384. *The Mass-law Effect in the Hydrolysis of Dichlorodiphenylmethane.*

By G. Kohnstam and B. Shillaker.

The rate of hydrolysis of dichlorodiphenylmethane is controlled by the rate at which one of the C–Cl linkages undergoes heterolysis. This process involves the unimolecular mechanism, S_N1, and the present study aimed at obtaining further information about the behaviour of the resulting carbonium ion, Ph_2ClC^+, in aqueous acetone. The mass-law constant,[1] which reflects the competition of chloride ions and water for this ion, decreases with increasing ionising power of the solvent, and its temperature coefficient is independent of the solvent composition. This behaviour is consistent with the assumption of Born charging for the solvated species involved, or with differences in the extent of their solvation; alternatively, both these factors may be responsible.

If the S_N1 heterolysis of the C–Cl linkage involves intermediate ion-pairs,[2] our results show that only the fully developed carbonium ion reacts with water and with anions.

In the S_N1 hydrolysis of an organic halide

$$\mathrm{RX} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{R^+ + X^-} \xrightarrow[\mathrm{H_2O}]{3} \mathrm{ROH + H^+ + X^-}$$

the competition of solvent molecules and " common " anions for the fully developed carbonium ion is of interest. The relevant information is contained in the mass-law constant ($\alpha^0 = k_2^0/k_3^0$, where the superscripts refer to zero ionic strength) which can be evaluated *via* the electrostatic treatment of Hughes, Ingold, and their co-workers.[1] Little is known of the variation of this constant with changing solvent composition and the present paper reports an extension of previous work on the hydrolysis of dichlorodiphenylmethane [3] to two further solvents, " 80% " and " 70% " aqueous acetone.† The rate-determining step in this reaction is the ionisation of one of the C–Cl linkages, and the resulting carbonium ion, Ph_2ClC^+, has a fairly large mass-law constant. The system is therefore well suited for studying the effects of solvent changes on α^0.

EXPERIMENTAL

The experimental methods were similar to those described previously.[3] The thermostat for temperatures below 0° consisted of a well-stirred ethanol–water mixture in a large Dewar vessel. Cooling was effected by filling the inner of two concentric glass tubes with solid carbon dioxide, and the outer with sufficient ethanol to keep the temperature of the bath just below the desired value in the absence of heating. A 5w intermittent heater was controlled by a conventional toluene–mercury regulator, and kept the temperature constant to within $\pm 0{\cdot}01°$.

The hydrolysis of *ca.* 0·005M-dichlorodiphenylmethane was studied at 0° in " 80% " acetone, and at $-9{\cdot}61°$ and $-21{\cdot}50°$ in the " 70% " solvent where the reaction at 0° was too rapid to permit accurate measurements. The reactions were followed by noting the development of acidity, and gave integrated first-order rate coefficients ($\bar{k}$) which always decreased as the hydrolysis proceeded (see Table 2). In the " 70% " solvent, experiments were also carried out at $-9{\cdot}61°$ in the presence of potassium chloride, potassium bromide, and their mixtures at an initial ionic strength of 0·0515. The instantaneous rates at this ionic strength were obtained by extrapolating the integrated first-order rate coefficients to " zero time," and followed the relation

$$10^4k = 3{\cdot}25/(1 + 32{\cdot}9[\mathrm{Cl^-}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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† Throughout this paper a " x% " solvent refers to a mixture of acetone and water in the ratio $x : 100 - x$ by vol.

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

[2] Winstein *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 169, 459; and earlier papers.

[3] Bensley and Kohnstam, *J.*, 1955, 3408.

This is illustrated in Table 1 where the values calculated from this equation are compared with those observed.

TABLE 1. *Instantaneous rates* (k, *in* sec.$^{-1}$) *at ionic strength* 0·0515 *in* " 70% " *acetone at* −9·61°.

[KBr] + [KCl] = 0·0500, $[\mathrm{Cl}^-]_0$ = [KCl] + 0·0015 ± 0·0005,† 0·0015 ⩽ $[\mathrm{Cl}^-]_0$ ⩽ 0·0510.

$10^3[\mathrm{Cl}^-]_0$	1·5	14·5	26·4	38·5	51·0
10^4k, obs.	3·12	2·16	1·72	1·47	1·20
10^4k, calc.	3·10	2·20	1·74	1·43	1·21

The subscript 0 refers to " zero time."
† Due to hydrolysis before the initial reading.

The results of any one kinetic run gave the rate of ionisation at zero ionic strength ($k_1°$) and the mass-law constant ($\alpha°$) from the equation

$$I/t = k_1{}^0 - \alpha^0 J/t \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)\dagger$$

where

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

and

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

$a = [\mathrm{Ph_2CCl_2}]$ at time $t = 0$, $a - x = [\mathrm{Ph_2CCl_2}]$ at time t, b and c are the initial bromide- and chloride-ion concentrations, respectively, $b + c + 2x$ is the ionic strength at time t,‡ $A = -1{\cdot}815 \times 10^6(DT)^{-3/2}$, $B = -0{\cdot}912 \times 10^{16}(DT)^{-2}$, D and T are the dielectric constant and absolute temperature, respectively, and σ is the ionic-strength constant [1] whose value was assumed to be the same ($1{\cdot}1 \times 10^{-8}$) as in the solvents previously examined. Eqn. (2) is readily deduced from the electrostatic treatment by Hughes, Ingold, and their co-workers,[1] and the evaluation of the integrals I and J has already been discussed.[3] Data for a typical run are given in Table 2, and our main results are summarised below ($k_1{}^0$ in sec.$^{-1}$, α^0 in mole^{-1} l.):

(i) " 80% " acetone at 0°, 4 experiments: $10^4k_1{}^0 = 1{\cdot}438 \pm 0{\cdot}004$, $\alpha^0 = 98{\cdot}8 \pm 0{\cdot}8$
(ii) " 70% " acetone at −9·61°, 10 experiments: $10^4k_1{}^0 = 2{\cdot}912 \pm 0{\cdot}020$, $\alpha^0 = 62{\cdot}7 \pm 0{\cdot}7$
(iii) " 70% " acetone at −21·50°, 4 experiments: $10^5k_1{}^0 = 5{\cdot}503 \pm 0{\cdot}038$, $\alpha^0 = 57{\cdot}2 \pm 2{\cdot}0$.

TABLE 2. *Reaction of dichlorodiphenylmethane with* " 80% " *aqueous acetone at* 0°. (Run C.)

(5 ml. samples titrated with 0·004988N-NaOH; $A = -1{\cdot}861$; $B\sigma = -1{\cdot}038$.)

t (sec.)	Titre (ml.)	10^4k (sec.$^{-1}$)	$10^4I/t$ (sec.$^{-1}$)	$10^7J/t$ (mole l.$^{-1}$ sec.$^{-1}$)	t (sec.)	Titre (ml.)	10^4k (sec.$^{-1}$)	$10^4I/t$ (sec.$^{-1}$)	$10^7J/t$ (mole l.$^{-1}$ sec.$^{-1}$)
0	0·37	—	—	—	5068	6·77	1·134	1·124	3·295
1461	2·87	1·280	1·276	1·775	5948	7·42	1·104	1·093	3·491
2058	3·69	1·249	1·242	2·133	6878	8·12	1·096	1·083	3·769
2643	4·41	1·222	1·215	2·427	8083	8·85	1·071	1·058	4·001
3263	5·06	1·184	1·176	2·649	∞	15·01	—	—	—
4163	6·00	1·166	1·157	3·037					

$10^4k_1{}^0 = 1{\cdot}441$ sec.$^{-1}$, $\alpha^0 = 99{\cdot}1$ mole^{-1} l.

DISCUSSION

The data now available for the ionisation of dichlorodiphenylmethane in aqueous acetone at 0° and zero ionic strength are summarised in Table 3. The rate of ionisation ($k_1{}^0$) changes almost 100-fold on passing from " 70% " to " 85% " acetone; Fainberg

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† We take this opportunity to correct errors in the earlier paper [3] which were inadvertently missed during proof-reading. Equation (ii) should be identical with the present equation (2), A (Tables 3 and 4) should be negative, and the constants C and D (p. 3416) should be given by

$$C = 10^4k_1{}^0\ \text{antilog}_{10}\,(-B\sigma\mu) \text{ and } D = \alpha^0\ \text{antilog}_{10}\,(A\mu^{\frac{1}{2}} - B\sigma\mu).$$

‡ The hydrolysis of dichlorodiphenylmethane yields benzophenone and, hence, two chloride ions per mole.

and Winstein's data for t-butyl chloride[4] lead to a similar change at this temperature. The activation energy of the ionisation process (E_1^0) is virtually independent of the solvent composition,† in agreement with previous observations on S_N1 reactions.[4,6,7] The difference between the activation energies for the reactions of chloride ions and water with the fully developed carbonium ion ($E_2^0 - E_3^0$) also appears to be insensitive to changes in the solvent. The most significant feature of the present results is the decrease in the mass-law constant, α^0, as the solvent is made more aqueous. Before this observation can be discussed in detail, it is necessary to consider whether it arises from some imperfection in the electrostatic treatment[1] adopted.

TABLE 3. *Effect of solvent composition on the rate of ionisation and mass-law constant in the reaction of dichlorodiphenylmethane with aqueous acetone at* 0°.

" % " Acetone	85% †	80%	75% †	70%
$10^4k_1^0$ (sec.$^{-1}$)	0·530	1·438	4·386	14·30 ‡
α^0 (mole^{-1} l.)	126 ± 4·2	98·8 ± 0·8	79·4 ± 0·6	67·2 ± 2·0 ‡
E_1^0 (kcal.)	17·60	—	—	18·40
$E_2^0 - E_3^0$ (kcal.) §	0·9 ± 0·4	—	—	1·0 ± 0·4

† From Bensley and Kohnstam's data.[3] ‡ Calculated from results at lower temperatures. § From the temperature coefficient of ln α^0.

Ionic Activity Coefficients.—Eqn. (2) assumes that ionic activity coefficients are given by Debye's limiting law, an assumption which becomes increasingly less valid as the ionic strength is increased, or the dielectric constant of the solvent reduced. " Limiting-law activity coefficients " are then too low, leading to too small a value for the integral J and, hence, to too large a value for α^0. This could account for the variation of α^0 with changes in the solvent composition. However, experiments in " 70% " and " 75% " acetone gave the same value of α^0 when carried out in the absence of added electrolytes and at ionic strength 0·05, and it does not therefore seem likely that the observed behaviour of α^0 results from the use of " limiting-law activity coefficients."

Ion-pair Formation by Electrolytes.—The present results have been calculated on the assumption that all electrolytes are completely dissociated. It can easily be shown that, if this is not the case, mass-law constants obtained from eqn. (2) are too small, the error increasing as the ion-pair dissociation constant of the electrolyte decreases. The values of α^0 should then decrease as the solvent is made less aqueous, contrary to our observations.

In any case, it is not considered that ion-association is large enough to have a significant effect on the value of α^0 in any of the systems under consideration. In " 75% " acetone, the dissociation of lithium bromide is virtually complete,[8] and this should therefore also apply to potassium bromide which has almost the same dissociation constant as the lithium salt in " 90% " acetone;[9] there is little reason to believe that potassium chloride is appreciably more associated than its bromide.‡ It also seems reasonable to assume that hydrochloric acid behaves in a similar manner to hydrobromic acid; the latter has a dissociation constant of 6×10^{-3} in " 90% " acetone and is completely dissociated in the " 70% " solvent.[9] The dissociation constant to be expected for hydrochloric acid in " 85% " acetone is then such that the neglect of association in the acid produced by the hydrolysis

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† The two values of E_1^0 in Table 3 were obtained from data at different temperatures. A negative temperature coefficient is to be expected for E_1^0 since the ionisation of C–Cl involves an increase in the polarity of the reacting system,[5,6] and it is therefore considered that the two values of E_1^0 will differ by less than 0·5 kcal. at 0°.

‡ Experiments in the presence of salts were only carried out in " 75% " and " 70% " acetone.

[4] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 5937.

[5] Robertson, *Canad. J. Chem.*, 1955, **33**, 1536; 1957, **35**, 613; Bensley and Kohnstam, *J.*, 1956, 287; 1957, 4747.

[6] Tommila, Tilikainen, and Voipio, *Ann. Acad. Sci. Fennicae*, 1955, *A*, No. II.

[7] Brown and Hudson, *J.*, 1953, 3352.

[8] Olson and Konecny, *J. Amer. Chem. Soc.*, 1953, **75**, 5801.

[9] Nash and Monk, *J.*, 1955, 1899.

of 0·005M-dichlorodiphenylmethane only affects the value of α^0 within the limits of the experimental error. The resulting error is even smaller in the more aqueous solvents.

Specific Salt Effects.—The electrostatic treatment on which eqn. (2) is based assumes that the acceleration of the ionisation of the C–Cl linkage by added electrolytes, the ionic-strength effect, results from ion-atmosphere stabilisation of the transition state and depends only on the ionic strength of the solution. Earlier criticisms of this assumption[10, 11] are often based on observations in systems where ion-pair formation may be significant, but highly specific salt effects have recently been observed by Duynstee and Grunwald for the ionisation of 1-methyl-2-phenylpropyl toluene-*p*-sulphonate in 50% aqueous dioxan.[12] These authors conclude that two additional factors may contribute to the ionic-strength effect: (i) a salt-induced medium effect which arises from the different effects of electrolytes on the activities of the solvent components,[13] similar to an earlier suggestion by Lucas and Hammett,[14] and (ii) short-range interactions, such as complex formation with the substrate.

Specific salt reactions do not, however, appear to be operating in the present reactions. First, the constant C in eqn. (5) (cf. eqn. 1) represents the initial rate of ionisation in 0·05M-potassium chloride and in 0·05M-potassium bromide. Secondly, the rate of ionisation at zero ionic strength, k_1^0, which was obtained from experiments on 0·005M-solutions containing no added salts, leads to a value for the rate at ionic strength 0·05 [$k_1^0 \text{ antilog}_{10} (-B\sigma\mu) = 3{\cdot}15 \times 10^{-4}$, where μ is the ionic strength] which agrees with the observed value ($C = 3{\cdot}25 \times 10^{-4}$) as well as can be expected for initial rates. The two additional effects proposed by Duynstee and Grunwald are therefore either negligibly small or of the same magnitude for hydrochloric acid, potassium chloride, and potassium bromide in the present systems, and thus have no significant influence on our values for the mass-law constant.

The Variation of the Mass-law Constant with Solvent Composition.—The observed decrease of the mass-law constant with increasing water content of the solvent confirms and extends previous findings.[3] A qualitative explanation of this result has already been given, and a more quantitative interpretation can now be attempted.

From the definition of the mass-law constant we have

$$\boldsymbol{R}T \ln \alpha^0 = \boldsymbol{R}T \ln (k_2^0/k_3^0) = \Delta G_3^* - \Delta G_2^*$$

where ΔG_2^* and ΔG_3^* are the free energies of activation for the reaction between the carbonium ion and chloride ions, and for the hydrolysis of the carbonium ion, respectively. Solvation of charged species is an essential feature of reaction by mechanism S_N1, and it seems reasonable to assume that the two processes now under consideration may involve changes in solvation by water, but not changes in solvation by acetone. The difference between the two free energies of activation then becomes the difference between the standard free-energy changes of the two processes:

$$\mathrm{R^+ \ (solv.) + Cl^- \ (solv.) \longrightarrow R^{z+}\text{---}Cl^{z-} \ (solv.)} + n_2\mathrm{H_2O}$$

$$\mathrm{R^+ \ (solv.) \longrightarrow R\text{-}\overset{+}{\text{-}}OH_2 \ (solv.)} + n_3\mathrm{H_2O}$$

where the parameter z represents the degree of charge development in the transition state of the ionic recombination and has a value between zero and unity; n_2 is most unlikely to be negative and is probably positive since a reduction of charge can be expected to lead to decreased solvation, and n_3 may well be zero.[1] Hence,

$$\boldsymbol{R}T \ln \alpha^0 = \bar{G}_a^* + \bar{G}_b^* - \bar{G}_c^* - (n_2 - n_3)\bar{G}(\mathrm{H_2O}) \quad . \quad . \quad . \quad . \quad (3)$$

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[10] Spieth and Olson, *J. Amer. Chem. Soc.*, 1955, **77**, 1412.

[11] Fainberg and Winstein, *ibid.*, 1956, **78**, 2763.

[12] Duynstee, Thesis, Amsterdam, 1959.

[13] Baughman, Grunwald, and Kohnstam, *ibid.*, in preparation.

[14] Hammett and Lucas, *ibid.*, 1942, **64**, 1928.

where the $\bar{G}^*$ terms represent standard chemical potentials, $\bar{G}(\mathrm{H_2O})$ is the chemical potential of water in the solvent, and the subscripts a, b, c refer to $\mathrm{Cl^-}$ (solv.), $\mathrm{R}\overset{+}{-}\mathrm{OH_2}$ (solv.) and $\mathrm{R}^{z+}\text{---}\mathrm{Cl}^{z-}$ (solv.), respectively.

The two transition-state structures being assumed to be constant over the range of solvents under consideration, the effect of solvent changes on the chemical potentials will be given by the Born equation [15] for the fully developed ions, and by the Kirkwood equation [16] for the dipolar structure.† Equation (3) then takes the form

$$\boldsymbol{R}T \ln \alpha^0 = \text{constant} + (\boldsymbol{N}e^2/2\varepsilon)[1/r_a + 1/r_b - 3(zd)^2/2r_c^{\,3}] - (n_2 - n_3)\boldsymbol{R}T \ln a \quad (4)\ ‡$$

where ε is the dielectric constant, a the activity of water in the solvent, zed the dipole moment of $\mathrm{R}^{z+}\text{---}\mathrm{Cl}^{z-}$ (solv.), and the r's the radii of the solvated species.

In the present solvents $1/\varepsilon$ is virtually a linear function of $\ln a$, and the " best " straight line obtained by plotting $\ln \alpha^0$ against $1/\varepsilon$, or against $\ln a$, predicts the observed values of α^0 within the limits of experimental error. If the transition state for the ionic recombination reaction carries fully developed charges (*i.e.*, $z = 1$),[18] the square bracket in eqn. (4) could be zero, whence $n_2 - n_3 = 4{\cdot}2$; this value is not impossibly large.§ Alternatively, if $n_2 - n_3 = 0$, the assumption that $d = r_c$ and reasonable values for the radii ($r_a = 4{\cdot}6$ Å,[17] $r_b = r_c = 7$ Å) lead to $z = 0{\cdot}63$, consistent with the usual view that this type of transition state carries approximately half-developed charges.[1] Our results are thus fully consistent with the considerations on which equation (4) is based, but it is unfortunately not possible to establish whether the variation of α^0 with solvent composition arises solely from the " electrostatic " effect (the term in $1/\varepsilon$), or whether differential solvation effects also contribute.

The constancy of $E_2^{\,0} - E_3^{\,0}$ within the limits of experimental error (see Table 3) does not alter this conclusion. From eqn. (4) we have

$$E_2^{\,0} - E_3^{\,0} = \boldsymbol{R}T^2 \mathrm{d} \ln \alpha^0/\mathrm{d}T = \text{constant} - (\boldsymbol{N}e^2/2\varepsilon)[1/r_a + 1/r_b - 3(zd)^2/2r_c^{\,3}](1 + T\,\mathrm{d} \ln \varepsilon/\mathrm{d}T) + (n_2 - n_3)\bar{L}$$

where $\bar{L}$ is the relative partial molar enthalpy of water in the solvent, and can be obtained from available data.[20] This equation predicts that a change from " 85% " to " 70% "

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† It has often been found that the Born equation does not apply to unsolvated ions, but it is generally taken to be valid for solvated ions.[17] It seems reasonable to assume that this also applies to the Kirkwood equation.

‡ The last term in the square bracket of equation (4), the Kirkwood term, arises as follows. The Kirkwood equation for the free-energy change on transferring a dipole of moment zed and radius r from vacuum to a medium of dielectric constant is

$$\Delta G_{\mathrm{D}} = -\frac{\varepsilon - 1}{2\varepsilon + 1} \cdot \frac{(zed)^2}{r^3} = \text{constant} + \frac{3}{2(2\varepsilon + 1)} \cdot \frac{(zed)^2}{r^3}$$
$$= \text{constant} + 3(zed)^2/4\varepsilon r^3$$

with negligible error for the dielectric constants now under consideration.

§ This value probably represents an overestimate, even for an upper limit, since it is likely that changes in the dielectric constant have a larger effect on the stabilities of two separate ions than on the stability of a dipole carrying fully developed charges. For $r_a = 4{\cdot}6$ Å, $r_b = r_c = d = 7$ Å, and $z = 1$, equation (4) yields $n_2 - n_3 = 2{\cdot}0$. Water activities were obtained from Ewert's data at 25°,[19] ideal behaviour of the vapours over aqueous acetone being assumed, and from Kister and Waldmann's thermal data;[20] dielectric constants are from Akerlof's data.[21]

[15] Born, *Z. Phys.*, 1920, **1**, 45.

[16] Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.

[17] Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093; Coulson and Everett, *ibid.*, 1940, **36**, 633; Oiwa, *J. Phys. Chem.*, 1957, **61**, 1587; Buckingham, *Discuss. Faraday Soc.*, 1958, **24**, 151.

[18] Baughan, Evans, and Polanyi, *Trans. Faraday Soc.*, 1941, **37**, 377; Evans, *ibid.*, 1946, **42**, 719; Franklin, *ibid.*, 1952, **48**, 443.

[19] Ewert, Thesis, Brussels, 1935.

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

[21] Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

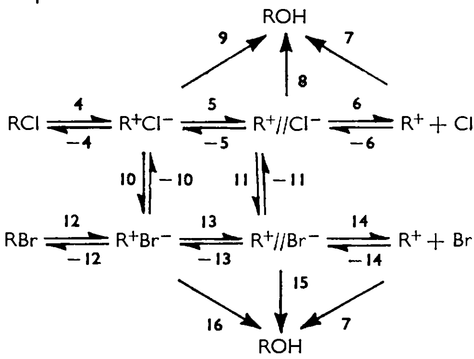
acetone alters $E_2^0 - E_3^0$ by less than 0·2 kcal. for all values of $n_2 - n_3$ between zero and 4·2; the standard error of the observed $E_2^0 - E_3^0$ is 0·4 kcal./mole.

Ion-pair Intermediates.—The present discussion has been based on Hughes and Ingold's scheme for the S_N1 reactions of the C–Cl linkage:

$$\mathrm{RCl} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{R^+ + Cl^-} \xrightarrow[\mathrm{H_2O}]{3} \mathrm{ROH + H^+ + Cl^-},\ \mathrm{R^+ + Br^-} \rightleftharpoons \mathrm{RBr} \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

Here only the fully developed carbonium ion reacts with water and with anions.

Results observed in the acetolysis of sulphonic esters led Winstein and his co-workers to conclude that ionisation proceeds *via* intermediate ion-pairs which are capable of reacting directly with water and anions.[2] This scheme can be represented as follows when applied to the present reactions: †



. . . . (ii)

where $\mathrm{R^+X^-}$ represents the " internal " ion-pair and $\mathrm{R^+//X^-}$ the " external " or " solvent-separated " ion-pair. If the present reactions follow this scheme, the conclusions reached in the preceding section could be seriously in error.

Any reaction scheme must, however, be consistent with the instantaneous hydrolysis rate observed in " 70% " acetone and ionic strength 0·051 over chloride-ion concentrations ranging from 0·0015M to 0·051M: *viz.*,

$$k = C/(1 + \alpha[\mathrm{Cl^-}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where C and α are constants (see Table 1). The rate coefficients of the individual reaction stages should be independent of chloride- and bromide-ion concentrations at constant ionic strength, and the application of the stationary state principle to the ion-pairs, the carbonium ion, and the organic bromide shows that scheme (ii) only leads to eqn. (5) if

$$C = \frac{k_4}{1 + k_{-45}k_5 + k_{-4}k_{-5}/k_5k_6}, \qquad \alpha = \frac{k_{-4}k_{-5}k_{-6}/k_5k_6k_7}{1 + k_{-4}k_5 + k_{-4}k_{-5}/k_5k_6} \quad . \quad . \quad (6)$$

This result is identical with that obtained for the scheme

$$\left.\begin{array}{l} \mathrm{RCl} \underset{-4}{\overset{4}{\rightleftharpoons}} \mathrm{R^+Cl^-} \underset{-5}{\overset{5}{\rightleftharpoons}} \mathrm{R^+//Cl^-} \underset{-6}{\overset{6}{\rightleftharpoons}} \mathrm{R^+ + Cl^-} \xrightarrow{7} \mathrm{ROH + H^+ + Cl^-} \\ \qquad \mathrm{R^+ + Br^-} \rightleftharpoons \mathrm{R^+//Br^-} \rightleftharpoons \mathrm{R^+Br^-} \rightleftharpoons \mathrm{RBr} \end{array}\right\} \quad . \quad . \quad \text{(iii)}$$

and requires that only the fully developed carbonium ion reacts with water and anions.‡

It is now necessary to express the mass-law constant, α^0, in terms of the rate coefficients of the individual reaction stages involved in solvolysis by scheme (iii). Mass-law constants

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† It is usually considered that the internal ion-pair, $\mathrm{R^+X^-}$, does not react with anions,[2] but this process has now been included to allow for all possibilities.

‡ A similar conclusion has already been reached for a simplified version of scheme (ii) on the basis of experiments in " 75% " acetone over the range 0·025—0·050M for the chloride-ion concentration.[3]

were obtained from eqn. (2) which is based on Hughes and Ingold's simpler scheme, (i), and on the electrostatic treatment proposed by these workers;[1] this approach is also consistent with eqn. (5) and requires that $\alpha = k_2/k_3 = \alpha^0$ antilog$_{10}$ $(A\mu^{\frac{1}{2}} - B\sigma\mu)$. Experiments at different ionic strengths gave the same value of α^0, within the limits of experimental error, and this value yields $\alpha = 33{\cdot}7$ in "70%" acetone at $-9{\cdot}61°$ and ionic strength 0·051, in good agreement with the observed value of 32·9 [see eqn. (1)]. It can therefore be concluded that reaction by scheme (iii) requires the same variation of α with changing ionic strength as scheme (i) and, hence, that α^0 represents the value of α at zero ionic strength whichever of the two schemes is operating.

Qualitatively, the observed behaviour of the mass-law constant with changing solvent composition is fully consistent with reaction by scheme (iii). Rate coefficients for processes involving the approach of opposite charges will increase less with increasing ionising power of the solvent than rate coefficients for their separation (or for the spreading of an existing charge); eqn. (6) shows that α, and hence α^0, should therefore decrease with increasing water content of the solvent, as observed. The more quantitative interpretation discussed in the preceding section also holds true for reaction by scheme (iii) provided that

$$k_{-4}/k_5 + k_{-4}k_{-5}/k_5k_6 \ll 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

we then have $\alpha^0 = k^0{}_{-4}k^0{}_{-5}k^0{}_{-6}/k^0{}_5k^0{}_6k^0{}_7$, whence it can easily be shown that $\boldsymbol{R}T \ln \alpha^0$ is still given by eqn. (3); the only difference is that R^{z+}----Cl^{z-} (solv.) now represents the transition state in step -4 and is not formed directly from the fully developed ions.

There is some evidence that inequality (7) is valid, at least as a first approximation,* but this evidence is not conclusive, and the denominator in equation (6) could be greater than unity; this would complicate any attempt to interpret the behaviour of α^0 quantitatively. It must, however, be stressed that the available evidence does not allow us to distinguish between schemes (i) and (iii) for the hydrolysis of dichlorodiphenylmethane. Since ion-pair intermediates have often been found to undergo direct solvolysis, the absence of any such reactions now (cf. p. 1920) may well arise from the fact that no ion-pairs are involved as intermediates in the present systems. This would mean hydrolysis by scheme (i), as originally envisaged by Hughes and Ingold.

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* If inequality (7) is valid, application of the Brönsted equation to the rate coefficients shows that schemes (i) and (iii) require the same variation of α^0 with changing ionic strength, as observed. Inequality (7) also demands that the rate of step 4 (k_4[RCl]) should be the same as the rate of hydrolysis in the absence of "common" ions (C[RCl]). For 1-methyl-2-phenylpropyl toluene-*p*-sulphonate in 50% aqueous dioxan step 4 occurs about 60% more rapidly than hydrolysis,[18] but Winstein's results [2] suggest that this discrepancy should be less for a substrate with a greater facility for ionisation and it may well vanish for dichlorodiphenylmethane. The identity of titrimetric and polarimetric rates in the reaction of 1-phenylethyl chloride with aqueous ethanol [22] is consistent with this view.

[22] Ward, *J.*, 1927, 445.