high reflux ratio from aluminium amalgam, it proved impossible to prevent some mercury from distilling over, so that 1 litre of distillate sometimes contained a visible droplet of the metal. For this reason most of the distillations were made from magnesium. The equivalent conductances of solutions of the hydrogen halides in the various batches of methanol used showed them to be pure and dry.



Vapour-free conductivity cell of Polythene and Perspex.

*Conductivity Cells.*—Most of the runs were carried out in Pyrex conductivity cells, by the method already described.[2] With solutions containing low concentrations of the halides, however, slight attack by the acids on the walls of the vessel seemed to occur, especially with very slow runs.[4] To overcome this complication, a vapour-free cylindrical cell of diameter 6 cm., and capacity 200 c.c. was made of Polythene (Figure). The lid, into which a pressure-controlling tap and electrical leads were sealed, consisted of Perspex, with a concave underside. Solutions of acids kept in this cell showed no change in conductivity during several weeks. The cell constant was 0·39007 ± 0·00006 $\text{cm.}^{-1}$.

*Analysis of Products.*—The amount of unsaturated substance in the product was estimated by a slight modification of the method of Lucas and Eberz.[5] A solution containing 0·1 mole of t-butyl bromide in 100 c.c. of dry methanol was allowed to react to completion at room

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[3] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1937, **35**, 358.

[4] Cf. Heppolette and Robertson, *Proc. Roy. Soc.*, 1959, *A*, **252**, 273.

[5] Lucas and Eberz, *J. Amer. Chem. Soc.*, 1954, **56**, 460.

temperature. Samples (5 c.c.) were added to 0·05N-bromate–bromide solution (10 c.c.) and 6N-sulphuric acid (5 c.c.) was then introduced before shaking in a glass-stoppered vessel. After 10 min., the sample required 23·7 ± 0·2 c.c. of 0·0212N-thiosulphate. Four tests were made. The four control experiments with pure methanol required 23·6 ± 0·55 c.c. of the same reagent. Thus the reaction products contained nothing that will react with bromine. As a check on the method, a few drops of 2-methylbut-2-ene were added to the sample for analysis: it required 67·7 c.c. of the standard thiosulphate under the same conditions.

The methods used to estimate the final concentrations of halogen ions formed were those selected in a previous study of the hydrolysis of the methyl halides.[6] 10 c.c. of a completely reacted solution of t-butyl iodide, for example, required 2·040 c.c. of 0·001469N-potassium iodate: $c = 0{\cdot}2997$ mmole/l. Repetition gave 2·058 c.c.; $c = 0{\cdot}3024$. Mean $c = 0{\cdot}301$. The end concentrations of halide ions agreed to within 0·1% with those expected from the weight of organic halide used.

70 c.c. of a methanol solution which was 0·1N with respect to t-butyl bromide were kept at room temperature until reaction was complete. It was then made alkaline by the addition of sodium, and fractionated 3 times through a short vacuum-insulated packed column. The sample collected at 51·5—53·5°/759 mm. had $n_D^{25} = 1{\cdot}36775$. Norris and Rigby[7] give 53·55°/760 mm. and $n_D^{25} = 1{\cdot}3667$ for methyl t-butyl ether. After 3 distillations there were 5·5 c.c. of the ether (theoretically possible 6·9 c.c.).

These analyses, though differing in method, are in complete agreement with the more extensive work of Speith and Olson,[8] who find that the fraction of ether formed increases regularly with the molar fraction of methanol.

*The Relation between the Apparent and the True Unimolecular Constant.*—Because the equivalent conductance depends on the electrolyte concentration, a quantitative relationship between them must be established before the rate of change of electrical conductivity, $\kappa$, can be converted into the rate of chemical change, which is what we are primarily interested in. By denoting the true unimolecular constant by $k_1$ and the apparent unimolecular constant by $k_1'$ we have the general equation (5),

$$k_1 = -\mathrm{d}\ln(c_\infty - c)/\mathrm{d}t = k_1' f \qquad (5)$$

where $c$ is the concentration of halide ion at time $t$, and $c_\infty$ is the final concentration,

$$k_1' = -\mathrm{d}\ln(\kappa_\infty - \kappa)/\mathrm{d}t \qquad (6)$$

and

$$f = \mathrm{d}\ln(c_\infty - c)/\mathrm{d}\ln(\kappa_\infty - \kappa) \qquad (7)$$

Measurements of the specific conductivities of the products of reaction after successive dilutions enabled us to calculate values of $f$ for all the solutions employed. Table 1 illustrates the continuous fall in $k_1'$ and rise in $f$ found in a particular instance. In the region where the square-root conductivity law is obeyed, we have

$$\Lambda = 10^6\kappa/c = \Lambda_0 - Ac^{\frac{1}{2}}, \qquad (8)$$

where $\kappa$ is the specific conductivity, and $c$ the concentration in mmoles/l. Consequently

$$f = \frac{\kappa_\infty - \kappa}{c_\infty - c} \cdot \frac{10^6}{\Lambda_0 - \frac{3}{2}Ac^{\frac{1}{2}}} \qquad (9)$$

This expression is more general than equation (4) of the previous paper,[2] which is applicable only to solutions weak enough to justify the use of the square-root law throughout the course of the reaction. In the present instance Kohlrausch's law becomes invalid after the first two hours of the reaction. Only the first three values of $f$ were therefore calculated by means of equation (9), using the constants $\Lambda_0 = 193{\cdot}5$ and $A = 11{\cdot}63$ obtained by Frazer and Hartley.[9] After 2 hours, the concentration of electrolyte exceeds 1 mmole/l. and the values of $f$ afforded by equation (9) greatly exceed the experimental values obtained graphically by means of equation (7).

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[6] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1953, *A*, **220**, 386.
[7] Norris and Rigby, *J. Amer. Chem. Soc.*, 1932, **54**, 2095.
[8] Speith and Olson, *J. Amer. Chem. Soc.*, 1955, **77**, 1412.
[9] Frazer and Hartley, *Proc. Roy. Soc.*, 1925, *A*, **109**, 351.

The procedure described above is laborious, and difficult because of the sensitivity of $\kappa$ to traces of moisture. Accurate and reproducible results can, moreover, be obtained with solutions containing 1 mmole/l. or less. Kohlrausch's law then becomes applicable throughout the course of the run, and the function $f$ may be calculated from the simple equation:

$$f = \left[1 - \frac{A}{\Lambda_0}\left(\frac{c_\infty^{\frac{3}{2}} - c^{\frac{3}{2}}}{c_\infty - c}\right)\right]\left[1 - \tfrac{3}{2}\frac{A}{\Lambda_0}c^{\frac{1}{2}}\right]^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

TABLE 1.

94·6 mmoles of t-butyl chloride per litre of pure methanol at 299·15° ± 0·01°K.

| $t$ (min.) | $\kappa \times 10^4$ (ohm$^{-1}$ cm.$^{-1}$) | $k_1' \times 10^6$ (sec.$^{-1}$) | $f$ | $k_1 \times 10^6$ (sec.$^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | | | |
| | | 1·679 | 0·601 | 1·01 |
| 8 | 0·0888 | | | |
| | | 1·700 | 0·631 | 1·07 |
| 78 | 0·8389 | | | |
| | | 1·604 | 0·645 | 1·04 |
| 133 | 1·416 | | | |
| | | 1·516 | 0·673 | 1·02 |
| 333 | 3·370 | | | |
| | | 1·471 | 0·694 | 1·02 |
| 393 | 3·932 | | | |
| | | 1·451 | 0·704 | 1·02 |
| 475 | 4·680 | | | |
| | | 1·348 | 0·754 | 1·02 |
| 1,605 | 13·90 | | | |
| | | 1·270 | 0·808 | 1·03 |
| 3,032 | 23·80 | | | |
| | | 1·237 | 0·847 | 1·05 |
| 4,810 | 34·45 | | | |
| | | 1·229 | 0·873 | 1·05 |
| 5,940 | 40·48 | | | |
| | | 1·124 | 0·926 | 1·04 |
| 20,820 | 84·47 | | | |
| ∞ | 109·93 | | | |
| | | | Average | 1·03 |

The initial value of $f$ is clearly

$$f_0 = 1 - \frac{A}{\Lambda_0}c_\infty^{\frac{1}{2}} = \Lambda_\infty/\Lambda_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $\Lambda_\infty$ is the equivalent conductance of the solution at the end of the reaction and $\Lambda_0$ the equivalent conductance at infinite dilution. During the course of runs within this concentration range, we have

$$f_{\frac{1}{4}} = \frac{1 - 1{\cdot}167\,(A/\Lambda_0)\,c_\infty^{\frac{1}{2}}}{1 - 0{\cdot}750\,(A/\Lambda_0)\,c_\infty^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$f_{\frac{1}{2}} = \frac{1 - 1{\cdot}293\,(A/\Lambda_0)\,c_\infty^{\frac{1}{2}}}{1 - 1{\cdot}060\,(A/\Lambda_0)\,c_\infty^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$f_{\frac{3}{4}} = \frac{1 - 1{\cdot}401\,(A/\Lambda_0)\,c_\infty^{\frac{1}{2}}}{1 - 1{\cdot}299\,(A/\Lambda_0)\,c_\infty^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$f_\infty = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The subscripts $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ refer to a system where the concentration of ions has reached these fractional values of the final concentration, and not to fractional increases in specific conductivity.

*The Effect of Moisture on* $\Lambda_\infty$ *and* $k_1'$.—It is well known from the work of Goldschmidt[10] that the presence of water, even in small quantities, reduces the equivalent conductance of solutions of electrolytes in methanol. Its presence has also been found to increase the reaction

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[10] Goldschmidt and Thuessen, *Z. phys. Chem.*, 1913, *A*, **81**, 30.

velocity $k_1'$, but the increase in $k_1'$ is much less than the decrease in $\Lambda$. A run with 10·55 mmoles/l. of t-butyl chloride was carried out in a sample of methanol (Kahlbaum, not dried). It was a pre-war *pro analysi* specimen, free from chloroform and aldehyde, and containing less than 0·005% by weight of acetone. The specific conductivity increased to one half of its final value of $1{\cdot}061 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$ in 12,000 min. at 24·77°: $\Lambda_\infty$ was thus 100·6, and $k_{\frac{1}{2}}'$ was $9{\cdot}63 \times 10^{-6}$ sec.$^{-1}$. A run at the same temperature, in methanol freshly distilled from magnesium, gave $c_\infty = 9{\cdot}454$ mmoles/l.: $\kappa_\infty = 1{\cdot}465 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$: $\Lambda_\infty = 155{\cdot}0$: $t$ $(\kappa = \kappa_\infty/2) = 12{,}550$ min.: $k_{\frac{1}{2}}' = 9{\cdot}21 \times 10^{-7}$ sec.$^{-1}$. Thus the water in the impure solvent had reduced $\kappa$ by 35% and increased the apparent unimolecular constant by nearly 4·5%. The increase in the true unimolecular constant is about 1%. Both observations indicate the presence of approximately 1 mmole of water per litre of methanol. Only runs carried out in dry methanol are recorded in this paper.

*t-Butyl Chloride.*—The physical properties of the purified specimen of t-butyl chloride used have been recorded.[2] Solutions of it in dry methanol gave, at the end of the reaction, equivalent conductivities lying close to, though significantly lower than, the equivalent conductivities of hydrogen chloride in the same solvent. The differences between the entries of lines 2 and 3 of Table 2 indicate that the presence of methyl t-butyl ether depresses the value of the equivalent conductivity of hydrogen chloride in methanol. Conductivity data for a typical run at a relatively low concentration are shown in Table 3. The run was started by injecting 0·01 c.c. of the solute into about 100 c.c. of freshly distilled (Hg–Al) methanol in a Pyrex conductivity cell (constant = 0·2738 cm.$^{-1}$) at 39·92° ± 0·005°. Resistances were read between $1{\cdot}05 \times 10^5$ and $1{\cdot}00 \times 10^3$ ohms. The zero-time error was less than 1 sec. After 10 days, when the conductivity had reached a constant value, the cell was transferred to a thermostat at 25·00°, where the solution gave $\kappa_{25^\circ} = 1{\cdot}644 \times 10^{-4}$ ohm$^{-1}$ cm.$^{-1}$. Analysis gave $[\mathrm{Cl}^-] = 0{\cdot}903$ mmole/l. at 25°, corresponding, at 39·92°, to the concentration recorded in Table 3. $\Lambda$ in this instance is 182·1 cm.$^2$ ohm$^{-1}$ mole$^{-1}$ at 25°.

TABLE 2.

Equivalent conductivities (cm.$^2$ ohm.$^{-1}$ mole$^{-1}$) at 25°.

| | | | |
|---|---|---|---|
| $[\mathrm{Bu^tCl}]_0$ (mmoles/l.) ............... | 1·03 | 7·31 | 9·45 |
| $\Lambda_{25}$ (products) ..................... | 178·9 | 157·7 | 155·0 |
| $\Lambda_{25}$ (HCl) .......................... | 180·8 [9] | 158·6 [10] | 155·4 [10] |

TABLE 3.

t-Butyl chloride in dry methanol at 313·08°; $[\mathrm{HCl}]_\infty = 0{\cdot}888$ mmole/l.

| $t$ (min.) | $\kappa \times 10^6$ (ohm$^{-1}$ cm.$^{-1}$) | $k_1' \times 10^6$ (sec.$^{-1}$) | $t$ (min.) | $\kappa \times 10^6$ (ohm$^{-1}$ cm.$^{-1}$) | $k_1' \times 10^6$ (sec.$^{-1}$) |
|---|---|---|---|---|---|
| 0 | 0 | | 180 | 14·81 | |
| | | (7·357) | | | 6·851 |
| 1 | 0·086 | | 270 | 21·50 | |
| | | — | | | 6·889 |
| 6 | 0·623 | | 440 | 33·54 | |
| | | — | | | 6·636 |
| 9 | 0·913 | | 550 | 40·63 | |
| | | — | | | 6·756 |
| 13 | 1·308 | | 1880 | 106·6 | |
| | | 7·298 | | | 6·819 |
| 17 | 1·654 | | 2870 | 137·4 | |
| | | 7·256 | | | 6·879 |
| 34 | 3·109 | | 3300 | 147·4 | |
| | | 7·155 | | | 6·773 |
| 40 | 3·613 | | 4685 | 166·9 | |
| | | 7·076 | | | — |
| 102 | 8·69 | | ∞ | 199·0 | |
| | | 6·981 | | | — |

The conductivity data were analysed as follows. Values of $k_1'$ were calculated between neighbouring observations by means of the incremental equation

$$k_1' = \frac{1}{t_2 - t_1} \ln \frac{\kappa_\infty - \kappa_1}{\kappa_\infty - \kappa_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The results, given in column 3, extrapolate to a value of $k_0' = 7{\cdot}357 \times 10^{-6}$ sec.$^{-1}$. The specific conductivities observed during the first 1·8% of the total conductivity change give $\mathrm{d}\kappa/\mathrm{d}t = 8{\cdot}70 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$ min.$^{-1}$, which affords a more accurate value of $k_0' = (1/\kappa_\infty) \times (\mathrm{d}\kappa/\mathrm{d}t)_0 = 7{\cdot}285 \times 10^{-6}$ sec.$^{-1}$. This is accepted as the apparent constant of the reaction at infinite dilution of the electrolyte. A logarithmic plot covering the 25—75% range gives $k_{\frac{1}{2}}' = 6{\cdot}942 \times 10^{-6}$ sec.$^{-1}$. From the time taken for $\kappa$ to reach one half of its limiting value, which is 1650 min., $k_{\frac{1}{2}}' = 7{\cdot}044 \times 10^{-6}$. We accept the mean value of $k_{\frac{1}{2}}' = (6{\cdot}99 \pm 0{\cdot}05) \times 10^{-6}$ sec.$^{-1}$.

The equivalent conductivity of hydrogen chloride in methanol at 25° according to Frazer and Hartley [9] is $\Lambda = 193{\cdot}5 - 368C^{\frac{1}{2}}$, where $C$ is the concentration in moles/l. If $c$ denotes the concentration in mmoles/l., we have $\Lambda = 193{\cdot}5 - 11{\cdot}63c^{\frac{1}{2}}$. The equation holds for values of $c$ up to 1·475. At concentrations below 0·217 mmole/l., Thomas and Marum [11] find for the same system at the same temperature $\Lambda = 196{\cdot}7 - 20{\cdot}24c^{\frac{1}{2}}$. The corresponding values of $A/\Lambda_0$ are 0·0601 and 0·1006, respectively. Our values of $\Lambda_\infty$ run close to those obtained by Wynne-Jones [12] at low concentrations, though giving a slightly lower value (190·7) for $\Lambda_0$, and to those of Goldschmidt and Thuessen [10] at values of $c$ up to 50. The experimental value of $A/\Lambda_0$ found by Wynne-Jones is the nearest yet recorded for this system to the theoretical slope of the limiting equation of Debye, Hückel, and Onsager: [13]

$$\frac{\Lambda}{\Lambda_0} = 1 - \left[\frac{2}{2+\sqrt{2}} \cdot \frac{e^2}{6DkT} + \frac{1}{9 \times 10^{11}\Lambda_0}\frac{N_0e^2}{3\pi\eta}\right]\frac{1}{1000} \cdot \left(\frac{8\pi N_0 e}{DkT}\right)^{\frac{1}{2}} c^{\frac{1}{2}}, \quad . \quad (17)$$

where $e$ is the electronic charge, $D$ the dielectric constant, $\eta$ the viscosity, and $N_0$ is Avogadro's number. According to this equation, $A/\Lambda_0 = 0{\cdot}0529$, if $\Lambda_0$ is given the mean value of 195 at 25°. The fraction $A/\Lambda_0$ increases slightly with a rise in temperature, being 0·0568 at 40° and 0·0607 at 55°. Because of the difference between the values of $\Lambda_0$ found by the various investigators, we have frequently used equation (17) to evaluate the function $f$. When applied to the data of Table 3, we find $f_0 = 0{\cdot}945$ and $f_{\frac{1}{2}} = 0{\cdot}986$. Thus $k_0'/f_0$ and $k_{\frac{1}{2}}'/f_{\frac{1}{2}}$ are both $6{\cdot}88 \times 10^{-6}$ sec.$^{-1}$, which is regarded as the true first-order constant, $k_1$, at this temperature.

TABLE 4.

First-order velocity constants for the solvolysis of t-butyl chloride in dry methanol.

| | $k_1$ (sec.$^{-1}$) | |
|---|---|---|
| $T$ (°K) | (Obs.) | (Calc.) |
| 297·96 | $8{\cdot}58 \times 10^{-7}$ | $8{\cdot}52 \times 10^{-7}$ |
| 313·08 | $6{\cdot}88 \times 10^{-6}$ | $6{\cdot}68 \times 10^{-6}$ |
| 317·24 | $1{\cdot}123 \times 10^{-5}$ | $1{\cdot}128 \times 10^{-5}$ |
| 326·73 | $3{\cdot}36 \times 10^{-5}$ | $3{\cdot}49 \times 10^{-5}$ |

Velocity constants determined at other temperatures, with solutions of nearly the same concentration, are summarised in Table 4, and can be reproduced empirically by the equation,

$$\log_{10}k_1 = 76{\cdot}4020 - 21{\cdot}9052\log_{10}T - 8424{\cdot}73/T \quad . \quad . \quad . \quad . \quad (18)$$

according to which the apparent energy of activation, in cal./mole, is

$$E_A = 38{,}549 - 43{\cdot}53T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

The estimated error in the coefficient of $T$ is ±19 cal. mole$^{-1}$ deg.$^{-1}$.

*t-Butyl Bromide.*—A specimen of t-butyl bromide provided by Schuchardt was shaken with mercury, filtered, dried, and distilled from anhydrous sodium sulphate. It gave the correct analysis for bromine, and, after hydrolysis, an equivalent conductivity only slightly lower than the standard value for hydrogen bromide. It had $n_D^{20} = 1{\cdot}42849$ and b. p. 72·25° ± 0·15°, which is lower by about 1° than the temperature given by Timmermans.[14] Though the technique employed in studying the rate of solvolysis of t-butyl bromide was the same as

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[11] Thomas and Marum, *Z. phys. Chem.*, 1929, *A*, **143**, 191.

[12] Murray-Rust, Wynne-Jones, and Hartley, *Proc. Roy. Soc.*, 1929, *A*, **126**, 40.

[13] See Davies, " The Conductivity of Solutions," Chapman and Hall, London, 1933.

[14] Timmermans, " Physicochemical Constants of Pure Organic Liquids," Elsevier, Amsterdam, 1950.

that used with the chloride, more accurate and consistent results were obtained, owing partly to the relative rapidity of the reaction, but also to some extent because of the greater precaution taken to ensure the absence of traces of water from the solvent.

From the results of a typical run (Table 5), it is seen that $k_1' \times 10^5$ falls from about 3·80 initially to 3·51 when the reaction is 96% complete. As there appears to be no directly measured equivalent conductivity of hydrogen bromide in dry methanol, the following equation was constructed from the ionic mobilities obtained by other workers and the conductivities measured by us at concentrations up to about 1·5 mmoles/l. at 25°:

$$\Lambda = 197{\cdot}5 - 11{\cdot}87c^{\frac{1}{2}}.$$

This gives $A/\Lambda_0 = 0{\cdot}0601$ at this temperature and affords all the values of $f$ given in Table 6, except those in the last line. The metals shown are those from which the methanol was distilled. Runs 40 and 37 are regarded as giving the most reliable results, because $\Lambda_\infty$ in these cases agree with standard data. In Run 35, the observed value of $\Lambda_\infty$ was 16·5 cm.$^2$ ohm$^{-1}$ mole$^{-1}$ too low. To determine $f$ for Run 41, a concentration–conductivity graph was constructed from observations after successive dilutions. $\Lambda_\infty$ for this run was 121·5. Equivalent conductances of hydrogen bromide in methanol have not previously been recorded in this region of concentration. The accepted value of $k_1$ at this temperature is $3{\cdot}604 \times 10^{-5}$ sec.$^{-1}$.

TABLE 5.

t-Butyl bromide in dry methanol at 298·25°; $[\mathrm{HBr}]_\infty = 0{\cdot}365$ mmole/l.

| $t$ (min.) | $\kappa \times 10^6$ (ohm$^{-1}$ cm.$^{-1}$) | $k_1' \times 10^5$ (sec.$^{-1}$) | $t$ (min.) | $\kappa \times 10^6$ (ohm$^{-1}$ cm.$^{-1}$) | $k_1' \times 10^5$ (sec.$^{-1}$) | $t$ (min.) | $\kappa \times 10^6$ (ohm$^{-1}$ cm.$^{-1}$) | $k_1' \times 10^5$ (sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | | 16′ 40″ | 2·454 | | 202 | 23·23 | |
| | | — | | | 3·659 | | | 3·498 |
| 6′ 50″ | 1·009 | | 30 | 4·290 | | 275 | 29·31 | |
| | | 3·754 | | | 3·639 | | | 3·494 |
| 9 | 1·327 | | 35 | 4·961 | | 326 | 33·04 | |
| | | 3·723 | | | 3·577 | | | 3·506 |
| 10 | 1·471 | | 45 | 6·258 | | 376 | 36·35 | |
| | | 3·838 | | | 3·578 | | | 3·497 |
| 11 | 1·619 | | 76 | 10·11 | | 402 | 37·92 | |
| | | 3·723 | | | 3·561 | | | 3·485 |
| 12 | 1·764 | | 90 | 11·76 | | 450 | 40·61 | |
| | | 3·934 | | | 3·693 | | | 3·514 |
| 14 | 2·067 | | 100 | 12·95 | | 491 | 42·72 | |
| | | 3·838 | | | 3·518 | | | 3·575 |
| 15 | 2·214 | | 177 | 20·92 | | 1477 | 63·27 | |
| | | 3·777 | | | 3·485 | | | — |
| | | | | | | ∞ | 66·09 | |

TABLE 6.

Apparent and true first-order constant for the methanolysis of t-butyl bromide at various concentrations at 298·25°.

| | | | | Velocity constant $\times 10^5$ (sec.$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|
| Run | $[\mathrm{HBr}]_\infty$ (mmoles/l.) | $f_0$ | $f_{\frac{1}{2}}$ | $k_0'$ | $k_{\frac{1}{2}}'$ | $f_0k_0'$ | $f_{\frac{1}{2}}k_{\frac{1}{2}}'$ |
| 35 (Mg) ............ | 0·365 | 0·9637 | 0·9913 | 3·802 | 3·506 | 3·664 | 3·474 |
| 40 (Al, Hg) ......... | 1·170 | 0·9350 | 0·9860 | 3·845 | 3·659 | 3·595 | 3·608 |
| 37 (Mg) ............ | 1·629 | 0·9223 | 0·9806 | 3·903 | 3·684 | 3·603 | 3·613 |
| 41 (Al, Hg) ......... | 66·51 | 0·615<br>±0·023 | 0·906<br>±0·057 | 5·60 | 4·086 | 3·44<br>±0·13 | 3·70<br>±0·24 |

Within the limits of accuracy of the data in the concentrated solution, there is no dilution effect when the initial concentration is varied by a factor of 182. This fact, and the constancy of $k_1$ over the complete course of reaction prove that the products of reaction exert no detectable effect on the velocity of chemical change. In this work, therefore, the necessity does not arise to invent hypotheses or to introduce a new terminology to explain the effect, on the rate of reaction, of the ions which the reaction produces. The corrected first-order constants for the reaction of t-butyl bromide with dry methanol at various temperatures are given in Table 7.

Little weight has been given to the first entry, which represents the results of a single experiment only. At each of the other temperatures, at least three concordant experiments were carried out. The empirical equation

$$\log_{10}k_1(\text{sec.}^{-1}) = 69{\cdot}9265 - 19{\cdot}354 \log_{10}T - 7899{\cdot}79/T \quad . \quad . \quad . \quad (21)$$

reproduces the observed velocity constants. It follows that

$$E_A = 36{,}147 - 38{\cdot}46T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The estimated error in the coefficient of $T$ is $\pm 5{\cdot}6$ cal. mole$^{-1}$ deg.$^{-1}$.

*t-Butyl Iodide.*—Commercial specimens of t-butyl iodide were purified by the method used with the other halides. Distillation without decomposition was carried out at 26·5°/46·5 mm.; the material had $n_D^{20} = 1{\cdot}49264$. Samples thus prepared remained colourless in glass-stoppered bottles in the dark for several weeks. After longer periods, however, iodine was produced, in quantities greatly exceeding what could be attributed to the enclosed oxygen. Some independent reaction clearly takes place slowly in the liquid phase, the initial step in which could be $\text{Bu}^t\text{I} \longrightarrow \text{Bu}^t + \text{I}$ or $\text{Bu}^t\text{I} \longrightarrow \text{Bu}^{t+} + \text{I}^-$. These possibilities and the bimolecular reaction $2\text{Bu}^t\text{I} \longrightarrow \text{Bu}^t{\cdot}\text{Bu}^t + \text{I}_2$ are being investigated in the liquid phase and in certain solvents. In dilute solution of the iodide in dry methanol, no trace of iodine was detected, analytically or visually, during the time required for complete etherification.

TABLE 7.

First-order velocity constants for the solvolysis of t-butyl bromide in dry methanol.

| $T$ (°K) | $k_1$ (sec.$^{-1}$) (Obs.) | $k_1$ (sec.$^{-1}$) (Calc.) | $T$ (°K) | $k_1$ (sec$^{-1}$). (Obs.) | $k_1$ (sec$^{-1}$). (Calc.) |
|---|---|---|---|---|---|
| 288·03 | $7{\cdot}93 \times 10^{-6}$ | $7{\cdot}741 \times 10^{-6}$ | 313·08 | $2{\cdot}460 \times 10^{-4}$ | $2{\cdot}469 \times 10^{-4}$ |
| 298·25 | $3{\cdot}604 \times 10^{-5}$ | $3{\cdot}599 \times 10^{-5}$ | 318·32 | $4{\cdot}640 \times 10^{-4}$ | $4{\cdot}660 \times 10^{-4}$ |
| | | | 326·33 | $1{\cdot}160 \times 10^{-4}$ | $1{\cdot}157 \times 10^{-4}$ |

TABLE 8.

t-Butyl iodide in dry methanol at 288·03°; $[\text{HI}]_0 = 0{\cdot}63$. $[\text{HI}]_\infty = 1{\cdot}97$ mmoles/l.

| $t$ (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.$^{-1}$) | $t$ (min.) | $\kappa \times 10^4$ (ohm$^{-1}$ cm.$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0 | 1·3716 | 12 | 1·390 | 70 | 1·473 | 240 | 1·676 |
| 1 | 1·373 | 14 | 1·393 | 80 | 1·487 | 260 | 1·696 |
| 1·5 | 1·374 | 16 | 1·396 | 100 | 1·512 | 285 | 1·720 |
| 3·5 | 1·377 | 19 | 1·401 | 120 | 1·538 | 305 | 1·739 |
| 4·5 | 1·379 | 22·9 | 1·406 | 140 | 1·563 | 349 | 1·781 |
| 5·5 | 1·380 | 25·9 | 1·411 | 160 | 1·586 | 375 | 1·797 |
| 7 | 1·383 | 28·9 | 1·415 | 180 | 1·610 | 395 | 1·812 |
| 8 | 1·384 | 33·9 | 1·423 | 200 | 1·633 | 450 | 1·851 |
| 9 | 1·386 | 37 | 1·427 | 220 | 1·655 | 480 | 1·870 |
| 10 | 1·387 | 40 | 1·432 | | | 501 | 1·881 |
| | | 50 | 1·446 | | | ∞ | 2·238 |

The data of Table 8 relate to conductivity measurements made in a Pyrex vessel. To a solution containing initially 0·63 mmole/l. of the products of reaction from a previous run was added sufficient t-butyl iodide to bring up the total concentration to 1·97 mmoles/l. From the calibration curve, the specific conductivity after 501 min.. indicates a concentration of 1·3 mmoles/l. of hydrogen iodide. Less than half of the observations are included in the Table, and the reaction has been followed in detail over the half-life. After allowance for the initial presence of hydrogen iodide, however, the run must be regarded as covering between 32 and 66% of the change possible had the initial concentration of solute been 1·97 mmoles/l.

The equivalent conductance at this temperature, obtained as described in a later section, is $\Lambda = 177{\cdot}5 - 8{\cdot}93c^{\frac{1}{2}}$. The initial value of $d\kappa/dt$, obtained from readings during the first 10 min., is $2{\cdot}65 \times 10^{-9}$ ohm$^{-1}$ cm.$^{-1}$ sec.$^{-1}$ and, since $\kappa_\infty - \kappa_0$ is $8{\cdot}665 \times 10^{-5}$ ohm$^{-1}$ cm.$^{-1}$, $k_0'$ becomes $3{\cdot}06 \times 10^{-5}$ sec.$^{-1}$. After 500 min., $k'$, found logarithmically or from the half-life

(385 ± 1 min.), is $(3{\cdot}00 \pm 0{\cdot}01) \times 10^{-5}$ sec.$^{-1}$. From equations (12)—(14), $f_{\frac{1}{4}} = 0{\cdot}959$, $f_{\frac{1}{2}} = 0{\cdot}982$, and $f_{\frac{3}{4}} = 0{\cdot}993$. By interpolation, the values of $f$ at 32% and 66% change are 0·967 and 0·990, respectively: hence $k_1$ is initially $2{\cdot}96 \times 10^{-5}$ and finally $2{\cdot}97 \times 10^{-5}$ sec.$^{1}$.

TABLE 9.

First-order velocity constants for the solvolysis of t-butyl iodide in dry methanol.

| $T$ (°K) | $k_1$ (sec.$^{-1}$) (Obs.) | $k_1$ (sec.$^{-1}$) (Calc.) | $T$ (°K) | $k_1$ (sec.$^{-1}$) (Obs.) | $k_1$ (sec.$^{-1}$) (Calc.) |
|---|---|---|---|---|---|
| 277·69 | $7{\cdot}06 \times 10^{-6}$ | $7{\cdot}123 \times 10^{-6}$ | 307·99 | $4{\cdot}140 \times 10^{-4}$ | $4{\cdot}192 \times 10^{-4}$ |
| 288·03 | $2{\cdot}97 \times 10^{-5}$ | $3{\cdot}222 \times 10^{-5}$ | 317·99 | $1{\cdot}309 \times 10^{-3}$ | $1{\cdot}305 \times 10^{-3}$ |
| 298·21 | $1{\cdot}258 \times 10^{-4}$ | $1{\cdot}258 \times 10^{-4}$ | 326·22 | $3{\cdot}141 \times 10^{-3}$ | $3{\cdot}117 \times 10^{-3}$ |

Table 9 shows that the mean value is 8% less than that calculated from the empirical equation:

$$\log_{10}k_1 = 64{\cdot}9881 - 17{\cdot}981 \log_{10}T - 7277{\cdot}58/T. \qquad (23)$$

For this reason, three further experiments were carried out at this temperature, with no hydrogen iodide initially present. They all confirmed this value. It is thus possible that the actual value of $-\mathrm{d}E_{\mathrm{A}}/\mathrm{d}T$ is greater than that represented in the equation:

$$E_{\mathrm{A}} = 33{,}330 - 35{\cdot}732T. \qquad (24)$$

Because of the relative slowness of the reaction at the lowest temperature recorded in the Table, values of $k_1$ were found chiefly from calculations at early stages of the reaction. With an initial concentration of 1·35 mmoles/l., for example, $k_1'$ at 277·69°K was found to be $7{\cdot}38 \times 10^{-6}$ sec.$^{-1}$. From the conductance equation $\Lambda = 150 - 73{\cdot}6c^{\frac{1}{2}}$, $f_0$ becomes 0·945, and $k_0 = 6{\cdot}97 \times 10^{-6}$ Duplicate runs gave values agreeing to within 2·5%. The lack of precision at the relatively low temperatures is probably connected with the inadequacy of the square-root law, or with errors in our conductance data.

*A Test of Walden's Rule applied to Strong Acids in Methanol.*—At the conclusion of each run, when a constant conductivity had been reached at temperature $t$, the cell was transferred to a thermostat kept at 25°, and the conductivity again measured. There thus accumulated much information on the temperature coefficient of the conductivity, particularly at temperatures above 25° where most of the runs were carried out. According to Walden,[15] the equivalent conductivity of most electrolytes varies inversely as the viscosity, $\eta$, of the solution. His rule, however, is known to be inapplicable to strong acids in water.[13] The temperature variation of $\Lambda$ is given experimentally by equation (25), where $\alpha$ is the coefficient of expansion

$$\mathrm{d}\ln\Lambda/\mathrm{d}T = \mathrm{d}\ln\kappa/\mathrm{d}T + \mathrm{d}\ln V/\mathrm{d}t = \mathrm{d}\ln\kappa/\mathrm{d}T + \alpha, \qquad (25)$$

of the solvent. According to Walden's rule

$$\mathrm{d}\ln\Lambda/\mathrm{d}T = -\mathrm{d}\ln\eta/\mathrm{d}T. \qquad (26)$$

From 12 experiments with the products of solvolysis of t-butyl chloride, bromide, and iodide at concentrations in the range 0·95—10·4 mmoles/l., we find the following values at 39·10°:

$$10^3\,\mathrm{d}\log_{10}\kappa/\mathrm{d}T = 5{\cdot}147 \pm 0{\cdot}045$$

$$10^3\,\mathrm{d}\log_{10}V/\mathrm{d}T = 0{\cdot}508 \pm 0{\cdot}008$$

$$\therefore\quad 10^3\,\mathrm{d}\log_{10}\Lambda/\mathrm{d}T = 5{\cdot}655 \pm 0{\cdot}053$$

The viscosities recorded by Thorpe and Rodger[16] yield the value $-10^3\mathrm{d}\log_{10}\eta/\mathrm{d}T = 5{\cdot}594 \pm 0{\cdot}009$. As far as this work can decide, therefore, Walden's rule is obeyed by hydrogen chloride, hydrogen bromide, and hydrogen iodide in methanol.

An example of its usefulness is to the conductivity of hydrogen iodide in methanol, for which independent data are not available. It is found in this work that $\Lambda = 204{\cdot}4 - 12{\cdot}6c^{\frac{1}{2}}$ at 25°. The value of $\Lambda_0$ exceeds the sum of the ionic mobilities[9] by 1·2 cm.$^2$ ohm$^{-1}$ mole$^{-1}$.

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[15] Walden, "Das Leitvermögen der Lösungen," Leipzig (1924).

[16] Landolt–Börnstein–Roth, "Physikalisch-chemische Tabellen," Springer, Berlin, 1914.

Equation (26) yields $\Lambda_0 = 177{\cdot}5$ at 14·87° and $A$, computed from equation (17), is 8·93, as used in the text.

## DISCUSSION

From the summarised data (Table 10) we note first that the relative rates of methanolysis of the t-butyl halides are in an order differing from that found for the hydrolysis of the methyl halides.[17] Secondly, for all the reactions examined, the apparent energy of activation, defined as $E_{\mathrm{A}} = \boldsymbol{R}T^2\,(\mathrm{d}\ln k_1/\mathrm{d}T)$, decreases as the temperature is raised. This effect appears to be a general one for unimolecular reactions in solution. One explanation offered [18] is that the number, $p$, of quantal oscillators and the number, $q$, of classical oscillators in the normal reactants are changed to $r$ and $s$, respectively, in the activated complex. Subject to the assumptions enumerated in the treatment, the equilibrium constant governing the conversion of normal reactants into activated complexes is:

$$K = \frac{n^*}{n} = \frac{\prod^{p}\,[2\sinh(\boldsymbol{h}\nu_p/2\boldsymbol{k}T)]\prod^{s}(\boldsymbol{k}T/\boldsymbol{h}\nu_s)}{\prod^{r}\,[2\sinh(\boldsymbol{h}\nu_r/2\boldsymbol{k}T)]\prod^{q}(\boldsymbol{k}T/\boldsymbol{h}\nu_q)}\cdot \mathrm{e}^{-\epsilon_{\mathrm{m}}/\boldsymbol{k}T} \quad . \;\; . \;\; . \quad (27)$$

when $n^*$ is the concentration of activated reactants and $n$ that of normal reactants. $\varepsilon_{\mathrm{m}}$ is the excess energy of the active reactants over that of the normal reactants, each in the hypothetical motionless state at the absolute zero of temperature. The observed energy of activation is

$$\varepsilon_0 = \varepsilon_{\mathrm{m}} + \sum^{r}(1/2)\boldsymbol{h}\nu_r - \sum^{p}(1/2)\boldsymbol{h}\nu_p \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (28)$$

Equation (27) consequently approximates to

$$K = (\boldsymbol{k}T/\boldsymbol{h}\bar{\nu})^{s-q}\cdot \mathrm{e}^{-\epsilon_0/\boldsymbol{k}T} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (29)$$

where

$$\bar{\nu} = \left(\prod^{s}\nu_s\Big/\prod^{q}\nu_q\right)^{\frac{1}{s-q}} \quad . \;\; . \;\; . \;\; . \;\; . \;\; . \;\; . \quad (30)$$

As the unimolecular constant, $k_1$, is simply $K\bar{\nu}$, we have

$$\ln k_1 = (q - s)\ln(\boldsymbol{h}/\boldsymbol{k}T) + (q - s + 1)\ln\bar{\nu} - \varepsilon_0/\boldsymbol{k}T, \quad . \;\; . \;\; . \quad (31)$$

which formally explains the effect if the empirical coefficient of $\ln T$ is identified with the number, $q - s$, of classical oscillators participating in the activation. With one exception, the mean frequencies found here lie near to the value of $1{\cdot}66 \times 10^{13}$ sec.$^{-1}$ found for the hydrolysis of methyl bromide.[19]

TABLE 10.

A summary of the kinetics of methanolysis.

$\log_{10}k_1\ (\mathrm{sec.}^{-1}) = a - b\log_{10}T - c/T.$

| | Bu$^t$Cl | Bu$^t$Br | Bu$^t$I |
|---|---|---|---|
| $a$ | 76·402 | 69·927 | 64·998 |
| $b$ | 21·905 | 19·354 | 17·981 |
| $c$ | 8424·7 | 7899·8 | 7277·6 |
| $(q - s)$ | 22 | 19 | 18 |
| $E_0$ (cal./mole) | 38,550 | 36,150 | 33,300 |
| $-\partial E_{\mathrm{A}}/\partial T$ (cal./mole-degree) | 43·53 ± 19 | 38·46 ± 5·6 | 35·73 ± 5·2 |
| $E_{\mathrm{A}}$ at 25° | 25,570 | 24,679 | 22,647 |
| $k_1$ (sec.$^{-1}$) at 25° | $8{\cdot}77 \times 10^{-7}$ | $3{\cdot}47 \times 10^{-5}$ | $1{\cdot}25 \times 10^{-4}$ |
| Relative $k_1$ | 1 | 40 | 143 |
| $\bar{\nu} \times 10^{-13}$ (sec.$^{-1}$) | 1·55 | 2·00 | 1·59 |
| $\Delta S^*$ (cal./mole-degree) at 25° | −3·76 | +6·35 | −2·26 |

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[17] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295.

[18] Johnson and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1940, *A*, **175**, 118.

[19] Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1940, *A*, **176**, 352.

The molar entropy of activation may be defined as the molar entropy of the activated complex less that of the normal reactants. From equation (29), we have

$$\Delta S^*/R = -(q - s)[1 + \ln (\boldsymbol{k}T/\boldsymbol{h}\bar{\nu})].$$

The resulting values for t-butyl chloride and iodide at 25° are negative, as could have been expected. t-Butyl bromide appears to be anomalous. If $\Delta S^\ddagger$ is computed from the equation [20]

$$k_1 = (\boldsymbol{k}T/\boldsymbol{h})\, e^{\Delta S^\ddagger/R}\, e^{-\Delta H^\ddagger/\boldsymbol{R}T} = (\boldsymbol{k}T e/\boldsymbol{h})\, e^{\Delta S^\ddagger/R}\, e^{-E_A/\boldsymbol{R}T} \quad . \quad . \quad . \quad (33)$$

the term $\Delta S^\ddagger$ at 298·16°K becomes 3·83 cal. mole$^{-1}$ deg.$^{-1}$ for the bromide, but is virtually zero for the chloride and iodide. The methanolysis of these halides would, according to the so-called absolute-rate theory, be regarded as normal. A disadvantage attaching to this seemingly convenient conclusion is the implication that, as the " entropy of activation " defined by equation (33) is zero, the free energy and heat of activation must be equal and independent of temperature, which is contrary to the facts.

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[20] Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1941.