

298. Rates and Activation Parameters in the Solvolysis of Organic Chlorides and Bromides.

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Rates, activation parameters, and their temperature coefficients have been obtained for S_N1 and S_N2 hydrolysis of a number of chlorides and bromides in aqueous acetone. The ratio of the heat capacity of activation (ΔC^\ddagger) to the entropy of activation (ΔS^\ddagger) is independent of the nature of the substrate in S_N1 hydrolysis but has a different value when mechanism S_N2 is operating. The recognition of solvolytic mechanisms from the values of $\Delta C^\ddagger/\Delta S^\ddagger$ is discussed.

For both mechanisms, the greater reactivity of the bromide than of the corresponding chloride arises mainly from a lower activation energy, and the increase in solvation on passage into the transition state does not appear to be quite as large for the bromide as for the chloride.

The mechanism of the hydrolysis of benzyl bromide is discussed.

RECENT work on the solvolysis of organic halides and sulphonates has shown¹⁻³ that these reactions are associated with a negative temperature coefficient for the activation energy, E , and hence with a negative heat capacity of activation, $\Delta C^\ddagger = dE/dT - R$. Bensley and Kohnstam tentatively suggested⁴ that the ratio $\Delta C^\ddagger/\Delta S^\ddagger$ (where ΔS^\ddagger is the entropy of activation) should be independent of the nature of the substrate for S_N1 solvolysis, and that this ratio should have a larger value than when reaction occurs by the bimolecular mechanism, S_N2 , under the same experimental conditions. This criterion, if valid, affords an additional test of solvolytic mechanism but little relevant information was available at the time. Since then the constancy of $\Delta C^\ddagger/\Delta S^\ddagger$ in S_N1 solvolysis has been demonstrated for the reactions of structurally different chlorides with 50% aqueous acetone¹ and substituted diphenylmethyl chlorides with the 70% solvent.⁵ The present paper reports solvolytic studies of a number of chlorides and bromides, aimed at obtaining further information about the effect of changes in the structure of the substrate and of changes in the reaction mechanism on the value of $\Delta C^\ddagger/\Delta S^\ddagger$. It was also hoped that the results would show whether changes in the energy or entropy of activation are mainly responsible for the increase in the rate of solvolysis when an organic chloride is replaced by the corresponding bromide. A preliminary summary of the results has already been reported⁶ and has also been included in a recent discussion of activation parameters in solvolytic reactions.⁷

Studies of S_N1 hydrolysis were carried out with diphenylmethyl chloride, 4-nitrodiphenylmethyl chloride and bromide, and t-butyl chloride and bromide. The evidence for the operation of this mechanism in these reactions has recently been summarised,¹ and it is not considered that the effect of changes in the solvent on the rate of solvolysis⁸ demands a different interpretation. Ethyl, n-propyl, and n-butyl bromide, and benzyl chloride and bromide were chosen as examples of compounds which undergo S_N2 solvolysis. This mechanism is generally considered to operate in the reactions between simple primary halides and aqueous organic solvents,⁹ and an examination of the available evidence led to the conclusion that the solvolysis of benzyl chloride also occurs mainly, if not entirely,

¹ Brittain, Kohnstam, Shillaker, and Queen, *J.*, 1961, 2045, and references there cited.

² Robertson and Scott, *J.*, 1961, 1596, and references there cited.

³ Moelwyn-Hughes, *J.*, 1961, 1517, and references there cited.

⁴ Bensley and Kohnstam, *J.*, 1957, 4747.

⁵ Kohnstam, *J.*, 1960, 2066.

⁶ Cowie, Fox, Fitches, Hooton, Hunt, Kohnstam, and Shillaker, *Proc. Chem. Soc.*, 1961, 222.

⁷ Kohnstam, "The Transition State," *Chem. Soc. Special Publ.*, No. 16, 1962, p. 179.

⁸ MacLachlan and Swain, *J. Amer. Chem. Soc.*, 1960, 82, 6095.

⁹ Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 352.

by the same mechanism.⁴ It seemed very likely that similar conclusions apply to the solvolysis of benzyl bromide, and this has been confirmed by the present results (cf. p. 1591)

EXPERIMENTAL

Preparation of Materials.—Ethyl bromide (b. p. 38.0°/759 mm.), n-propyl bromide (b. p. 70.5°/751 mm.), n-butyl bromide (b. p. 101.3°/760 mm.), t-butyl chloride (n_D^{20} 1.3870) and bromide (n_D^{25} 1.4260), benzyl chloride (n_D^{15} 1.5420) and bromide (m. p. -4°) were commercial samples which had been dried and fractionated, sometimes under reduced pressure. 4-Nitrodiphenylmethyl bromide was prepared by passing dry hydrogen bromide into a benzene solution of the alcohol¹ in the presence of lithium bromide for *ca.* 6 hr. The solution was washed and dried (Na₂SO₄), the solvent distilled off, the residue passed in light petroleum (b. p. 60–80°) down a Celite column, and the solvent removed; the product had m. p. 32°. Diphenylmethyl chloride and its 4-nitro-derivative were prepared and purified as previously described.^{1,5}

The acid produced by the complete hydrolysis of these halides was always greater than 99% of the calculated amount, and vapour-phase chromatography of the more volatile compounds also indicated purities better than 99%.

Measurement of Reaction Rates and Activation Parameters.—The methods employed in the determination of reaction rates, and in the calculation of the activation parameters and their errors, were similar to those previously described.¹ The hydrolysis of *ca.* 0.02M-halides was studied in aqueous acetone; “*x*%” acetone refers to the mixture in the proportions *x* volumes of purified acetone¹⁰ to (100 - *x*) volumes of water. Reactions were followed over *ca.* three “half-lives” by noting the development of acidity and always yielded constant first-order rate coefficients. Check experiments showed no evidence of reversibility in the prevailing experimental conditions.

The sealed-ampoule technique was employed in kinetic runs above 30°. For the most volatile compound, ethyl bromide, the free space above the solution was kept very small by the use of special ampoules in order to minimise loss of the substrate by evaporation at the relatively high temperatures used, and the ampoules were filled at 0°. Nevertheless, the results for this compound were the least accurate which were obtained.

The rate coefficients obtained from the development of acidity refer to the overall decomposition of the halide. Olefin elimination may accompany hydrolysis in the reactions of the n-alkyl bromides and the evaluation of rates of hydrolysis therefore requires a knowledge of the amounts of olefin produced. A modification of the aspiration method¹¹ showed that olefins did not account for more than 0.3% of the products of the complete reaction of initially 0.05M-n-butyl and n-propyl bromide with “50%” acetone; check experiments confirmed the reliability of the method. Similarly, no propene could be detected by vapour-phase chromatography of the products from a mixture of 12 g. of n-propyl bromide and 100 ml. of “50%” acetone. The observed rate coefficients for the S_N2 reactions could therefore be accepted as the rate coefficients for hydrolysis.

The rate coefficient observed in the S_N1 reactions were taken as the rate coefficients for the ionisation of the substrate, it being assumed that mass-law and ionic-strength effects¹² could be ignored. The relevant data are available for the t-butyl halides,¹² diphenylmethyl chloride and its 4-nitro-derivative,¹³ and show that this assumption is justified under the present experimental conditions. This also applies to the bromides studied since, in general, the mass-law constants of these compounds do not differ greatly from those of the corresponding chlorides.¹³

As each solvent was made up by volume, different batches of the “same” solvent did not have exactly the same composition. Each batch was therefore monitored by studying the rate of hydrolysis of benzotrchloride or diphenylmethyl chloride. The sensitivity of the rate of hydrolysis of these compounds and of the substrate in question to small changes in the solvent composition gave the necessary correction factor which allowed all rates to be calculated for hydrolysis in the same “50%,” “70%,” or “80%” acetone. The first two of these solvents were chosen to be the same as those previously studied.^{1,4} The resulting mean rate coefficients (*k*, in sec.⁻¹) are given below together with their standard errors.

¹⁰ Bunsley and Kohnstam, *J.*, 1955, 3408.

¹¹ Hughes, Ingold, and Shapiro, *J.*, 1936, 230.

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

¹³ Kohnstam, Queen, and Tidy, unpublished work.

(a) *Hydrolysis in "50%" acetone.*

Ethyl bromide: $10^6k = 1.882 \pm 0.011_2$ (50.05°), $5.152 \pm 0.015_5$ (59.91°), $13.62 \pm 0.047_1$ (70.06°), $32.97 \pm 0.34_6$ (80.00°), $75.88 \pm 0.62_0$ (90.00°).

n-Propyl bromide: $10^6k = 0.8957 \pm 0.0047_8$ (50.02°), $2.382 \pm 0.0092_2$ (59.63°), $6.263 \pm 0.027_2$ (69.84°), $15.53 \pm 0.068_5$ (80.06°), $35.30 \pm 0.10_1$ (90.00°).

n-Butyl bromide: $10^6k = 0.7708 \pm 0.0031_4$ (50.02°), $2.060 \pm 0.0065_9$ (59.63°), $5.415 \pm 0.023_2$ (69.84°), $13.37 \pm 0.056_8$ (80.06°), $30.40 \pm 0.13_2$ (90.00°).

Benzyl bromide: $10^6k = 9.447 \pm 0.018_7$ (29.95°), $25.61 \pm 0.053_3$ (39.67°), $65.12 \pm 0.097_6$ (49.42°), $157.2 \pm 0.20_0$ (59.37°), $348.3 \pm 0.30_8$ (68.97°).

(b) *Hydrolysis in "70%" acetone.*

Benzyl chloride: $10^6k = 4.294 \pm 0.010_2$ (74.74°), $10.18 \pm 0.021_3$ (85.05°), $21.85 \pm 0.033_4$ (94.82°), $45.89 \pm 0.068_5$ (104.90°), $91.95 \pm 0.084_7$ (114.97°).

Benzyl bromide: $10^6k = 8.701 \pm 0.0037_1$ (44.82°), $21.95 \pm 0.021_7$ (54.86°), $52.33 \pm 0.076_2$ (65.01°), $116.0 \pm 0.20_8$ (74.94°), $243.1 \pm 0.32_6$ (84.88°).

t-Butyl chloride: $10^6k = 4.490 \pm 0.011_1$ (16.84°), $13.22 \pm 0.031_9$ (25.08°), $44.46 \pm 0.088_2$ (35.07°), $131.6 \pm 0.33_5$ (44.73°), $371.4 \pm 0.76_0$ (54.74°).

t-Butyl bromide: $10^5k = 2.717 \pm 0.0073_9$ (−0.03°), $12.07 \pm 0.017_5$ (10.92°), $37.76 \pm 0.11_3$ (20.07°), $112.2 \pm 0.29_7$ (29.62°), $282.2 \pm 0.81_5$ (38.25°).

4-Nitrodiphenylmethyl chloride: $10^6k = 5.710 \pm 0.0022_6$ (45.00°), $18.31 \pm 0.025_1$ (55.18°), $45.43 \pm 0.13_8$ (63.70°), $209.4 \pm 0.45_0$ (79.44°), $814.3 \pm 1.8_0$ (95.10°).

4-Nitrodiphenylmethyl bromide: $10^6k = 2.769 \pm 0.0036_0$ (15.21°), $10.17 \pm 0.020_3$ (24.79°), $38.32 \pm 0.057_5$ (35.34°), $116.5 \pm 0.33_8$ (44.90°), $340.7 \pm 0.68_1$ (54.87°).

(c) *Hydrolysis in "80%" acetone.*

Diphenylmethyl chloride: $10^6k = 0.4771 \pm 0.0017_2$ (−10.90°), $2.544 \pm 0.0037_7$ (0.00°), $20.18 \pm 0.040_2$ (15.00°), $68.73 \pm 0.17_9$ (24.95°), $366.4 \pm 1.0_9$ (40.12°).

t-Butyl chloride: $10^6k = 3.474 \pm 0.0083_4$ (29.99°), $11.08 \pm 0.026_0$ (39.66°), $36.10 \pm 0.084_4$ (50.27°), $98.05 \pm 0.24_9$ (59.97°), $254.3 \pm 0.58_8$ (69.95°).

t-Butyl bromide (Measurements by Mr. D. HUNT): $10^6k = 4.385 \pm 0.010_2$ (0.00°), $16.23 \pm 0.040_6$ (9.37°), $67.06 \pm 0.18_8$ (20.54°), $198.6 \pm 0.64_0$ (29.77°), $594.0 \pm 0.81_5$ (39.85°).

Experimental values of the energy ($E_{\text{obs.}}$) and entropy of activation ($\Delta S^\ddagger_{\text{obs.}}$) were obtained from the rates at adjacent temperatures, as previously described,¹ and were assumed to refer to the mean temperature of the *ca.* 10° interval. It can easily be shown that this assumption causes only a negligibly small error even if dE/dT (or ΔC^\ddagger) varies according to the expression, $dE/dT = a + bT + cT^2$, where a , b , and c are only constant over the temperature interval in question. All our experiments gave linear plots of $E_{\text{obs.}}$ against T within the limits of experimental error; *i.e.*, dE/dT and ΔC^\ddagger were constant, within these limits, over the experimental temperature range.

Our results are summarised in Table 1 where rates and activation parameters are quoted for reaction at 50°; all the errors are standard errors. Values of k at 50° were calculated from k at the nearest experimental temperature and the appropriate activation parameters. The figures for E and ΔS^\ddagger were obtained from the "best" straight lines for $E_{\text{obs.}}$ against T and $\Delta S^\ddagger_{\text{obs.}}$ against $\log T$, respectively. This procedure involved extrapolation beyond the experimental temperature range in a few cases, and the resulting values of E and ΔS^\ddagger are therefore subject to an additional uncertainty which arises from the implicit assumption of a constant ΔC^\ddagger . However, errors from this cause are likely to be very small, if not entirely negligible, since the temperature coefficient of ΔC^\ddagger is clearly not large and since 50° was never very far outside the experimental range.

The results for the n-alkyl bromides are less accurate than those for the other compounds studied, probably because these relatively volatile halides had to be examined at high temperatures where some loss of the substrate from the solution may have occurred during reaction. In spite of precautions to minimise this effect in the hydrolysis of ethyl bromide (see p. 1586), the results for this compound are the least accurate which were obtained and lead to an error in ΔC^\ddagger which is large enough to make the value of this parameter unreliable.

Previous rates of hydrolysis for ethyl bromide,¹⁴ t-butyl bromide and chloride,¹⁴ benzyl

¹⁴ Tommila, Tiliäinen, and Voipio, *Ann. Acad. Sci. Fennicae*, 1955, AII, No. 65.

TABLE 1.
Kinetic data for reaction with aqueous acetone at 50°.
(k in sec.⁻¹, E in kcal. mole⁻¹, ΔS^\ddagger and ΔC^\ddagger in cal. mole⁻¹ deg.⁻¹.)

	$-\log k$	E	$-\Delta S^\ddagger$	$-\Delta C^\ddagger$	$\Delta C^\ddagger/\Delta S^\ddagger$
(a) " 50% " Acetone.					
EtBr	5.7277	22.00 ₂ ± 0.22 ₃	18.82 ± 0.67	23.6 ± 11.4	1.25 ± 0.66
Pr ⁿ Br	6.0488	21.85 ₀ ± 0.12 ₃	20.78 ± 0.36	23.4 ± 6.2	1.13 ± 0.30
Bu ⁿ Br	6.1140	21.93 ₅ ± 0.11 ₉	20.82 ± 0.35	27.6 ± 6.0	1.32 ± 0.31
Ph·CH ₂ Cl *	5.5086	20.60 ₄ ± 0.07 ₇	22.41 ± 0.21	21.2 ± 3.6	0.95 ± 0.16
Ph·CH ₂ Br	4.1632	19.02 ₇ ± 0.00 ₁	20.85 ± 0.00	23.5 ± 2.4	1.13 ± 0.10
(b) " 70% " Acetone.					
Ph·CH ₂ Cl	6.3800	21.30 ₁ ± 0.11 ₂	23.96 ± 0.32	21.7 ± 2.9	0.91 ± 0.13
Ph·CH ₂ Br	4.8494	19.11 ₂ ± 0.04 ₃	23.75 ± 0.12	23.4 ± 2.8	0.99 ± 0.12
Bu ⁿ Cl	3.6392	21.48 ₁ ± 0.04 ₇	10.89 ± 0.15	38.0 ± 3.2	3.49 ± 0.30
Bu ⁿ Br	2.0502	19.35 ₃ ± 0.16 ₂	10.20 ± 0.53	38.3 ± 5.3	3.75 ± 0.56
4-NO ₂ ·C ₆ H ₄ ·CHPhCl	4.9888	23.77 ₂ ± 0.04 ₅	9.96 ± 0.13	39.8 ± 2.6	4.00 ± 0.27
4-NO ₂ ·C ₆ H ₄ ·CHPhBr	3.6904	22.36 ₇ ± 0.03 ₄	8.38 ± 0.11	30.4 ± 2.3	3.62 ± 0.28
(c) " 80% " Acetone.					
Ph ₂ CHCl	3.0080	19.88 ₂ ± 0.15 ₃	12.96 ± 0.50	39.4 ± 4.2	3.04 ± 0.36
Bu ⁿ Cl	4.4550	22.18 ₄ ± 0.00 ₀	12.41 ± 0.00	32.5 ± 3.2	2.62 ± 0.26
Bu ⁿ Br	2.7838	20.02 ₇ ± 0.12 ₀	11.23 ± 0.40	31.5 ± 4.0	2.80 ± 0.37

* Recalculated from Bensley and Kohnstam's data.⁴

bromide and chloride,¹⁵ and diphenylmethyl chloride¹⁶ in aqueous acetone of similar composition to that now employed agree with the present values as well as can be expected for solvents made up by volume. The earlier energies and entropies of activation refer to the mean temperatures of the experimental ranges^{7,15a} and agree tolerably with our values for benzyl and diphenylmethyl halides at the same temperatures. This does not apply to the other three compounds, but the values in Table I are preferred since the previous data show indiscriminate increases and decreases of E with changing T and therefore appear to be subject to some inaccuracy. The values of ΔC^\ddagger now found for the hydrolysis of the n-alkyl bromides are not as negative as those previously reported for reaction in water.^{3,15} There is, however, no reason why ΔC^\ddagger should be independent of the solvent composition, especially as it seems very likely that its magnitude is controlled by different factors when solvolysis occurs in water and when it occurs in aqueous acetone.⁷

DISCUSSION

The Ratio $\Delta C^\ddagger/\Delta S^\ddagger$.—The S_N1 reaction of t-butyl and 4-nitrodiphenylmethyl chlorides and bromides with " 70% " acetone shows a constant value of $\Delta C^\ddagger/\Delta S^\ddagger$, within the limits of experimental error (see Table I). At 50°, this value (3.71) is almost the same as the value of 3.59 obtained under the same conditions for diphenylmethyl chloride, its 4-chloro-, 4-bromo-, and 4-iodo-derivatives, and 4-phenoxy- and 4-methoxy-benzyl chloride.^{5,6} Similar considerations apply to the S_N1 reaction of t-butyl chloride and bromide and diphenylmethyl chloride with " 80% " acetone where the value for this ratio (2.82) is also constant within the limits of experimental error and nearly the same as that for 4-methoxy-benzyl chloride (2.59).⁶ These results represent a part of the evidence for the conclusion^{6,7} that $\Delta C^\ddagger/\Delta S^\ddagger$ is independent of the nature of the substrate in S_N1 hydrolysis. It must, however, be stressed that the validity of this conclusion has, so far, only been demonstrated for reaction with aqueous acetone containing not more than 50% (v/v) of water.

The S_N2 hydrolysis of n-alkyl bromides, and benzyl chloride and bromide in " 50% " acetone at 50° yield $\Delta C^\ddagger/\Delta S^\ddagger = 0.9 - 1.3$ (see Table I), while the value of 2.89 is obtained for S_N1 reaction under these conditions.¹ Similar considerations apply to hydrolysis in

¹⁵ (a) Tommila, Paakala, Virtanen, Erva, and Varila, *ibid.*, 1959, AII, No. 91; (b) Koshy and Anantaraman, *J. Amer. Chem. Soc.*, 1960, **82**, 1574; (c) Hine and Lee, *ibid.*, 1951, **73**, 22.

¹⁶ Hughes, Ingold, and Taher, *J.*, 1940, 949.

“70%” acetone where the two benzyl compounds show a much smaller $\Delta C^\ddagger/\Delta S^\ddagger$ than the halides which undergo S_N1 reaction (see Table 1). It therefore appears that the value of $\Delta C^\ddagger/\Delta S^\ddagger$ can be employed for the recognition of solvolytic mechanism, as originally suggested by Bensley and Kohnstam.⁴

It must be stressed that this new test of mechanism can only be employed once it has been established that $\Delta C^\ddagger/\Delta S^\ddagger$ for S_N1 solvolysis is independent of the nature of the substrate. The general observation that ΔS^\ddagger is considerably more negative in S_N2 solvolysis than in the S_N1 reaction of a structurally similar compound^{4,7,17} then allows the conclusion that mechanism S_N2 is operating if solvolysis yields a value of ΔS^\ddagger which is less than that calculated from the observed ΔC^\ddagger and $(\Delta C^\ddagger/\Delta S^\ddagger)_{S_N1}$, the value of this ratio for compounds known to undergo S_N1 reaction under the same experimental conditions. If ΔS^\ddagger for S_N1 solvolysis is negative at the temperature under consideration, $(\Delta C^\ddagger/\Delta S^\ddagger)_{S_N1} > (\Delta C^\ddagger/\Delta S^\ddagger)_{S_N2}$, the form in which this mechanistic test was originally proposed.⁴

Robertson and Scott² have criticised mechanistic conclusions based on $\Delta C^\ddagger/\Delta S^\ddagger$ on the grounds that ΔS^\ddagger increases as the temperature is reduced (ΔC^\ddagger is always negative in solvolysis) and ultimately changes its sign. On this view, $\Delta C^\ddagger/\Delta S^\ddagger$ will be a discontinuous function which may be positive or negative, depending on the temperature. The arguments given in the preceding paragraph, however, show that even if this type of behaviour applies in the experimentally accessible temperature range,* it does not *per se* invalidate the present test of mechanism. In spite of this, we note that Robertson and Scott's results refer to solvolysis in water where this mechanistic criterion may not apply, though for quite different reasons. The constancy of $(\Delta C^\ddagger/\Delta S^\ddagger)_{S_N1}$ for solvolysis in aqueous acetone is consistent with a simple solvation model which assumes that the magnitudes of ΔC^\ddagger and ΔS^\ddagger are mainly, if not entirely, controlled by the increase in solvation by water associated with the activation process.⁷ Insufficient data are available at present to establish whether this ratio depends on the nature of the substrate for S_N1 solvolysis in water, but the positive ΔS^\ddagger for the hydrolysis of *t*-butyl chloride^{3,14,18} appears to argue against the validity of the simple solvation model for reaction in this solvent. This suggests that different factors control solvolysis in water and in aqueous organic solvents, and possible differences between these factors have already been discussed.⁷ On the other hand, it is conceivable that the assumed replacement of water-water interactions in the initial state by water-substrate interactions in the transition state lead to changes in entropy and heat capacity which, in S_N1 solvolysis, depend mainly on the number of water molecules involved. Under these conditions, $(\Delta C^\ddagger/\Delta S^\ddagger)_{S_N1}$ for solvolysis in water would be independent of the nature of the substrate, and the present mechanistic test could be applied to reaction in this solvent.

Solvolysis of Chlorides and Bromides.—The results in Table 1 show that the rate of solvolysis of *n*-alkyl bromides decreases with increasing chain-length, as expected. Replacement of ethyl bromide by *n*-propyl bromide changes the rate of solvolysis by almost

* Robertson and Scott obtain ΔS^\ddagger from the expression

$$\Delta S^\ddagger = \Delta S_0^\ddagger + \Delta C^\ddagger \ln T \quad \dots \quad (1)$$

As ΔS_0^\ddagger is always positive, they argue that ΔS^\ddagger must pass through zero at a temperature T_a , given by $\ln T_a = -\Delta S_0^\ddagger/\Delta C^\ddagger$. However, ΔS_0^\ddagger is an integration constant and not the value of ΔS^\ddagger at 0°K ,⁷ and we have no evidence to support the view [implied by eqn. (1)] that ΔC^\ddagger remains constant over wide ranges of temperature. Strictly, eqn. (1) is valid only over the experimental temperature range and a value of T_a well outside this range may well be unreliable. Moreover, T_a often lies well below the freezing point of the solvent and is therefore of no practical significance.

The summarised data for solvolysis in water¹⁸ show that a few reactions may have zero ΔS^\ddagger in the experimentally accessible temperature range, but the two examples mentioned by Robertson and Scott must be treated with reserve. The hydrolysis of allyl iodide appears to be complicated by side reactions, and their method of calculating ΔS^\ddagger , from an expression for $\log k$ in terms of T , leads to errors which are of similar magnitude to the positive values of ΔS^\ddagger at 0° . Additional errors may arise from the errors in the observed k 's, but the relevant data are unfortunately not given.

¹⁷ For references, see ref. 7.

¹⁸ Robertson, Heppollette, and Scott, *Canad. J. Chem.*, 1959, **37**, 803.

the same factor as it changes the rate of bromide-ion exchange in acetone,¹⁹ and a decrease in ΔS^\ddagger is entirely responsible for the change in rate in both sets of reactions. The exchange reaction is considered to occur by the more extreme form of mechanism S_N2 , and the calculation of the differences between the activation parameters for ethyl and n-propyl bromide leads to quantitative agreement with the observations.²⁰ The present results are therefore fully consistent with the operation of the same mechanism for hydrolysis in "50%" acetone.

The kinetic effects of replacing chlorine by bromine as the leaving group are illustrated in Table 2. It can be seen that these effects are not independent of the composition of the solvent and any comparisons should therefore refer to the same medium. There appears to be no connection between the increase in rate and the reaction mechanism; in "70%" acetone, $\Delta \log k$ has virtually the same value for the benzyl and t-butyl halides. The smaller $\Delta \log k$ found for the 4-nitrodiphenylmethyl compounds may arise from the presence of the electron-attracting nitro-group which could stabilise the initial state of the bromide to a greater extent than the initial state of the less polarisable chloride.

TABLE 2.
Differences between rates and activation parameters in the hydrolysis of RBr and RCl at 50°.

R·	Mechanism	Acetone (%)	$\Delta \log k$	$-\lambda \Delta E/2.303RT$	$\Delta \Delta S/2.303R$
Ph·CH ₂ ·	S_N2	50	1.3454	1.0678	0.3409
"	"	70	1.5306	1.4843	0.0459
Bu ^t ·	S_N1	70	1.5890	1.4390	0.1508
"	"	80	1.6712	1.4586	0.2579
4-NO ₂ ·C ₆ H ₄ ·CHPh·	"	70	1.2984	0.9501	0.3453

The results in Table 2 also show that 80%, or more, of the greater reactivity of the bromides arises from their lower activation energy.* The greater inductomeric polarisability of bromine than of chlorine can be expected to facilitate the heterolysis of the C-Hal linkage, but it is noteworthy that ΔE for the S_N2 hydrolysis of the benzyl compounds in "70%" acetone is almost the same as for the S_N1 reaction of the t-butyl halides with the same solvent. This observation emphasises the great importance of the bond-breaking process in S_N2 reactions.

Contrary to the present observations, Fainberg and Winstein²² have concluded that, on the average, changes in the energy and entropy of activation make roughly the same contribution to the increase in the rate of solvolysis when a chloride is replaced by the corresponding bromide. In many of the reactions considered by these workers, however, the activation parameters for RBr refer to a lower temperature than those for the RCl. Since ΔC^\ddagger is negative in solvolysis, this yields too small a change in E and too large a change in ΔS^\ddagger . It therefore seems very likely that the discrepancy between the Americans' conclusion and ours arises from the neglect of the temperature-dependence of the activation parameters in their work. It must, however, be stressed that the present reactions also show a small increase in ΔS^\ddagger on passing from RCl to RBr; $\Delta \Delta S^\ddagger \sim 1$ cal. mole⁻¹ deg.⁻¹ at 50° (Table 2). This suggests that passage into the transition state requires slightly less additional solvation by water in the hydrolysis of RBr than in the hydrolysis of RCl. It is fully consistent with this view that k_{RBr} is less sensitive to changes in the water content of the solvent than k_{RCl} (see Table 3, and refs. 22, 23), resulting in an increase of $\Delta \log k$ as the

* Similar considerations apply to the reaction between chloride ions and alkyl bromides and chlorides in acetone.²¹

¹⁹ de la Mare, *J.*, 1955, 3186.

²⁰ Fowden, de la Mare, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

²¹ de la Mare, *J.*, 1955, 3169; Hughes, Ingold, and Mackie, *J.*, 1955, 3173.

²² Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, (a) 1602, (b) 1608, (c) 4146.

²³ Streitwieser, *Chem. Rev.*, 1956, **56**, 571.

solvent is made less aqueous (see Table 2). This applies to both mechanisms of hydrolysis. Similarly, a smaller degree of transition-state solvation (relative to the initial state) for the bromide accounts for the relatively large value of $\Delta \log k$ (ca. 2.2) in the exchange reaction with chloride ions in acetone,²¹ a poor solvating agent for charged species, and for the relatively small $\Delta \log k$ (ca. 0.6—1.0) for S_N1 solvolysis in carboxylic acids^{22a,b} which are known to be particularly favourable to the solvation of incipient anions.* If the transition states in the solvolysis of RBr and RCl are associated with the same degree of charge development, the difference in the solvation of the transition states can be explained by analogy with the generally accepted relation between the degree of solvation of fully developed ions and their size. It is considered unlikely that this difference arises from additional steric hindrance to solvation of the incipient cation (resulting from the presence of the larger bromine atom) since there seems to be little connection between the extent of solvation of S_N1 transition states and the sizes of the groups attached to the reaction centre.⁷ There is, however, no reason to believe that the two compounds must show the same charge development in the activated complex, and the differences in solvation could arise from a less polar transition state in the solvolysis of RBr. The experimental results available at present do not allow us to favour either of these two possibilities.

TABLE 3.

The effect of solvent changes on the rate of hydrolysis at 50°
(The subscripts refer to the “%” acetone used as solvent.)

Substrate	Mechanism	$k_{50\%}/k_{70\%}$	$k_{70\%}/k_{80\%}$
Ph·CH ₂ Cl	S_N2	7.44	—
Ph·CH ₂ Br	„	4.86	—
4-MeO·C ₆ H ₄ ·CH ₂ Cl	S_N1	—	6.86 †
Bu ^t Cl	„	13.36 *	6.54
Bu ^t Br	„	—	5.42
Ph ₂ CHCl	„	—	6.83 §
4-NO ₂ ·C ₆ H ₄ ·CHPhCl	„	16.43 *	—

* Data for “50%” acetone from ref. 1. † Ref. 24. § Data for “70%” acetone from ref. 5.

Mechanism in the Hydrolysis of Benzyl Chloride and Bromide.—A consideration of the available information has already led to the conclusion that the reaction of benzyl chloride with aqueous organic solvents occurs mainly, if not entirely, by mechanism S_N2 .⁴ Many of the arguments then employed can also be applied to the bromide. Comparison of the hydrolysis with that of compounds known to undergo S_N1 reaction, including the structurally similar 4-methoxybenzyl chloride, shows that the rate of reaction of benzyl bromide is much less sensitive to solvent changes (see Table 3) and that the entropy of activation of this compound is ca. 10 cal. mole⁻¹ deg.⁻¹ more negative than that of the others (see Table 1 †). α -Chlorination and α -bromination in benzyl bromide alter the rate of hydrolysis by increasing both the energy and the entropy of activation; ^{15c} the dihalides undergo S_N1 hydrolysis, and α -halogen substituents would increase the rate of reaction by this mechanism through reduction of the activation energy.⁴ All these observations, and the value of $\Delta C^\ddagger/\Delta S^\ddagger$ (see Table 1), argue strongly in favour of similar mechanisms in the hydrolysis of benzyl chloride and bromide. This conclusion is supported by the rates which are to be expected if the two halides react entirely by mechanism S_N1 . These rates can now be calculated fairly reliably, and they are found to correspond to only a small fraction of the observed rates; details are given in the Appendix.

It has often been suggested that the operation of mechanism S_N1 is facilitated if the group X in RX is replaced by a better leaving group, X', such that the ionisation of the

* A similar explanation has already been proposed to account for the decrease in $\Delta \log k$ on passing from hydroxylic solvents to carboxylic acids.^{22b}

† For the hydrolysis of 4-MeO·C₆H₄·CH₂Cl in “70%” acetone, $\Delta S^\ddagger \sim -12$ cal. mole⁻¹ deg.⁻¹ at 50°.*

* Fox, Kohnstam and Shillaker, unpublished results.

C-X' linkage occurs more readily than the ionisation of C-X. Although the hydrolysis of benzyl chloride occurs near the border-line region which marks the transition from mechanism S_N2 to mechanism S_N1 , the present results show that the use of a better leaving group, bromine, does not significantly alter the reaction mechanism. This seems to arise from the fact that the heterolysis of C-X is also an important factor in determining the rate of S_N2 reaction, so that the use of a better leaving group may well facilitate the operation of mechanism S_N1 only slightly more than the operation of mechanism S_N2 . These considerations also account for the observation that the replacement of Cl by a still better leaving group, $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3$, only invokes completely S_N1 reaction at a slightly earlier stage in a series of increasing electron release towards the reaction centre.²⁵ It therefore appears that the nature of the leaving group is not a major factor in determining the mechanism of S_N reactions.

[*Added in Proof.*] The activation parameters discussed in this paper were obtained from the observed rates *via* the conventional form of Eyring's absolute rate equation for reactions in solution (cf. ref. 1). Biordi and Moelwyn-Hughes have recently reported²⁶ that the use of this equation yields $\Delta S^\ddagger = 0$ for the methanolysis of *t*-butyl chloride and iodide at 25° and that, therefore, "the free energy (ΔG^\ddagger) and heat of activation (ΔH^\ddagger) must be equal and independent of temperature, which is contrary to the facts." If this conclusion were correct, any arguments based on parameters derived from the Eyring equation would be unjustified. However, although $\Delta G^\ddagger = \Delta H^\ddagger$ at the temperature for which $\Delta S^\ddagger = 0$, the temperature coefficients of ΔG^\ddagger and ΔH^\ddagger are not equal at this temperature since they are defined by $d(\Delta G^\ddagger)/dT = -\Delta S^\ddagger$ and $d(\Delta H^\ddagger)/dT = \Delta C^\ddagger$, irrespective of the value of ΔS^\ddagger . Biordi and Moelwyn-Hughes's objection to the use of the Eyring equation is therefore not valid.

APPENDIX

Rates of entirely S_N1 hydrolysis can be obtained from the appropriate activation parameters, E_1 and ΔS_1^\ddagger .

Calculation of ΔS_1^\ddagger .—The change from "50%" to "70%" acetone hardly alters ΔS^\ddagger for the S_N1 hydrolysis of Bu^tCl and $4\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHPhCl}$ (see Table I and ref. 1). This mechanism also operates in the hydrolysis of $4\text{-PhO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ and $4\text{-MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$; $\Delta S^\ddagger = -12$ cal. deg.⁻¹ in "70%" acetone at 50°. The introduction of alkoxy-substituents decreases ΔS^\ddagger in S_N1 reactions⁷ and we therefore assumed, for "50%" and "70%" acetone at 50°:

$$\Delta S_1^\ddagger(\text{PhCH}_2\text{Cl}) = -10 \text{ cal. mole}^{-1} \text{ deg.}^{-1}.$$

$$\Delta S_1^\ddagger(\text{PhCH}_2\text{Br}) = -9 \text{ cal. mole}^{-1} \text{ deg.}^{-1}, \text{ since } \Delta\Delta S^\ddagger \sim 1 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \text{ (see p. 1590).}$$

Calculation of E_1 .—The assumption⁴ that α -chlorination always alters the S_N1 activation energy by the same amount yields, for "50%" acetone at 50°:

$$E_1(\text{Ph}\cdot\text{CH}_2\text{Cl}) = 26.52 \text{ kcal. mole}^{-1}, \text{ from the results for Ph}\cdot\text{CHCl}_2 \text{ and Ph}\cdot\text{CCl}_3,⁴$$

$E_1(\text{Ph}\cdot\text{CH}_2\text{Br}) = 26.52 \text{ kcal. mole}^{-1}$, from the results for $\text{Ph}\cdot\text{CHClBr}$ and $\text{Ph}\cdot\text{CCl}_2\text{Br}$,^{15c} corrected to refer to 50°.

On the average, the S_N1 activation energy of organic chlorides increases by 1.75 kcal. mole⁻¹ at 50° on passing from "50%" to "70%" acetone (see Table I and ref. 1). Hence, in "70%" acetone at 50°:

$$E_1(\text{Ph}\cdot\text{CH}_2\text{Cl}) = 28.27 \text{ kcal. mole}^{-1}, \text{ whence}$$

$$E_1(\text{Ph}\cdot\text{CH}_2\text{Br}) = 26.14 \text{ kcal. mole}^{-1}, \text{ from } E_{t\text{-BuCl}} - E_{t\text{-BuBr}} = 2.13 \text{ kcal. mole}^{-1} \text{ (see Table 1).}$$

$E_1(\text{Ph}\cdot\text{CH}_2\text{Cl})$ for "70%" acetone can also be obtained by another method. The S_N1 hydrolysis of $4\text{-PhO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ and $4\text{-MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ in "70%" acetone shows the same rate ratio ($k_{\text{MeO}}/k_{\text{PhO}}$) and the same activation energy difference ($E_{\text{MeO}} - E_{\text{PhO}}$) as the S_N1 solvolysis of the 4-substituted derivatives of 4'-nitrodiphenylmethyl chloride in similar solvents.²⁴ As the unsubstituted nitro-compound also reacts by this mechanism it seems reasonable to

²⁵ Kohnstam and Tidy, *Chem. and Ind.*, 1962, 1193.

²⁶ Biordi and Moelwyn-Hughes, *J.*, 1962, 4291.

assume that $E_{\text{PhO}} - E_{\text{H}}$ for the $S_{\text{N}}1$ hydrolysis of the benzyl chlorides has the same value as for the 4'-nitro-compounds. The resulting value of E_1 ($\text{Ph}\cdot\text{CH}_2\text{Cl}$) differs by less than 0.2 kcal. mole⁻¹ from that obtained in the preceding paragraph.

Rates.—The rate coefficients calculated for $S_{\text{N}}1$ hydrolysis (k_1) are always much less than those observed (k). At 50°, $k_1/k = 0.045$ and 0.022 for $\text{Ph}\cdot\text{CH}_2\text{Cl}$ in "50%" and "70%" acetone, respectively; for $\text{Ph}\cdot\text{CH}_2\text{Br}$ the corresponding figures are 0.053 and 0.029. The fact that two different methods of calculation yield virtually the same value of E_1 suggests that the figures for k_1/k are not seriously in error.

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