Mass-law and Ionic-strength Effects in the Hydrolysis of Dichlorodiphenylmethane.

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The rate of hydrolysis of dichlorodiphenylmethane is controlled by the rate of heterolysis of one of the C–Cl linkages. This process involves the unimolecular mechanism, S_N1, and is subject to the operation of significant mass-law and ionic-strength effects (cf. Hughes, Ingold, *et al.*, *J.*, 1940, 979). The rate of ionisation and the mass-law constant are larger than for chlorodiphenylmethane under similar conditions, and the ionic-strength constant is less. These observations are consistent with electron-donation by the α-chloro-substituent towards the reaction centre.

The energy of activation for the reaction of the carbonium ion, Ph_2ClC^+, with chloride ions is about 1 kcal. less than for its hydrolysis. The ionic recombination can also be expected to be the more sensitive to changes in the solvent composition and this is considered to account for the observed increase of the mass-law constant as the ionising power of the solvent is reduced.

In aqueous acetone, any contribution to the overall reaction due to the direct solvolysis of ion-pairs (Winstein *et al.*, *Chem. and Ind.*, 1954, 664) is negligibly small.

THIS paper reports a kinetic investigation of the hydrolysis of dichlorodiphenylmethane and the effect of salt additions on the rate. It has long been known that this reaction occurs fairly readily with the formation or benzophenone (Kekulé and Franchimont,

Ber., 1872, **5**, 908). More recently, the solvolysis in ethanol has been investigated by Andrews and Kaeding (*J. Amer. Chem. Soc.*, 1951, **73**, 1007) who found that the reaction followed first-order kinetics, the rate being greater than for monochlorodiphenylmethane by a factor of about 15, and unaltered by the addition of ethoxide ions. The rate-determining stage, the heterolysis of one of the C⁻Cl linkages, must therefore involve the unimolecular mechanism, S_N1, (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603) and there is no reason to assume a different mechanism in the reaction with water.

Hughes, Ingold, and their co-workers (*J.*, 1940, 960 *et seq.*; 1952, 2488 *et seq.*) have shown that S_N1 solvolysis of the C–Cl bond is associated with the operation of mass-law and ionic-strength effects which are characteristic of this mechanism and may lead to appreciable deviations from the first-order rate law. In the absence of added salts these effects are more apparent in hydrolysis than in ethanolysis (cf. Hughes, Ingold, and Taher, *J.*, 1940, 949) and the present investigation aimed at establishing the influence of an α-chloro-group on their magnitude.

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

Preparation of Materials.—Dichlorodiphenylmethane was prepared by the conventional method from phosphorus pentachloride and benzophenone (Gattermann and Schultz, *Ber.*, 1896, **29**, 2944; Andrews and Kaeding, *loc. cit.*). The hydrolysable chloride of two different samples was 99·6% and 99·8% of the theoretical amount.

Chlorodiphenylmethane was prepared by the method of Hughes, Ingold, and Taher (*loc. cit.*). The hydrolysable chloride was 99·8% of the theoretical amount.

Acetone was obtained from the commercial product by Conant and Kirner's method (*J. Amer. Chem. Soc.*, 1924, **46**, 245) and fractionated through a 20-plate column. The addition of 250 ml. of water to 750 ml. of this acetone gave " 75% " aqueous acetone, and the other solvent, " 85% " aqueous acetone, was prepared in an analogous manner.

Inorganic chlorides and bromides, which were added to some of the reaction mixtures, were dried *in vacuo* over phosphoric oxide at elevated temperatures, " AnalaR " products being used when possible.

Products of Hydrolysis.—Dichlorodiphenylmethane (0·2214 g.) was allowed to react in the " 85% " solvent. After completion of the reaction, the solution was made alkaline with ammonia and most of the acetone pumped off. The remaining mixture was poured into an excess of ice-water, and the precipitated product filtered off, washed, dried over phosphoric oxide, and weighed. 0·1624 g. of product was obtained (calc. for benzophenone 0·1701 g.), having m. p. and mixed m. p. 47·5°. Extraction of the residues with ether failed to yield any further product.

There was no evidence for any reversibility of the hydrolysis. The acidity of a mixture of hydrochloric acid and benzophenone in the " 85% " solvent did not change for 24 hr. at 25°.

Rate Measurements.—The hydrolysis of dichlorodiphenylmethane was examined at 0° and 24·76°, the thermostats being of conventional design. The inital concentrations varied from 0·0025 to 0·02M. When inorganic halides were added the ionic strength at complete reaction was never greater than 0·06; usually it was much less. In a kinetic run the appropriate amount of the organic chloride was added to the solvent after this had attained the thermostat temperature, and samples (5 ml.) were withdrawn from time to time, run into cold, neutral acetone (200 ml.) to stop the reaction, and titrated with standard sodium hydroxide (lacmoid as indicator). The first reading was taken as " zero time " and the initial concentration of dichlorodiphenylmethane obtained from the " infinity " reading, *i.e.*, after more than 10 half-lives had elapsed. The concentration of any salt added to the reaction mixture was determined argentometrically, except when chlorides and bromides were added together. Such solutions were made up by weight. Several batches of the two solvents were employed and each batch was monitored by examining the rate of hydrolysis of chlorodiphenylmethane (good first-order kinetics were observed for initial concentrations of 0·02M), the necessary correction being applied to the runs with the dichloride.

Integrated first-order rate coefficients (integrated rates, $\bar{k}_1$) were calculated from the experimental results by means of the equation $\bar{k}_1 t = \ln(a/a - x)$, where the symbols have their usual meaning. Initial rates, $(k_1)_0$, were obtained from these quantities by extrapolation to " zero time." The subscript 0 will be used throughout this paper to refer to values at " zero time."

Results.—The kinetic form of the hydrolysis of dichlorodiphenylmethane is illustrated below

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for reaction in the " 75% " solvent at 0° with $[Ph_2CCl_2]_0 = 0.0164$ (Run 3). 5 ml. of the reaction mixture were titrated with 0.01109N-sodium hydroxide; t is in sec., $\bar{k}_1$ in sec.$^{-1}$.

$10^{-3}t$ ...	0.000	0.240	0.540	0.840	1.1145	1.460	1.750	2.040	2.355	2.680	3.100	3.515	∞
Titre...	0.84	2.02	3.30	4.30	5.23	6.03	6.71	7.31	7.90	8.40	9.10	9.70	15.39
$10^4\bar{k}_1$...	—	3.512	3.430	3.232	3.135	3.020	2.952	2.883	2.820	2.735	2.705	2.672	—

It is seen that $\bar{k}_1$ decreases as the reaction proceeds. Similar results were observed even when the initial concentration was as low as 0.0024M (cf. Table 3), in the presence of inorganic bromides, and also in the " 85% " solvent. When ionised chlorides were added to the reaction mixture this decrease became progressively less as the salt concentration increased (cf. Table 4).

The initial rate was not independent of the initial concentration of the organic chloride. This is illustrated in Table 1 where it is shown that this is entirely due to the retarding effect of the chloride ions which are inevitably formed in the time interval between the mixing of the reactants and the first reading at " zero time." The initial rate depends only on $[Cl^-]_0$ and is independent of $[Ph_2CCl_2]_0$.

TABLE 1. *The effect of initial concentration on the initial rate* $[(k_1)_0$ *in sec.$^{-1}$].*

Runs F, 4, and G were carried out in the " 75% " solvent at 0°; 25, 23, and V in the " 85% " acetone at 24.76°.

Run	Addition	$[Ph_2CCl_2]_0$	$[Cl^-]_0$	$10_4(k_1)_0$	Change (%)
F	—	0.00237	0.00026	4.35	—
4	—	0.01600	0.00250	3.75	−16
G	LiCl, 0.00228M	0.00241	0.00249	3.70	−17
25	—	0.00260	0.00045	7.55	—
23	—	0.01540	0.00280	5.80	−23
V	LiCl, 0.00226M	0.00242	0.00252	5.90	−21

It is of interest that the retardation of the reaction by chloride ions is more marked in the less aqueous solvent.

The effect of added salts, at 0.0165M, on the initial rate $[(k_1)_0$ in sec.^{1}] is illustrated below for reaction in the " 75% " solvent at 0° with $[Ph_2CCl_2]_0 = 0.016$M :

Added salt	—	NaBr	NaCl
$10^4(k_1)_0$	3.75	4.15	2.40

These results are quite general; ionised bromides accelerate the reaction, chlorides retard it.

When chloride and bromide ions were present in the same reaction mixture at ionic strength 0.0515, the initial rate in the " 75% " solvent at 0° followed the relation

$$10^4(k_1)_0 = 4.820/(1 + 36.9[Cl^-])$$

This is demonstrated in Table 2 where the values thus calculated are compared with those observed.

TABLE 2. *Initial rates at constant ionic strength in* " 75% " *aqueous acetone at* 0°.

$[Ph_2CCl_2]_0 \sim 0.005$, $[KCl] + [KBr] = 0.0507$, $[Cl^-]_0 = [KCl] + 0.0008$,* $0.80 \leqslant 10^3$ $[Cl^-]_0 \leqslant 26.2$.

$10^3[Cl^-]_0$	0.80	5.88	10.95	16.02	21.10	26.20
$10^4(k_1)_0$, obs.	4.71	3.91	3.44	3.04	2.71	2.45
$10^4(\bar{k}_1)_0$, calc.	4.68	3.96	3.43	3.03	2.71	2.45

* Due to hydrolysis before the first reading. This quantity was constant within ± 0.0001.

All these results are fully consistent with an S_N1 reaction subject to the operation of a powerful mass-law effect.

Mass-law and Ionic-strength Constants.—(a) *Calculations.* $\alpha°$, the mass-law constant, and σ, the ionic-strength constant, were calculated by means of the equation of Bateman, Church, Hughes, Ingold, and Taher (*J.*, 1940, 979, eqn. 14). For the hydrolysis of dichlorodiphenylmethane this equation can be written in the form

$$\frac{d[Ph_2CO]}{dt} = \frac{k_1°[Ph_2CCl_2]}{\alpha°[Cl^-] \text{ antilog}_{10} (A\mu^{\frac{1}{2}}) + \text{antilog}_{10}(B\sigma\mu)} \qquad . \quad . \quad . \quad (i) *$$

* This equation was employed in all calculations though, strictly, it is not applicable in the presence of bromide ions where the processes $R^+ + Br^- \rightleftharpoons RBr$ should be taken into account. Alkyl bromides, however, are known to undergo ionisation much more rapidly than the corresponding chlorides and it therefore appeared reasonable to apply the stationary-state principle to RBr. Under these conditions the resulting rate equation is easily shown to be identical with equation (i).

where k_1° is the rate constant, at zero ionic strength, of the rate-determining ionisation $Ph_2CCl_2 \longrightarrow Ph_2ClC^+ + Cl^-$, $A = -1\cdot815 \times 10^6 (DT)^{-3/2}$, $B = -0\cdot912 \times 10^{16}(DT)^{-2}$ and μ, D, and T are the ionic strength, dielectric constant, and absolute temperature, respectively.

Writing $[Ph_2CO] = x$, $[Ph_2CCl_2]_0 = a$, $[Cl^-]_0 = c$, and $[Br^-]_0 = b$, we have $[Ph_2CCl_2] = a - x$, $[Cl^-] = c + 2x$, and $\mu = b + c + 2x$.

The integrated form of equation (i) can then be written in the form

$$I/t = k_1^\circ + \alpha^\circ (J/t) \qquad \qquad \text{. . . . . (ii)}$$

where

$$I = \int_0^x \frac{\text{antilog}_{10} \, B\sigma(b + c + 2x)}{a - x} \cdot dx$$

and

$$J = \int_0^x \frac{(c + 2x) \, \text{antilog}_{10} \, A(c + b + 2x)^{\frac{1}{2}}}{a - x} \cdot dx$$

Equation (ii) contains three unknown parameters : σ (in the integral I), k_1°, and α°. If σ is known the other two may be obtained from the results of any one run as the slope and intercept of the straight line I/t as a function of J/t. Now, σ can be expected to be of the order of 10^{-3} (*idem, loc. cit.*) and B is 1—2×10^8 under our experimental conditions. The error in the integral I caused by taking σ as zero will therefore be very small in the most dilute solutions employed where $b = c \simeq 0$, $2x \leqslant 0\cdot005$. In the first place, k_1° and α° were therefore determined from the results observed in such reaction mixtures on the assumption that σ was zero. That value of σ which led to the same values for these parameters at the highest ionic strength employed, $(b + c = 0\cdot05, 2x \leqslant 0\cdot01)$, was then used for their recalculation from the results in the dilute solutions. This procedure did not significantly change their value. The σ thus obtained was therefore accepted and utilised in their calculation from the results observed in other reaction mixtures. The method of least squares was employed in each case to give the " best " straight line, A and B being evaluated from Akerlof's data for the dielectric constants of acetone-water mixtures (*J. Amer. Chem. Soc.*, 1932, **54**, 4125). The integral I was obtained from the expression

$$I = (\bar{k}_1 t - 4\cdot606 \, B\sigma x) \text{antilog}_{10} \, B\sigma(b + c + 2a)$$

which represents the first two terms of the series for that integral, the contribution of all other terms being negligibly small; $\bar{k}_1$ is the integrated first-order rate coefficient. J was obtained by graphical integration.

The values of these integrals in a typical run are given in Table 3.

TABLE 3. *Reaction of dichlorodiphenylmethane in " 75% " aqueous acetone at 0° (Run F).*

$a = 0\cdot002365$, $b = 0$, $c = 0\cdot000263$; $A = 1\cdot588$, $B\sigma = -0\cdot8402$.

t *	$10^4 x$ †	$10^4 \bar{k}_1$ ‡	$10^7 J/t$ §	$10^4 I/t$ ‡	t *	$10^4 x$ †	$10^4 \bar{k}_1$ ‡	$10^7 J/t$ §	$10^4 I/t$ ‡
230	2·19	4·226	1·810	4·220	2040	12·94	3·885	5·638	3·869
540	4·82	4·218	2·703	4·210	2405	14·39	3·899	6·050	3·882
835	6·98	4·116	3·406	4·107	2760	15·48	3·853	6·720	3·834
1125	8·65	4·046	4·100	4·036	3180	16·64	3·825	7·200	3·807
1440	10·34	3·990	4·708	3·978	3610	17·61	3·780	7·560	3·761
1745	11·83	3·973	5·280	3·959					

$k_1^\circ = 4\cdot376 \times 10^{-4}$ sec.$^{-1}$, $\alpha^\circ = 81$ mole^{-1} l.

* Sec. † Mole l.$^{-1}$. ‡ Sec.$^{-1}$. § Mole l.$^{-1}$ sec.$^{-1}$.

When ionised chlorides had been added to reaction mixtures, the variation of J/t was small over the course of the run. Under these conditions, the value obtained for k_1° was liable to considerable inaccuracy as its determination now involved extrapolation over a much greater range than that covered by the experimental points. For such systems the value of k_1° from other experiments was accepted, and only α° was calculated by means of equation (ii). This is illustrated in Table 4.

Our method for the calculation of α° and k_1° differs from that previously employed (Bateman *et al., loc. cit.*) where k_1° was obtained from the initial rates in the absence of added salts. In view of the marked effect of even small quantities of chloride ions on the rate (cf. Table 1), this procedure would only have been valid for the most dilute solutions where the accuracy was not of the highest order. The relatively small effect of changes in σ on the results of this investigation also led us to prefer the present method which, here, gives more accurate values of α°.

TABLE 4.   *Reaction of dichlorodiphenylmethane in " 85% " aqueous acetone at* $24 \cdot 76°$
in the presence of LiCl *(Run U).*

$a = 0 \cdot 002712$, $b = 0$, $c = 0 \cdot 005144$; $A = 2 \cdot 307$, $B\sigma = -1 \cdot 382$, $10^4 k_1° = 8 \cdot 08$ * sec.$^{-1}$. Units as in Table 3.

t	$10^4 x$	$10^4 \bar{k}_1$	$10^6 J/t$	$10^4 I/t$	$\alpha°$	t	$10^4 x$	$10^4 \bar{k}_1$	$10^6 J/t$	$10^4 I/t$	$\alpha°$
175	2·35	5·160	1·894	5·090	(158)	1920	16·71	4·997	2·249	4·900	142
415	5·30	5·245	2·005	5·172	146	2240	18·22	4·981	2·295	4·888	139
675	8·03	5·204	2·074	5·125	143	2520	19·24	4·916	2·302	4·825	142
895	9·96	5·118	2·096	5·035	146	2825	20·27	4·872	2·325	4·770	143
1330	13·33	5·088	2·172	5·002	142	3170	21·34	4·844	2·355	4·740	142
1600	15·07	5·072	2·225	3·991	139						

$\alpha°$ (mean) $= 142 \cdot 5$.

* This refers to the solvent employed in the present experiment. The value quoted later in this paper, 7·780, applies to a different batch of solvent.

(b) *Results.* In " 75% " aqueous acetone at $0°$, $\sigma = 1 \cdot 1 \times 10^{-8}$, and it was assumed that the same value applied in the " 85% " solvent. This figure is subject to an error of 5—10% as changes in the magnitude of σ had only a relatively small effect on $k_1°$ and $\alpha°$ under the existing experimental conditions. For example, in the " 75% " solvent at $0°$, with the ionic strength at 0·05, the term involving this parameter (the integral I) is only altered by 25% when its value is reduced to zero.

The mean values of $k_1°$ (in sec.$^{-1}$) and $\alpha°$ (in mole^{-1} l.), together with their standard deviations, are given below for the experiments carried out in the " 75% " solvent at $0°$. The initial concentration of the organic chloride varied in the range 0·0025—0·02, any salts added were at 0·002—0·05M, and the ionic strength was never greater than 0·06 :

(i) No addition, or +LiBr, NaBr, KBr; 12 experiments :

$$10^4 k_1° = 4 \cdot 386 \pm 0 \cdot 053, \ \alpha° = 80 \cdot 3 \pm 3$$

(ii) +LiCl, HCl, NaCl, KCl + KBr; 16 experiments :

$$\alpha° = 78 \cdot 7 \pm 2$$

The consistent results obtained in this solvent confirm the value of σ which was calculated from a smaller number of experiments and also show that equation (i) is applicable under these conditions.

The investigation of the reaction in the " 85% " aqueous acetone was not as extensive as in the more aqueous solvent. In the absence of added salts the following results were obtained :

(iii) At 24·76°, [Ph$_2$CCl$_2$]$_0$ = 0·0025 or 0·016, 8 experiments :

$$10^4 k_1° = 7 \cdot 780 \pm 0 \cdot 276, \ \alpha° = 140 \cdot 3 \pm 5 \cdot 5$$

(iv) At 0°, [Ph$_2$CCl$_2$]$_0$ = 0·005, 2 experiments :

$$10^4 k_1° = 0 \cdot 530 \ (\pm 0 \cdot 001), \ \alpha° = 126 \ (\pm 6).$$

The probable error in $k_1°$ is greater than before but it can be reduced a little by the choice of a slightly lower value for σ than in the " 75% " solvent. In view of the lack of sufficient experimental results it is difficult to justify such a procedure which, in any case, does not appreciably alter $\alpha°$. In the presence of small quantities of lithium chloride ($\leqslant 0 \cdot 005$M) $\alpha°$ is the same as in the absence of added electrolytes, but its value increases with increasing salt concentration. Thus for [LiCl] = 0·0040, $\alpha° = 142$, and for [LiCl] = 0·0215, $\alpha° = 155$; and a reasonable reduction of σ does not reduce this increase to any significant extent. Hughes, Ingold, and their co-workers (*locc. cit.*) have pointed out that equation (i) is, strictly, applicable only to very dilute solutions as it involves assumptions similar to those of Debye's limiting theory of the activity coefficients of electrolytes. These assumptions become increasingly less justified as the ionic strength is increased or the dielectric constant of the solvent reduced. Under these conditions the ionic activity coefficients are too low and hence the integrals I and J, which contain these quantities, also have too small a value. In these experiments $\alpha°$ was evaluated from the expression $\alpha° = (k_1°t - I)/J$; any factor which tends to make I and J too small will therefore tend to increase $\alpha°$, and our observations in the presence of the larger quantity of lithium chloride are consistent with this prediction. Similar deviations from equation (i), arising from an underestimate of the ionic activity coefficients, have already been reported in this solvent (*idem, locc. cit.*) though they became apparent at rather higher values of the ionic

strength than here. This is probably because the present method allows a more sensitive check of the applicability of this equation. The absence of such deviations in the more aqueous solvent is considered to result from its greater ionising power.

The conductance of lithium bromide solutions (Olson and Konecny, *J. Amer. Chem. Soc.*, 1953, **75**, 5801) leads to the conclusion that this salt is almost completely dissociated in " 75% " aqueous acetone, but not in the " 85% " solvent. If lithium chloride can be expected to be a weaker electrolyte than the bromide (Spieth and Olson, *ibid.*, 1955, **77**, 1412), the value of J (calculated on the assumption of complete ionisation) is subject to two errors : incomplete ionisation implies an overestimate of the ionic strength and thus tends to reduce J below its real value, but the concomitant overestimate of the chloride-ion concentration tends to make J too large. It can easily be shown that the second factor has the greater effect on J, which should therefore be too large. As a first approximation the error in I can be neglected,* and incomplete dissociation of lithium chloride should therefore lead to a reduction of α°. This is not consistent with the observed increase in this parameter on the addition of this salt.

Two experiments in the presence of lithium bromide, however, showed a decrease in α°, and an increase in k_1°, with increasing salt concentration. The same arguments can be employed to show that this cannot be due to an underestimate of the ionic activity coefficients, and that this result is to be expected if lithium chloride is a weaker electrolyte than the bromide—some of the reaction products are then present as undissociated lithium chloride. This contradicts the conclusions reached from the results observed in the presence of lithium chloride where in six experiments there was no indication of the reduction in α° required by the assumption of the incomplete dissociation of this salt. Further work appears to be necessary before this discrepancy can be resolved, and in the present investigation only α° values obtained from reaction mixtures containing no added electrolytes were accepted as the mass-law constant in the " 85% " solvent.

DISCUSSION

The Rate of Ionisation of Dichlorodiphenylmethane.—The results of this investigation show that the introduction of an α-chloro-group in chlorodiphenylmethane considerably increases the rate of ionisation in aqueous acetone and reduces the Arrhenius activation energy of this process (see Table 5).

TABLE 5. *The ionisation of chlorodiphenylmethane and chlorodiphenyl limethane in aqueous acetone.*

	Expt. conditions	Ph_2CCl_2	Ph_2CHCl
$10^6 k_1^\circ$ (sec.$^{-1}$)	" 75% " Aq. acetone, 0°	438	7·61
$10^6 k_1^\circ$ (sec.$^{-1}$)	" 85% " Aq. acetone, 24·76°	778	21·0
E_A (kcal.)	" 85% " Aq. acetone, 0—25°	17·5 *	21·4 †

    * This value may be subject to an error of ± 1 kcal. as the solvent used at 0° was inadvertently not monitored in the usual manner.

    † Hughes, Ingold, and Kohnstam, unpublished work.

These results are in agreement with the predictions of Hughes (*loc. cit.*) who pointed out that the replacement of a hydrogen atom, attached to a C–Cl bond, by chlorine should increase S_N1 reactivity as the expected increase in the electron release to the reaction centre would lower the activation energy of the rate-determining ionisation.

Similar increases in the rate, caused by α-chlorination, have been reported in the ethanolysis of chlorodiphenylmethane (Andrews and Kaeding, *loc. cit.*), in the reaction of benzylidene chloride with aqueous acetone and ethanol (Olivier and Weber, *Rec. Trav. chim.*, 1934, **53**, 869; Hine and Lee, *J. Amer. Chem. Soc.*, 1951, **73**, 22; Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25), and of allyl chloride in moist formic acid (Vernon, *J.*, 1954, 223). Hine and Lee, and Vernon, also reported a decrease in the activation energy. Evans and Hamann, on the other hand, found an increase in this parameter but a repetition of their work (Bensley and Kohnstam, unpublished work) reverses this conclusion.

It is also of interest to compare these results with the effect of p-chloro-substituents on

    * The error in I is due only to the overestimate of the ionic strength, and can be shown to be small when compared to the corresponding error in J.

the rate of S_N1 reactions. For example, chloro-*p*-chlorodiphenylmethane undergoes hydrolysis at about one-third of the rate of the parent compound and with a larger activation energy (Ingold, " Structure and Mechanism in Organic Reactions," G. Bell and Sons Ltd., London, 1953, p. 332). In general no compound has yet been reported in which a chlorine atom in the *para*-position relative to the reaction centre acts as an overall electron-donor with respect to hydrogen. It therefore appears that the conjugative electron-release by chlorine can outweigh the attraction due to the inductive effect when the atom is directly attached to the site of reaction. As the *p*-chloro-group acts as an overall attractor in a similar reaction it seems that the demand for electrons is less powerful in that position or, alternatively, that the relay of the conjugative effect to the reaction centre is less efficient.

The Ionic-strength Constant, σ.—The ionic-strength constant, σ, is a measure of the ion-atmosphere stabilisation of the transition state of the rate-determining ionisation. A comparison of our results for chlorodiphenyldimethane with those reported by Hughes, Ingold and their co-workers for chlorodiphenylmethane (*locc. cit.*) shows that this stabilisation is less for the dichloro-compound, $10^8\sigma$ being $1\cdot1$ and $1\cdot61$, respectively.

σ was evaluated by means of equation (i) which is derived by treating the transition state of ionisation as a dipole with charges $\pm ze$ separated by a distance d, and defining $\sigma = z^2d$. This parameter can therefore be regarded as a measure of the charge separation in the transition state, and it has already been shown that the changes in its value caused by the introduction of *p*-alkyl substituents in chlorodiphenylmethane are consistent with this assumption and with the known polar effects of these groups (*idem, locc. cit.*). The present results show that the introduction of an α-chloro-group in this compound reduces σ, and it therefore appears that the substituent releases electrons towards the reaction centre in the transition state. Such a process will tend to move the effective positive charge out of the benzene rings towards the reaction centre, thus leading to a reduction in the charge separation, relatively to that in the parent compound, as observed. Electron-attraction by this group can be expected to have the converse effect.

The Mass-law Constant, $\alpha°$.—The carbonium ion, which is formed by the heterolysis of the C–Cl linkage, can undergo one of two reactions; ionic recombination $R^+ + Cl^- \xrightarrow{k_1}$ RCl, or hydrolysis, $R^+ + H_2O \xrightarrow{k_2}$ ROH. The mass-law constant, $\alpha°$, represents the relative efficiencies of these two processes at zero ionic strength and is defined by $\alpha° = k_2°/k_3°$. The values of this parameter for a number of carbonium ions are compared in Table 6.

TABLE 4. $\alpha°$ *for diphenylmethyl cations in aqueous acetone.*

Cation	Solvent	Temp.	$\alpha°$
Ph_2CH^+	" 80%," " 90% "	25, 50°	11·5 *
$p\text{-}Me\cdot C_6H_4\cdot CHPh^+$	" 80% "	25	32 *
$(p\text{-}Me\cdot C_6H_4)_2CH^+$	" 80%," " 85%," " 90% "	0	74 *
Ph_2CCl^+	" 75% "	0	79
Ph_2CCl^+	" 85% "	25	140
Ph_2CCl^+	" 85% "	0	126

* Hughes, Ingold, *et al., locc. cit.*

It can be seen that the introduction of α-chloro- or *p*-methyl groups in the diphenylmethyl cation considerably increases the mass-law constant. The changes in this parameter due to *p*-alkylation have already been discussed by Hughes, Ingold, and their co-workers (*locc. cit.*) who pointed out that they are a direct consequence of the greater electron-release towards the central carbon atom, which enhances the stability of the carbonium ion. This ion is therefore capable of a longer existence, and thus more liable to penetration of its solvation shell by a chloride ion before this shell collapses to yield the alcohol. On this view the present results again indicate that the α-chloro-substituent acts as an electron-donor relative to hydrogen.
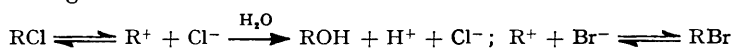
If it can be accepted that electron-release towards the central carbon atom is the principal factor controlling the magnitude of $\alpha°$, it can also be concluded that the α-chloro-group is capable of at least the same electron-release in the fully developed carbonium ion

as two *p*-methyl groups. In the transition state of the ionisation, where the demand for electrons is less than in the fully developed ion, *p*-alkyl groups are the more efficient electron-donors; the rate of ionisation of chlorodi-*p*-tolylmethane in " 85% " aqueous acetone at 0° is about ten times that of dichlorodiphenylmethane, ($10^5 k_1° = 47$ and $5\cdot3$ respectively), and it is unlikely that this is entirely due to purely steric factors. It therefore seems that an α-chlorine atom is capable of a greater response to an increased demand for electrons than a *p*-methyl group. As chlorine, unlike the methyl group, possesses unshared electrons this conclusion appears reasonable.

As $\alpha° = k_2°/k_3°$, the change in the value of this parameter with changing temperature may be employed to calculate the difference in the activation energies of the reactions of the carbonium ion with chloride ions and water. The results obtained in the " 85% " solvent at 0° and 25° show that for the chlorodiphenylmethyl cation the activation energy for the ionic recombination is 0·9 kcal. greater than for the hydrolysis. This figure cannot be regarded as very accurate as only two experiments were carried out at the lower temperature but it is unlikely to be in error by more than 0·4 kcal. For the same solvent, Hawdon, Hughes, and Ingold (*J.*, 1952, 2499) found that the activation energy for the combination of di-*p*-tolylmethyl ions with azide ions was 4 kcal. greater than for their hydrolysis. Both investigations show that the ionic reaction is associated with the greater activation energy. The energy difference is less in the present case but it must be borne in mind that different cations and anions are involved. There is no reason why the two ionic reactions, or even the two hydrolyses, should have the same activation energy.

The results quoted in Table 6 show that the mass-law constant of the chlorodiphenyl-methyl ion increases as the ionising power of the solvent is reduced, its value at 0° being 79 in the " 75%," and 126 in the " 85% " solvent. Although this type of behaviour has not been reported before it is consistent with the definition of α° as the ratio of the rates of ionic recombination ($k_2°$) and hydrolysis of the carbonium ion ($k_3°$). The passage into the transition state involves a decrease of electric charge for the ionic reaction, and a spreading of charge for the hydrolysis. In general, reactions associated with such changes in charge are accelerated by the use of less powerfully ionising solvents, and this acceleration is greater when a diminution of charge occurs than when the charge is merely rendered more diffuse (Ingold, *op. cit.*, p. 347). A change from " 75% " to " 85% " aqueous acetone can therefore be expected to produce a greater increase in $k_2°$ than in $k_3°$, and hence a larger α°.

The Intervention of Ion-pairs.—In the present discussion it has been assumed that the component processes in the S_N1 reactions of the C–Cl linkage are those originally proposed by Hughes and Ingold :

$$\text{RCl} \rightleftharpoons \text{R}^+ + \text{Cl}^- \xrightarrow{\text{H}_2\text{O}} \text{ROH} + \text{H}^+ + \text{Cl}^-; \quad \text{R}^+ + \text{Br}^- \rightleftharpoons \text{RBr}$$

In this scheme only the carbonium ion, R⁺, reacts with anions or the solvent.

Recent work on the S_N1 acetolysis of sulphonic esters led Winstein and his co-workers (*Chem. and Ind.*, 1954, 664) to conclude that it is also necessary to take into account the reactions of the " external," or " solvent-separated," ion-pairs, R⁺ Cl⁻, which they regard as intermediate in the formation of the carbonium ion. The application of these views to the present investigation can be represented as follows : *
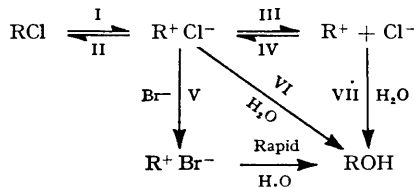
* Strictly, process V can be expected to be reversible, and the " external " ion-pairs, R⁺ Br⁻, should undergo a series of reactions analogous to those involving R⁺ Cl⁻. It has however been assumed, as by Winstein, that the direct hydrolysis of R⁺ Y⁻ can be regarded as instantaneous if RY is hydrolysed much more rapidly than the initial reactant.

The " internal " ion-pair, which does not react with water or other ions, has been omitted from the present scheme.

Qualitatively it is difficult to distinguish between these two views. The Hughes–Ingold scheme requires a retardation of the overall reaction by added chloride ions, but this retardation is not proportional to their concentration as the concomitant increase in the ionic strength reduces their activity coefficient, and also increases the ion-atmosphere stabilisation of the transition state of the ionisation process. These factors also lead to an increase in the hydrolysis rate on the addition of bromide ions. Winstein's scheme predicts similar results but now these are at least partly due to the intervention of the ion-pairs. Equation (i), which is derived from the Hughes–Ingold scheme was found to apply to the present results but this cannot be regarded as conclusive evidence in favour of this scheme. The observed agreement could conceivably arise out of a cancellation of the errors caused by a neglect of the ion-pair reactions and an overestimate of the effect of ionic strength on the activity coefficients of charged species, the most likely error in equation (i) (Hughes, Ingold, *et al.*, *locc. cit.*).

It is however possible to decide which of these schemes applies to the present investigation by considering the results observed in the hydrolysis of dichlorodiphenylmethane at constant ionic strength (cf. Table 2). It was found that the hydrolysis rate was given by the equation

$$10^4 (k_1)_0 = C/(1 + D[\text{Cl}^-]) \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

with $C = 4 \cdot 820$ and $D = 36 \cdot 9$, at an ionic strength of $0 \cdot 0515$ in " 75% " aqueous acetone at $0°$.

An expression for the hydrolysis rate can be obtained on the basis of Winstein's scheme by applying the stationary-state principle to the carbonium ion and the ion-pair $\text{R}^+ \text{Cl}^-$. For the range of chloride- and bromide-ion concentrations used in these experiments (cf. Table 2) this expresion only reduces to equation (iii), with $D \sim 35$, if $k_{\text{II}} + k_{\text{III}} \gg k_{\text{VI}} + k_{\text{V}}[\text{Br}^-]$. Under these conditions the expression is identical with that which is obtained if only the hydrolysis of the carbonium ion is considered, the contribution due to the hydrolysis of the ion-pairs being negligibly small. The same conclusion can be reached even if process V is considered to be reversible. There is therefore no evidence for the participation of ion-pairs in the hydrolysis of dichlorodiphenylmethane in " 75% " aqueous acetone.

On the other hand, the expression for the hydrolysis rate derived from equation (i) is of the same form as (iii), with $C = 10^4 k_1°$ antilog$_{10}$ $(B\sigma\mu)$ and $D = \alpha°$ antilog$_{10}$ $(A\mu^{\frac{1}{2}})$. If the previously determined values of $k_1°$ and $\alpha°$ are used, this leads to $C = 4 \cdot 840$ and $D = 38 \cdot 2$, in good agreement with the experimental observations. It therefore appears that the Hughes–Ingold scheme for the component processes in the $S_\text{N}1$ reactions of the C–Cl linkage is applicable to the present investigation.

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