

31. *The Elimination of Chlorine in the Hydrolysis of Aqueous Solutions of Chloroacetic Acid and the Chloroacetates.*

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IN previous papers (Dawson and Dyson, J., 1933, 49, 1133; 1934, 778) an account has been given of kinetic observations relative to the removal of bromine from the $\text{CH}_2\text{Br}\cdot\text{CO}_2$ group in neutral, acid, and alkaline solution. By making use of solutions with a constant total-salt concentration and by restricting the measurements of velocity to the very early stages of the reaction (0.5—2%), the complications arising from inert-salt effects and from the intervention of the reaction products have been largely avoided. In these circum-

stances it was found that the kinetic data can be satisfactorily interpreted in terms of four independent reactions corresponding with the equation

$$v = v_1 + v_2 + v_3 + v_4 = k_1[A'] + k_2[A']^2 + k_3[HA] + k_4[HA][A'] \quad (1)$$

in which $[A']$ and $[HA]$ represent the concentrations of the bromoacetic ion and the undissociated bromoacetic acid respectively. The coefficients k_1 and k_3 probably correspond with reactions in which the solvent molecules are involved, and include the molar concentration of the water.

The experiments to be described show that analogous processes are effective in the elimination of chlorine from the $\text{CH}_2\text{Cl}\cdot\text{CO}_2$ group in aqueous solution. The evidence for this is provided by measurements of the initial velocity in solutions which contain (A) undissociated molecules only, (B) ions only, and (C) both molecules and ions. These were made at 45° and for the most part also at 25° with solutions in which the total-salt concentration was kept constant at 1 g.-equiv. per l. by the requisite addition of sodium nitrate.

(A) When the hydrogen-ion concentration of a moderately dilute solution of chloroacetic acid is sufficiently raised by the addition of a suitable strong acid (nitric acid), the concentration of the chloroacetic ions is reduced below the limit at which they play any effective part, and in these circumstances the initial velocity is found to be proportional to the concentration (x) of the chloroacetic acid as required by the third term $v = v_3 = k_3[HA]$ of equation (1). This is evident from the results in Table I.

TABLE I.
Velocities for $xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + 0.5M\text{-HNO}_3 + 1.0M\text{-NaNO}_3$ (45°).

x	0.0204	0.0306	0.050	0.0612	0.0707	0.0909
$10^7 \times v_{\text{obs.}}$	0.238	0.360	0.572	0.715	0.829	1.06
$10^7 \times v_{\text{calc.}}$	0.239	0.358	0.585	0.716	0.827	1.06

The above calculated velocities are based on $k_3 = 11.7 \times 10^{-7}$, but it is probable that this value is affected to some extent by the presence of the nitric acid, in that the experimental data for solutions in which the ionisation of the chloroacetic acid is reduced by the addition of chloroacetate lead to the higher value $k_3 = 13.5 \times 10^{-7}$. The depressing effect of the nitric acid on k_3 is, however, difficult to estimate, for free chlorine appears when the concentration of the nitric acid is further increased. If perchloric acid is substituted for the latter, and sodium perchlorate for the nitrate, no free chlorine is formed, but the value of k_3 diminishes markedly as the concentration of the perchloric acid increases. With regard to the above discrepancy, it is noteworthy that the values obtained for k_3 at 25° by the two methods are much closer than at 45° , but the relations have not been further examined.

(B) Solutions which contain the reactive group entirely in the ionic form are represented by neutral solutions of chloroacetate and in this case the general equation for the velocity reduces to the form $v = v_1 + v_2 = k_1x + k_2x^2$. Measurements in which the ionic concentration (x) was varied from 0.02 to 1.0 g.-equiv./l. have given results in close agreement with this equation, according to which v/x is a linear function of the chloroacetate concentration x . The actual graphs lead to the values of k_1 and k_2 shown in Table II, which affords a comparison of the calculated and the observed initial velocities.

TABLE II.
Velocities for $xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{Na} + (1-x)M\text{-NaNO}_3$.
Temp. 45° ; $k_1 = 16.5 \times 10^{-7}$, $k_2 = 57.0 \times 10^{-7}$.

x	0.02	0.04	0.05	0.07	0.10	0.15	0.20	0.30
$10^7 \times v_{\text{obs.}}$	0.36	0.76	0.97	1.47	2.22	3.81	5.57	9.95
$10^7 \times v_{\text{calc.}}$	0.35	0.75	0.97	1.43	2.22	3.76	5.58	10.1
x	0.40	0.50	0.60	0.70	0.80	0.90	1.00	
$10^7 \times v_{\text{obs.}}$	15.5	22.4	30.1	39.0	49.5	61.4	73.6	
$10^7 \times v_{\text{calc.}}$	15.7	22.4	30.4	39.5	49.7	61.0	73.5	

Temp. 25° ; $k_1 = 0.95 \times 10^{-7}$, $k_2 = 3.9 \times 10^{-7}$.

x	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$10^7 \times v_{\text{obs.}}$	0.13	0.34	0.63	0.99	1.44	1.99	2.52	3.22	4.00	4.91
$10^7 \times v_{\text{calc.}}$	0.134	0.345	0.635	1.00	1.45	1.97	2.58	3.26	4.01	4.85

From the results in the above table it is apparent that the initial rate of chloride formation in neutral chloroacetate solutions can be adequately represented in terms of the two reactions corresponding with v_1 and v_2 . The close agreement suggests that there can be no appreciable difference between the inert-salt effects produced by the nitrate and the chloroacetate.

(C) For solutions which contain both the acid and the salt in comparable quantities, the observed initial velocity is usually much greater than the sum of the velocities for the two corresponding solutions which contain only the acid or the salt. The difference increases with the product of the two concentrations, and this suggests that chloride is produced by the interaction of ions and molecules as represented by $v_4 = k_4[A'][HA]$ in equation (1).

When the acid and the salt are present in equivalent concentration (x), this equation reduces to the form $v = (k_1 + k_3)x + (k_2 + k_4)x^2$, and in accordance with this, the experimental data yield a straight line when v/x is plotted against x . The slope of this gives the value of $(k_2 + k_4)$, and the intercept gives $(k_1 + k_3)$. In combination with k_1 and k_2 of Table II, these lead to the values of k_3 and k_4 which have been used in the calculation of the partial and total velocities recorded in subsequent tables.

TABLE III.

Velocities for $xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{Na} + (1-x)M\text{-NaNO}_3$.
Temp. 45°; $k_1 = 16.5 \times 10^{-7}$, $k_2 = 57.0 \times 10^{-7}$, $k_3 = 13.5 \times 10^{-7}$, $k_4 = 220 \times 10^{-7}$.

x	0.02	0.04	0.10	0.20	0.30	0.40	0.50	0.60	0.80	1.00
$10^7 \times v_1$	0.33	0.66	1.65	3.30	4.95	6.60	8.25	9.90	13.2	16.5
$10^7 \times v_2$	0.02	0.09	0.57	2.28	5.13	9.12	14.3	20.5	36.5	57.0
$10^7 \times v_3$	0.27	0.54	1.35	2.70	4.05	5.40	6.75	8.10	10.8	13.5
$10^7 \times v_4$	0.09	0.35	2.20	8.80	19.8	35.2	55.0	79.2	141	220
$10^7 \times v_{\text{calc.}}$	0.71	1.64	5.77	17.1	33.9	56.3	84.3	118	201	307
$10^7 \times v_{\text{obs.}}$	0.72	1.68	5.91	17.2	34.5	57.2	84.8	117	193	298

Temp. 25°; $k_1 = 0.95 \times 10^{-7}$, $k_2 = 3.9 \times 10^{-7}$, $k_3 = 0.69 \times 10^{-7}$, $k_4 = 15.0 \times 10^{-7}$.

x	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
$10^7 \times v_1$	0.095	0.19	0.28	0.38	0.47	0.57	0.66	0.76	0.85	0.95
$10^7 \times v_2$	0.039	0.16	0.35	0.62	0.97	1.40	1.91	2.50	3.16	3.90
$10^7 \times v_3$	0.069	0.14	0.21	0.28	0.34	0.41	0.48	0.55	0.62	0.69
$10^7 \times v_4$	0.150	0.60	1.35	2.40	3.75	5.40	7.35	9.60	12.1	15.0
$10^7 \times v_{\text{calc.}}$	0.35	1.09	2.19	3.68	5.55	7.79	10.4	13.4	16.8	20.5
$10^7 \times v_{\text{obs.}}$	0.36	1.11	2.26	3.73	5.65	7.99	10.5	13.6	16.9	20.7

From Table III it is apparent that v_1 and v_3 are jointly responsible for about 85% of the observed velocity when $x = 0.02$, but that this diminishes to less than 10% when $x = 1$. In spite of the wide variations in the relative importance of the component reactions, the concordance between $v_{\text{calc.}}$ and $v_{\text{obs.}}$ is good over the entire range.

Observations have also been made with series of solutions in which the ion concentration is kept constant whilst that of the acid molecule is varied. If the ratio of acid to salt is not too large, the ionisation of the acid may be neglected, and the reaction velocity is found to be a linear function of the concentration of the acid as required by equation (1) in these circumstances. The results for two such series of solutions are given in Table IV.

TABLE IV.

$0.2M\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{Na} + xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + 0.8M\text{-NaNO}_3$ (45°).

x	0	0.05	0.10	0.15	0.20	0.25	0.30
$10^7 \times v_{\text{obs.}}$	5.60	8.53	11.4	14.3	17.2	20.0	22.9
$10^7 \times v_{\text{calc.}}$	5.58	8.46	11.3	14.2	17.1	20.0	22.8

$0.4M\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{Na} + xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + 0.6M\text{-NaNO}_3$ (25°).

x	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
$10^7 \times v_{\text{obs.}}$	0.99	1.34	1.68	2.02	2.36	2.71	3.10	3.40	3.73
$10^7 \times v_{\text{calc.}}$	1.00	1.34	1.67	2.01	2.34	2.68	3.01	3.34	3.68

The concordance between the observed and the calculated velocities for the molecule-free solutions of Table II, and for the solutions containing molecules and ions of Tables III

and IV, shows no appreciable difference, and there can be little doubt that the constancy of the total-salt concentration of the solutions is partly responsible for the simplicity of the relations which have been found. In Table III the concentration of chloroacetic acid shows, however, a large variation (0.02—1.0 mol. per litre), and this represents a change in the reaction medium which might reasonably be expected to have an appreciable influence on the magnitude of the several velocity coefficients. In the more concentrated solutions of this series, the observed rate of change is mainly due to the partial velocities v_2 and v_4 , and hence it would seem legitimate to infer that the coefficients k_2 and k_4 for the ion-ion and the molecule-ion reaction are not much affected by the change in the medium resulting from the presence of chloroacetic acid.

The behaviour of solutions of chloroacetic acid which contain no chloroacetate is not nearly so simple, in that the measured velocities for the more concentrated solutions are appreciably less than the calculated values. For these solutions, the initial velocity cannot be determined directly, because the hydrochloric acid which is formed reduces the concentration of the chloroacetate ion and thus has a very marked retarding effect on the reaction rate in the very early stages of hydrolysis. The required velocity has been obtained by a method which involves the measurement of the mean velocities for successive short periods corresponding with the liberation of 0.5, 1.0, 1.5, and 2.0% of the total chlorine. These mean velocities when plotted against the corresponding hydrochloric acid concentrations give a straight line which on extrapolation to $[HCl] = 0$ leads to a value for the true initial velocity. The disturbing effect in question increases with the concentration of the chloroacetic acid and is almost negligible when the solution is less than 0.1M.

The results for 0.1—1.0M solutions of chloroacetic acid at 45° and 25° are given in Table V. The calculated velocities derived from equation (1) are based on degrees of ionisation given by $K_c = 2.40 \times 10^{-3}$, which is the value of the ionisation constant indicated by measurements of the rate of hydrolysis of ethyl acetate in 1M-sodium chloride solution at 25° with chloroacetic acid as catalyst (Dawson and Lowson, J., 1929, 393). Since the ionisation of acetic acid is very nearly the same in equivalent solutions of sodium chloride and sodium nitrate, it is assumed that this value of K_c will apply to the standard salt solutions used in the present experiments, and also that the influence of temperature can be neglected.

TABLE V.

		Velocities for $xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + 1.0M\text{-NaNO}_3$.									
x		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
45°	$10^7 \times v_{\text{obs.}}$	1.54	3.17	5.24	7.05	9.02	11.1	—	14.8	—	18.9
	$10^7 \times v_{\text{calc.}}$	1.49	3.28	5.22	7.30	9.51	11.8	—	16.8	—	22.1
25°	$10^7 \times v_{\text{obs.}}$	0.098	0.212	0.326	0.459	0.582	0.708	0.840	0.984	1.12	1.24
	$10^7 \times v_{\text{calc.}}$	0.091	0.201	0.322	0.453	0.593	0.740	0.895	1.05	1.22	1.39

In explanation of the systematic divergence between $v_{\text{obs.}}$ and $v_{\text{calc.}}$ for the more concentrated solutions which contrasts very markedly with the concordance shown by the corresponding solutions in Table III, it may be noted that the observed velocities in Table V are mainly due to $v_3 = k_3[HA]$ and $v_4 = k_4[HA][A']$. The results in Table III suggest that k_4 is not affected by the chloroacetic acid content of the reaction medium, but on the other hand, there are grounds for the belief that the ionisation constant K_c in the case of the weaker acids falls appreciably as the concentration increases, and if this occurs with chloroacetic acid, it may be expected that v_4 will be reduced as a result of the lower value of $[A']$.

Such diminution in the value of K_c will have relatively little influence on v_3 , but, on the other hand, there is evidence to support the view that k_3 becomes smaller as the concentration of the chloroacetic acid increases. If the hydrogen-ion concentration of the series of solutions in Table V is increased by the addition of a small amount of a strong acid (e.g., 0.2M-perchloric acid), the resulting fall in the concentration of the chloroacetic ion leads to a very considerable diminution in the importance of v_4 as compared with v_3 , but the divergence between the values of $v_{\text{obs.}}$ and $v_{\text{calc.}}$ is still in evidence at the higher concen-

trations. It thus appears that k_3 is reduced by the presence of chloroacetic acid in much the same way as it is by the strong acids, nitric and perchloric, to which reference has already been made (p. 154). This reduction is probably due, in part, to the fall in the concentration of the water which is inevitably associated with an increase in the chloroacetic acid content of the solution, for it is to be remembered that k_3 is in all probability represented by the product $k_3'[\text{H}_2\text{O}]$, where k_3' is the bimolecular coefficient corresponding with the interaction of the molecules of water and chloroacetic acid. The above considerations seem to offer a reasonable explanation of the medium effects which are responsible for the discrepancy between the observed and calculated velocities in the case of the more concentrated solutions of the free acid.

In further support of the view that the observed rate of formation of chloride by the hydrolysis of aqueous chloroacetate solutions can, in general, be accounted for in terms of the four reactions represented by equation (1), a brief reference may be made to the results obtained with a series of solutions in which chloroacetic acid is gradually replaced by sodium chloroacetate. Such a series corresponds with the general formula $(a - x)M\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + xM\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$, in which a represents the total chloroacetic concentration. Provided that x/a be not too small, equation (1) for this series takes the form

$$v = k_1x + k_2x^2 + k_3(a - x) + k_4x(a - x) \\ = k_3a + (k_1 + k_4a - k_3)x - (k_4 - k_2)x^2$$

according to which the velocity passes through a maximum when $x = (k_1 + k_4a - k_3) / 2(k_4 - k_2)$. On substitution of the numerical values of the velocity coefficients, it is found that the maximum velocity corresponds with the neutralisation of a fraction given by $x/a = 0.675 + 0.0092/a$. Table VI gives the results for such a series with $a = 1$.

TABLE VI.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$10^7 \times v_{\text{obs.}}$...	18.9	32.5	48.9	63.7	74.6	84.3	88.7	90.5	88.6	83.4	73.6
$10^7 \times v_{\text{calc.}}$...	22.1	34.2	51.6	65.7	76.6	84.2	88.6	89.7	87.6	82.2	73.5

The curve obtained by plotting $v_{\text{obs.}}$ against the fraction of neutralised acid x passes through a maximum in the neighbourhood of $x = 0.70$, whilst the theoretical relation leads to $x = 0.685$. The divergence between $v_{\text{obs.}}$ and $v_{\text{calc.}}$ at the lower values of x is, of course, to be attributed to the influence of those factors which have been discussed in connexion with the results in Table V.

Apart from secondary disturbances due to uncompensated changes in the reaction medium, the experimental data in the previous tables seem to justify the conclusion that equation (1) includes all the collisional processes which lead to the separation of covalent chlorine from the $\text{CH}_2\text{Cl}\cdot\text{CO}_2$ group in the form of the chloride ion. The processes in which the water molecule appears to be involved are much less effective than the other two processes, as may be seen if the values of the bimolecular velocity coefficients are compared. The relative values at 45° are :

Reactants	Mol.- H_2O .	Ion- H_2O .	Ion-Ion.	Mol.-Ion.	Mol.-Mol.
Relative bimol. vel. coeffs.	1	1.22	228	880	(0)

The kinetic measurements afford no evidence of the liberation of chlorine by collisions in which the hydrogen ion takes part or by collisions between pairs of chloroacetic acid molecules. If the effectiveness of such intermolecular collisions, as measured by the bimolecular velocity coefficient, is of the same order of magnitude as that for the molecule-water collisions, it is evident that the high concentration of the solvent molecules would preclude the detection of any effect which might result from collisions between pairs of chloroacetic acid molecules. The relations disclosed are similar to those for the liberation of bromine ion, but further data are required for the discussion of the quantitative differences.

EXPERIMENTAL.

The general method of experiment has been previously described (*loc. cit.*). Since, however, chloride cannot be determined accurately by the Volhard method, Drechsel's procedure (*Z. anal.*

Chem., 1877, 16, 351) was adopted. The samples of reaction mixture were run into a measured volume of *M*/20-silver nitrate mixed with sufficient nitric acid to coagulate the silver chloride on stirring. This was filtered off, thoroughly washed, and the filtrate titrated with thiocyanate. This procedure increases considerably the volume of the solution, but apart from a loss of sharpness, the dilution does not affect the end-point. The same method was followed in the use of carefully purified potassium chloride for the standardisation of the silver solution.

SUMMARY.

Measurements of the rate at which chloride is liberated from the $\text{CH}_2\text{Cl}\cdot\text{CO}_2$ group show that in aqueous solution it is, in general, due to the four independent processes represented by the equation $v = k_1[A'] + k_2[A']^2 + k_3[\text{HA}] + k_4[\text{HA}][A']$. The first and the third term represent, in all probability, bimolecular processes in which the water molecule is involved. The experimental data relate to conditions in which there are no disturbances resulting from the products of reaction or from variations in the salt content of the reaction medium. Collisions in which the hydrogen ion is involved, and those between pairs of chloroacetic acid molecules, are not measurably effective.

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