299. *Activation Parameters in the Hydrolysis of Diphenylmethyl* p-*Nitrobenzoate.*

By J. R. Fox and G. Kohnstam.

Operation of the ionisation mechanism, S_N1 ($B_{AL}1$) has been confirmed for the reactions of diphenylmethyl *p*-nitrobenzoate and its 4-methoxy-derivative with aqueous acetone. The ratio of the heat capacity of activation to the entropy of activation for the hydrolysis of the parent compound has the same value as in other S_N1 reactions, in agreement with the hypothesis that the ratio is independent of the nature of the substrate when this mechanism is operating.

Previous work has shown that the ratio of the heat capacity of activation ($\Delta C^‡$) to the entropy of activation ($\Delta S^‡$) in the ionisation (S_N1 reaction) of a number of chlorides, bromides, and sulphonates in aqueous acetone is independent of the nature of the substrate.[1] The neutral solvolysis of diphenylmethyl *p*-nitrobenzoate has now been studied in an attempt to obtain further evidence for, or against, the view that the structure of the substrate does not affect the value of $\Delta C^‡/\Delta S^‡$ in reaction by this mechanism. The solvolysis of the 4-methoxy-derivative was also briefly studied, mainly in order to confirm the reaction mechanism.

There were good reasons for believing that the reactions under consideration occur by mechanism $B_{AL}1$ which requires a rate-determining ionisation of the alkyl–oxygen linkage and is thus identical with the unimolecular mechanism of nucleophilic substitution, S_N1. The neutral solvolysis of t-butyl 2,4,6-triphenylbenzoate [2] and 1-phenylethyl hydrogen phthalate [3] has already been shown to involve this mechanism, and similar considerations should therefore apply to the present reactions where the leaving group and the alkyl groups are more favourable to ionisation (cf. ref. 4). Previous workers have already assigned mechanism $B_{AL}1$ to the solvolysis of diphenylmethyl *p*-nitrobenzoates from the relatively high reactivity and from the changes in rate caused by the introduction of substituents or by alterations in the composition of the solvent,[5] and this conclusion is supported by the present results (see below). The parent compound undergoes internal ion-pair return more rapidly than hydrolysis in " 90% " acetone * but this does not argue

---

* Throughout this paper, " X% " acetone refers to the mixture in the proportions X volumes of acetone to ($100-X$) volumes of water.

[1] (*a*) Kohnstam, " The Transition State," *Chem. Soc. Special Publ., No.* 15, 1962, p. 179, and references there cited; (*b*) Kohnstam and Tidy, *Chem. and Ind.*, 1962, 1193; (*c*) Cowie, Fitches, and Kohnstam, *J.*, preceding paper.

[2] Graham, Hughes, and Quayle, unpublished results, quoted in Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 764.

[3] Balfe, Bevan, and Kenyon, *J.*, 1951, 376.

[4] Ref. 2, p. 762.

against solvolysis *via* the fully developed carbonium ion.[5a] Similar observations have already been reported for halides which are generally accepted as undergoing S_N1 solvolysis,[6] but the direct combination between ion-pairs and solvent molecules has not yet been demonstrated for reaction by this mechanism in aqueous systems, and it has already been shown that such a process does not contribute to the hydrolysis of dichlorodiphenylmethane.[7]

RESULTS AND DISCUSSION

4-*Methoxydiphenylmethyl* p-*Nitrobenzoate*.—The presence of 0·03M-potassium *p*-nitrobenzoate retarded the hydrolysis of the 4-methoxy-compound in " 85% " acetone by a factor of 4·0 at 71·33°. This is consistent with the operation of the mass-law effect [8] and therefore confirms reaction by mechanism S_N1 ($B_{AL}1$).

A knowledge of the extent of retardation of S_N1 hydrolysis by added anions allows the calculation of the mass-law constant, α, which represents the rate of reaction of the carbonium ion with the anion relative to its rate of reaction with water.[8] If all activity coefficients are assumed to be unity, our results yield $\alpha(NO_2{\cdot}C_6H_4{\cdot}CO_2^-) = 100$ in " 85% " acetone at 71·33° and ionic strength 0·03, while for the same carbonium ion in the same solvent $\alpha(Cl^-) \sim 700$ at 0° and ionic strength 0·001.[9] Pocker [10] has shown that the affinities of chloride, bromide, and azide ions for a fully developed carbonium ion in nitromethane are not very sensitive to the nucleophilic powers of these ions. If this also applies in aqueous systems, the 7-fold difference * now observed between $\alpha(NO_2{\cdot}C_6H_4{\cdot}CO_2^-)$ and $\alpha(Cl^-)$ suggests that the *p*-nitrobenzoate ion is a very much poorer nucleophile than the chloride ion. On the other hand, at least a part of this difference may arise from the fact that a chloride ion can penetrate the solvation shell of a carbonium ion more easily than the much larger *p*-nitrobenzoate ion.

Diphenylmethyl p-*Nitrobenzoate*.—(*a*) *Reaction rates*. The rate of hydrolysis of the parent compound was found to depend considerably on the solvent composition. At 140°, a change from " 70% " to " 85% " acetone decreased the rate by a factor of 12·8, compared with a 16·5-fold decrease in the rate of hydrolysis of 4-nitrodiphenylmethyl chloride.[9] As hydrolysis of the chloride occurs by the mechanism S_N1, the same mechanism is therefore indicated for the *p*-nitrobenzoate. The slightly smaller sensitivity of the rate of hydrolysis of the ester to changes in the solvent probably arises from the fact that this compound appears to require less additional solvation on activation than the chloride (see p. 1595): as a result the solvating power of the medium becomes a less important factor in determining the rate. Analogous considerations have already been advanced to account for the smaller effect of solvent changes on the rate of hydrolysis of organic bromides than of the corresponding chlorides.[1c]

Diphenylmethyl *p*-nitrobenzoate undergoes solvolysis much more slowly than its 4-methoxy-derivative, consistently with the operation of mechanism S_N1 in both reactions. It is noteworthy that introduction of this substituent increases the rate of hydrolsysis of the ester and of the corresponding chloride by almost the same amounts; $k_{MeO}/k_H = 2890$ for the nitrobenzoate and 3290 for the chloride,[9] in " 85% " acetone at 71·33°. Similarly,

---

* Strictly, the two values of α should be compared at the same ionic strength and the same temperature. In " 85% " acetone at 70°, $\alpha(NO_2{\cdot}C_6H_4{\cdot}CO_2^-)$ can be expected to be 1·5—1·8 larger at zero ionic strength than at ionic strength 0·03, but $\alpha(Cl^-)$ should be greater at 70° than at 0° since this parameter always increases as the temperature is raised.[7, 11] As a first approximation, the two corrections have been assumed to cancel each other.

[5] (*a*) Goering and Levy, *Tetrahedron Letters*, 1961, No. 18, 644; (*b*) Silver, *J. Amer. Chem. Soc.*, 1961, **83**, 404.

[6] Winstein, Hojo, and Smith, *Tetrahedron Letters*, 1960, No. 22, 12; Pocker, *Proc. Chem. Soc.*, 1961, 140.

[7] (*a*) Bensley and Kohnstam, *J.*, 1955, 3408; (*b*) Kohnstam and Shillaker, *J.*, 1959, 1915.

[8] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

[9] Fox, Thesis, Durham, 1962.

[10] Pocker, *J.*, 1959, 3943.

[11] Hawdon, Hughes, and Ingold, *J.*, 1952, 2499.

almost the same change in the rate of S_N1 solvolysis is observed when a 4-phenoxy- is replaced by a 4-methoxy-substituent in benzyl toluene-*p*-sulphonate and in benzyl chloride, and on the introduction of 4-fluoro-groups in diphenylmethyl bromide and chloride.[12] Silver [5b] has given other examples which show that changes in the rate caused by changes in the structure of the alkyl group are relatively insensitive to the nature of the leaving group in S_N1 reactions, but the available information is not yet sufficient to permit the conclusion that this will always apply in reaction by this mechanism.

(*b*) *Activation parameters*. The hydrolysis of diphenylmethyl *p*-nitrobenzoate in "70%" acetone was studied at six temperatures between 140° and 84°. The kinetic data are compared in Table 1 with those for the S_N1 hydrolysis of some halides at 50°, the temperature usually employed by us in such comparisons. At this temperature, the activation parameters for the benzoate are subject to larger errors than those generally observed for other compounds reacting by this mechanism (see Table 1 and ref. 1), but this arises mainly from the fact that the benzoate had to be studied at relatively high temperatures (details are given in the Experimental section). Within the limits of experimental error, however, $\Delta C^\ddagger/\Delta S^\ddagger$ for the hydrolysis of diphenylmethyl *p*-nitrobenzoate is the same as for the other compounds listed in Table 1 and agrees, within these limits, with the mean value of this ratio (3·68 ± 0·14) for all the S_N1 reactions previously studied in this solvent. The present results thus confirm the view that $\Delta C^\ddagger/\Delta S^\ddagger$ is independent of the nature of the substrate in reaction by this mechanism in aqueous acetone and consequently strengthen mechanistic conclusions based on the value of this ratio.[1]

TABLE 1.

Kinetic data for S_N1 reactions in "70%" acetone at 50°.

All substituents are in the 4-position, and all errors are standard errors.

k in sec.$^{-1}$, E in kcal. mole^{-1}, $\Delta S^\ddagger$ and $\Delta C^\ddagger$ in cal. mole^{-1} deg.$^{-1}$.

Substrate	$-\log k$	E	$-\Delta S^\ddagger$	$-\Delta C^\ddagger$	$\Delta C^\ddagger/\Delta S^\ddagger$
$Ph_2CH\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$	7·4966	$28{\cdot}80_4 \pm 0{\cdot}25_5$	5·87 ± 0·72	26·5 ± 4·0	4·51 ± 0·92
$Ph_2CH\cdot Cl$ (ref. 13)	2·1773	$19{\cdot}52_1 \pm 0{\cdot}09_8$	10·26 ± 0·28	37·6 ± 2·7	3·66 ± 0·28
$NO_2\cdot C_6H_4\cdot CHPh\cdot Cl$ (ref. 1*c*) ...	4·9888	$23{\cdot}77_2 \pm 0{\cdot}04_5$	9·96 ± 0·13	39·8 ± 2·6	4·00 ± 0·27
$NO_2\cdot C_6H_4\cdot CHPh\cdot Br$ (ref. 1*c*)...	3·6904	$22{\cdot}36_7 \pm 0{\cdot}03_4$	8·38 ± 0·11	30·4 ± 2·3	3·62 ± 0·28

The constancy of $\Delta C^\ddagger/\Delta S^\ddagger$ in S_N1 solvolysis and the alterations in the value of this ratio caused by changes in the composition of the solvent are consistent with a simple solvation model which assumes that the magnitudes of $\Delta C^\ddagger$ and $\Delta S^\ddagger$ in reaction by this mechanism are mainly, if not entirely, controlled by the increase in solvation by water associated with the activation process.[1a] On this view, the observation that $\Delta S^\ddagger$ is less in the hydrolysis of the nitrobenzoate than in the hydrolysis of the halides (see Table 1) therefore suggests that this increase in solvation is not as extensive for the carboxylic ester as for the other compounds. This could arise from hydrogen-bonding between water molecules and the ester group in the initial state of hydrolysis. Such water molecules will already be correctly oriented for solvating the incipient anion in the transition state, which will therefore require less additional solvation than the activated complex in the ionisation of halides where such interactions are much less likely in the initial state. Similar explanations have already been proposed to account for "abnormal" values of $\Delta S^\ddagger$ in the S_N1 solvolysis of sulphonates [1a] and alkyl halides containing α-carboxylate-ion substituents.[14]

The activation parameters discussed in the preceding paragraphs were obtained by assuming that $\Delta C^\ddagger$ is independent of the temperature. The validity of this assumption has recently been questioned [15] and it is therefore necessary to discuss its implications.

---

[12] Fox, Kohnstam, and Tidy, unpublished results.
[13] Kohnstam, *J.*, 1960, 2066.
[14] Gripenberg, Hughes, and Ingold, *Nature*, 1948, **161**, 480.
[15] Hulett, ref. 1*a*, p. 207.

All the reliable data at present available for solvolysis show that in each case $\Delta C^\ddagger$ is constant, within the limits of experimental error, over the experimental temperature range. This range is, however, always small when compared with the absolute values of T and the observations are therefore equally consistent with the requirements of eqn. (1) over quite a wide range of values of β:

$$\Delta C^\ddagger = \alpha + \beta T \qquad (1)$$

This is illustrated for the hydrolysis of diphenylmethyl *p*-nitrobenzoate in Table 2, where it can also be seen that $\Delta C^\ddagger$ at the mean temperature of the experimental range, T_m, is independent of the value chosen for β. Thus, if $\Delta C^\ddagger$ is a linear function of T, the usual assumption that $\beta = 0$ yields $\Delta C^\ddagger$ at T_m and the values calculated for the activation parameters at a temperature $T_a \neq T_m$ will be subject to errors which depend on the difference between T_a and T_m, and on the magnitude of β. Our results for S_N1 reactions in aqueous acetone suggest that β is numerically small since $\Delta C^\ddagger/\Delta S^\ddagger$ at some temperature T_a has the same value for reactions with $T_m \sim T_a$ as for reactions with $T_m - T_a \sim -60°$;[1,12] this conclusion is supported by analogy with the temperature coefficients of partial molar heat capacities of electrolytes in water.[16] A rough estimate of the value of β in the present solvent, "70%" acetone, can be obtained by the *a priori* reasonable assumption that the hydrolysis of the structurally highly similar diphenylmethyl chloride and its 4-nitro-derivative should show the same $\Delta C^\ddagger$ at the same temperature. The values of $\Delta C^\ddagger$ given in Table 1 refer to T_m (286·82°and 340·22°K, respectively) and thus yield $\beta = -0{\cdot}045 \pm 0{\cdot}069$ cal. mole^{-1} deg.$^{-2}$. Even if $\beta = -0{\cdot}10$ cal. mole^{-1} deg.$^{-2}$, it can be shown that the neglect of this parameter causes an error no larger than the experimental error in $\Delta C^\ddagger$, $\Delta S^\ddagger$, and $\Delta C^\ddagger/\Delta S^\ddagger$ when $T_m - T_a \sim 30°$. For the hydrolysis of diphenylmethyl *p*-nitrobenzoate at 50° ($T_m - T_a \sim 60°$), this value of β does not alter the conclusions reached earlier in this paper on the assumption of a constant $\Delta C^\ddagger$; *i.e.*, $\Delta C^\ddagger/\Delta S^\ddagger$ has the same value as for other S_N1 reactions, and $\Delta S^\ddagger$ is less negative than in the hydrolysis of halides. Details are given on p. 1598.

It must be stressed that our results neither prove nor disprove a significant temperature-dependence of $\Delta C^\ddagger$; an unambiguous demonstration must await results of much greater accuracy than we have been able to achieve. The present arguments merely show that the assumption of a constant $\Delta C^\ddagger$ is unlikely to cause serious errors in the calculated values of rates and activation parameters at temperatures not too far outside the experimental range.

EXPERIMENTAL

Preparation of Materials.—All reagents were dried and purified by standard methods. Diphenylmethyl *p*-nitrobenzoate was prepared by refluxing equimolar amounts of diphenylmethanol and *p*-nitrobenzoyl chloride in benzene for 2 hr. in the presence of a 100% excess of pyridine. After cooling, the excess of pyridine was removed as the hydrochloride by passing dry hydrogen chloride into the solution and filtering, and the filtrate was washed and dried ($MgSO_4$). The residue left on the evaporation of the solvent was recrystallised twice from acetone–light petroleum (b. p. 60—80°) and dried under reduced pressure; it had m. p. 132° (lit.,[17] 131—132°). 4-Methoxydiphenylmethyl *p*-nitrobenzoate was similarly obtained and, recrystallised from light petroleum (b. p. 80—100°), had m. p. 82° (lit.,[5b] 79—82°). The infrared spectra of both esters showed the frequencies expected for C=O and C–O stretching, and the acid produced by complete hydrolysis was always 99·2%, or more, of the calculated amount.

The solvent employed in the hydrolysis experiments was prepared from "equilibrium" water and acetone which had been purified [7a] and fractionated over quinol.

Rate Measurements.—Rates of hydrolysis were determined for initially *ca.* 0·01M-solutions by the sealed-ampoule technique. Ampoules were broken under carbon tetrachloride (20 ml.), an excess of water was added, and the mixture titrated with standard alkali under a stream of

---

[16] Randall and Rossini, *J. Amer. Chem. Soc.*, 1929, **51**, 323.
[17] Meisenheimer and Schmidt, *Annalen*, 1929, **475**, 177.

nitrogen, with *o*-cresolphthalein as indicator. Check experiments showed that the esters were not hydrolysed under these conditions.

All kinetic runs were carried out in duplicate, with separate determinations of acidity at 11 or 12 different times in each run. The " zero " reading was taken as soon as the tubes had attained thermostat temperature, and the " first " and last readings at *ca.* 15% and 80% reaction, respectively. Rate coefficients, *k*, were obtained from the integrated form of the first-order rate equation and were constant, within the limits of experimental error, for any one run. This suggests that the *p*-nitrobenzoic acid formed is too weak an acid in our solvents to produce sufficient hydrogen ions for significant acid-catalyst (reaction by mechanism $A_{\text{AL}}1$) at the prevailing concentrations ($\not> 0{\cdot}012$M). There was no evidence for the production of acid by our solvents at high temperatures, possibly because the acetone had been purified by distillation over quinol (cf. ref. 5*b*). All batches of the " 70% " solvent were monitored and the observed rates corrected (cf. ref. 1*c*) to refer to the same " 70% " acetone as employed in previous work.[1]

Results and Calculations.—All rate coefficients are in sec.$^{-1}$, X = $NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}$, and all errors are standard errors.

For reaction with " 85% " acetone: 10^5k (Ph_2CHX) = 3·096 (140·02°); 10^5k ($MeO{\cdot}C_6H_4{\cdot}CHPhX$) = 10·78 (71·33°, no added salt), 2·696 (71·33°, 0·03M-KX).

The rate for Ph_2CHX at 71·33° was calculated from the rate at 140·02° by assuming that the activation energy at the mean of these two temperatures was 0·2 kcal. mole^{-1} greater in " 85% " than in " 70% " acetone. Results for halides [9] suggested that this assumption was justified for S_N1 hydrolysis.

For Ph_2CHX reacting with " 70% " acetone: $10^6k = 395{\cdot}3 \pm 0{\cdot}93_7$ (140·02°), $169{\cdot}1 \pm 0{\cdot}94_0$ (129·52°), $74{\cdot}02 \pm 0{\cdot}14_3$ (119·88°), $29{\cdot}26 \pm 0{\cdot}046_2$ (109·69°), $8{\cdot}775 \pm 0{\cdot}019_8$ (97·33°), $2{\cdot}119 \pm 0{\cdot}0027_5$ (83·90°).

Experimental values for the energy and entropy of activation ($E_{\text{obs.}}$ and $\Delta S^{\ddagger}_{\text{obs.}}$) were obtained from rates at adjacent temperatures, as previously described,[18] and refer to the mean temperature of the interval.[1c] Each $E_{\text{obs.}}$ is subject to an error, $\sigma(E)$, given by [19]

$$\sigma(E) = \frac{\boldsymbol{R}T_1T_2}{T_2 - T_1}\left[\left(\frac{\sigma_1}{k_1}\right)^2 + \left(\frac{\sigma_2}{k_2}\right)^2\right]^{\frac{1}{2}}$$

where the σ's are the errors in the rate coefficients and the subscripts refer to the two temperatures. For a given experimental accuracy, σ/k, reactions studied at higher temperatures show higher values of $\sigma(E)$.

The assumption that $\mathrm{d}E/\mathrm{d}T$ or $\Delta C^{\ddagger}$ ($=\mathrm{d}E/\mathrm{d}T - \boldsymbol{R}$) is independent of the temperature allows the evaluation of these parameters from the " best " straight line, $E_{\text{obs.}}$ against T, and hence the calculation of energies and entropies of activation from

$$E = E_{\text{m}} + (T - T_{\text{m}})\mathrm{d}E/\mathrm{d}T,$$

and

$$\Delta S^{\ddagger} = \Delta S^{\ddagger}{}_{\text{m}} + \Delta C^{\ddagger}[\ln T - (\ln T)_{\text{m}}], \qquad (2)$$

where the subscripts m refer to the mean values of the experimental quantities. It can be seen from Table 2, column (i), that the agreement between $E_{\text{obs.}}$ and E is much better than the experimental accuracy warrants, and the error in $\mathrm{d}E/\mathrm{d}T$ (and $\Delta C^{\ddagger}$) was therefore obtained from $\sigma(E)$, as previously described.[20] This error represents a larger fraction of $\Delta C^{\ddagger}$ than usual (see Table 1), partly because the hydrolysis of the nitrobenzoate was examined at much higher temperatures than that of other compounds previously studied, and partly because of the abnormally large error in the rate of reaction at 129·52° (*q.v.*).

The figures in Table 1 for hydrolysis at 50° were obtained from eqn. (2), and their errors therefore depend on the error in $\mathrm{d}E/\mathrm{d}T$ (or $\Delta C^{\ddagger}$) and on the difference between T and T_{m}. This difference is much larger for the nitrobenzoate than for the other compounds listed, and therefore the inferior accuracy of the results for this compound arises, at least partly, from the poor reactivity which made it necessary to work at high temperatures.

---

[18] Bensley and Kohnstam, *J.*, 1956, 287.

[19] Purlee, Taft, and de Fazio, *J. Amer. Chem. Soc.*, 1955, **77**, 837.

[20] Brittain, Kohnstam, Shillaker, and Queen, *J.*, 1961, 2045.

TABLE 2.

Activation parameters for the reaction of diphenylmethyl *p*-nitrobenzoate with " 70% " acetone.

T in °K, E in kcal. mole^{-1}, α and $\Delta C^{\ddagger}$ in cal. mole^{-1} deg.$^{-1}$, β in cal. mole^{-1} deg.$^{-2}$.

		$E_{\text{obs.}} - E$ *					
T (K)	$E_{\text{obs.}}$	(i)	(ii)	(iii)	(iv)	(v)	(vi)
407·93°	26·735 ± 0·191	+0·009	+0·014	+0·019	+0·031	+0·056	+0·105
397·86	26·964 ± 0·193	−0·010	−0·013	−0·015	−0·021	−0·032	−0·054
387·94	27·233 ± 0·074	+0·016	+0·010	−0·004	−0·008	−0·033	−0·082
376·67	27·470 ± 0·064	−0·013	−0·017	−0·019	−0·028	−0·043	−0·074
363·77	27·816 ± 0·052	+0·007	−0·007	+0·019	+0·029	+0·053	+0·097
α		−26·5	−7·2	12·1	50·7	127·9	282·4
$-\beta$		0·0	0·05	0·10	0·20	0·40	0·80
$-\Delta C^{\ddagger}$ at 386·83°K ...		26·5	26·4	26·6	26·7	26·9	27·3

* E calculated from eqn. (3).

If $\Delta C^{\ddagger}$ is a linear function of temperature, integration of eqn. (1) yields

$$E = A + (\alpha + \boldsymbol{R})T + \tfrac{1}{2}\beta T^2$$

where A is a constant. Taking mean values of the experimental quantities, we have

$$E_{\text{m}} = A + (\alpha + \boldsymbol{R})T_{\text{m}} + \tfrac{1}{2}\beta(T^2)_{\text{m}},$$

and hence

$$E = E_{\text{m}} + (\alpha + \boldsymbol{R})(T - T_{\text{m}}) + \tfrac{1}{2}\beta[T^2 - (T^2)_{\text{m}}]. \tag{3}$$

Similarly,

$$\Delta S^{\ddagger} = \Delta S^{\ddagger}{}_{\text{m}} + \alpha[\ln T - (\ln T)_{\text{m}}] + \beta(T - T_{\text{m}}). \tag{4}$$

The results in Table 2 show that, within the limits of experimental error, E calculated from eqn. (3) agrees well with $E_{\text{obs.}}$ over a fairly wide range of values of β. It can also be seen that $\Delta C^{\ddagger}$ at T_{m} (386·83°K) is virtually independent of the value assigned to β.

The errors in the calculated values of activation parameters caused by assuming $\Delta C^{\ddagger}$ to be constant in a reaction for which $\beta = -0{\cdot}10$ cal. mole^{-1} deg.$^{-2}$ are illustrated below for the hydrolysis of diphenylmethyl *p*-nitrobenzoate in " 70% " acetone (E in kcal. mole^{-1}, $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ in cal. mole^{-1} deg.$^{-1}$).

(*a*) When $T = 356{\cdot}83$°K ($T - T_{\text{m}} = -30°$):

	E	$-\Delta S^{\ddagger}$	$-\Delta C^{\ddagger}$	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
$\beta = -0{\cdot}10$	27·951	8·58	23·6	2·8
$\beta = 0$	27·979	8·49	26·5	3·1

(*b*) When $T = 323{\cdot}16$°K ($T - T_{\text{m}} = -63{\cdot}67°$):

	E	$-\Delta S^{\ddagger}$	$-\Delta C^{\ddagger}$	$\Delta C^{\ddagger}/\Delta S^{\ddagger}$
$\beta = -0{\cdot}10$	28·622	6·40	20·3	3·2
$\beta = 0$	28·804	5·87	26·5	4·5

It can be seen that the neglect of β does not yield errors greater than the experimental errors usually found by us in hydrolyses when T and T_{m} differ by 30°, but this does not apply when the difference is *ca.* 60°. Since the experimental error in the reaction under consideration is larger than usual, the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ at 323·16°K for $\beta = -0{\cdot}10$ agrees (within the limits of these errors) with the mean value of this ratio (3·7) for $S_{\text{N}}1$ reactions in the same solvent and at the same temperature.

The award of a Research Studentship by the Department of Scientific and Industrial Research (to J. R. F.) is gratefully acknowledged.

SCIENCE LABORATORIES, SOUTH ROAD, DURHAM. [*Received, October 5th,* **1962**.]