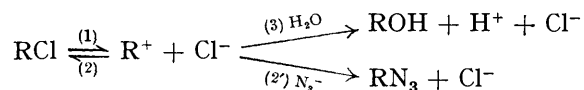**472.** *Mechanism of Substitution at a Saturated Carbon Atom. Part XXXV.* Effect of Temperature on the Competition between Unimolecular Solvolytic and Non-solvolytic Substitutions of Di-p-tolylmethyl Chloride. Activation in the Fast Step of Unimolecular Non-solvolytic Substitution.*

By Audrey R. Hawdon, E. D. Hughes, and C. K. Ingold.

In continuation of previous work directed to the determination of the kinetic characteristics of the separate processes involved in the unimolecular mechanism of nucleophilic substitution, an attack has been made on the question of whether the immeasurably fast processes have finite energies of activation. Theory suggests that the union of oppositely charged ions should be activated, though the cation–solvent reaction might not be. It has been shown in the case experimentally studied that the combination of a carbonium ion with an anion has an energy of activation. Di-p-tolylmethyl (pp'-dimethylbenzhydryl) chloride has been allowed to undergo solvolysis in aqueous acetone in the presence of sodium azide, and the ratio of the rates at which the ditolylmethyl azide and the ditolylmethanol appear has been measured as a function of temperature. An application of the Arrhenius equation to these results shows that the energy of activation of the ionic association exceeds that of the cation–water reaction by 4·0 kcal./g.-mol., and therefore must have at least this value.

THE study of salt effects in nucleophilic substitutions, both solvolytic and non-solvolytic, was developed in our former group of papers (*J.*, 1940, 960 *et seq.*), not only in order to diagnose mechanism, but also for the purpose of building up a picture of the unimolecular mechanism, notably with respect to those of its component processes, which, because they are fast, cannot be kinetically isolated.

A preliminary explanation of how the present work extends the latter type of study can be made simpler, if, instead of expressing it in general terms, we introduce at once, and employ for the purpose of illustration, the particular form of example with which we have operated in extension of earlier work. This is the unimolecular solvolysis of an alkyl chloride in an aqueous solvent, with a competing unimolecular non-solvolytic substitution by azide ions :

$$RCl \underset{(2)}{\overset{(1)}{\rightleftharpoons}} R^+ + Cl^- \quad \overset{(3)\ H_2O}{\longrightarrow} ROH + H^+ + Cl^-$$
$$\overset{(2')\ N_3^-}{\longrightarrow} RN_3 + Cl^-$$

The main points already established with respect to the four component processes here represented are as follows.

The rate-determining ionisation, process (1), is unimolecular, the alkyl chloride being the only molecule which suffers covalency change in this reaction stage. It is a slow and activated process. Its energy of activation, although considerable, is not inaccessible; and this is because there is an off-setting of ionic solvation energy against the covalent bonding energy (*J.*, 1935, 252).

The ionic recombination process (2), which restores the alkyl halide, and the ionic association process (2′), which is product-forming for the non-solvolytic substitution, are close analogues. Indeed, the main reason for introducing process (2′) is that it generalises process (2), and provides a convenient case for the investigation of reactions of ionic union. These reactions are much too fast to be isolated; but it has been shown by the study of salt effects that each is unimolecular with respect to each participating ion, and is thus bimolecular overall (*J.*, 1940, 979).

* Part XXXIV, preceding paper.

Process (3), which is product-forming for the solvolytic substitution, is also much too fast to be isolated. But it has been shown by the salt-effect method that it is unimolecular with respect to the carbonium ion, and multimolecular with respect to water (*loc. cit.*). The reaction is described as an internal collapse of the solvation shell, which for a certain time protects the carbonium ion.

The next two points on which we would like to be informed relate to whether the fast ionic associations, (2) and (2'), on the one hand, and the fast cation–solvent reaction (3), on the other, have finite energies of activation.

In the papers of 1940 it was briefly mentioned that we had found the ionic associations to be activated. But the observations were not complete enough to be reported at the time and hence they are presented on this, the first subsequent occasion on which we have returned to the discussion of salt effects. The rest of the present paper deals with the evidence on this matter. We are still without any definite evidence as to whether or not the cation–solvent reaction is activated.

The theoretical proposition, that the combination of oppositely charged ions in solution must be activated, is probably less in need of defence now than it was in the 1930's (cf. *Trans. Faraday Soc.*, 1938, **34**, 226). However, this principle is such an essential part of the theory of unimolecular substitution that we thought we should try to establish it definitely for this type of reaction. It has often been explained how, in a rate-controlling ionisation, energy must be supplied to the bond at smaller interatomic separations than those at which solvation energy eventually becomes liberated in excess (*J.*, 1935, 252, and subsequently). An equivalent statement is that in ionic recombination, some energy of desolvation must be supplied before the ions can get sufficiently close to each other to commence the release of bond energy in excess. Either description implies that an energy hill separates the molecule from its ions.

The theory of the cation–solvent reaction is quite different. It does not exclude, but does not require, the presence of any energy of activation in this process.

We have examined the kinetic course of the reactions which di-*p*-tolylmethyl (*pp'*-di-methylbenzhydryl) chloride undergoes in aqueous acetone in the presence of sodium azide. The experiments reported in 1940 showed that the di-*p*-tolylmethyl cation has a degree of stability towards water which makes it fairly easy to arrange that ionic combination processes, such as (2) and (2'), will have speeds comparable to that of the cation–water reaction (3). This being the case, competitions between the fast processes, for example, between reactions (2') and (3), can be studied with some precision. Our plan has been to examine the effect of temperature on the manner in which the carbonium ion is partitioned between azide ions and water, that is, on the ratio of the rates of the fast processes (2') and (3), and thus, by the use of the Arrhenius equation, to determine the difference between the energies of activation of processes (2') and (3).

The analytical procedure is simple. We determine the concentration $a - x$ of the alkyl chloride at any time t by measuring the concentration x of liberated chloride ions. We also determine the concentration x' of liberated acid, which is the same as the concentration of formed alcohol. The difference, $x'' = x - x'$, is the concentration of formed alkyl azide, $c - x''$ being the concentration of azide ion. The ionic strength, needed for the purpose of an activity correction, is $c + x'$.

By the stationary-state principle,

$$v_1 = v_2 + v_3 + v_{2'}$$

These rates are connected with observable quantities as follows

$$v_1 - v_2 = \mathrm{d}x/\mathrm{d}t; \ v_3 = \mathrm{d}x'/\mathrm{d}t; \ v_{2'} = \mathrm{d}x''/\mathrm{d}t.$$

The rates may be expressed in terms of rate constants and concentrations, in accordance with the already determined molecularities of the reactions :

$$v_1 = k_1(a - x) \qquad v_3 = k_3[\mathrm{R^+}]$$
$$v_2 = k_2[\mathrm{R^+}]x \qquad v_{2'} = k_2[\mathrm{R^+}](c - x'')$$

Our concern will be with the ratio,

$$\alpha = \frac{k_{2'}}{k_3} = \frac{v_{2'}}{v_3} \cdot \frac{1}{c - x''} = \frac{dx''}{dx'} \cdot \frac{1}{c - x''} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (i)$$

Evidently we can determine α, if we can measure x' and x'', with sufficient precision to obtain good values of dx''/dx'.

Here we introduce the activity correction, which is necessitated by the circumstance that the ionic strength $c + x'$ increases during reaction. On this account the rate constants, $k_{2'}$ and k_3, are not strict constants. Moreover, since they apply to reactions of different molecularities and charge distributions, they will drift according to different laws, and therefore their ratio, α, will itself drift as reaction proceeds. In fact, α is found to drift by the expected few units per cent. We therefore must work, not with the slowly varying function, α, but with the constant $\alpha°$, the ratio of the rate constants $k_{2'}°$ and $k_3°$ of reactions (2') and (3) at zero ionic strength. This can be calculated from α, on the basis of electrostatic principles, as explained in our former discussion of salt effects (*J.*, 1940, 979). The formulæ are as follows :

$$\left. \begin{array}{l} \alpha° = k_{2'}°/k_3° = \alpha° \text{ antilog}_{10}\,[X(c + x')^{1/2} - Y\sigma(c + x')] \\ X = 1\cdot815 \times 10^6 \cdot D^{-3/2}T^{-3/2} \\ Y = 0\cdot912 \times 10^{16} \cdot D^{-2}T^{-2} \\ \sigma = 2\cdot7 \times 10^{-8} \text{ cm.} \end{array} \right\} \quad \cdot \quad \cdot \quad (ii)$$

Here D is the dielectric constant of the solvent and T the absolute temperature. The ionic-strength constant σ is as experimentally determined for di-p-tolylmethyl (pp'-dimethylbenzhydryl) chloride (*loc. cit.*), since the value for the azide must be nearly the same (*loc. cit.*), and an exact value is not important for the purposes of the present somewhat small correction.

Our procedure, then, is to determine $\alpha°$ as a function of temperature. From the Arrhenius equations,

$$k_{2'}° = A_{2'} \exp\,[-E_{2'}/RT] \text{ and } k_3° = A_3 \exp\,[-E_3/RT]$$

we have the relation

$$\alpha° = k_2°/k_3° = (A_{2'}/A_3) \exp\,[-(E_{2'} - E_3)/RT] \quad \cdot \quad \cdot \quad \cdot \quad (iii)$$

Hence a plot of log $\alpha°$ against $1/T$ will give the activation-energy difference $E_{2'} - E_3$. If this should be positive, then the energy of activation $E_{2'}$ of the ionic union must be finite, and not smaller than the determined difference.

In the main series of experiments, the solvent was a mixture of 9 volumes of acetone with 1 of water, a mixture designated below as " 90% " aqueous acetone. The results obtained in this solvent are summarised in Table 1 (for details, see Experimental section).

TABLE 1. *Effect of temperature on relative rates of non-solvolytic and solvolytic substitutions of di-*p-*tolylmethyl chloride in " 90% " aqueous acetone containing sodium azide.*

Runs No.	Temp.	$a° = k_{2'}°/k_3°$ in l./g.-mol.	
		Individual values	Mean
10, 11, 12	0·00°	102, 105, 105	104
18, 19	4·95	115, 114	115
4, 5, 6	9·97	138, 134, 134	135
16, 17	14·95	152, 149	151
13, 14, 15	19·98	170, 168, 170	169

The corresponding Arrhenius plot, essentially the graph of equation (iii), is in Fig. 1. It shows that the energy of activation of the ionic association (2') exceeds that of the cation–water reaction (3) by 4·0 kcal./g.-mol. A similar though rather rough value, 3·9 kcal./g.-mol., was obtained as the final result of another series of experiments, which were made in " 85% " aqueous acetone, but are unrecorded because the runs were so fast * that the accuracy of measurements was somewhat low. Our general conclusion is that the ionic union, although it is very fast, has an energy of activation of at least 4 kcal./g.-mol.

* The use of lower temperatures was precluded by the limited solubility of the alkyl chloride.

EXPERIMENTAL

Materials.—These were prepared and purified as previously recorded (*J.*, 1940, 974).

Analyses.—Generally the methods were those of the previous work (*loc. cit.*), though some special routines were adopted. No attempt was made to determine acidity and chloride ion on the same sample. First, 5 c.c. of the reaction solution were run into 50 c.c. of dry acetone at $-10°$, and titrated with potassium hydroxide, bromothymol-blue being the indicator. The temperature is of some importance, for if it is much lower the indicator does not work well, while if it is much higher the reaction does not stop. Then, about 30 seconds later, a second similar sample was run into 50 c.c. of carbon tetrachlorde at $-20°$, and an ice-cold aqueous extract of this solution was employed for the determination of chloride ion by the usual Volhard procedure. Later analyses were made similarly in pairs, the sample for the determination of acid being taken first, and that for the measurement of chloride ion about 30 seconds later. Eventually the chloride-ion measurements were interpolated to the times of the acidity determinations, and the time of the first chloride-ion measurement was treated as the time zero.

Calculations.—*Method* (1). The first method we used was the obvious one : the chloride ion x, the acidity x', and their difference x'', were all plotted as functions of the time. Then x''

FIG. 1. *Arrhenius plot of the rate-ratios* ($a° = k_2°/k_3°$ *in l./g.-mol.*) *of the competing fast stages of unimolecular substitution.*
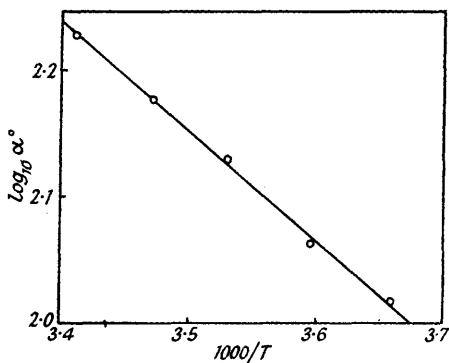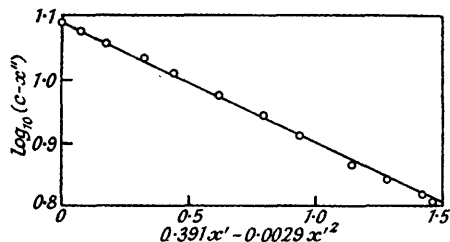
FIG. 2. *Illustrating the determination of* $a°$ *by method* (2). (*Run no.* 11.)

was plotted against x', and, tangents being drawn with the help of a mirror, values of dx''/dx' were obtained. From these, and the relevant values of x'', α was computed by means of equation (i). From this $\alpha°$ was calculated by means of equation (ii). The dielectric constant of " 90% " aqueous acetone at θ °c was taken as $27 \cdot 5 - 0 \cdot 10\,\theta$.

Method (2). This method was invented in order to avoid the risk of introducing subjective errors during the drawing of tangents. The general idea is to separate the differentials in equation (i), and then integrate it. It is true that to do this directly would be most tedious, because α is the somewhat complicated function of x' expressed in equation (ii). But we can effect great simplification by taking advantage of the cirumstance that the graphs of α against x', as drawn from equation (ii), for the relevant ranges of x', are in practice indistinguishable from straight lines :

$$\alpha = \alpha°(m - nx') \qquad \text{. . . . . . . (iv)}$$

They are, indeed, not quite horizontal straight lines, falling in height, usually by about 5%, as x' rises from zero to its largest value. Using equation (ii), we can draw such a line for the conditions of any experiment, and thus determine the constants m and n which appear in the expression (iv). Then, substituting for α in equation (i) by means of equation (iv), we obtain an equation which can easily be integrated to give equation (v) :

$$\alpha°(mx' - \tfrac{1}{2}nx'^2) = -\ln(c - x'') + \text{constant} \qquad \text{. . . . . (v)}$$

This equation tells us that if, having measured x' and x'', we plot log $(c - x'')$ against $mx' - \tfrac{1}{2}nx'^2$, we should get a straight line, the slope of which will give the value of $\alpha°$. An example of such a plot is shown in Fig. 2.

For the purpose of comparing the graph in Fig. 2, or such other graphs as could be constructed from the data given below, with the final results, as entered in Table 1, it is necessary to know that our practice was to carry through the calculations with all concentrations expressed as that

volume of a solution of the normality of the employed silver nitrate which is equivalent to the amount of the material in the sample analysed. The resulting α° is thus obtained in units which are the reciprocal of these units; and it has therefore to be multiplied by the volume of the sample, and divided by the normality of the silver solution, for conversion into the standard units, l./g.-mol.

Preferred procedure. The two methods of calculation, when applied to the same run, gave similar results. Thus for run no. 4, α° was obtained as 135 and 138 l./g.-mol. by the two methods, for run no. 6, 133 and 134, and for run no. 10, 105 and 102 l./g.-mol. However, after some experience of both methods, we came to prefer the second, as depending less on personal judgment. Method (2) has been used consistently for the derivation of the figures in Table 1.

Results.—In all runs the initial concentrations of di-*p*-tolylmethyl chloride and of sodium azide were about 0·05M, the samples taken for analysis were about 5 c.c., and the solutions of silver nitrate and of potassium hydroxide used for titration were about 0·02N.

In illustration, the record of a run, and of the calculations based upon it, are given in Table 2. Tabulated quantites are expressed in the following units : x = Titre of $AgNO_3$ in c.c., reckoned from the first such titration as zero; y = titre of KOH in c.c.; y' = titre of KOH in c.c., reckoned from the titre at the time of the first $AgNO_3$ titration as zero; $x' = y'$, re-expressed as equivalent c.c. of the $AgNO_3$; $x'' = x - x'$, reckoned as above.

The initial concentrations a and c are expressed in the same units as x, x', and x''. Times are in seconds, but are denoted by t only when reckoned from the time of the first $AgNO_3$ titration. Values of α° have been converted into l./g.-mol.

TABLE 2. *Details of run No. 4.*

Experimental Results.—Solvent : " 90% " aqueous acetone. Temperature, 9·97°. Initially, [RCl] = 0·0463M, [NaN₃] = 0·0512M. Analytical solutions, $AgNO_3$ = 0·02137N, KOH = 0·0184N. Samples, 5·037 c.c.

Acid						Chloride					
Time	y	Time	y	Time	y	Time	x	Time	x	Time	x
0	0·00	1048	1·53	4816	3·43	35	0·00	1081	4·35	4850	8·50
154	0·32	1723	2·19	6147	3·53	188	1·03	1755	5·75	6177	8·99
308	0·60	2583	2·61	7749	3·65	344	1·84	2615	6·90	7779	9·42
619	1·01	3636	3·07	∞	3·68	649	3·04	3669	7·72	∞	9·93

The time 35 seconds was taken as $t = 0$.

Calculations.—Method 1 :

Data from the graphs of x and x' against t.

$100x/a$	10·1	18·1	30·2	40·0	49·5	58·9	70·5	80·6	90·4	100·0
$100x'/x$	28·0	28·4	28·6	29·1	30·5	31·4	32·6	33·6	33·4	31·3

Data from the graphs of x'' against t and against x'.

$100x/a$	10·6	17·6	27·7	34·4	40·7	49·5	57·9	63·3	76·6	83·4
α°	135	135	135	135	135	135	135	134	134	(132)

Mean α° = 135 l./g.-mol.

Method 2. From the graph of equation (ii) the constants of equations (iv) are evaluated as $m = 0·391$ and $n = 0·0061$.

t	x	x'	x''	$c - x''$	$\log_{10} (c - x'')$	$mx' - \frac{1}{2}nx'^2$
0	0·00	0·00	0·00	12·04	1·081	0·000
119	0·79	0·22	0·57	11·47	1·060	0·086
273	1·66	0·46	1·20	10·84	1·035	0·179
584	2·92	0·81	2·11	9·93	0·997	0·315
1003	4·22	1·26	2·96	9·08	0·958	0·488
1688	5·68	1·83	3·85	8·19	0·913	0·705
2647	6·96	2·19	4·77	7·27	0·861	0·842
3601	7·75	2·58	5·17	6·87	0·837	0·989
4781	8·48	2·79	5·69	6·35	0·803	1·068
6112	8·98	2·98	6·00	6·04	0·781	1·131
7714	9·41	3·08	6·33	5·71	0·757	1·176
∞	9·93	3·11	6·82	5·22	0·718	1·188

From the graph of equation (v), α° = 138 l./g.-mol.

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