297. *The Kinetics of the Hydrolysis of t-Butyl Chloride.*

By E. A. Moelwyn-Hughes.

The kinetics of the hydrolysis of t-butyl chloride in water has been measured conductimetrically. A drift in the apparent unimolecular constant has been quantitatively related to the interionic electrolyte effect, and the rate of chemical change is found to be strictly unimolecular over the complete reaction. Unimolecular constants at 0° and 25° are in reasonable agreement with those measured potentiometrically by Winstein and Fainberg. Those measured at intervening temperatures show that the energy of activation decreases as the temperature is raised. Hydroxyl ions have no effect on the rate, in agreement with the original observation by Hughes on the solvolysis of t-butyl chloride in mixed solvents.

The mechanisms of hydrolysis and substitution at a saturated carbon atom are briefly discussed in terms of hypotheses advanced in earlier papers of this series and in terms of the theory of Hughes and Ingold with which they are not in conflict.

The work described here was undertaken in order to compare the velocity and energy of activation of the hydrolysis of butyl chloride with the corresponding values for other alkyl halides,[1] particularly methyl chloride.[2] Although numerous papers have been published on the rates of reaction of t-butyl chloride with mixed solvents containing water,[3] only one attempt appears to have been made [4] to study the kinetics of its hydrolysis in water alone. The present results, obtained by the method of electrical conductivity, confirm and extend those obtained potentiometrically.

Experimental

Materials and Method.—(1) Purchased t-butyl chloride, proving to be grossly impure, was fractionally distilled, and the sample boiling at 50·5° retained. This was redistilled from anhydrous sodium sulphate, and the middle fraction (b. p. 50·3—50·4°) was used. It had n_D^{20} 1·38411; Timmermans [5] gives $n_{H\alpha}^{15}$ 1·38557.

(2) The Pyrex conductivity cells held 30—300 c.c., but in each the electrodes were at a

---

[1] Moelwyn-Hughes, *J.*, 1933, 1576.

[2] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295; 1953, *A*, **220**, 386; Heppolette and Robertson, *ibid.*, 1959, *A*, **252**, 273; and papers cited in Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1947.

[3] E. D. Hughes, *J.*, 1935, 255, and other papers cited by Ingold in " Structure and Mechanism in Organic Chemistry," Bell, London, 1953; Olson and Halford, *J. Amer. Chem. Soc.*, 1937, **59**, 2644.

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

[5] Timmermans, " Physicochemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

distance of 10 cm. apart. The neck of each cell was in the middle, and ended in a ground-glass stopper fitted with a mercury cup. The cell and a variable resistance in a 5-decade resistance box reading from 10^{-2} to 10^5 ohms were balanced in a circuit which included a Wien bridge R.C. oscillator tuned to 1000 cycles per second and a detector capable of dealing with a wide range of signal intensity. Cell constants, *C*, were determined by using 0·10043m-potassium chloride [6] of specific conductivity of 0·028849 ohm^{-1} cm.$^{-1}$ at 25°. Most of the runs were carried out in four cells, for which the *C* values were 0·9767, 2·679, 3·452, and 5·219 cm.$^{-1}$.

(3) In a typical run, conductivity water (~50 c.c.) was degassed and placed in a 100 c.c. glass-stoppered conical flask in the thermostat bath. After the water had reached a steady temperature, t-butyl chloride (about 0·05 c.c.) was added from a syringe; the solution was shaken and rapidly transferred to the cell. A stop-clock was started at the moment of mixing. In the fast runs, the procedure was to set fixed resistances on the box and read the time of balance. In the slow runs, resistances were measured at fixed times. The cells were first filled to overflowing, and the ungreased glass stopper forced in before the first reading was taken. Mercury was placed in the annular cup during the course of the run. To avoid heterogeneity, concentrations were not allowed to exceed 4 mmoles/l.

(4) All runs were followed to completion, *i.e.*, until the resistance was constant, and the contents of the cell were analysed. Owing to the escape of vapour on dissolution of the organic liquid, the superfluous solution left in the mixing flask contained considerably less solute than that in the cell. The concentrations of hydrogen ion and chloride ion, determined by the methods used with methyl chloride, proved to be equal. The specific conductivity κ of the completely hydrolysed solutions led to equivalent conductivities, Λ, which agreed, within the accuracy of the analysis, with the standard values,[6] as the following data at 25° show:

c (mmoles/l.)	3·04	3·81	8·75
$10^3\kappa$ (ohm^{-1} cm.$^{-1}$)	1·268	1·581	3·591
Λ (cm.^{2} ohm^{-1} mole^{-1})	417	415	411
Λ (McInnes)	418·0	416·7	412·6

The concentrations of hydrogen chloride in some of the later runs, particularly those followed in dilute solutions, were consequently obtained from the measured values of κ found after the cell had been transferred into a thermostat bath at 25°:

$$c = 10^6\kappa_\infty/\Lambda \qquad (1)$$

(5) The products of reaction were also analysed for olefins, by the method of Lucas and Eberz [7] and a slight modification of it, which dispensed with the evacuation and used glass-stoppered titration vessels with a controlled volume of air. The results were negative, but, because of the errors in the analytical method and the small concentrations involved, cannot be taken as conclusive evidence of the complete absence of an elimination reaction. Control experiments with saturated aqueous solutions of 2-methylbut-3-ene gave satisfactory results. Moreover, the product of solvolysis of t-butyl chloride at a concentration of 430 ± 2 mmoles/l. in equimolar methanol–water contained 25·8 mmoles/l. of olefin, indicating an elimination reaction of 6% of the total. A repetition with an initial concentration of 381 gave 27·1 mmoles/l. of olefin. In the mixed solvent, therefore, the percentage elimination is 6·6 ± 0·6%. If the same proportion were formed in pure water, the concentration of olefin would be about 0·26 mmole/l., which is beyond the analytical accuracy. Circumstantial evidence that the presence of olefin in pure water is improbable is provided by Lucas and Eberz,[7] who have shown that isobutene reacts to completion with water to give t-butyl alcohol in acid solution. On the whole, it seems highly probable that the reaction in water is simply $\mathrm{Bu^tCl} + \mathrm{H_2O} \longrightarrow \mathrm{Bu^tOH} + \mathrm{HCl}$.

RESULTS

Examples of results by the fast and the slow technique described above are given in Tables 1 and 2. They are both necessary to illustrate two characteristic features of the experiments, which are a gradual decline of from 1 to 4% in the apparent first-order constant

$$k_1' = \frac{1}{t}\ln\frac{\kappa_\infty - \kappa}{\kappa_\infty} \qquad (2)$$

---

[6] McInnes, "The Principles of Electrochemistry," Reinhold Publ. Inc., New York, 1939.

[7] Lucas and Eberz, *J. Amer. Chem. Soc.*, 1934, **56**, 460.

when the complete reaction has been followed, and the appearance of a false value of κ_0 when linear extrapolation of ln $(\kappa_\infty - \kappa)$ ignores the data obtained in the early stages of reaction.

The times listed in the first column of each Table are those from the moment when the stop-clock was started, which is as near as is possible to the instant of dissolution. A plot of $\log_{10} (\kappa_\infty - \kappa)$ derived from Table 1 against t (sec.), is strictly linear with a gradient of $-1{\cdot}2605 \times 10^{-3}$, indicating a constant value of $k_1' = 2{\cdot}904 \times 10^{-2}$ sec.$^{-1}$, in agreement with the separate values given in the Table. Equation 2 is seen to be obeyed from the time of the first reading, which corresponds to 67% reaction, to that corresponding to 99·1% reaction. The values in parentheses, which correspond to 99·5 and 99·9% change are ignored. The extrapolated value of $\log_{10} (\kappa_\infty - \kappa)$ is found to be $\bar{4}{\cdot}886$, which is seen to be greater than the true value by 0·021. The difference can be accounted for if a zero-time error of 1·66 sec. is allowed. With most of the fast runs, zero-time errors fell in the range ±2 sec., and were as often positive as negative.

TABLE 1.

Temp. = 298·20° K. [HCl] = 1·758 mmoles/l. C = 3·452 cm.$^{-1}$.

Time (sec.)	R (ohms)	$10^4\kappa$ (ohm^{-1} cm.$^{-1}$)	$10^2 k_1'$ (sec.$^{-1}$)	Time (sec.)	R (ohms)	$10^4\kappa$ (ohm^{-1} cm.$^{-1}$)	$10^2 k_1'$ (sec.$^{-1}$)
0	—	—	—	152	4770	7·238	2·91
40	7000	4·931	2·91	165	4751	7·266	2·89
65	5600	6·165	2·90	190	4731	7·297	(2·85)
78	5300	6·513	2·87	240	4714	7·323	(2·86)
90	5100	6·769	2·89	300	4710	7·330	—
100	5000	6·904	2·89	600	4709	7·331	—
126	4840	7·134	2·91	900	4709	7·331	—

The data of Table 2, on being similarly analysed, yield, not a constant, but a slowly changing, gradient. For simplicity, we shall analyse the results in two sections, (i) that between $t = 0$ and $t = 390$ sec., when c varies from 0 to 0·66 mmole/l., and (ii) that between $t = 390$ and $t = 5400$ sec., when c changes from 0·66 to 2·49 mmoles/l. In the first section the gradient affords a value of $k_1' = 7{\cdot}41 \times 10^{-4}$ sec.$^{-1}$, and an experimentally permissible zero-time error of 1·05 sec. In the second section, the gradient gives $k_1' = 7{\cdot}03 \times 10^{-4}$ sec.$^{-1}$, and an inadmissibly large zero-time error of 49·4 secs. There is thus a decrease of about 4·5% in k_1' as the reaction proceeds.

TABLE 2.

Temp. = 273·22° K. $[\text{HCl}]_\infty$ = 2·55 mmoles/l. C = 3·452 cm.$^{-1}$.

Time (sec.)	R (ohms)	$10^4\kappa$ (ohm^{-1} cm.$^{-1}$)	$k_1' \times 10$ (sec.$^{-1}$)	Time (sec.)	R (ohms)	$10^4\kappa$ (ohm^{-1} cm.$^{-1}$)	$k_1' \times 10$ (sec.$^{-1}$)
0	(822,800)	(0·041)	—	1210	8600	4·015	7·06
60	100,000	0·3452	7·37	1432	7800	4·426	7·03
195	36,000	0·9592	7·36	1580	7400	4·666	7·03
275	26,100	1·323	7·48	1765	7000	4·931	7·03
390	19,600	1·761	7·43	1932	6700	5·152	7·03
0	(147,500)	(0·234)	—	2075	6500	5·311	7·05
600	13,900	2·484	6·94	2400	6137	5·624	7·05
656	13,000	2·656	6·96	2700	5892	5·860	7·06
870	10,600	3·257	7·03	3000	5710	6·046	7·06
918	10,280	3·359	6·98	3600	5460	6·323	7·09
986	9800	3·523	6·99	4000	5353	6·449	7·06
1016	9600	3·596	7·00	5400	5159	6·691	7·01
1068	9300	3·712	7·00	∞	5047	6·841	—
1125	9000	3·858	7·07				

If the equivalent conductance, Λ, of hydrogen chloride in water were independent of its concentration, c, it could be concluded that the rate of chemical change also decreases as the reaction proceeds. Such, of course, is not the case, and the unimolecular constant, k_1, governing the chemical change is related to the apparent constant k_1' as follows:

$$k_1 = -\frac{d \ln (c_\infty - c)}{dt} = -\frac{d \ln (\kappa_\infty - \kappa)}{dt} \cdot \frac{d \ln (c_\infty - c)}{d \ln (\kappa_\infty - \kappa)} = k_1' f \quad . \quad . \quad (3)$$

To evaluate the function f, it will suffice to assume the validity of the limiting conductance law $\Lambda = \Lambda_0 - Ac^{\frac{1}{2}}$, although in fact a more elaborate equation is required to cover the complete run. Then

$$f = \left[1 - \frac{A}{\Lambda_0}\left(\frac{c_\infty^{\frac{3}{2}} - c^{\frac{3}{2}}}{c_\infty - c}\right)\right]\left[1 - \frac{3}{2}\frac{A}{\Lambda_0}\cdot c^{\frac{1}{2}}\right]^{-1} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For hydrogen chloride in water at 25°, $A/\Lambda_0 = 0{\cdot}0113$. Thus in a solution for which $c_\infty =$ 2·5 mmoles/l., f increases from an initial value of 0·982 to a final value of 1·028, *i.e.*, by 4·7%. For the same electrolyte at 0°, a theoretical estimate of A/Λ_0 based on Onsager's equation is 0·01056. At this temperature, f for a solution of the same concentration increases from 0·983 at $c = 0$ to 1·026 at $c = 2{\cdot}5$, *i.e.*, by 4·3%. That these corrections from conductivity data should lie so very close to the kinetic deviations may be to some extent fortuitous, because no allowance has been made for the presence of t-butyl alcohol. This effect, however, has been shown to be very small, and the magnitude and direction of change of the function f are consequently taken as firm evidence that the unimolecular velocity coefficient k_1 governing the hydrolysis of t-butyl chloride in water is in fact a true constant.

Effect of Added Electrolytes.—The results summarised in Table 3 show that there is a slight positive electrolyte effect, the gradient of $\log_{10} k_1/\mathrm{d}c$ being approximately 520 ± 20. Two theories which strive at a quantitative formulation of the salt effect in reactions of this type have been critically compared and found to be almost equally adequate.[8] The Table also shows that alkali at concentrations exceeding that of the reactant has no effect on the rate of hydrolysis. The result is similar to that first found by E. D. Hughes [3] for the first-order constant governing the solvolysis of t-butyl chloride in mixed solvents.

Effect of Temperature.—The temperature effect cannot be summarised in the form of the integrated equation of Arrhenius, $k_1 = A \exp(-E_A/\boldsymbol{R}T)$, but is adequately reproduced (Table 4) by the equation:

$$\log_{10} k_1 \text{ (in sec.}^{-1}) = 280{\cdot}870 - 91{\cdot}586 \log_{10} T - 16631{\cdot}75/T \quad . \quad . \quad . \quad (5)$$

It follows that the apparent energy of activation, defined as $-\boldsymbol{R}[\mathrm{d} \ln k_1/\mathrm{d}(1/T)]$, is

$$E_A \text{ (cal./mole)} = 76{,}102 - 182T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In this respect the hydrolysis of t-butyl chloride resembles that of methyl chloride and the other methyl halides. According to equation (5), k_1 at 0° and 25° are $6{\cdot}94 \times 10^{-4}$ and $2{\cdot}91 \times 10^{-2}$ sec.$^{-1}$ respectively, which differ by only a few per cent from the values of $7{\cdot}27 \times 10^{-4}$ and $2{\cdot}70 \times 10^{-2}$ found by Winstein and Fainberg.[4] At the mid-point of this temperature range, their data give $E_A = 23{,}400$ cal. mole^{-1}, which again differs little from the value of 24,112 given by equation 6. If, however, we accept the empirical equation used by them, their E_A value would appear to be 23,790, which is in closer agreement with the present value. Their data at the two temperatures used are thus, on the whole, fully corroborated.

TABLE 3. *The effect of dilution and of added electrolytes at* 292·90° K.

[Bu^{t}Cl]	Electrolyte	[Electrolyte] (mmole/l.)	Mean $k_1 \times 10^2$	Standard error
0·64	None		1·4460	0·0114
1·06	,,		1·4675	0·0036
3·91	,,		1·4637	0·0082
4·08	,,		1·4959	0·0072
4·36	HCl	8·75	1·5173	0·0060
4·46	NaOH	13·5	1·4817	0·0037
2·04	KCl	100·0	1·6749	0·0135

TABLE 4. *Observed and calculated unimolecular constants for the hydrolysis of t-butyl chloride in water.*

Temp. (°K)	273·22°	281·33°	287·01°	292·90°	298·20°
$10^4 k_1$ (sec.$^{-1}$): obs.	7·02	27·3	64·9	148	292
eqn. (5)	6·984	27·38	64·97	147·8	292·1

---

[8] Nash and Monk, *J.*, 1955, 1899.

The values of k_1 and E_A found by Heppolette and Robertson [2] for the hydrolysis of methyl chloride lie approximately midway between the two values published by the present author. As their method is probably more accurate than his, their results are here accepted. They lead to the comparison summarised in Table 5. t-Butyl chloride is seen to be hydrolysed faster than methyl chloride by a factor of at least 10^6. To attribute the observed ratio entirely to a difference in activation energies would require the difference to be 8312 cal./mole. Thus the change in k_1 is due in roughly equal measure to a change in E_A and to a change in those terms which correspond to the first constant A of the integrated equation of Arrhenius.

TABLE 5. *Comparison of the rates and energies of activation for the hydrolysis of methyl and t-butyl chloride.*

Solute	k_1 at 298·16° K (sec.$^{-1}$)		E_A at 298·16° K (cal./mole)	
MeCl	$2 \cdot 35 \times 10^{-8}$	Ratio = $1 \cdot 24 \times 10^6$	26,562	Difference = 4725
Bu^{t}Cl	$2 \cdot 91 \times 10^{-2}$		21,837	

DISCUSSION

(1) *Hydrolysis.*—The unimolecular constants, k_1, of uncatalysed reactions which have been accurately examined in aqueous solutions can usually be represented by equations of the form:

$$\log_{10} k_1 = a_1 - b_1 \log_{10} T - c_1/T$$

They include the hydrolysis of methyl fluoride,[9] the remaining methyl halides,[2] methyl nitrate,[10] and methylene dichloride,[11] and the following reactions not generally regarded as hydrolyses: the mutarotation of α-xylose, α-mannose, α-glucose, and α-lactose; [12] the decarboxylation of trichloroacetic acid, tribromoacetic acid, and trinitrobenzoic acid; [13] and the decomposition of benzenediazonium chloride.[14] The average value of b_1 for the hydrolyses is 26·6, indicating that the heat capacity of the activated complex is less by about 53 cal. mole^{-1} degree^{-1} than that of the reactants in their normal state. In the equation independently adopted by Pitzer [15] and the writer [16] to express the temperature variation of the ionisation constant of numerous weak electrolytes in water,

$$\log_{10} K = A - B \log_{10} T - C/T$$

the term B has an average value of about 20·6, indicating that the sum of the C_P terms for the products of ionisation is less than that for the un-ionised molecule by about 41 cal. mole^{-1} degree^{-1}. Both b_1 and B have been interpreted in terms of the freezing-in of certain degrees of freedom of the water molecules.[17] Since ΔC_P for the fusion of ice at 25° C is about 8·1 cal. mole^{-1} degree^{-1}, the activation of solutes during hydrolysis and the ionisation of weak electrolytes could be ascribed to the freezing-in of between 5 and 7 molecules of liquid water. There are, of course, many other factors to be reckoned with and different explanations discussed in the papers cited [2,3] are possible. This crude method suffices to emphasise the analogy between the unimolecular hydrolysis of solutes in water and the process of ordinary ionisation. The principal difference between them

---

[9] Glew and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **211**, 254.

[10] McKinley-McKee and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247.

[11] Fells and Moelwyn-Hughes, *J.*, 1958, 1326.

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

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

[14] Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, 1940, **36**, 948.

[15] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

[16] Moelwyn-Hughes, *Trans. Faraday Soc.*, 1938, **34**, 91.

[17] Ulich, *Z. Elektrochem.*, 1930, **36**, 497.

is that only the anion formed in the primary process is present in solution at the end of a hydrolytic change, whereas both anion and cation are present after the establishment of an ionisation equilibrium. Since the hydrolyses hitherto examined show no trace of consecutive reactions, it is to be inferred that the cation initially formed in hydrolytic reactions reacts rapidly with water. This conclusion,[2] it will be appreciated, is precisely that drawn from evidence of quite a different nature by Hughes and Ingold.[3] An upper limit to the half-life of the t-butyl ion can be estimated from the results given here, since the method is sensitive enough to have detected a consecutive change if it were 100 times faster than the first change. At 25° C, therefore, the half-life of the ion cannot exceed 0·2 sec.

(2) *Substitution.*—In aqueous solutions of methyl and ethyl halides containing reactive ions[18] such as $S_2O_3^{2-}$ or OH^-, the unimolecular hydrolysis $RX + H_2O \longrightarrow ROH + H^+ + X^-$ is accompanied by the bimolecular substitution $RX + Y^- \longrightarrow RY + X^-$. In aqueous solutions containing moderate concentrations of hydroxyl ions, however, the substitution reaction $Bu^tCl + OH^- \longrightarrow Bu^tOH + Cl^-$ does not occur. This result fully confirms for the reaction in water the effect first noted by E. D. Hughes[3] for the same solute in ethanol–water and in acetone–water mixtures. The energy of activation of such substitutions has not yet been satisfactorily evaluated, but it is thought to consist of a number of components, among which is the energy required to overcome the intrinsic repulsion between the ion and the molecule when they are in the close contact necessary for reaction. It is natural to expect this energy to be much greater for the pair OH^-, Bu^tCl than for the pair OH^-, MeCl, and the velocity of substitution reaction may become so small as to be negligible. This is the plausible interpretation of the steric effect given by Hughes and Ingold.[3] In the present example, even if the velocity of the reaction $Bu^tCl + OH^- \longrightarrow Bu^tOH + Cl^-$ were to be no slower than that of the reaction $MeCl + OH^- \longrightarrow MeOH + Cl^-$, it would still be many hundreds of times too slow to affect the net rate of reaction by a few per cent.

Another explanation of the effect may be given in terms of the idea of partial desolvation. If one water molecule of the four that are attached to the hydroxyl ion has to be removed before the ion can effect substitution, a lower limit to the energy of activation is automatically set, irrespective of the facility with which the carbon–halogen bond is broken.

The author is indebted to Mr. G. G. Yates of the Cavendish Laboratory for designing the circuit.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, October 5th,* 1960.]

---

[18] Moelwyn-Hughes, *J.*, 1933, 1576; Nielsen, *J. Amer. Chem. Soc.*, 1936, **58**, 206; Moelwyn-Hughes, *J.*, 1938, 779; *Proc. Roy. Soc.*, 1949, *A*, **196**, 540.