388. *Activation Parameters for S_N1 Solvolysis in 50% Aqueous Acetone.*

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The rates of hydrolysis of t-butyl chloride, *p*-nitrodiphenylmethyl chloride and *p*-methylbenzylidene chloride have been examined in 50% aqueous acetone. Comparison with earlier results for benzylidene chloride and benzotrichloride in the same solvent shows that, within the limits of experimental error, the ratio of the heat capacity of activation to the entropy of activation is independent of the nature of the substrate for S_N1 reactions.

Evidence has been accumulating showing that the solvolysis of organic halides and sulphonates is associated with a negative temperature coefficient for the activation energy,[1-4] and hence with a negative heat capacity of activation, $\Delta C^{\ddagger} = (\mathrm{d}E/\mathrm{d}T) - \boldsymbol{R}$. It has been suggested that the decrease in heat capacity on passing into the activated complex arises mainly, if not entirely, from the increase in solvation associated with the development of electric charges,[2,3a] and that this factor is also almost entirely responsible for the entropy of activation, $\Delta S^{\ddagger}$, in S_N1 reactions.[3b,5] On this view, the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ should be independent of the nature of the substrate in reaction by mechanism S_N1.[3b] This hypothesis is supported by the results for the solvolysis of benzylidene chloride and benzotrichloride in 50% aqueous acetone and 50% aqueous ethanol,[3b] and by results for the reactions of substituted diphenylmethyl chlorides with 70% aqueous acetone.[3c] The reactions of t-butyl chloride, *p*-nitrodiphenylmethyl chloride, and *p*-methylbenzylidene chloride with 50% aqueous acetone have now been studied in order to obtain further information about the effect of substrate-structure on the value of $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ in S_N1 reactions.

Some comment on the reaction mechanism is necessary before discussing the present results since the assignment of mechanism S_N1 to the reaction between aqueous solvents and benzylidene chloride and benzotrichloride has been queried as a result of solvolytic studies in water and deuterium oxide.[6] Much of the evidence that the rate-determining step in the solvolysis of these compounds (and, by analogy, in the solvolysis of *p*-methylbenzylidene chloride) is the ionisation of one of the C–Cl linkages has already been discussed.[3a] Abstraction of an α-hydrogen atom, as in the hydrolysis of chloroform,[7] might be considered as rate-determining in the hydrolysis of benzylidene chloride but the absence of any accelerating effect by added hydroxide ions [8] argues strongly against this mechanism which could also not operate in the solvolysis of benzotrichloride, a compound without α-hydrogen atoms. Complete hydrolysis of both compounds yields the amount of hydrochloric acid to be expected on the assumption of nucleophilic substitution, the effect of α-chlorination on the rate of hydrolysis of benzylidene chloride is similar to that in other compounds known to react by mechanism S_N1, and it will be shown later in this paper that the introduction of a *p*-methyl group alters the rate of hydrolysis in a manner entirely consistent with the assumption of S_N1 hydrolysis for the parent compound and

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[1] Robertson, *Proc. Roy. Soc.*, 1959, *A*, **252**, 273; Hamilton and Robertson, *Canad. J. Chem.*, 1959, **37**, 966, and earlier papers.

[2] (*a*) Tommila, Tilikainen, and Voipio, *Ann. Acad. Sci. Fennicae*, 1955, *A*, II, No. 65; (*b*) Tommila, Paakkala, Virtanen, Erva, and Varila, *ibid.*, 1959, *A*, II, No. 91.

[3] (*a*) Bensley and Kohnstam, *J.*, 1956, 287; (*b*) *J.*, 1957, 4747; (*c*) Kohnstam, *J.*, 1960, 2066.

[4] McKinley-McKee and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247; Glew and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **211**, 254; Moelwyn-Hughes, *ibid.*, 1953, *A*, **220**, 386.

[5] Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25; Buchanan and Hamann, *ibid.*, 1953, **49**, 1425; Burris and Laidler, *ibid.*, 1955, **51**, 1497.

[6] Laughton and Robertson, *Canad. J. Chem.*, 1959, **37**, 1491.

[7] Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438.

[8] Olivier and Weber, *Rec. Trav. Chim.*, 1934, **53**, 869.

its substituted derivative. It therefore seems likely that factors, which have yet to be explained, complicate mechanistic interpretations based on the results of isotopic changes in the solvent. t-Butyl chloride and diphenylmethyl chloride have long been assumed to undergo S_N1 solvolysis, both compounds show considerable steric hindrance with respect to bimolecular (S_N2) reaction,[9] and it has recently been shown that not more than a small fraction of the racemisation of *p*-chlorodiphenylmethyl chloride in acetone, a poor ionising solvent, could occur bimolecularly.[10] It seems reasonable to assume that analogous considerations apply to *p*-nitrodiphenylmethyl chloride. Evidence has recently been presented to show that the reaction of diphenylmethyl bromide with nucleophilic reagents in nitromethane involves both first- and second-order components, the latter being interpreted as arising from bimolecular attack on the partially heterolysed substrate.[11] The very rapid bimolecular attack by azide ions in nitromethane is, however, not observed with diphenylmethyl chloride in aqueous acetone where, within the limits of experimental error, all the azide intervention occurs by the unimolecular mechanism.[12] Water, a much less powerful nucleophilic agent than azide ions, is even less likely to show bimolecular attack. It is therefore considered that the reaction between 50% aqueous acetone and the present compounds (as well as the two compounds previously studied in this solvent [3a]) occurs entirely by mechanism S_N1.

TABLE 1. *Kinetic data for solvolysis in 50% aqueous acetone.*

(*k* in sec.$^{-1}$, *E* in kcal., d*E*/d*T* in cal. °K^{-1}.)

(i) *p*-Nitrodiphenylmethyl chloride.

Temp.	10^6k	Temp.	$E_{obs.}$	$E_{calc.}$
20·60°	$5{\cdot}318 \pm 0{\cdot}012_3$	25·12°	$22{\cdot}48_5 \pm 0{\cdot}060$	$22{\cdot}48_6$
29·65	$16{\cdot}81 \pm 0{\cdot}034_5$	34·48	$22{\cdot}18_7 \pm 0{\cdot}056$	$22{\cdot}19_1$
39·31	$52{\cdot}55 \pm 0{\cdot}10_6$	44·35	$21{\cdot}88_9 \pm 0{\cdot}049$	$21{\cdot}88_0$
49·39	$158{\cdot}1 \pm 0{\cdot}22_8$	54·90	$21{\cdot}54_3 \pm 0{\cdot}052$	$21{\cdot}54_8$
60·41	$480{\cdot}0 \pm 0{\cdot}85_9$			

$dE/dT = -31{\cdot}5 \pm 2{\cdot}4$

(ii) t-Butyl chloride.

Temp.	10^6k	Temp.	$E_{obs.}$	$E_{calc.}$
0·00°	$9{\cdot}120 \pm 0{\cdot}021_4$	5·00°	$21{\cdot}08_5 \pm 0{\cdot}041$	$21{\cdot}09_7$
10·00	$35{\cdot}95 \pm 0{\cdot}046_4$	14·90	$20{\cdot}84_2 \pm 0{\cdot}048$	$20{\cdot}84_9$
19·81	$124{\cdot}2_5 \pm 0{\cdot}31_6$	24·68	$20{\cdot}65_0 \pm 0{\cdot}061$	$20{\cdot}60_4$
29·55	$389{\cdot}0 \pm 0{\cdot}85_6$	34·70	$20{\cdot}32_6 \pm 0{\cdot}051$	$20{\cdot}35_4$
39·86	$1183{\cdot}_7 \pm 2{\cdot}0_6$			

$dE/dT = -25{\cdot}0 \pm 2{\cdot}1$

(iii) *p*-Methylbenzylidene chloride.

Temp.	10^6k *	Temp.	$E_{obs.}$	$E_{calc.}$
0·00°	$2{\cdot}682 \pm 0{\cdot}0060_9$	5·02°	$21{\cdot}82_5 \pm 0{\cdot}051$	$21{\cdot}80_7$
10·05	$11{\cdot}17 \pm 0{\cdot}026_9$	14·75	$21{\cdot}46_8 \pm 0{\cdot}057$	$21{\cdot}44_6$
19·46	$38{\cdot}08 \pm 0{\cdot}081_9$	24·68	$20{\cdot}98_6 \pm 0{\cdot}043$	$21{\cdot}07_8$
29·90	$132{\cdot}0 \pm 0{\cdot}17_4$	34·84	$20{\cdot}75_4 \pm 0{\cdot}053$	$20{\cdot}70_1$
39·77	$391{\cdot}4 \pm 0{\cdot}95_1$			

$dE/dT = -37{\cdot}1 \pm 3{\cdot}5$

* Per replaceable chlorine atom.

The kinetic results now obtained are summarised in Table 1; all the errors quoted are standard errors. Energies of activation, $E_{obs.}$, were obtained from rates at adjacent temperatures by use of the Arrhenius equation and refer to the mean temperature of the interval,[3a] the temperature coefficient of the activation energy, d*E*/d*T*, was obtained from the slope of the " best " straight plot of *E* against *T*, and $E_{calc.}$ refers to the activation

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[9] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200; Hughes and de la Mare, *J.*, 1956, 845.

[10] Gall and Winstein, *Tetrahedron Letters*, 1960, No. 2, 31.

[11] Pocker, *J.*, 1959, 3939, 3943.

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

energies required by this line. This method of calculation assumed that dE/dT is constant over the temperature range investigated, and it can be seen that the observed and calculated activation energies agree within the limits of experimental error. The temperature dependence of dE/dT is therefore small and the present results are not sufficiently accurate to allow its recognition.

The reaction of t-butyl chloride with a number of acetone–water mixtures has already been studied by Tommila and his co-workers.[2a] Their values for the energy and entropy of activation in 46% (w/w) acetone agree fairly well with those calculated from the present results in our solvent [which corresponds to 44·2% (w/w) acetone] at 32·5°, the mean temperature of the previous work; unfortunately, the results in 46% (w/w) acetone are not sufficiently accurate to yield a value for the temperature coefficient of the activation energy. In the present solvent, this coefficient is about one-half the mean value previously reported for a number of highly aqueous acetone–water mixtures,[2a] and is also less than the value already estimated for reaction with pure water.[13] There is however no reason why this coefficient should be independent of the solvent composition.

DISCUSSION

p-*Methylation in Benzylidene Chloride.*—The effect of a *p*-methyl substituent on the rate of hydrolysis of benzylidene chloride can be found by combining the present results with those obtained earlier for the parent compound.[3a] The changes in the rate of solvolysis resulting from this substitution are given in Table 2 for a number of compounds known to react by mechanism S_N1. It can be seen that the relative rates (k_{Me}/k_H) decrease with increasing facility for electron donation to the reaction centre by the groups, other than the phenyl group to be substituted, which are directly attached to the central carbon atom, probably because of the resulting reduction in the demand for electrons at the site of substitution (cf. ref. 3*c*). Admittedly, the largest value of k_{Me}/k_H also corresponds to the best ionising solvent in this series but the effect of *para*-substituents on the rates of S_N1 reactions is usually fairly insensitive to changes in solvent.[3c,14] It is also noteworthy that the acceleration caused by *p*-methylation in benzylidene chloride almost entirely results from a reduction in the activation energy, the entropy of activation being virtually unchanged (see Table 3). This type of behaviour is to be expected in S_N1 reactions—and

TABLE 2. *The effect of* p-*methyl substituents on the rates of* S_N1 *reactions at* 25°

Compound	$Ph{\cdot}CHCl_2$	$Ph{\cdot}CHMe{\cdot}Cl$ [a]	$Ph{\cdot}CHPh{\cdot}Cl$ [b]	$Ph{\cdot}CMe_2{\cdot}Cl$ [c]	$Ph{\cdot}CPh_2{\cdot}Cl$ [d]
Solvent	50% acetone *	79·5% dioxan *	80% acetone *	90% acetone *	60% ether †
k_{Me}/k_H	79·2	56·2	21·4	26·0	4·1

* Water as second component. † Ethanol as second component.

[a] Mechelynk-David and Fierens, *Tetrahedron*, 1959, **6**, 232. [b] Hughes, Ingold, and Taher, *J.*, 1940, 949. [c] Brown, Brady, Grady, and Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897. [d] Branch and Nixon, *ibid.*, 1936, **58**, 492.

TABLE 3. *Activation parameters for* S_N1 *solvolysis in* 50% *aqueous acetone at* 50°.

E and $\Delta S^‡$ from the "best" straight plots of $E_{obs.}$ against T and $\Delta S^‡_{obs.}$ against log T, respectively. The standard errors which are quoted for E and $\Delta S^‡$ arise from the standard error in dE/dT. E is in kcal., $\Delta S^‡$ in cal. °K^{-1}.

Compound	E	$-\Delta S^‡$	$-\Delta C^‡$	$\Delta C^‡/\Delta S^‡$
$PhCCl_3$ *†	19·315 ± 0·129	16·17 ± 0·42	45·8 ± 4·3	2·83 ± 0·28
$PhCHCl_2$ *†	22·917 ± 0·018	11·33 ± 0·05	29·7 ± 3·6	2·62 ± 0·32
p-$MeC_6H_4{\cdot}CHCl_2$ *	20·140 ± 0·105	11·97 ± 0·35	39·1 ± 3·5	3·27 ± 0·31
p-$NO_2{\cdot}C_6H_4{\cdot}CHPhCl$	21·702 ± 0·032	10·81 ± 0·21	33·5 ± 2·4	3·10 ± 0·22
Bu^tCl	19·971 ± 0·063	10·28 ± 0·09	27·0 ± 2·1	2·63 ± 0·21

* $\Delta S^‡$ and $\Delta C^‡/\Delta S^‡$ per replaceable chlorine atom. † Calculated from Bensley and Kohnstam's data.[2a]

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[13] Robertson, Heppolette, and Scott, *Canad. J. Chem.*, 1959, **37**, 803.

[14] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1909.

is also observed with the other compounds listed in Table 2—and therefore supports the assignment of mechanism S_N1 to the hydrolysis of benzylidene chloride.

$\Delta C^{\ddagger}/\Delta S^{\ddagger}$.—Activation parameters for S_N1 solvolysis in 50% aqueous acetone are given in Table 3 for the compounds for which the temperature-dependence of these parameters has been studied. It can be seen that, within the limits of experimental error, $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ is independent of the nature of the substrate, in agreement with the earlier prediction.[3b]

This prediction was based on the assumption that the entropy and heat capacity of activation in S_N1 reactions are almost entirely controlled by the increase in solvation associated with passage into the more polar transition state. This view is not supported by Robertson and his co-workers for solvolysis in water.[13,15] Most of the reactions considered by these workers occur by the bimolecular mechanism, but their analysis of the contributions to $\Delta S^{\ddagger}$ and $\Delta C^{\ddagger}$ which arise from interactions between the solvent and the initial and transition states suggests that $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ should depend on the structure of the substrate for all nucleophilic substitution reactions, contrary to the present observations. It may well be that the factors controlling the magnitude of $\Delta C^{\ddagger}$ and $\Delta S^{\ddagger}$ are not the same in water as in aqueous acetone where one of the solvent components can " solvate " an organic substrate. For example, the entropy of activation for the hydrolysis of t-butyl chloride in water decreases rapidly when small amounts of acetone are added to the solvent,[2a] although the partial molar entropy of water changes little under these conditions; this can be readily demonstrated by combining Ewert's vapour-pressure data [16] with the results of Kister and Waldmann's thermal measurements.[17] A detailed discussion of this point is deferred till current work on solvolysis in other acetone–water mixtures has been completed, but the results already available show that the ratio $\Delta C^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 reactions in such mixtures depends only on the solvent and the temperature, for both chlorides and bromides.

EXPERIMENTAL

Preparation of Materials.—*p*-Nitrodiphenylmethane was prepared by Friedel–Crafts reaction between *p*-nitrobenzyl chloride and benzene,[18] and converted into *p*-nitrodiphenylmethyl bromide by reaction with *N*-bromosuccinimide in carbon tetrachloride in the presence of a small quantity of benzoyl peroxide.[19] The bromide was hydrolysed by refluxing it with aqueous acetone, and the alcohol obtained after removal of the acetone and extraction of the residue with ether. It was purified by recrystallisation from petroleum (b. p. 80—100°) and had m. p. 73—74° (uncorr.). A sample prepared by Meerwein–Ponndorf reduction of *p*-nitrobenzophenone had the same m. p. and mixed m. p. The pure alcohol was chlorinated for 8 hr. in benzene–ether (8 : 1) in the presence of anhydrous zinc chloride by a stream of dry hydrogen chloride. The solution was washed and dried ($MgSO_4$), and the solvent removed under reduced pressure. Repeated recrystallisation of the residue from light petroleum (b. p. 40—60°) gave *p*-nitrodiphenylmethyl chloride, m. p. 43·5—44·5°. *p*-Methylbenzylidene chloride was obtained by the action of phosphorus pentachloride on *p*-tolualdehyde in light petroleum,[20] and purified by distillation under reduced pressure and recrystallisation from light petroleum; it had m. p. 47·5°. t-Butyl chloride, purified by fractional distillation, had n_D^{18} 1·3865. The acid produced by the complete hydrolysis of these chlorides was never less than 99·3% of the theoretical amount.

Acetone was purified as previously described,[3a] and 50% aqueous acetone was prepared by mixing equal volumes of acetone and water.

Rate Measurements and Calculations.—Rates of hydrolysis were measured by methods similar to those employed in the previous work,[3a] and the " observed " values of energies and entropies of activation were calculated from rate coefficients at adjacent temperatures and

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[15] Robertson, *Suomen Kem.*, 1960, **33**, *A*, 44.

[16] Ewert, Thesis, Brussels, 1936.

[17] Kister and Waldmann, *J. Phys. Chem.*, 1958, **62**, 245.

[18] Bayer and Villiger, *Ber.*, 1904, **37**, 605.

[19] Dauben and Layton, *J. Amer. Chem. Soc.*, 1959, **81**, 5404.

[20] Auwers and Keil, *Ber.*, 1903, **36**, 1861.

assumed to refer to the mean temperature of the interval. The standard error in E is then given by

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

where σ is the standard error of k, and the subscripts 1 and 2 refer to the temperatures T_1 and T_2, respectively.[21] The standard error of $\mathrm{d}E/\mathrm{d}T$ was obtained in one of two ways:

(i) from the " best " straight plot of E against T, then

$$\sigma(\mathrm{d}E/\mathrm{d}T) = \left[\frac{\sum(E_{\text{obs.}} - E_{\text{calc.}})^2}{(n-2)\sum\theta^2}\right]^{\frac{1}{2}}$$

where n is the number of determinations, θ the difference between the temperature and the mean temperature for all the determinations, and $E_{\text{calc.}}$ the value given by the " best " straight plot of E against T.

(ii) from the standard error in E, whereupon

$$\sigma(\mathrm{d}E/\mathrm{d}T) = \{\sum[\theta.\sigma(E)]^2\}^{\frac{1}{2}}/\sum\theta^2$$

The value of $\sigma(\mathrm{d}E/\mathrm{d}T)$ quoted in Table 1 and employed to obtain the errors in the values given in Table **3** was always the larger of the values obtained from (i) and (ii).

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