957. *Nucleophilic Substitution Reactions of Benzyl Halides. Part I. The Reaction of Benzyl Chloride with Partly Aqueous Solvents.*

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The heat capacity of activation for the solvolysis of benzyl chloride in 50% aqueous acetone and 50% aqueous ethanol has been determined. Two mechanistic explanations can be advanced to account for all the data now available for these reactions. Hydrolysis (or ethanolysis) may involve a single bimolecular reaction path, with an appreciable contribution of the valence-bond structure involving the carbonium ion, $Ph \cdot CH_2^+$, to the structure of the transition state. Alternatively, a continuous " spectrum " of transition states may be available to the reactant, but only a small fraction, at most, of the total solvolysis can proceed by unimolecular mechanisms. Concurrence of only the extreme forms of the two mechanisms is not supported by the evidence.

THE solvolysis of benzyl chloride has often been studied, and it is generally accepted that the reaction with partly aqueous solvents occurs in, or near, the border-line region which marks the transition from the bimolecular (S_N2) to the unimolecular (S_N1) mechanism. No agreement exists on whether the reaction path corresponds more closely to that of a

typical S_N1 or a typical S_N2 process, and both mechanisms have been proposed.[1-5] The present paper reports the determination of the temperature coefficient of the activation energy for reaction with " 50% " acetone * and " 50% " ethanol, and discusses the conclusions which can be drawn about the reaction mechanism from the evidence now available.

EXPERIMENTAL

Benzyl chloride was dried ($CaCl_2$) and distilled under reduced pressure; the content of hydrolysable chloride was 99·6% of the theoretical amount; n_D^{23} was 1·5375. The methods employed in the purification of solvents and in the measurement of reaction rates were similar to those already described.[6]

Solvolysis in " 50% " Acetone and " 50% " Ethanol.—Rate measurements were carried out in duplicate or triplicate. In any one kinetic run the rate coefficient (k) was obtained from the integrated first-order rate equation as the mean of at least ten separate determinations. The results of two typical runs are given below (t in sec., k in sec.$^{-1}$):

(i) " 50% " Acetone at 80·01°; 3·765 ml. samples titrated with 0·00490N-NaOH:

$10^{-3}t$	0	2·400	4·560	6·960	9·360	12·36	14·16
Titre	0·13	1·23	2·12	3·02	3·76	4·60	5·06
10^5k	—	4·60	4·61	4·62	4·53	4·48	4·47
$10^{-3}t$	17·70	22·80	26·46	28·56	32·10	35·70	∞
Titre	5·95	6·93	7·52	7·73	8·23	8·63	10·64
10^5k	4·56	4·57	4·59	4·50	4·52	4·63	—

10^5k (mean) = 4·557; duplicate runs gave 4·581, 4·575.

(ii) " 50% " Ethanol at 80·06°, 3·765 ml. samples titrated with 0·00528N-NaOH:

$10^{-3}t$	0	0·600	1·200	1·800	2·400	3·000	4·500
Titre	0·25	1·35	2·35	3·24	4·04	4·69	6·19
10^4k	—	1·846	1·859	1·853	1·867	1·832	1·853
$10^{-3}t$	5·700	6·900	8·100	9·360	10·92	∞	
Titre	7·12	7·85	8·38	8·86	9·38	10·75	
10^4k	1·864	1·865	1·838	1·832	1·865	—	

10^4k (mean) = 1·850; a duplicate run gave 1·841.

Rate coefficients were multiplied by a small correction factor (which was determined by examining the solvolytic rate of benzotrichloride in the present solvents) in order to ensure that the results referred to the same " 50% " solvents as were employed in our earlier study of benzylidene chloride and benzotrichloride.[6] The resulting final rate coefficients are (in sec.$^{-1}$):

" 50% " Acetone	Temp.	50·01°	60·08°	69·89°	80·01°	89·90°	—
	10^6k	3·103	8·115	19·58	45·56	98·61	—

" 50% " Ethanol	Temp.	39·99°	49·99°	60·05°	69·75°	80·06°	90·02°
	10^6k	4·521	12·74	33·32	78·52	183·6	396·8

Energies and entropies of activation were calculated as previously described.[6] The observed activation energies ($E_{obs.}$) decreased with increasing temperature and did not differ by more than 0·11 kcal. mole^{-1} from the values corresponding to the " best " straight line, $E_{obs.}$ against T (see Table 1). Only a linear E–T relation can therefore be postulated since each $E_{obs.}$ was obtained from two rate coefficients (standard deviation ≤0·25%) measured at temperatures *ca.* 10° apart, and is thus subject to a standard deviation of 0·08—0·10 kcal. mole^{-1}.[7] In " 50% " acetone $dE/dT = -19 \pm 2.5$ cal. mole^{-1}, in " 50% " ethanol $dE/dT = -29 \pm 4$ cal. mole^{-1}.

* Throughout this paper a " x% " solvent refers to the mixture made up in the proportions x ml. of pure solvent to $(100 - x)$ ml. of water.

[1] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 329.

[2] Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.

[3] Charlton and Hughes, *J.*, 1956, 850.

[4] Wilputte-Steinert and Fierens, *Bull. Soc. chim. belges*, 1956, **61**, 719.

[5] Simonetta and Favini, *J.*, 1954, 1840; Miller and Bernstein, *J. Amer. Chem. Soc.*, 1948, **70**, 3500.

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

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

TABLE 1. *Activation energies (E, in kcal. mole^{-1}) for the overall solvolysis of benzyl chloride.*

Temp.	45·00°	55·00°	65·00°	75·00°	85·00°
" 50% " Acetone $\{ E_{obs.}$	—	20·45	20·40	20·09	19·89
$\ E_{calc.}$ *	—	20·50	20·30	20·11	19·92
" 50% " Ethanol $\{ E_{obs.}$	20·83	20·44	20·06	19·83	19·70
$\ E_{calc.}$ *	20·74	20·46	20·17	19·88	19·60

* From the " best " straight line, $E_{obs.}$ against temp.

The heat capacity of activation (ΔC^*), which represents the increase in the heat capacity of the reacting system on passage into the transition state, was obtained from the expression $\Delta C^* = dE/dT - R$. This expression is readily derived from the conventional form of the absolute rate equation for reactions in solution.[8]

DISCUSSION

A comparison of the present results with our earlier data [6] for the S_N1 reactions of benzylidene chloride and benzotrichloride (see Table 2) shows that α-chlorination in benzyl chloride increases the rate, energy, and entropy of activation,* confirming previous observations in " 50% " acetone.[9] The negative heat capacities of activation (ΔC *) have already been discussed in the earlier paper, where it was concluded that the loss in heat capacity on passage into the transition state arises from the increased solvation associated with the development of electric charges. This view has also been adopted to account for similar observations in the hydrolysis of *tert.*-butyl chloride [10] and esters of toluene-*p*-sulphonic acid.[11] Since both S_N1 and S_N2 solvolyses require an increase in polarity on activation, the negative ΔC^* now found in the solvolysis of benzyl chloride is to be expected and does not, by itself, provide any information about the reaction mechanism.

Mechanistic Evidence.—A considerable part of the available data suggests that the reactions of benzyl chloride with the present solvents do not occur by the unimolecular mechanism, S_N1. The rate-increase caused by *para*-methylation [12] and α-chlorination (see Table 2) results from an increase in the entropy of activation, ΔS^*, but electron-releasing substituents should accelerate S_N1 solvolysis by reducing the activation energy, E. Mechanism S_N1 for benzyl chloride is also made unlikely by the fact that here α-chlorination does not increase the solvolytic rate nearly as much as α-chlorination in benzylidene chloride (see Table 2). The accelerating effect of added hydroxide ions [9a] also argues against this mechanism, but does not exclude it completely.[13]

The present results appear to support this conclusion. Within the limits of experimental error the ratio $\Delta C^*/\Delta S^*$ is independent of the nature of the substrate for the S_N1 solvolysis of benzylidene chloride and benzotrichloride in " 50% " acetone and " 50% " ethanol (see Table 2), and in the S_N1 reactions of *para*-substituted diphenylmethyl chlorides with " 70% " and " 80% " acetone.[14] In reactions by this mechanism, and in the absence of complicating features, the degree of solvation of the transition state relatively to the

* Throughout this paper the entropy of activation refers to the quantity calculated from the observed first-order rate coefficient. This corresponds to defining the standard state of the nucleophilic reagent as its state in the solvent under consideration.

[8] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill, New York, 1941 p. 199.
[9] (a) Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 867; (b) Hine and Lee, *J. Amer. Chem. Soc.*, 1951, **73**, 22.
[10] Tommila, Tilikainen, and Voipio, *Ann. Acad. Sci. Fennicae*, 1955, A, No. II.
[11] Robertson, *Canad. J. Chem.*, 1955, **33**, 1536; *J. Chem. Phys.*, 1956, **25**, 375.
[12] (a) Bennett and Jones, *J.*, 1935, 1815; (b) Olivier, *Rec. Trav. chim.*, 1930, **49**, 697.
[13] Ballinger, de la Mare, Kohnstam, and Presst, *J.*, 1955, 3641.
[14] Hughes, Ingold, and Kohnstam, unpublished results; cf. Kohnstam, Thesis, London, 1948.

initial state is by far the most important factor controlling the magnitude of ΔC^* [6,11] and ΔS^*,[6,15] and it therefore seems reasonable to assume that $\Delta C^*/\Delta S^*$ in the S_N1 reactions of organic chlorides depends only on the solvent and temperature.† On this view, the decrease in $\Delta C^*/\Delta S^*$ in passing from benzylidene chloride to benzyl chloride (see Table 2) suggests that the latter compound does not react by mechanism S_N1. This decrease can be tentatively explained in terms of some covalent attachment of a solvent molecule in the rate-determining step. Such an attachment requires a less random arrangement of this molecule than its participation in solvation, and hence a greater loss of entropy (ΔS^* is

TABLE 2.   *Kinetic data for the overall solvolysis of benzyl chloride and its α-chloro-derivatives at 50°.*

(E, ΔS^*, and ΔC^* from the " best " straight line, E against T; k in sec.$^{-1}$, E in kcal., ΔS^* and ΔC^* in cal. deg.$^{-1}$.)

	" 50% " Acetone			" 50% " Ethanol		
	Ph·CH₂Cl	Ph·CHCl₂	Ph·CCl₃ ‡	Ph·CH₂Cl	Ph·CHCl₂	Ph·CCl₃ ‡
$10^5 k$	0·3103	1·988 †	47·50 †	1·274	7·775 †	128·5 †
E	20·60	22·91	19·31	20·61	22·76	20·18
$-\Delta S^*$	22·8	11·4 †	16·2 †	19·3	9·01 †	11·5 †
$-\Delta C^*$	21 ± 2·5	29 ± 3	46 ± 4	31 ± 4	59 ± 3	73 ± 6
$\Delta C^*/\Delta S^*$	0·9	2·5 †	2·9 †	1·6	6·6 †	6·3 †

† Per replaceable chlorine atom.
‡ Data for Ph·CCl₃ extrapolated from results at lower temperatures.

generally lower in S_N2 than in S_N1 solvolysis [17]), but the loss in heat capacity is probably not greatly altered. Further work is required before mechanistic interpretations based on $\Delta C^*/\Delta S^*$ can be finally accepted. The assumption of a constant value for this ratio in S_N1 reactions is probably correct, but data for recognised S_N2 reactions are not yet available. It is also possible that ΔC^* is not a measure of the number of solvent molecules associated with the transition state in the present reactions (see p. 4752), but this would only apply if mechanism S_N1 is not operating.

On the other hand, the solvolysis of benzyl chloride in partly aqueous media also shows characteristics which are generally associated with the operation of the unimolecular mechanism. The constancy of the rate-increase on successive *ortho*-methylation has been interpreted as showing a predominantly, if not entirely, unimolecular reaction with " 50% " ethanol,[3] the introduction of *para*-substituents [12] alters the rate by factors which approach the magnitude to be expected in S_N1 solvolysis, and the retarding action of added chloride ions [18] suggests the operation of the mass-law effect which is generally considered to be specific to this mechanism;[19] it has, however, been proposed that a neutral salt effect may be responsible for this last observation.[20] Unimolecular solvolysis is usually much more sensitive to changes in the ionising power of the medium than the bimolecular process, and the data in Table 3 show that benzyl chloride behaves very much like ethyl bromide on passing from pure ethanol to " 50% " ethanol, but more like *tert.*-butyl chloride than like ethyl bromide for the other three solvent pairs. *tert.*-Butyl chloride reacts by mechanism S_N1 with all these solvents while ethyl bromide undergoes S_N2 solvolysis, except in formic acid where the reaction is largely unimolecular. The behaviour of benzyl chloride

† The S_N1 solvolysis of *tert.*-butyl chloride in " 50% " acetone also gives the required value of $\Delta C^*/\Delta S^*$.[16]

[15] (a) Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25; (b) Buchanan and Hamann, *ibid.*, 1953, **49**, 1425; Burris and Laidler, *ibid.*, 1955, **51**, 1497.
[16] Brittain and Kohnstam, unpublished work.
[17] Gold and Jefferson, *J.*, 1953, 1409; Brown and Hudson, *ibid.*, p. 3352.
[18] (a) Beste and Hammett, *J. Amer. Chem. Soc.*, 1940, **62**, 2481; (b) Kohnstam and Rosser, unpublished results.
[19] Ref. 1, p. 365.
[20] Coburn, Grunwald, and Marshall, *J. Amer. Chem. Soc.*, 1953, **75**, 5735.

is thus consistent with an increasing tendency to react unimolecularly as the ionising power of the solvent increases,† and this conclusion derives support from the increase of $k_{50\% \text{ EtOH}}/k_{50\% \text{ Me}_2\text{CO}}$ for its substituted derivatives in the order p-$NO_2 < p$-$H < p$-Me.[12b]

TABLE 3. *The effect of solvent changes on the rate.*

(Data from the literature for Bu^{t}Cl,[22] for Ph·CH$_2$Cl,[4, 15a, 23] and for EtBr [10, 2, 24].)

	Bu^{t}Cl (25°)	Ph·CH$_2$Cl (50°)	EtBr (55°)
$k_{\text{H}_2\text{O}}/k_{50\% \text{ Me}_2\text{CO}}$	125	71	6·1
$k_{\text{H}_2\text{O}}/k_{50\% \text{ EtOH}}$	70	17	2·6
$k_{\text{HCO}_2\text{H}}/k_{50\% \text{ Me}_2\text{CO}}$	4·6	1·6 ‡	0·04 §
$k_{50\% \text{ EtOH}}/k_{\text{EtOH}}$	4750	26·8 †	21·9

† At 80°. ‡ At 25°. § At 100·2°.

Mechanism.—The reactions of benzyl chloride with the present solvents can be explained by assuming that the valence-bond structures (I) and (II) both make an appreciable contribution to the structure of the transition state for hydrolysis.‡ Since the rate-determining step requires covalency change by two molecules the reaction must be regarded as bimolecular (S_N2), but this is by no means inconsistent with the similarities

(I) $\quad$ H$_2$O$^+$—C$\overset{\displaystyle H}{\underset{\displaystyle Ph}{\diagup}}\overset{\displaystyle H}{}$ Cl$^-$ $\qquad\qquad$ H$_2$O $\;\;$ C$^+\overset{\displaystyle H}{\underset{\displaystyle Ph}{\diagup}}\overset{\displaystyle H}{}$ Cl$^-$ (II)

between some of the reactions of benzyl chloride and S_N1 solvolysis. Most of the generally accepted characteristics of mechanism S_N2 have been established from studies on primary alkyl halides where the analogue of structure (II) is relatively unimportant. However, a bimolecular reaction in which this does not apply may approach the behaviour of a unimolecular process since the effect of changing experimental conditions on the stability of (II) is now an important factor in determining the rate.

† The values of $k_{\text{H}_2\text{O}}/k_{50\% \text{ EtOH}}$ and $k_{\text{H}_2\text{O}}/k_{50\% \text{ Me}_2\text{CO}}$, however, appear to indicate that this tendency is less in "50%" ethanol than in "50%" acetone, in spite of the fact that the latter solvent is the poorer ionising medium. This contradiction can be resolved if it is assumed that steric effects oppose solvation of the ionising *tert.*-butyl chloride by ethanol to a greater extent than they oppose solvation by water. $k_{\text{H}_2\text{O}}/k_{50\% \text{ EtOH}}$ for this compound then reflects not only the effect of a better ionising medium but also the change to conditions sterically more favourable for solvation, and will therefore be larger than in compounds where this factor is less important. It has already been proposed that steric effects of this type play a greater part in the solvolysis of benzotrichloride than in the solvolysis of benzylidene chloride,[6] and the following results suggest that they are more important still when the reactant is *tert.*-butyl chloride:

Compound	Ph·CHCl$_2$	Ph·CCl$_3$	Bu^{t}Cl
$k_{50\% \text{ EtOH}}/k_{50\% \text{ Me}_2\text{CO}}$ (25°)	3·0	2·3	1·8

Most organic halides known to undergo S_N1 solvolysis are also sterically unfavourable to bimolecular attack by nucleophilic reagents. Under these conditions steric inhibition of solvation is likely to be an important factor in determining the rate, and it is therefore necessary to treat with caution any quantitative conclusions drawn from a comparison of rates in media which differ in the nature of the solvating agent or in the proportions in which several such agents are present. This may well be at least partly responsible for the observation that the use of S_N1 rates for establishing the ionising power, Y, of a solvent [2] often leads to different values of Y when different reactants are employed, but leaves Y virtually unchanged when a reactant is replaced by a structurally similar compound.[21a]

Added, October 15th, 1957.—Other limitations of the use of Y values for the quantitative interpretation of solvolysis rates were discussed recently by Winstein *et al.*[21b]

‡ Reactions of benzyl halides with better nucleophilic reagents, and in poorer ionising solvents, have already been explained in similar terms.[25-27]

[21] (*a*) Streitwieser, *Chem. Rev.*, 1956, **56**, 618; (*b*) Winstein, Fainberg, and Grunwald, *J. Amer. Chem. Soc.*, 1957, **79**, 4146.
[22] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.
[23] Kohnstam and Robinson, succeeding paper.
[24] Bateman and Hughes, *J.*, 1940, 940.
[25] Baker, *Trans. Faraday Soc.*, 1941, **37**, 632.
[26] de la Mare and Hughes, *J.*, 1956, 845; and references cited in ref. 3 of that paper.
[27] Swain and Langsdorf, *J. Amer. Chem. Soc.*, 1951, **73**, 2812.

The effect of solvent changes on the rate (see Table 3) suggests that the contribution of (II) to the transition-state structure in " 50% " acetone is at least as great as that of (I), and it should therefore be considerably greater than that of (I) in " 50% " ethanol, a better ionising solvent. The latter conclusion is in qualitative agreement with the views of Charlton and Hughes.[3]

At least two concurrent processes must contribute to solvolysis in " 50% " ethanol, one for hydrolysis and the other for ethanolysis. These two processes are associated with different activation energies [23] and therefore result in a positive contribution to the observed heat capacity of activation, ΔC^*, which is calculated from the overall rate. Under these conditions ΔC^* cannot be regarded as a measure of the increase in the number of solvent molecules associated with the reactant on passage into the activated complex. This earlier interpretation also requires a constant transition-state structure, independent of temperature, and may not be justified for reaction with " 50% " acetone since there is no guarantee that the contributions of (I) and (II) are always the same. It must however be stressed that these considerations only apply once the transition state requires some covalent attachment of a solvent molecule. The earlier conclusion that the reactions do not occur unimolecularly is therefore unaffected.

The solvolytic behaviour of benzyl chloride is however also consistent with the view that hydrolysis (and ethanolysis) occurs by several reaction paths. A simple physical interpretation of ΔC^* is then impossible, but the conclusion that the whole solvolysis does not occur unimolecularly is again unaltered (see preceding paragraph). It is of interest to establish to what extent, if any, S_N1 processes contribute to the overall rate, and an upper limit for the fraction of the total solvolysis which may proceed by this mechanism (k_1/k) can be obtained from the observed value of ΔC^*. Details are given in the Appendix. All the likely errors in the assumptions made in these calculations lead to an overestimate of k_1/k, but the figures may be in error up to a factor of two in view of the accuracy with which ΔC^* is known.

The simplest case arises when S_N1 reaction, S_N2 hydrolysis, and S_N2 ethanolysis (when applicable) each occur by a single reaction path. The data for this model are given below, and it can be seen that the values of k_1/k are much too small to permit the view that only

Temp.		90°	70°	50°
100 k_1/k	{ " 50% " Acetone	7	4·2	2·3
	{ " 50% " Ethanol	22	14	8

the S_N1 processes are responsible for the marked " S_N1 character " observed at 50° or less (*e.g.*, substituent and solvent effects). It therefore seems unlikely that the S_N2 processes involve the extreme form of that mechanism [*i.e.*, a very small contribution from (II)], in agreement with the general predictions by Gleave, Hughes, and Ingold about the concurrence of mechanistic extremes.[28]

Alternatively, the individual acts of molecular substitution can be considered to occur *via* any one of a continuous series of transition states which differ in the relative contributions of (I) and (II). It has already been postulated that reactions in the S_N1–S_N2 borderline region may involve a range of transition states in which both (I) and (II) are important (*i.e.*, bimolecular reaction paths only),[29] but an extension of this range to cover the mechanistic extremes has also been proposed.[30, 31] If the latter view is correct, the values of k_1/k in the present reactions are certainly not greater than for the simpler model, and probably much less (for details, see Appendix).

So far there is no unambiguous evidence that S_N reactions can occur by simultaneous S_N1 and S_N2 processes. Results indicating this type of behaviour in bromine exchange

[28] Gleaves, Hughes, and Ingold, *J.*, 1935, 236.
[29] Bird, Hughes, and Ingold, *J.*, 1954, 634.
[30] Gold, *J.*, 1956, 4633.
[31] Crunden and Hudson, *J.*, 1956, 501.

with *tert.*-butyl bromide [32] are not confirmed by more recent work,[33] and the interpretation of the simultaneous hydrolysis and ammonolysis of benzoyl chloride in such terms [34] appears to require re-examination as it has been shown that at least a part of the reaction does not involve an S_N mechanism.[35] Our calculations merely give an upper limit to the fraction of S_N1 solvolysis in the present reactions *if* the two mechanisms operate concurrently: they do not prove that this concurrence exists.

It must be stressed that neither of the two mechanistic explanations now proposed for the solvolytic behaviour of benzyl chloride can explain the retarding action of added chloride ions. Passage through a single bimolecular transition state should not be subject to a mass-law effect (cf. ref. 19), and the assumption of several reaction paths leads to too small a fraction of S_N1 solvolysis to account for the observation that the presence of 0·05M-potassium chloride reduces the rate by 5% in " 50% " acetone at 70°.[18b] Further work is necessary before this difficulty can be resolved.

<div align="center">APPENDIX</div>

<div align="center">*Calculation of the Fraction of S_N1 Solvolysis.*</div>

If solvolysis in " 50% " acetone occurs by one unimolecular and one bimolecular reaction path (subscripts 1 and 2, respectively), the overall rate $k = k_1 + k_2$. Hence,

$$E = \mathbf{R}T^2(\mathrm{d} \ln k/\mathrm{d}T) = (E_1k_1 + E_2k_2)/k \quad \ldots \ldots (1)$$

$$\Delta C^* = \mathrm{d}E/\mathrm{d}T - \mathbf{R} = (E_1 - E_2)^2 k_1 k_2/\mathbf{R}T^2k^2 + (k_1\Delta C_1^* + k_2\Delta C_2^*)/k$$

If we assume that $\Delta C_1^* = \Delta C_2^*$, this equation becomes:

$$\Delta C^* - \Delta C_1^* = (E_1 - E_2)^2 k_1 k_2/\mathbf{R}T^2k^2 \quad \ldots \ldots (2)$$

ΔC_1^* was taken to be equal to ΔC^* for the ionisation of benzylidene chloride, and E_1 was obtained by assuming that α-chlorination in benzyl chloride increases the S_N1 activation energy by the same amount as α-chlorination in benzylidene chloride. By arbitrarily choosing a number of values of k_1/k at a given temperature, T_a, the corresponding values of the parameters on the right of equation (2) can be obtained at all the experimental temperatures from the overall rate at T_a, the Arrhenius equation, and equation (1). Equation (2) was considered to be satisfied when the mean of the right-hand terms over the experimental temperature range equalled $\Delta C^* - \Delta C_1^*$. k_1/k is then readily deduced.

The assumptions employed may be subject to the following errors. It is very likely that $\Delta C_1^* < \Delta C_2^*$ since the smaller dispersal of electric charges in the S_N1 transition state leads us to expect a greater degree of solvation.[36] α-Chlorination decreases ΔC^* for the ionisation of the C–Cl linkage (see Table 2), and ΔC_1^* may therefore be greater than $\Delta C^*(\mathrm{Ph\cdot CHCl_2})$. Any steric inhibition of solvation would be greater in benzotrichloride than in benzylidene chloride; this would partially obscure the effect of α-chlorination in the S_N1 activation energy, leading to too small a value for E_1. All these errors overestimate k_1/k.

If reaction with " 50% " ethanol involves only one additional reaction path (S_N2 ethanolysis, subscript 3), k_1/k can be obtained by analogous methods. k_2/k_3 and $E_2 - E_3$ were assumed to have the values corresponding to the overall rates and activation energies for hydrolysis and ethanolysis; [23] errors resulting from these assumptions are small. In " 50% " ethanol steric inhibition of solvation is much more marked for benzotrichloride than for benzylidene chloride,[6] and we therefore assumed that α-chlorination affected the S_N1 activation energy to the same extent as in " 50% " acetone.

Alternatively, ΔC_1^* can be employed as the arbitrary parameter; k_1 is then obtained from E_1 and the constancy of the ratio $\Delta S^*/\Delta C^*$ for S_N1 reactions. This procedure reduces k_1/k by a factor of two for " 50% " ethanol, and also gives a slight reduction for " 50% " acetone.

Calculations for a continuous range of transition states were only carried out for solvolysis

[32] Le Roux and Swart, *J.*, 1955, 1475.
[33] de la Mare, *J.*, 1955, 3180.
[34] Gold, Hilton, and Jefferson, *J.*, 1954, 2756.
[35] Bunton, Lewis, and Llewellyn, *Chem. and Ind.*, 1954, 1154; Bunton and Lewis, *ibid.*, 1956, 180.
[36] Ref. 1, p. 346.

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in " 50% " acetone. If we describe the various reaction paths by their activation energy,
$E' = \Delta H^* + \boldsymbol{R}T$,

$$k = (1/\boldsymbol{N}\boldsymbol{h})\int_{E'_m}^{\infty} \exp\left(-\Delta G^*/\boldsymbol{R}T\right) . \mathrm{d}E' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where E'_m is the smallest value of E', and the other symbols have their usual meaning. This equation was derived by analogy with Tolman's treatment of unimolecular gas reactions [37] and reduces to the conventional form of the absolute rate equation when ΔS^* is independent of E'.

If the relation between ΔG^* and E' is known, E'_m can be obtained from the expression for the observed activation energy, E. k_1/k can then be found by assuming that mechanism S_N1 operates when $E' \geqslant E_1$, where E_1 has the same value as in the simpler model already discussed. Unfortunately ΔG^* is not a known function of E'. We therefore employed a number of arbitrary, but *a priori* reasonable, functions which involved an unknown parameter, and accepted those values of this parameter which satisfied the analogue of equation (2) with $\Delta C_1^* = \Delta C^*(\text{Ph·CHCl}_2)$, as before.

The use of a number of different functions for ΔG^* gave smaller k_1/k values than the simpler model. The values are probably too large for the reasons already discussed, and also because we always chose ΔG^* as a single-value function of E'. It is quite likely that E' passes through a minimum with changing transition-state structure, and contributions from some bimolecular processes to the rate may therefore have been neglected. Errors in k_1/k from the assumptions involved in setting up equation (3) are probably not unduly large.

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[37] Fowler and Guggenheim, " Statistical Thermodynamics," Cambridge Univ., London, 1939, p 521.