354. *The Hydrolysis of t-Butyl Chloride in Water: Temperature-dependence of the Energy of Activation* *

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This Paper reports the results of a careful determination of the temperature-dependence of the rate of hydrolysis of t-butyl chloride in water at 1° intervals between 0 and 20°.

This work was initiated to check the large difference between the value of the temperature coefficient of the energy of activation reported by Moelwyn-Hughes [1] for this reaction and the average value of the coefficients found so far for the hydrolysis of all other halides.[2]

Experimental

Rate determinations involved an adaptation of the normal conductance method to the problem of measuring rates having a half-life from 45—900 sec. To meet this requirement two experimental problems had to be solved: (1) that of introducing the halide into the solution and achieving a homogeneous solution with a minimum disturbance of temperature equilibrium; (2) a method for recording changing conductance–time data. The first problem was solved by use of a 500 ml. reaction vessel (Figure) with a magnetic stirrer. This was supported in the bath in a frame above a rotating magnet. Before it was put in the bath, about 0·05 g. of halide was frozen in C and the system evacuated with stirring. Tap A was closed and the vessel permitted to come to the temperature of the thermostat for an arbitrary time of one hour.

To initiate a run, the cut-off tap B was opened permitting the halide to pass quickly into the solution from the vapour phase. After stirring for 60—75 seconds, taps A and D were opened; stirring was discontinued and the solution was forced into the cell by applying a slight positive pressure. During runs with a $t_{\frac{1}{2}} < 100$ seconds the stirring was continued throughout the entire experiment. An internal valve (E) consisting of a ground glass bead resting on a ground glass seat isolated the solution in the cell from the bulk. The need for this cut-off was not proven.

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* Issued as N.R.C. No. 8293.

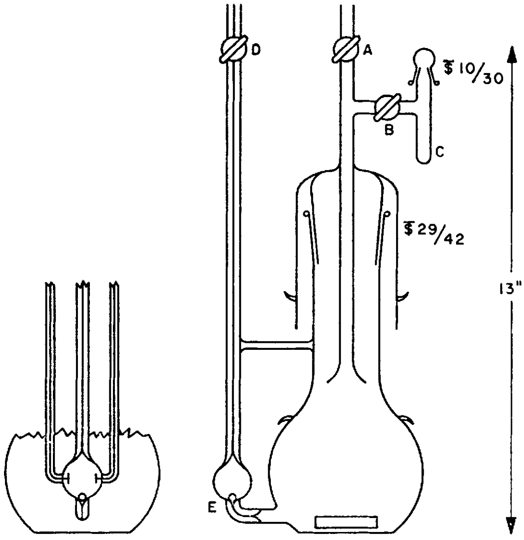
[1] E. A. Moelwyn-Hughes, *J.*, 1961, 1517.

[2] R. E. Robertson, R. L. Heppolette, and J. M. W. Scott, *Canad. J. Chem.*, 1959, **37**, 803.

The change in conductance with time was followed by an A.C. bridge of the Janz and McIntyre type[3] but using a Leeds and Northrup 5-decade resistance box rather than General Radio components. Each dial of the latter was modified by the addition of a modified L. and N. 31–3–01 Thermocouple switch which permitted any reading to be recorded on 5 lines of a 11-figure 565A Hewlett-Packard Digital Recorder.

Registration of time to 0·1 sec. could not be done directly because the digital electronic clock could not be stopped during the printing cycle. Accordingly a slave clock was so arranged that it would store any given time indication during the printing cycle (0·2 sec.) and " catch-up " to the master clock on release (see ref. 4). On visual indication of balance on an oscilloscope, corresponding time and resistance values were printed by depressing a micro-switch controlling the recorder. This step could have been automated but since capacity and presetting of resistance values were manually controlled, such automation offered no particular advantage.

After initiation the first series of points are taken at intervals of 4 sec. or longer during the first half-life. After the passage of one or two half-lives a second set of points is recorded over the same time as covered in the primary series. These latter resistance readings were then plotted against time on a sufficiently large graph and the resistance values read off the graph at the times of the primary series. Since the total change in resistance during the secondary series is small compared with the changes in the primary series, such an interpolation method does not introduce a significant error. Rate data were then calculated by plotting $\log [(1/R)_{t+\alpha} - (1/R)_t)]$ against time.



t-Butyl chloride (reagent grade) was purified by passage through alumina for absorption and shown to be kinetically pure. This purified sample was shielded from light and kept in a dry box at low temperature. The containers were brought to room temperature before removing aliquot portions.

Water.—The solvolysing medium was distilled water used without the addition of backing electrolyte.

Temperature control was to within ±0·002° or better, as measured on a Meyers platinum resistance thermometer in conjunction with a Leeds–Northrup 8069 Mueller Bridge.

RESULTS

In Table 1 are given all the rate data (with the exception of one run at 15°) for an initial concentration of about 0·001M. At the end of the series a new sample of t-butyl chloride was

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[3] G. J. Janz and J. D. E. McIntyre, *J. Electrochem. Soc.*, 1961, **108**, 272.

[4] B. Weston, unpublished work.

prepared and the rate determined at 12°. The rate constant was found to be identical with the earlier determination ($4{\cdot}82_9 \times 10^{-3}$ sec.$^{-1}$). No allowance has been made for the decrease in the equivalent conductivity attending the reaction. Application of equations used in earlier work[1] show that this may affect the rate constant by as much as 0·6% over the whole run, but the actual effect over the region examined is considerably less. Omission of this factor has a negligible effect on the temperature coefficient.

TABLE 1

Average rate data for solvolysis of t-butyl chloride in water

Temp.	10^3k (sec.$^{-1}$) (obs.*)	10^3k (sec.$^{-1}$) (calc.)	Temp.	10^3k (sec.$^{-1}$) (obs.*)	10^3k (sec.$^{-1}$) (calc.)
1·008°	0·8418 ± 0·0016	0·8397	11·012	4·145 ± 0·001	4·143
2·014	0·9925 ± 0·0019	0·9935	12·025	4·829 ± 0·007	4·826
3·010	1·174 ± 0·002	1·171	13·016	5·602 ± 0·009	5·594
4·009	1·379 ± 0·001	1·380	14·020	6·491 ± 0·012	6·486
5·015	1·618 ± 0·005	1·624	15·016	7·488 ± 0·012	7·501
5·961	1·896 ± 0·002	1·890	16·010	8·667 ± 0·007	8·659
7·029	2·241 ± 0·002	2·239	17·006	9·964 ± 0·035	9·984
8·016	2·609 ± 0·002	2·614	18·012	$11{\cdot}54_0 \pm 0{\cdot}02_7$	11·51
9·019	3·051 ± 0·007	3·055	19·008	$13{\cdot}23_8 \pm 0{\cdot}03_8$	13·23
10·023	3·569 ± 0·002	3·564	20·013	$15{\cdot}19_4 \pm 0{\cdot}03_9$	15·21

* Average rates for 3 consecutive determinations.

These data have been fitted by the method of least squares to an equation of the form

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

where a, b, and c are empirical constants and T is the absolute temperature.

The result is

$$\log_{10} k_1(\text{sec.}^{-1}) = 134{\cdot}490 - 40{\cdot}92755 \log_{10} T - 10359{\cdot}0955/T \qquad (2)$$

The close agreement between the observed velocity constants and those reprodued by this equation is shown in Table 1. At 14·85°, a temperature at which Clarke, Williams, and Taft[5] have summarized previous results, the calculated rate is $7{\cdot}32 \times 10^{-3}$ sec.$^{-1}$.

The apparent, or Arrhenius, energy of activation, defined by the equation,

$$E_A = \boldsymbol{R}T^2 \left(\frac{\mathrm{d} \ln k_1}{\mathrm{d}T}\right)_P \qquad (3)$$

becomes

$$E_A = 2{\cdot}302585\, \boldsymbol{R}c - b\boldsymbol{R}T \qquad (4)$$

where $\boldsymbol{R} = 1{\cdot}9872$ cal./mole-degree. Using the constants of equation (2), we have

$$E_A(\text{cal./mole}) = 47{,}400{\cdot}1 - 81{\cdot}3312\, T \qquad (5)$$

Then

$$\left(\frac{\mathrm{d}E_A}{\mathrm{d}T}\right)_P = \Delta C_P{}^* = -b\boldsymbol{R} = -81{\cdot}33$$

The value of $-\Delta C_P{}^*$, though cinsiderably less than the earlier estimate, is still significantly greater than $-\Delta C_P{}^*$ for methyl chloride (44·47 cal. mole-degree).

Hitherto, we have used no hypothesis. We may now, in the first place, adopt Herzfeld's expression ($\boldsymbol{k}T/\boldsymbol{h}$) for the pre-exponential term in the Arrhenius equation, and following Glasstone, Laidler, and Eyring,[6] write

$$\boldsymbol{k}_1 = (\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta F^{\ddagger}/\boldsymbol{R}T) \qquad (6)$$

where $\boldsymbol{k}$ and $\boldsymbol{h}$ are the constants of Boltzmann and Planck, respectively, and $\Delta F^{\ddagger}$ is defined as a free energy of activation. The heat of activation becomes

$$\Delta H^{\ddagger} = E_A - \boldsymbol{R}T \qquad (7)$$

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[5] G. A. Clarke, T. R. Williams, and Robert W. Taft, *J. Amer. Chem. Soc.*, 1952, **84**, 2292.

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

and the increase in heat capacity attending activation is now

$$\left(\frac{\mathrm{d}\Delta H^{\ddagger}}{\mathrm{d}T}\right)_P = \Delta C_p{}^{\ddagger} = \Delta C_p{}^{*} - \boldsymbol{R} \tag{8}$$

According to this convention, the entropy of activation is defined as

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T} = \boldsymbol{R} \ln \left(\frac{k_1 \boldsymbol{h}}{\boldsymbol{k}T}\right) + \frac{E_A}{T} \tag{9}$$

In the second place we may use an approximate statistical expression [7]

$$k_1 = \bar{\nu}(\boldsymbol{k}T/\boldsymbol{h}\bar{\nu})^{s-q}e^{-E_0/\boldsymbol{k}T} \tag{10}$$

where $q - s$ is the number of classical oscillators participating in the activation, $\bar{\nu}$ is a mean frequency derivable from the constant a of equation (1), and E_0 is the energy of activation at zero temperature. In the present reaction $(q - s) = 41$, and $\bar{\nu} = 1{\cdot}91 \times 10^{13}$ sec.$^{-1}$. The difference between the entropy of the activated complex and that of normal reactants, according to this formulation, is

$$\Delta S^{*} = -\boldsymbol{R}(q - s)[1 + \ln(\boldsymbol{k}T/\boldsymbol{h}\bar{\nu})] \tag{11}$$

Kinetic parameters for the hydrolysis of t-butyl chloride derived by both methods are given in Table 2. Values in parentheses are from the earlier work.

TABLE 2

Kinetic parameters for the hydrolysis of t-butyl chloride in water

	At 12·5°	At 25·0°
10^3k_1 (sec.$^{-1}$)	5·18 (5·33)	31·2 (29·1)
E_A (cal./mole)	24,167 (24,111)	23,150
$\Delta H^{\ddagger}$	23,599	22,555
$\Delta C_p{}^{*}$ (cal./mole-deg.)	−81·3 (−182)	−81·3
$\Delta C_p{}^{\ddagger}$,,	−83·3	−83·3
ΔS^{*} ,,	13·2	9·7
$\Delta S^{\ddagger}$,,	13·7	10·2

DISCUSSION

The value of $\mathrm{d}(\Delta E_A/\mathrm{d}T)_P$ found here is less negative than that previously reported by one of us,[1] but confirms this earlier indication that solvent reorganization about the t-butyl chloride at the transition state for hydrolysis in water is significantly different from that about the primary and secondary halides. The nature and magnitude of this difference appear to require changes in the traditional concept of solvent reorganization and transition state solvation. Two questions are of particular interest: (1) What is the source of the large negative temperature coefficient for such ionogenic reactions? (2) Why should this coefficient be more negative for solvolytic displacement reactions involving a tertiary than for a primary or secondary halide? The authors have not approached these questions from the same point of view. The interpretation of E. A. Moelwyn-Hughes is based on Papers published since 1938,[8,9] that of R. E. Robertson on these and on conclusions drawn from more recent work.[10,11] Rather than attempt to reach finality or to dilute our complementary hypotheses so as to make differences disappear, it was thought to be of greater value to state, briefly, these individual opinions as such.

Moelwyn-Hughes considers first the interaction energy, ϕ_{12}, between one solvent molecule and the solute molecule, and the interaction energy, ϕ_{11}, between neighbouring solvent molecule. As 3 out of 4 of the solvent–solvent contacts are in the shell of the c solvent molecules round the solute (or round the relevant part of it), the main part of the potential

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[7] E. A. Moelwyn-Hughes, " The Kinetics of Reactions in Solution," 2nd end., Oxford, 1947.

[8] E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, 1938, **34**, 91.

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

[10] R. L. Heppolette and R. E. Robertson, *J. Amer. Chem. Soc.*, 1961, **83**, 1834.

[11] R. E. Robertson, *Soumen Kemistilehti*, 1960, *A*, **33**, 63.

energy of the solute–solvent cluster is $u = c\phi_{12} + (3/4)c\phi_{11} = c[\phi_{12} + (3/4)\phi_{11}]$. A similar expression, with all the symbols starred, holds for the potential energy, u^*, of the cluster in the activated state. The energy of activation, E, thus contains the term $(u^* - u)$. There is experimental evidence, quantitatively established for the hydrolysis of methyl bromide, that u^* is approximately constant, independent of temperature. If that is true generally $\mathrm{d}E/\mathrm{d}T$ is effectively $-(\mathrm{d}u/\mathrm{d}T)$. This means that the variation, with respect to temperature, of the energy of activation is due principally to the variation, with respect to temperature, of the ground energy levels of the reactants. In reactions involving ions, it may well be that c^* is less than c, indicating partial desolvation in the critically active complex. In solvolysis, on the other hand, it may be assumed that c^* and c are equal, and the energy of activation arises from the difference in the magnitude and nature of the ϕ terms. For example, ϕ in the ground state may be due to the electrostatic interaction of the dipoles of the solute and solvent molecules, while ϕ^* may arise from the electrostatic interaction of the dipoles of the solvent molecules with localised charge elements in the solute molecule. Since all ϕ's are complicated functions of distances, angles of inclination, and polarities, a formal treatment is impossible. A simplified approximation is possible if each ϕ is regarded as dependent only on the intermolecular distance, a, for, in that case, the contribution to $\mathrm{d}E/\mathrm{d}T$ becomes

$$-c\left[\frac{\mathrm{d}\phi_{12}}{\mathrm{d}T} + \left(\frac{3}{4}\right)\frac{\mathrm{d}\phi_{11}}{\mathrm{d}T}\right]$$

Let us further assume that $\phi_{12} = -B_{12}/a_{12}^{n_{12}}$ and $\phi_{11} = -B_{11}/a_{11}^{n_{11}}$. Then $\mathrm{d}E/\mathrm{d}T$ contains the term

$$-c\left[n_{12}\frac{B_{12}}{a_{12}^{n_{12}}}\frac{\mathrm{d}\ln a_{12}}{\mathrm{d}T} + \frac{3}{4}n_{11}\frac{B_{11}}{a_{11}^{n_{11}}}\frac{\mathrm{d}\ln a_{11}}{\mathrm{d}T}\right]$$

which is negative, and of the correct order of magnitude. The last term in this expression is approximately $-(3/8)cn_{11}L_1\alpha$, where L_1 is the heat of vaporization and α_1 the cofficient of isobaric expansion of the solvent.

The pre-exponential term in the Arrhenius equation, may, like the activation energy, be a function of temperature. If, for example, it is a relaxation frequency, varying inversely as the viscosity, the apparent energy of activation will contain the term $B = -\boldsymbol{R}T^2(\mathrm{d}\ln\eta/\mathrm{d}T)$, and $\Delta C_P{}^*$ will contain the term $\mathrm{d}B/\mathrm{d}T$, which is negative, and becomes less negative as the temperature is raised. This effect diminishes, without removing, the difference between the $\Delta C_P{}^*$ values of primary and tertiary halides, as may be seen from the following comparison:

$(CH_3)_3CCl$ at 12·5°	CH_3Cl at 87·5°
$\Delta C_p{}^* = -81{\cdot}3$	$\Delta C_p{}^* = -44{\cdot}5$
$\frac{\mathrm{d}B}{\mathrm{d}T} = -41{\cdot}2$	$\frac{\mathrm{d}B}{\mathrm{d}T} = -11{\cdot}6$

As a basis for developing a working hypothesis, Robertson begins with the concept of the solute surrounded by an initial state solvation shell.[12–14] When a neutral molecule such as t-butyl chloride is dissolved in water, the presence of the solute interferes with the dynamic interchange of hydrogen bonds characteristic of bulk water, an effect which is greatest at low temperatures and decreases as temperature rises. Because solute–solvent interaction is relatively unimportant in such solutions and water–water interaction is enhanced, this description resembles the iceberg hypothesis of Frank and Evans.[13] This picturesque term emphasizes the necessity of breaking down the initial state of solvation shell in the activation process of such ionogenic reactions. The difference between the S_N1 and S_N2 mechanism appears to lie (as has long been recognized) in the different paths

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[12] D. D. Eley, *Trans. Faraday Soc.*, 1944, **40**, 184.

[13] H. C. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507.

[14] D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **211**, 254.

by which this disorganization is initiated, and the difference in the number of water molecules involved.

Primary and secondary halides require some degree of nucleophilic interaction to achieve a critical charge level on the anion

$$\left.\begin{array}{c}\text{Water–water interaction}\\ \text{in the initial state}\\ \text{solvation shell}\end{array}\right\} \begin{array}{l} \xrightarrow{S_N1} \left\{\begin{array}{l}\text{Water–cation}\\ \text{interaction in the}\\ \text{transition state}\end{array}\right. \qquad (12a) \\[2em] \xrightarrow{S_N2} \left\{\begin{array}{l}\text{Water–anion}\\ \text{interaction in the}\\ \text{transition state}\end{array}\right. \qquad (12b)\end{array}$$

such that equation (12*b*) will be satisfied. Beyond this condition no important increase in free energy is required, bond making and breaking proceeding concurrently to give products. Part of the free energy of activation will be that required to break down the initial state solvation shell. According to our interpretation, it is the temperature-dependence of this part which is an important factor in determining the negative temperature coefficient of $\Delta H^\ddagger$.

It is recognized that t-butyl chloride hydrolysing in a medium such as water does not require or permit nucleophilic interaction for activation. Presumably the critical condition will be similar to that for the S_N2 mechanism, but there must be a break-down of initial state solvent shell about the cation as well as about the anion. Critical charge level will be reached on the latter first as a consequence of favourable collision, and anion-water interaction may be assumed to facilitate achievement of the critical condition of (eqn. 12*a*). In the S_N1 mechanism, the same work will be required to break down the corresponding initial state solvation shell about the developing anion as for the primary and secondary halides, and this will have the same temperature coefficient, *i.e.*, $\Delta C_p^\ddagger = -50$ cal./mole deg., approximately, a value some -30 cal./mole deg. less negative than observed (Table 2).* It is consistent with the above hypothesis to assume that this negative increment to $\Delta C_p^\ddagger$ arises from the necessity of breaking down the initial-state solvation shell in whole or in part about the t-butyl group. Since the value of $\Delta C_p^\ddagger$ for primary and secondary halides does not show any systematic dependence on the size of the cationic moiety, we conclude that the S_N2 mechanism does not impose the same requirement. Alternatively, nucleophilic interaction may replace one form of water–water interaction by another.

Since the forming t-butyl ion is larger than the Cl^-, it is in accord with accepted ideas that charge development at the transition state on Cl^- will be greater in this S_N1 reaction than for a corresponding displacement by an S_N2 mechanism, a situation which might be described as electrophilic displacement of the quasi-cation by water. Equation (12*a*) does not imply, as is frequently assumed, that exothermic-solvation of the forming cation will have occurred at the transition state, and this deduction is consistent both with the large positive shift in entropy of activation ($\Delta S^\ddagger$) found for the hydrolysis of the t-butyl chloride compared to the corresponding value of $\Delta S^\ddagger$ for isopropyl chloride,[2] with the more negative heat capacity of activation ($\Delta C_p^\ddagger$) reported here, and with the differences in the secondary deuterium isotope effects in the two systems.[15,17] With the collapse of the solvation shell about the forming t-butyl ion (rather than about the anion in the S_N2 mechanism), the

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* The corresponding value for t-pentyl chloride is -93 cal. mole deg.[16]

[15] K. T. Leffek, R. E. Robertson, and S. Sugamori, *Chem. and Ind.*, 1961, 259.

[16] K. T. Leffek, R. E. Robertson, and S. Sugamori, unpublished work.

[17] L. Hakka, A. Queen, and R. E. Robertson, to be published.

reaction will proceed to products without requiring any further increase in free energy of activation.

In summary, the large negative heat capacity of activation which characterizes ionogenic reactions in water is related to the temperature dependence of the work required to break down the initial state solvation shell; the more negative value observed for the hydrolysis of the t-butyl chloride (S_N1) compared with the average for primary and secondary halides (S_N2) is attributed to the larger number of water–water bonds to be broken about the forming cation in the S_N1 mechanism.

We acknowledge the assistance of Mr. G. Charette of the National Research Council Pure Chemistry Electronic shop for the construction of electronic devices.

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[*Received, June* 29*th*, 1964.]