

60. *The Effect of α -Chloro-substituents on the S_N1 Reactivity of the C-Cl Linkage.*

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Kinetic study of the solvolysis of benzylidene chloride and benzotrichloride in aqueous acetone and ethanol, and of the ethanolysis of chloro- and dichloro-diphenylmethane, shows that replacement of an α -hydrogen atom by chlorine accelerates the ionisation of C-Cl linkages by reducing the activation energy, E . This is consistent with the view that, relatively to hydrogen, the additional chlorine atom acts as an electron donor in the transition state.¹

The activation energy was temperature-dependent in the solvolysis of benzylidene chloride and its α -chloro-derivative, dE/dT being negative. This indicates a decrease in heat capacity on passage from the initial to the transition state, probably owing to increase in solvation associated with the development of electric charge. Similar behaviour is to be expected in all reactions having a transition state which is more polar than the initial state.

The effect of changes in the solvent on the rate, energy, and entropy of activation is consistent with the assumption that, for a given C-Cl separation, α -chlorination impedes the solvation of the incipient ions by ethanol molecules to a greater extent than it impedes solvation by water.

THERE is now considerable evidence² that the replacement of an α -hydrogen atom by chlorine accelerates the solvolysis of the C-Cl linkage when the reaction occurs by the ionisation mechanism, S_N1 . The effect of such a substitution on the energy (E) and entropy of activation (ΔS^*) is however not clear. An examination of the hydrolysis of

¹ Cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

² (a) Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 869; (b) Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25; (c) Hine and Lee, *J. Amer. Chem. Soc.*, 1951, **73**, 22; (d) Andrews and Kaeding, *ibid.*, p. 1007; (e) Vernon, *J.*, 1954, 423.

benzylidene chloride and benzotrichloride in aqueous acetone showed that α -chlorination accelerates ionisation by reducing E , ΔS^* being virtually unchanged.^{2c} A study of the same compounds in aqueous ethanol, however, showed that this acceleration is due to an increase in ΔS^* , E being also increased.^{2b} In a recent investigation of the ionisation of allyl chloride in slightly aqueous formic acid, the increased reactivity of the α -chloro-derivative is seen^{2c} to be due as much to a reduction of E as to a rise in ΔS^* .

The present paper reports a kinetic investigation of the solvolysis of benzylidene chloride and benzotrichloride in aqueous acetone and ethanol. The reactions were studied at a number of different temperatures, as there was reason to suppose that E is not constant when the transition state is more polar than the initial reactant, and it was thought that this might account for the lack of concordance between the earlier results. The ethanolysis of chloro- and dichloro-diphenylmethane was also examined, though in less detail.

EXPERIMENTAL

Materials.—Commercial benzylidene chloride and benzotrichloride were dried (CaCl_2). Chlorodiphenylmethane was prepared by the method of Hughes, Ingold, and Taher,³ and diphenyldichloromethane by that of Gattermann and Schultz.⁴ All the organic chlorides were purified by distillation *in vacuo*, large head and tail fractions being discarded: $\text{Ph}\cdot\text{CHCl}_2$, $\text{Ph}\cdot\text{CCl}_3$, Ph_2CHCl , and Ph_2CCl_2 , had n_D^{25} 1.5500, 1.5574, 1.5938, and 1.6034, respectively; the hydrolysable chloride was always within 99.6—99.8% of the theoretical amount.

Acetone was purified by Conant and Kirner's method⁵ followed by fractionation through a 15-plate column; and ethanol by Manske's method⁶ with precautions against the entrance of atmospheric moisture. An " $x\%$ " solvent was prepared by the addition of x ml. of the pure solvent to $100 - x$ ml. of water at room temperature.

Rate Measurements.—The thermostats were of conventional design, except that a well-stirred bath of melting ice was used for 0° . The temperatures, which were constant within $\pm 0.01^\circ$, were measured with thermometers, standardised by the National Physical Laboratory to $\pm 0.02^\circ$.

For the runs at the higher temperatures the reaction mixture was made up at 0° , and 3.76-ml. samples were pipetted into glass tubes which were sealed off and introduced, with vigorous shaking, into the thermostat in such quantities that the temperature regained its value within 2 min. Tubes were withdrawn from time to time, cooled rapidly to -80° , cleaned, broken under 200 ml. of cold, neutral acetone, and titrated with standard sodium hydroxide with lacmoid as indicator. For each batch of tubes, the zero reading was taken after 2—3 min., all the tubes having by then reached the thermostat temperature.

At the lower temperatures the reactant was added to the solvent in the thermostat, and 5-ml. samples were withdrawn from time to time, run into 200 ml. of cold, neutral acetone, and titrated as before. For the runs in absolute ethanol, it was desirable to prevent the entrance of moisture during sampling. The pipette was therefore attached to the flask through a ground-glass joint and fitted with a three-way tap, guard-tubes preventing the absorption of moisture.

Approximately the following initial concentrations were employed: $\text{Ph}\cdot\text{CHCl}_2$, 0.008M; $\text{Ph}\cdot\text{CCl}_3$, 0.005M; Ph_2CHCl , 0.012M; Ph_2CCl_2 , 0.006M. The exact value of the initial concentration was usually obtained from an "infinity reading" which was always carried out in duplicate.

Integrated first-order rate coefficients were calculated from the equation $k_1 t = \ln [a/(a - x)]$, where the symbols have their usual meaning. In any one run, k_1 was generally obtained as the mean of ten separate determinations. At least two runs were always carried out for any given set of experimental conditions; if the two mean rate coefficients differed by more than $\frac{1}{2}\%$ a further run was done.

The solvolysis of benzylidene chloride and benzotrichloride was studied in "50%" acetone, and "80%" and "50%" ethanol; that of chlorodiphenylmethane and its α -chloro-derivative in absolute ethanol. Several batches of each aqueous solvent were used, and each batch was monitored by examining the rate of solvolysis of a reactant which had already been studied in the previous batch. Any necessary correction was applied to the results.

The experimental data for two typical runs are given on p. 289: t in sec., k_1 in sec.⁻¹.

³ Hughes, Ingold, and Taher, *J.*, 1940, 949.

⁴ Gattermann and Schultz, *Ber.*, 1896, 29, 2944.

⁵ Conant and Kirner, *J.*, *Amer. Chem. Soc.*, 1924, 46, 232.

⁶ Manske, *ibid.*, 1931, 53, 1104.

(i) Benzotrichloride in "50%" aqueous acetone at 30.05°; 5 ml. of reaction mixture titrated with 0.006427N-NaOH.

10 ⁻³ <i>t</i>	0	0.900	1.620	2.340	3.055	3.955	5.165	6.435	7.740	9.120	10.500	∞
Titre (ml.)	0.44	2.13	3.28	4.26	5.13	6.05	7.13	7.96	8.73	9.27	9.76	11.34
10 ⁴ <i>k</i> ₁	—	1.871	1.864	1.844	1.842	1.827	1.842	1.820	1.847	1.821	1.852	—

10⁴*k*₁ (mean) = 1.843; a duplicate run gave 1.850.

(ii) Dichlorodiphenylmethane in absolute ethanol at 0.00°; 4.11 ml. of reaction mixture titrated with 0.004933N-NaOH.

10 ⁻³ <i>t</i>	0	3.66	7.98	14.58	16.02	18.84	21.96	24.55	28.62	31.62	35.04	37.50	∞
Titre (ml.)	0.16	1.32	2.49	4.02	4.31	4.81	5.38	5.76	6.35	6.72	7.13	7.38	10.54
10 ⁵ <i>k</i> ₁	—	(3.241)	3.186	3.192	3.187	3.153	3.184	3.159	3.170	3.162	3.176	3.172	—

10⁵*k*₁ (mean) = 3.174; a duplicate run gave 3.164.

The solvolytic rates are summarised in Table 1, where the specific rates per replaceable chlorine atom, *k*, are quoted; they were obtained from the integrated rate coefficients by dividing by the number of chlorine atoms in the reactant molecule. The figures in each column refer to the same solvent, and each represents the mean of the results from, at least, two runs.

TABLE 1. *Specific rates (10⁶k, in sec.⁻¹) per replaceable chlorine atom.*

"50%" Aqueous acetone			"50%" Aqueous ethanol			"80%" Aqueous ethanol		
Temp.	Ph·CHCl ₂	Ph·CCl ₃	Temp.	Ph·CHCl ₂	Ph·CCl ₃	Temp.	Ph·CHCl ₂	Ph·CCl ₃
0.00°	—	1.359	0.00°	—	2.348	25.02°	—	1.633
9.94	—	5.380	10.08	—	10.80	35.00	—	5.550
20.00	—	19.14	20.04	1.802	42.77	45.01	—	19.32
30.05	1.830	61.53	30.00	7.040	146.6	50.00	2.489 ^b	34.43 ^b
39.92	6.225	174.4	39.99	24.64	454.0 ^a	54.96	—	54.00
50.04	19.88	—	49.99	77.75	—	60.13	7.785 ^b	99.47 ^b
60.04	57.20	—	60.07	223.9	—	64.81	—	155.0
69.74	149.4	—						
80.08	389.9	—						

^a At 40.04°. ^b A different solvent which was not monitored.

Absolute ethanol

Temp.	Ph ₂ CHCl	Ph ₂ CCl ₂
0.00°	1.732	15.85
19.97	28.20	209.2

The rate coefficients were virtually independent of the initial concentration of the organic chloride. An increase in this quantity of a factor of 2 decreased *k* by 1% for Ph·CHCl₂, and by 2.5% for Ph·CCl₃.

Energies, Entropies, and Heat Capacities of Activation.—The activation energy, *E*, was calculated from the equation

$$E = [RT_a T_b / (T_b - T_a)] \ln k_b / k_a \dots \dots \dots (i)$$

where *k_a* and *k_b* are the specific rates at the absolute temperatures *T_a* and *T_b*, respectively. *E* was not independent of *T_a* and *T_b* and was always found to obey the relation

$$E = E_0 + c(T_a + T_b) / 2 \dots \dots \dots (ii)$$

where *E₀* and *c* are constants. The "best" values of *E₀* and *c*, obtained by the method of least squares, are given in Table 2 for those cases in which the rate of solvolysis was examined at more

TABLE 2. *E₀ and c (in cal.) for the solvolysis of Ph·CHCl₂ and Ph·CCl₃.*

Solvent	"50%" Acetone		"50%" Ethanol		"80%" Ethanol
Reactant	Ph·CHCl ₂	Ph·CCl ₂	Ph·CHCl ₂	Ph·CCl ₃	Ph·CCl ₃
10 ⁻³ <i>E₀</i>	31.63	33.53	41.20	43.13	35.94
<i>c</i>	-27 ± 3	-44 ± 4	-57 ± 3	-71 ± 6	-41 ± 2

than two temperatures. The standard deviation of *c* is also quoted. The agreement between the values of *E* calculated by these two equations is illustrated below for the solvolysis of benzotrichloride in "80%" ethanol.

<i>T_a</i> (°K)	298.18	308.16	318.17	328.12
<i>T_b</i> (°K)	308.16	318.17	328.12	337.97
10 ⁻³ <i>E</i> (cal.), from eqn. (i)	23.47	23.16	22.69	22.26
10 ⁻³ <i>E</i> (cal.), from eqn. (ii)	23.51	23.10	22.69	22.29

The temperature-dependence of E , as calculated by means of equation (i), makes it necessary to establish the temperature to which this parameter refers. Strictly, the activation energy is defined by the differential equation $E = RT^2(d \ln k/dT)$. If E is a linear function of temperature in the range T_a to T_b , and $(dE/dT)(T_a - T_b)^2/(T_a + T_b) \ll E$, it can be shown that equation (i) gives E at $(T_a + T_b)/2$, the mean of the two temperatures employed. Equation (ii) then implies a linear E - T relation over the whole experimental range with $dE/dT = c$. The results in Table 2 show that, within the limits of experimental error, this equation applies to all the reactions listed [$c(T_a - T_b)^2/(T_a + T_b)$ is always very much less than E], and it was therefore assumed that all activation energies obtained from equation (i) referred to the mean of the two appropriate temperatures.

The heat capacity of activation, ΔC^* , was calculated from the expression $\Delta C^* = dE/dT - R$, which is readily derived from the relation between the energy and enthalpy of activation.^{7a}

The entropy of activation, ΔS^* , at the temperature $(T_a + T_b)/2$, was obtained from the expression

$$\ln k_a = \ln (k/h) + \ln (T_a + T_b)/2 + 1 + \Delta S^*/R - E/RT_a$$

where k_a refers to the temperature T_a , and E to $(T_a + T_b)/2$. This expression was derived from the conventional form of the absolute rate equation for reactions in solution⁸ by assuming that ΔS^* varies with the temperature according to $d(\Delta S^*)/dT = \Delta C^*/T$. If E refers to the mean of the two temperatures employed in its calculation by equation (i), it can be shown that the above expression does in fact give ΔS^* at $(T_a + T_b)/2$.

Values of E , ΔS^* , and ΔC^* are given in Table 3 for the reactions studied in this investigation. E and ΔS^* are quoted at temperatures which are within the experimental range, and common to the two reactants investigated in the same solvent. E and ΔC^* are the "least squares" values obtained from equation (ii) after substitution from equation (i). ΔS^* was always

TABLE 3. *Energies, entropies, and heat capacities of activation.*

Solvent	" 50% " Acetone		" 50% " Ethanol		" 80% " Ethanol		Absolute ethanol	
Reactant	Ph·CHCl ₂	Ph·CCl ₃	Ph·CHCl ₂	Ph·CCl ₃	Ph·CHCl ₂	Ph·CCl ₃	Ph ₂ ·CHCl	Ph ₂ ·CCl ₂
Temp.	35·00°	35·00°	35·00°	35·00°	55·06°	55·06°	9·99°	9·99°
E (kcal.)	23·31	19·97	23·63	21·24	24·11 ^a	22·43 ^a	22·23	20·56
ΔS^* (cal. °K ⁻¹)	- 9·97	- 14·0	- 6·22	- 8·07	- 11·8 ^a	- 11·8 ^a	- 5·43	- 7·12
ΔC^* (cal. °K ⁻¹)	- 29 ± 3	- 46 ± 4	- 59 ± 3	- 73 ± 6	—	- 43 ± 2	—	—

^a A different solvent which was not monitored.

calculated from the specific rate per replaceable chlorine atom. Where ΔC^* has been determined, E and ΔS^* can be obtained at temperatures other than those given in Table 3, but such a procedure is only justified for temperatures which are not too far outside the experimental range, as there is no reason to suppose that ΔC^* has the same value at all temperatures.

DISCUSSION

The rate of reaction between hydroxylic solvents and compounds having more than one chlorine atom directly attached to the reaction centre is entirely controlled by the heterolysis of one of the C-Cl linkages, the subsequent stages taking place very rapidly.⁹ Hydroxide ions do not accelerate the hydrolysis of benzylidene chloride and benzotrichloride,^{2a} and ethoxide ions have no effect on the ethanolysis rate of dichlorodiphenylmethane.^{2d} The rate-determining step in these reactions must therefore involve the unimolecular mechanism, S_N1 ; ¹ the ethanolysis of chlorodiphenylmethane has also been shown to occur by this mechanism.¹⁰ In the present investigation, all the reactions followed the first-order rate-law and large changes in the initial concentration had only a small effect on the rate. This shows that mass-law and ionic-strength effects¹¹ are not

⁷ Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941, (a) p. 198; (b) p. 419-423.

⁸ *Op. cit.*, p. 199.

⁹ Cf. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 329.

¹⁰ Bateman, Hughes, and Ingold, *J. Amer. Chem. Soc.*, 1938, **60**, 3080.

¹¹ Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

operating to any significant extent, and it is therefore possible to identify the specific rate per replaceable chlorine atom with the specific rate of ionisation of one of the C-Cl linkages.

The Effect of α -Chlorination on the Rate.—The results given in Table 4 show that the replacement of an α -hydrogen atom by chlorine, in benzylidene chloride and chlorodiphenylmethane, accelerates the ionisation by reducing the activation energy. The accompanying changes in the entropy of activation are, relatively, much smaller and tend, in general, to retard ionisation.†

TABLE 4. *Effect of α -chlorination on the ionisation of the C-Cl linkage.*

(The subscripts _H and _{Cl} refer to a compound and its α -chloro-derivative, respectively.)

Solvent	" 50% " Acetone	" 50% " Ethanol	" 80% " Ethanol	Ethanol
Reactant ^a	Ph·CHCl ₂	Ph·CHCl ₂	Ph·CHCl ₂	Ph ₂ CHCl
Temp.	30·05°	30·00°	55·06°	9·99°
k_{Cl}/k_H	33·65	20·75	13·1	8·31
$E_{Cl} - E_H$ (kcal.)	-3·26	-2·32	-1·68	-1·67
$\Delta S^*_{Cl} - \Delta S^*_H$ (cal. °K ⁻¹)	-3·83	-1·63	0·00	-1·69

^a Only the compound containing the replaceable α -hydrogen atom is quoted.

Because of the temperature-dependence of E and ΔS^* (see Experimental section), it is necessary to compute changes in these quantities (resulting from α -chlorination) from data at the same temperature. If the figures for the α -chloro-derivative refer to a lower temperature than those for the parent compound, the negative heat capacity of activation (cf. Table 3) leads to apparent changes in these quantities which become increasingly more positive as the temperature difference is increased. This accounts for the slightly smaller changes in E and ΔS^* reported by Hine and Lee ^{2c} for the effect of α -chlorination on the rate of ionisation of benzylidene chloride in " 50% " acetone. At the temperatures appropriate to their work,† our values of E and ΔS^* for the two compounds do not differ from theirs by more than 0·14 kcal. and 0·5 e.u., respectively. Similarly, the observation ^{2c} that the accelerating effect of α -chlorination on the ionisation of allyl chloride in slightly aqueous formic acid is as much due to an increase in ΔS^* as to a decrease in E is considered to arise out of the fact that the two compounds were examined at temperatures which differed by about 50°. It is pointed out in the following section that a negative heat capacity of activation is to be expected whenever the transition state is more polar than the initial state, and the assumption of a reasonable value for ΔC^* leads to the conclusion that a comparison of the two compounds at the same temperature can be expected to show that the increase in rate is almost completely, if not entirely, due to a reduction of E , as in the present investigation.

Our results in " 80% " ethanol do not confirm those of Evans and Hamann ^{2b} who found that α -chlorination in benzylidene chloride accelerates the ionisation in this solvent by increasing ΔS^* ; the accompanying change in E tended to retard the reaction. For the ionisation of one of the C-Cl linkages, their data actually lead to a slightly smaller increase in ΔS^* than reported || but, a reasonable value being assumed for ΔC^* (cf. Table 3), this increase is still so large that it can be only partially accounted for by the fact that E and ΔS^* refer to a temperature which is 30° lower for the α -chloro-derivative than for the parent

† The magnitude of the changes in E and ΔS^* , resulting from α -chlorination, depends to some extent on the temperature under consideration, as ΔC^* is more negative for benzotrichloride than for benzylidene chloride (cf. Table 3). These changes therefore become more positive as lower temperatures are chosen. The choice of temperatures for this comparison is, however, restricted to those which are not too far outside the experimental range, as ΔC^* was determined from experimental data and is unlikely to have the same value at all temperatures. It can readily be verified that, within the limits imposed by these restrictions, the predominant cause of the acceleration of the ionisation is the reduction of E .

‡ E and ΔS^* , calculated from rate data at two temperatures, refer to the mean of these two temperatures (cf. Experimental section).

|| At first sight, the rate constants reported by Evans and Hamann appear to refer to the ionisation of one of the C-Cl linkages. They were obtained from the " experimental " rate constants by dividing by n , the number of replaceable chlorine atoms in the reactant molecule, but the method employed for the calculation of the " experimental " constants can be shown to lead to values which are greater than rate constants for solvolysis by a factor of n . When $n > 1$, ΔS^* for the ionisation of one C-Cl linkage is thus smaller than ΔS^* reported by these authors. The difference is $R \ln n$; the value of E is the same.

compound. A comparison of their rates of ionisation with those of the present investigation in the same solvent, and at the same temperature, shows good agreement for the reaction of benzotrichloride but serious discrepancies when the reactant is benzylidene chloride; at, e.g., 60° their rate of ionisation for this compound is almost twice as great as ours. Our observation that α -chlorination accelerates the ionisation in "80%" ethanol by reducing E is consistent with our findings in the other solvents employed, and our rates of ionisation for benzylidene chloride are in good agreement with those previously reported in "50%" acetone^{2a, c} and "50%" ethanol.¹² The present results in "80%" ethanol are therefore regarded as the more reliable.

The results of this investigation are fully consistent with the predictions of Hughes¹ who suggested that the replacement of an α -hydrogen atom by chlorine accelerates the rate of ionisation of the C-Cl linkage by conjugatively releasing electrons towards the reaction centre, a process which increases the stabilisation of the transition state. In agreement with the present observations, and those of Hine and Lee,^{2c} this requires that the acceleration results mainly from a reduction of E . The view that the additional chlorine atom increases the rate of ionisation by increasing steric hindrance to solvation in the transition state—the conclusion to be drawn from the work of Evans and Hamann^{2b}—involves an appreciable increase in ΔS^* on α -chlorination and is, therefore, not supported by our results. An acceleration of the reaction arising out of a reduction of E would, however, also have been observed if the replacement of hydrogen by the larger chlorine atom decreases the stability of the initial state because of steric effects.¹³ There is some steric compression between chlorine and the o -hydrogen atoms in benzotrichloride, though not in benzylidene chloride, but the non-bonding energy, calculated according to the methods of Dostrovsky, Hughes, and Ingold,¹⁴ is only 110 cal. It has been suggested¹⁵ that these methods underestimate the interatomic penetration energy but, even if it is assumed that chlorine and hydrogen atoms are as difficult to compress as two helium atoms, the substitution of Slater's data¹⁶ in Buckingham's equation¹⁷ does not increase the non-bonding energy beyond 800 cal. This is less than half the smallest observed decrease in E on α -chlorination (cf. Table 4), and it does not, therefore, seem likely that increased steric compression in the initial state of the α -chloro-derivative is mainly responsible for the present observations.

The Temperature Effect.—It has already been pointed out that the solvolysis of benzylidene chloride and benzotrichloride involves temperature-dependent activation energies, dE/dT being negative and constant within the limits of experimental error. These observations cannot be due to a composite chemical mechanism in the rate-determining stage—this requires positive dE/dT values—and it is therefore necessary to discuss them in more detail. On purely theoretical grounds several workers have stressed that E is not constant if the heat capacity of the activated complex differs appreciably from that of the initial reactants.¹⁸ The conventional form of the absolute rate equation⁸ leads to the same conclusion, with $dE/dT = \Delta C^* + R$. Temperature-dependent values of E have been reported on a number of occasions though not all the claims to have observed this effect can be accepted; summaries of the earlier work are available,¹⁹ and some of the more recent investigations in this field are discussed later in this section.

In the present reactions, the rate is determined by the ionisation of one of the C-Cl linkages, and the rate coefficients for this process, rather than for the overall solvolysis, have been quoted throughout this paper. It is an essential feature of reaction by this mechanism that the activation energy is reduced to accessible values by the solvation of the

¹² Andrews and Linden, *J. Amer. Chem. Soc.*, 1947, **69**, 2091.

¹³ Cf. Brown *et al.*, *ibid.*, 1949, **71**, 1845; 1950, **72**, 5068; Hughes, Ingold, Martin, and Meigh, *Nature*, 1950, **166**, 679.

¹⁴ Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173.

¹⁵ Westheimer, *J. Chem. Phys.*, 1947, **15**, 252.

¹⁶ Slater, *Phys. Rev.*, 1928, **32**, 349.

¹⁷ Buckingham, *Proc. Roy. Soc.*, 1938, *A*, **168**, 264.

¹⁸ Trautz, *Z. anorg. Chem.*, 1918, **102**, 81; Brandsma and Scheffer, *Rec. Trav. chim.*, 1926, **45**, 522; La Mer, *J. Chem. Phys.*, 1933, **1**, 289.

¹⁹ (a) Kohnstam, Thesis, London, 1948; (b) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Clarendon Press, Oxford, 1947, chap. 2; La Mer and Miller, *J. Amer. Chem. Soc.*, 1935, **57**, 2664.

transition state,²⁰ and it is generally accepted that this process requires a definite orientation of the solvent dipoles around the incipient ions. These oriented molecules are less free to move than those in the bulk of the solvent and can therefore be expected to have a lower entropy and heat capacity. Analogous considerations apply to fully developed ions in solution, and this "freezing-out" of solvent molecules in the immediate neighbourhood of charged particles has been stated to account for the negative partial molar heat capacities of electrolytes²¹ and the negative heat capacity of ionisation of weak acids.²² Similarly, reactions which involve an increase in electric charge, and hence in solvation, on passing into the transition state should show negative ΔC^* values;²³ Moelwyn-Hughes²⁴ also regards this as one possible explanation of the negative temperature coefficient of E , observed in the hydrolysis of methyl fluoride.

Negative ΔC^* values have also been observed for a few other reactions in which the transition state is more polar than the initial reactants. In the hydrolysis of acetic anhydride in water and aqueous acetone ΔC^* varies between -85 and -55 cal. depending on the solvent composition;²⁵ its value is about -60 for the solvolysis of 1-methylallyl chloride in "50%" aqueous ethanol,²⁶ about -40 for the hydrolysis of diphenylchloromethane in aqueous acetone,²⁷ -45 for the hydrolysis of methyl nitrate in water,²⁸ and about -70 for the same reaction of the methyl halides,²⁹ though in a later investigation over the same temperature range ΔC^* was found to increase with increasing temperature, finally attaining positive values.³⁰ In view of the number of reactions of this type which have been investigated it is perhaps surprising that more examples are not available. On the other hand, the use of small temperature ranges and some inaccuracy in the rates— E values are often quoted as accurate to ± 0.5 kcal.—may have prevented the observation of this effect when ΔC^* is numerically small. The determination of E from the Arrhenius plot may also have obscured its temperature-dependence, but an examination of a number of previous investigations does not lead to any further, reliable examples. Thus, with the exception of the most recent work on the methyl halides, all the available evidence is consistent with the prediction that an increase of electric charge on passing over into the transition state reduces the heat capacity.

The same prediction, however, arises out of the electrostatic approach, based on the Born relation which treats the solvent as a continuous medium of dielectric constant D . This approach considers a contribution to E , E_D , due to electrostatic effects in a continuous dielectric. For all known solvents D decreases with increasing temperature, so that E_D , and hence E , can be expected to be temperature-dependent. In general, the electrostatic theory leads to good agreement with experimental observations. It has been employed in a discussion of the effect of D on the rates of bimolecular reactions between dipolar molecules and on the rate of ionisation of *tert.*-butyl chloride,^{7b} in the calculation of the electrostatic contribution to ΔS^* in similar bimolecular processes³¹ where there is an additional negative contribution to ΔS^* due to the combination of two reactant molecules to form a single activated complex, in the calculation of ΔH^* and ΔS^* for the ionisation of alkyl halides,³² and in the discussion of a large number of ionic and ion-dipole reactions.³³

In applying the electrostatic approach to the present problem, the ionisation of the

²⁰ Ref. 9, p. 312.

²¹ Randall and Rossini, *J. Amer. Chem. Soc.*, 1928, **51**, 323.

²² (a) Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380; (b) Coulson and Everett, *ibid.*, 1940, **36**, 663.

²³ Ingold, personal communication, see ref. 19a; Caldin, Long, and Trowse, *Nature*, 1953, **171**, 1124.

²⁴ Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, **A**, **211**, 254.

²⁵ Gold, *Trans. Faraday Soc.*, 1948, **44**, 506.

²⁶ Vernon, personal communication.

²⁷ Hughes, Ingold, and Kohnstam, unpublished work; cf. ref. 19a.

²⁸ McKinley-McKee and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 246.

²⁹ Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, **A**, **164**, 295; ref. 24.

³⁰ *Idem*, *ibid.*, 1953, **A**, **220**, 386.

³¹ Pearson, *J. Chem. Phys.*, 1952, **20**, 1478.

³² Franklin, *Trans. Faraday Soc.*, 1952, **48**, 443.

³³ For summary, see Amis, "Kinetics of Chemical Change in Solution," Macmillan, New York, 1949, chap. 4—6, 8, 9.

C-Cl linkage, the electrostatic contribution to ΔS^* is obtained by differentiating Kirkwood's equation³⁴ with respect to temperature:³¹ †

$$\Delta S_D = \left\{ \frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3} \right\} \cdot \frac{3D}{(2D+1)^2} \cdot \frac{d \ln D}{dT}$$

where μ and r are the dipole moment and molecular radius, and the subscripts i and t refer to the initial and the transition state, respectively. The electrostatic contribution to ΔC^* is then given by:

$$\Delta C_D = \left\{ \frac{\mu_t^2}{r_t^3} - \frac{\mu_i^2}{r_i^3} \right\} \cdot \frac{3DT(2D-1)}{(2D+1)^3} \cdot \left\{ \frac{d \ln D}{dT} \right\}^2$$

as $(d \ln D/dT)$ is independent of T for our solvents.³⁵

Our experimental values for ΔS^* and ΔC^* at 55° are compared in Table 5 with those calculated for ΔS_D and ΔC_D , it being assumed that $(\mu_t^2/r_t^3 - \mu_i^2/r_i^3)$ is 82 kcal. It is to be expected that the stretching of the C-Cl bond in the transition state results in a positive contribution to ΔS^* , but this is unlikely to be greater than 2—3 cal. ΔC_D should be identical with ΔC^* .

TABLE 5. *Electrostatic and experimental entropies and heat capacities of activation (in cal. °K⁻¹) for the ionisation of the C-Cl linkage at 55°.*

Solvent	" 50% " Acetone	" 50% " Ethanol	" 80% " Ethanol
D^a	45	45	27
$10^3 (d \ln D/dT)^a$	- 5.4	- 5.4	- 6.1
ΔS_D	- 7.24	- 7.24	- 12.5
$\Delta S^* \left\{ \begin{array}{l} \text{Ph} \cdot \text{CHCl}_2 \\ \text{Ph} \cdot \text{CCl}_3 \end{array} \right.$	- 11.8	- 9.9	- 11.8
ΔC_D	- 12.5	- 12.5	- 23.7
$\Delta C^* \left\{ \begin{array}{l} \text{Ph} \cdot \text{CHCl}_2 \\ \text{Ph} \cdot \text{CCl}_3 \end{array} \right.$	- 29	- 59	—
	- 46	- 73	- 43

^a Akerlof, ref. 35.

The figures in Table 5 show that the predictions of the theory are not supported by our observations. This might be thought to be due to the choice of an inappropriate value for $(\mu_t^2/r_t^3 - \mu_i^2/r_i^3)$ which may vary from solvent to solvent. A change of solvent should, however, affect ΔS^* and ΔC^* in the same manner irrespective of the value of this term and it can be seen that both compounds show an *increase* in ΔS^* and an appreciable *decrease* in ΔC^* on going from " 50% " acetone to " 50% " ethanol. It is also noteworthy that, even if this term is chosen so that ΔS_D is 3 cal. less than ΔS^* , ΔC_D is usually much less than ΔC^* . ‡ This conclusion is analogous to previous findings that temperature-dependent E values are not generally associated with constant isodielectric activation energies || as required by the theory,^{25,36} though this requirement is occasionally obeyed.³⁷ Similarly, it has already been reported^{22a} that the Born relation only accounts for part of the heat capacity of ionisation of weak acids.

† Kirkwood's equation gives the free energy of a dipole in a medium of dielectric constant D relative to its value in a vacuum. Differentiation with respect to temperature gives its entropy relative to the same reference state, but this quantity is equal to ΔS_D as electrostatic entropy effects are zero when the dielectric constant of the medium is independent of temperature.

‡ *Added in Proof.*—Enthalpies and entropies of activation derived from Kirkwood's equation have recently been compared with the experimental values for a number of bimolecular reactions which involve an increase in polarity on passage into the transition state (Caldin and Peacock, *Trans. Faraday Soc.*, 1955, **51**, 1217). Here too the predictions of the theory are not confirmed by the experimental observations.

|| Determined by varying the solvent composition in such a way that D is independent of the temperature.

³⁴ Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.

³⁵ Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

³⁶ Amis *et al.*, *J. Phys. Chem.*, 1943, **47**, 333; *J. Amer. Chem. Soc.*, 1941, **63**, 2231, 2621, 2883; also ref. 25.

³⁷ Amis and La Mer, *J. Amer. Chem. Soc.*, 1939, **61**, 905; Winstrom and Warner, *ibid.*, p. 1205.

It is also noteworthy that the ionisation of triphenylmethyl chlorides and the rate of ionisation of *tert.*-butyl chloride, in widely different solvents, does not vary with D in the expected manner.³⁸ These, and other deviations from the behaviour predicted for a continuous dielectric,^{33, 7b} are now regarded as due to specific solvent effects. The Born relation accounts well for the long-range forces between charged particles in solution but is only applicable beyond the first solvation shell.^{22b, 39}

The considerations outlined in the preceding paragraphs lead to the conclusion that the temperature-dependence of E , observed in ionisation reactions, arises out of the operation of specific solvation forces in the transition state. On this view, the magnitude of ΔC^* for the ionisation of molecules of similar size in the same solvent can be regarded as a measure of the increase in the extent of solvation on passing into the transition state. The results in Table 5 then indicate that this solvation is greater for benzotrichloride than for benzylidene chloride in both "50%" acetone and "50%" ethanol, and this conclusion is supported by the values of ΔS^* for these reactions. Although a small positive contribution to ΔS^* is to be expected, arising out of the bond stretching in the transition state, increased solvation should decrease ΔS^* , as observed. Our results do not permit a discussion of the dependence of the extent of this solvation on the nature of the solvent; acetone is a poor solvating medium, but both constituents are involved in the ethanolic solvents. It does, however, seem likely that the appreciable increase in ΔC^* on going from "50%" to "80%" ethanol is not entirely due to a decrease in solvation, as the excess heat capacity of mixing is considerably larger in the more aqueous solvent.⁴⁰

Our values for ΔC^* in aqueous acetone refer to an incomplete ionisation, but are much the same as the partial molar heat capacity of hydrochloric acid in water,⁴¹ and the heat capacity of ionisation of weak acids in the same solvent.^{22a} It may be that the extent of solvation in the transition state is not unduly different from that of fully developed ions, and the known variation of partial molar heat capacities with cationic size²¹ could also be responsible for part of these observations. It may also be that the partial molar heat capacity of water is greater in aqueous acetone than when it is pure, but this view is not supported by the decrease of ΔC^* with increasing water content, observed in the hydrolysis of acetic anhydride in aqueous acetone.²⁵ It has recently been suggested³⁰ that the transition state for the hydrolysis of methyl halides has zero heat capacity, and that, therefore, ΔC^* is numerically equal to the partial molar heat capacity of the initial reactant. In our reactions, it is difficult to accept a scheme which does not envisage the participation of additional solvent molecules in the activated complex, but it is possible that part of the loss of heat capacity on passing into the transition state arises out of a reduction in the heat capacity of the organic chloride. At present there is not sufficient information available to allow us to decide why our values for ΔC^* are so close to the corresponding values when ionisation is complete.

The Solvent Effect.—The results given in Table 4 show that the acceleration of the ionisation of the C-Cl linkage, caused by α -chlorination in benzylidene chloride, decreases along the solvent series "50%" acetone > "50%" ethanol > "80%" ethanol. The corresponding changes in E and ΔS^* increase in the same order. This is illustrated below for the reaction at 55°; the subscript _H refers to benzylidene chloride, _{Cl} to benzotrichloride.

Solvent	"50%" Acetone	"50%" Ethanol	"80%" Ethanol
$E_{Cl} - E_H$ (kcal.)	-3.69	-2.65	-1.67
$\Delta S^*_{Cl} - \Delta S^*_H$ (cal. °K ⁻¹)	-5.0	-2.9	0.0

The transition state of ionisation of benzotrichloride is more heavily solvated than that of benzylidene chloride (see preceding section), and it might be thought that a decreasing capacity for solvating such transition states is responsible for our observations. This,

³⁸ Brown and Hudson, *J.*, 1953, 3352; Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **51**, 481.

³⁹ Eley and Evans, *ibid.*, 1938, **34**, 1093.

⁴⁰ Prigogine and Defay, "Chemical Thermodynamics," Longmans Green and Co., London, 1954, p. 431.

⁴¹ Ramage and Randall, *J. Amer. Chem. Soc.*, 1927, **49**, 92.

however, requires an increase in E along the solvent series, while it is found that, in the ionisation of benzylidene chloride, E is unaltered by changing from "50%" acetone to "50%" ethanol at 35° and is actually reduced a little when the change at 55° is considered (cf. Table 3).

Our findings are consistent with the view that, for a given C-Cl separation, the replacement of an α -hydrogen atom by the larger chlorine results in increased steric hindrance to the solvation of the incipient ions. Any steric opposition to the approach of solvent molecules will be greater for the bulkier ethanol molecules than for water, and if this impedance of solvation is enhanced by α -chlorination, $E_{Cl} - E_H$ should increase with increasing participation of ethanol in the solvation process. This participation increases along our solvent series. The same explanation accounts for the observation that $E_{Cl} - E_H$ is -1.67 kcal. for the ionisation of chloro- and dichloro-diphenylmethane in absolute ethanol at 10° (cf. Table 4), and not greater than -3 kcal. in "85%" acetone at 12.5°.42 The observation that $\Delta S^*_{Cl} - \Delta S^*_H$ increases along this solvent series is also consistent with this view. It is, however, worth noting that the overall effect of increased steric hindrance to solvation is a retardation of the ionisation process.

The assumption that α -chlorination enhances steric effects of this type is not inconsistent with our earlier conclusion that it also leads to increased solvation in the transition state of ionisation. This state corresponds to that C-Cl separation for which the energy is a maximum, and two different contributions to this energy may be considered; one is the same as when the ionisation occurs in the gaseous phase, the other arises out of the solvation forces. Both increase with increasing charge development and bond extension. Relative to hydrogen, the additional chlorine atom in the α -chloro-derivative releases electrons towards the reaction centre and thus permits an increased C-Cl separation without increasing the "gaseous" ionisation energy; the greater bond extension also favours solvation. It thus seems reasonable to suppose that the transition state of the α -chloro-derivative is associated with a greater C-Cl separation which is sufficient to outweigh any steric hindrance to solvation arising out of the replacement of hydrogen by the larger chlorine atom. On this view, α -chlorination should lead to a reduction of E , and increased solvation in the transition state, as observed. Even in the absence of such steric effects † it is difficult to visualise the same bond extension in the transition states of the two compounds, as then no factors which tend to favour increased solvation are apparent in the α -chloro-derivative.

In the ionisation of benzotrichloride, these arguments could be employed to justify the assumption that the increasing participation of ethanol in the solvation process results in increasing C-Cl separation in the transition state, such that the solvation energy is independent of the solvent composition. The increase in E along the solvent series, "50%" acetone, "50%" ethanol, "80%" ethanol, then arises out of an increase in the "gaseous" ionisation energy. This view, however, is not supported by the observed increase in $\Delta S^*_{Cl} - \Delta S^*_H$, which is regarded as too large to be solely due to increasing bond extension. It is therefore considered that these changes in solvent involve some decrease in the extent of solvation of the transition state.

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† Our results do not allow us to draw any conclusions regarding the operation of these effects in "50%" acetone, where only water is involved in the solvation process.

42 Bensley and Kohnstam, *J.*, 1955, 3408.