118. *The Progressive Elimination of Bromine in the Aqueous Hydrolysis of Sodium Bromoacetate.*

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THE hydrolysis of sodium bromoacetate is represented stoicheiometrically by equation (A),

$$CH_2Br{\cdot}CO_2Na + H_2O = CH_2(OH){\cdot}CO_2H + NaBr \quad . \quad . \quad . \quad (A)$$

but kinetic observations indicate that the actual mechanism by which the reaction products are formed involves a number of simultaneous processes some of which occur in stages.

The initial velocities for solutions of varying concentration (Dawson and Dyson, J., 1933, 49) show that the formation of bromide in neutral solution is the result of two independent processes in which the primary reactants are, respectively, the bromoacetate ion and the water molecule (reaction 1) and two bromoacetate ions (reaction 2). As the hydrolysis proceeds and the solution becomes increasingly acid, the actual rates of bromide formation at successive stages are much greater than those calculated on the assumption that the observed rate is determined by reactions (1) and (2). In the case of 1·0*M*-sodium bromoacetate, the actual rate at the stage represented by the liberation of 50% of the total bromine is approximately twice as great as the rate calculated on this basis.

There can be no doubt that the glycollic acid formed is in part responsible for the discrepancy, and an attempt has been made to ascertain the nature of the processes which collectively determine the actual rate of bromide formation. The results show clearly that a large number of processes are involved. Some of these are associated with complex intermediate compounds the formation of which makes it impossible to give a complete account of the mechanism. It has, however, been established with very considerable probability that there are four other bimolecular processes, involving directly or indirectly the original bromoacetate and the final product glycollic acid, which play an effective part in the elimination of bromine as bromide in the progressive hydrolysis of the bromoacetate.

Although glycollic is a weaker acid than bromoacetic the difference is not very great and the equilibrium (B) is without doubt a factor of the first importance in determining

$$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H \rightleftharpoons CH_2(OH){\cdot}CO_2' + CH_2Br{\cdot}CO_2H \quad . \quad . \quad (B)$$

the rate of formation of bromide in the acid solutions. The establishment of this equilibrium is directly responsible for the incidence of three further processes previously described (cf. Dawson and Dyson, J., **1933**, 1133), which lead to the formation of bromide. The reactants in these are, respectively, the bromoacetic acid and water molecules (reaction 3), the bromoacetic acid molecule and the bromoacetate ion (reaction 4), and the bromoacetate and glycollate ions (reaction 5). For these five primary processes, the characteristic velocity coefficients have already been determined at 25° under " standard " conditions, *i.e.*, with a total salt concentration of 1·0 mol. per litre, and it seemed possible that the actual velocities at successive stages in the hydrolysis of a given original solution of sodium bromoacetate would be accounted for on the basis of the corresponding five partial velocities, provided that complications arising from the formation of intermediate compounds are avoided. That this is not the case is clearly shown by measurements of the initial velocities for solutions of sodium bromoacetate to which glycollic acid has been added. For all such mixtures the observed initial velocity is appreciably greater than that represented by the sum of the velocities of reactions (1) to (5). This may be illustrated by the data for $0{\cdot}5M$-sodium bromoacetate + $0{\cdot}5M$-glycollic acid, in which case the observed initial velocity at 25° is $11{\cdot}7 \times 10^{-6}$ mol./l./min., whilst the calculated velocity is $9{\cdot}3 \times 10^{-6}$. It thus appears that some other collisional process (or processes) must play a part in the liberation of bromine.

For convenience of reference the established reactions (1) to (5) and the corresponding bimolecular velocity coefficients are shown in Table I, which includes a number of other possible bimolecular processes, which might be considered responsible for the above discrepancy between the observed and calculated rates of elimination of bromine in the acid solution which results from the hydrolysis of sodium bromoacetate.

TABLE I.

(1)	$CH_2Br{\cdot}CO_2' + H_2O$	$k_1 = 0{\cdot}059 \times 10^{-6}$
(2)	$CH_2Br{\cdot}CO_2' + CH_2Br{\cdot}CO_2'$	$k_2 = 19{\cdot}3 \times 10^{-6}$
(3)	$CH_2Br{\cdot}CO_2H + H_2O$	$k_3 = 0{\cdot}041 \times 10^{-6}$
(4)	$CH_2Br{\cdot}CO_2H + CH_2Br{\cdot}CO_2'$	$k_4 = 72 \times 10^{-6}$
(5)	$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2'$	$k_5 = 35 \times 10^{-6}$
(6)	$CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2'$	$k_6 = 136 \times 10^{-6}$
(7)	$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H$	$k_7 = (0)$
(8)	$CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2H$	$k_8 = (0)$
(9)	$CH_2Br{\cdot}CO_2H + CH_2Br{\cdot}CO_2H$	$k_9 = (0)$
(10)	$CH_2Br{\cdot}CO_2H + OH_3^{\cdot}$	$k_{10} = (0)$

With regard to the several bimolecular processes (6)—(10) it is to be noted that measurements of the reaction velocity for solutions of widely varying hydrogen-ion concentration afford no evidence for the elimination of bromine by the interaction of the bromoacetic acid molecule with the hydrogen ion (10), or by the interaction of pairs of bromoacetic acid molecules (9). Since the latter process is ineffective under the experimental conditions used, as is implied by the symbol (0), it seemed unlikely that collisions of the bromoacetic acid molecule with the glycollic acid molecule (8), or, indeed, with any other un-ionised acid molecule would lead to the liberation of bromide, and the ineffectiveness of such collisional processes is shown by the results obtained with mixtures of bromoacetic acid and other weak acids under conditions in which the acids are practically un-ionised.

Previous experiments (Dawson and Dyson, *loc. cit.*) with bromoacetic acid in presence of nitric acid have shown that the rate of formation of bromide is accurately represented in terms of reaction (3), and it has now been established that the rate of formation remains sensibly unchanged in the presence of glycollic acid. The same result is obtained when other acids are substituted for the glycollic acid. Table II gives the initial velocities in mols./l./min. at 25° for these mixed acids in presence of $0{\cdot}5M$-nitric acid and $1{\cdot}0M$-sodium nitrate to provide as far as possible the " standard " conditions which characterise these experiments so far as salt content is concerned. It is probable that the nitric acid, which is added to prevent ionisation of the weak acids, has itself an inert-salt effect, but this is small and has been neglected. In this and subsequent tables the velocity v represents the actual velocity $\times 10^6$.

TABLE II.

Initial velocities for mixtures of bromoacetic and other un-ionised acids; 25°.

	v.
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H$	0·110
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}1M$-$CH_2(OH){\cdot}CO_2H$	0·1095
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}2M$-$CH_2(OH){\cdot}CO_2H$	0·109
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}3M$-$CH_2(OH){\cdot}CO_2H$	0·1085
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}1M$-$CH_3{\cdot}CO_2H$	0·109
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}2M$-$CH_3{\cdot}CO_2H$	0·1075
$0{\cdot}05M$-$CH_2Br{\cdot}CO_2H + 0{\cdot}2M$-$C_2H_4(CO_2H)_2$	0·106

The slight fall observed in the presence of the second acid is probably due to the small change in the reaction medium, and the obvious conclusion from these results is that bromide ion is not liberated with appreciable velocity by the interaction of the bromoacetic acid molecule with the molecules of other carboxylic acids. This result is in line with the ineffectiveness of the collisions between pairs of bromoacetic acid molecules (9).

For all the solutions in Table II, the observed velocity would therefore seem to be attributable to the action of water on the bromoacetic acid molecule. In view of the inactivity of the un-ionised weak acids it might be suggested that reaction (3) is somewhat anomalous, but this is probably not the case, for if the concentration of the water were of the same order as that of the acids in Table II ($<$ 1 mol. per litre) the velocity due to (3) would scarcely be measurable. The effectiveness of this reaction under the conditions of these experiments is thus attributable to the very large concentration of the solvent molecules. Similar considerations apply to reaction (1), in which bromide ion is eliminated from the bromoacetate ion by the action of the water molecule.

With regard to reactions (6) and (7), it is to be noted that the two sets of reactants are the reversible pairs involved in the equilibrium (B), and since the concentration products of the two pairs have a fixed ratio, it is evident that the differentiation between (6) and (7) as the cause of bromide formation is attended by peculiar difficulties. The effectiveness of one (or both) of these reactions has, however, been established with certainty by measurements of the initial velocities for solutions represented stoicheiometrically by

$$aM\text{-}CH_2Br{\cdot}CO_2Na + bM\text{-}CH_2(OH){\cdot}CO_2H.$$

Provided that the ratio b/a in these solutions is not greater than *ca.* 10 the equilibrium (B) takes the form

$$(a-x)CH_2Br{\cdot}CO_2' + (b-x)CH_2(OH){\cdot}CO_2H \rightleftharpoons xCH_2(OH){\cdot}CO_2' + xCH_2Br{\cdot}CO_2H$$

for which the constant K is given by

$$K = K_g/K_b = x^2/(a-x)(b-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)$$

in which K_g and K_b are the ionisation constants of glycollic acid and bromoacetic acid respectively in the " standard " solution. From equation (C), x may be derived, and the sum of the velocities of reactions (1)—(5) is then given by

$$v_{\text{calc.}} = k_1w(a-x) + k_2(a-x)^2 + k_3wx + k_4x(a-x) + k_5x(a-x) \quad . \quad (D)$$

If the difference between $v_{\text{obs.}}$ and $v_{\text{calc.}}$ is denoted by v_r and attributed to reactions (6) and (7) then

$$v_r = v_6 + v_7 = k_6x^2 + k_7(a-x)(b-x) \quad . \quad . \quad . \quad . \quad . \quad (E)$$

whence

$$v_r/x^2 = k_6 + k_7/K = \text{const.}$$

The initial velocities obtained for mixtures of sodium bromoacetate and glycollic acid agree closely with the above deduction, as may be seen from Table III, in which the values of a and b are shown in cols. 1 and 2. Col. 3 gives the values of x derived from $K = K_g/K_b = 0{\cdot}125$, where $K_g = 2{\cdot}6 \times 10^{-4}$ and $K_b = 2{\cdot}05 \times 10^{-3}$ are the ionisation constants for glycollic and bromoacetic acid in $1M$-sodium nitrate solution. The ratio of these ionisation constants for the " standard " salt solution is practically identical with the ratio for pure aqueous solutions of the acids. Col. 4 gives the observed initial velocities (mols./l./min.), and col. 5 records the velocities calculated from equation (D) by using the velocity coefficients recorded in Table I and $w = 54$. Col. 6 shows the difference v_r between the observed and calculated velocities, and col. 7 gives the values of v_r/x^2.

TABLE III.

Initial reaction velocities for aM-$CH_2Br{\cdot}CO_2Na + bM$-$CH_2(OH){\cdot}CO_2H$.

a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.	a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.
0·05	0	0	0·206	0·208	—	—	0·10	0	0	0·516	0·513	—	—
0·05	0·20	0·0239	0·297	0·217	0·080	140	0·10	0·20	0·0362	0·787	0·610	0·177	135
0·05	0·30	0·0276	0·313	0·209	0·104	136	0·10	0·30	0·0429	0·843	0·602	0·241	131
0·05	0·40	0·0302	0·323	0·201	0·122	134	0·10	0·40	0·0479	0·888	0·591	0·297	130
0·05	0·50	0·0322	0·334	0·195	0·139	134	0·10	0·50	0·0519	0·923	0·580	0·343	128

From the table it is clear that the differences between the observed velocities and those calculated on the basis of reactions (1)—(5) are very considerable and increase in each series with the concentration of the glycollic acid. At the same time, the approximate constancy of v_r/x^2 affords strong support for the view that the differences are due to the formation of bromide by either reaction (6) or reaction (7) or possibly by both. The fact that the values of v_r/x^2 tend to fall slightly with increasing glycollic acid concentration is possibly due to the gradually changing character of the reaction medium, which probably slightly affects all the velocity coefficients.

In order to obtain further evidence in support of the results which are summarised in the above table, similar experiments have been made with corresponding series of solutions in which the glycollic acid is replaced by acetic acid. The results are presented in Table IV, the form of which is identical with that of Table III. For this series of solutions the values of x are derived from $K = K_a/K_b = 0{\cdot}0132$ where $K_a = 2{\cdot}7 \times 10^{-5}$ is the ionisation constant of acetic acid in $1M$-sodium nitrate solution. The velocities are calculated from equation (D) with the substitution of $k_5 = 50 \times 10^{-6}$ for the reaction represented by $CH_2Br{\cdot}CO_2' + CH_3{\cdot}CO_2'$ which takes the place of reaction (5) of Table I in the glycollic acid series.

TABLE IV.

Initial reaction velocities for aM-$CH_2Br{\cdot}CO_2Na + bM$-$CH_3{\cdot}CO_2H$ (25°).

a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.	a.	b.	x.	$v_{obs.}$.	$v_{calc.}$.	v_r.	v_r/x^2.
0·05	0	0	0·206	0·208	—	—	0·10	0·2	0·0145	0·640	0·593	0·047	225
0·05	0·2	0·0100	0·251	0·230	0·021	210	0·10	0·3	0·0175	0·674	0·611	0·063	205
0·05	0·3	0·0120	0·263	0·232	0·031	215	0·10	0·5	0·0221	0·728	0·620	0·108	220
0·05	0·4	0·0137	0·270	0·233	0·037	200	0·20	0	0	1·39	1·41	—	—
0·05	0·5	0·0150	0·280	0·233	0·047	210	0·20	0·4	0·0289	1·965	1·78	0·185	220
0·10	0	0	0·516	0·513	—	—	0·20	0·5	0·0321	2·05	1·81	0·24	230

The relations shown by Table IV are evidently quite similar to those in Table III and thus support the conclusion that bromide is formed by reaction (6) or (7) when glycollic acid is added to a bromoacetate solution. The kinetic data *per se* do not, however, permit of a distinction between (6) and (7) as the cause of the reaction velocity represented by v_r. On the other hand, since the liberation of bromide ion is very probably associated with the formation of an intermediate complex (cf. p. 503), reaction (6) would represent the simpler mechanism, in that (7) would seem to involve the simultaneous transfer of proton from one molecule to another.

Definite evidence in favour of (6) seems to be provided by experiments in which the bromoacetic acid in (6) has been replaced by ethyl bromoacetate, and the glycollic acid in (7) by ethyl glycollate. In these circumstances there is no complication due to the acid–base equilibrium, and the experiments show that bromide is readily liberated in the interaction of ethyl bromoacetate and the glycollate ion, but that no change takes place which can be attributed to the interaction of the bromoacetate ion with ethyl glycollate. It thus appears probable that v_r is attributable to the mechanism represented by (6). If this be accepted, the data in Table III lead to $k_6 = 136 \times 10^{-6}$, and the corresponding coefficient for the interaction between the bromoacetic acid molecule and the acetate ion (Table IV) is approximately 220×10^{-6}.

Idealised Hydrolysis of Sodium Bromoacetate.—Having thus obtained evidence of a sixth reaction which gives rise to bromide in acid solutions containing bromoacetate and glycollate, it will now be shown that the rate of elimination of bromine as bromide in solutions which correspond with successive idealised stages in the hydrolysis of sodium bromoacetate can be interpreted very satisfactorily in terms of the six reactions (1)—(6). In accordance with the established facts, it is assumed that reactions (7)—(10) are of negligible significance under the conditions of the experiments to be described.

The experimental data represent the initial velocities for synthetic solutions which contain the final reaction products in quantities such as would result from actual hydrolysis in the absence of intermediate compound formation. The only difference is that the synthetic solutions contain sodium nitrate instead of sodium bromide. It should be clearly recognised that these " idealised " solutions contain no complexes and therefore are not identical with those which are produced at the same stage (measured by the silver titration) in the progressive hydrolytic change. These " idealised " solutions correspond stoicheiometrically with the formula $aM\text{-CH}_2\text{Br}{\cdot}\text{CO}_2\text{Na} + bM\text{-CH}_2(\text{OH}){\cdot}\text{CO}_2\text{H} + (1 - a)M\text{-NaNO}_3$, in which $(a + b)$ is constant throughout the series. The value of x corresponding with equilibrium (B) is derived in the manner previously described, and in terms of a and x the total velocity due to reactions (1)—(6) is then given by

$$v_{\text{calc.}} = k_1w(a - x) + k_2(a - x)^2 + k_3wx + k_4x(a - x) + k_5x(a - x) + k_6x^2 \quad . \quad \text{(F)}$$

The results obtained for two such series of solutions with $a + b = 0{\cdot}5$ and 1·0 severally are shown in Table V. The first two columns give the values of a and x; the next six give the partial velocities attributable to reactions (1)—(6), and the sum of these ($v_{\text{calc.}}$) is shown in the penultimate column. The observed initial velocities for the various solutions are recorded in the last column.

TABLE V.

Velocity of bromide formation at successive idealised stages of the hydrolysis of sodium bromoacetate. Standard conditions and 25°.

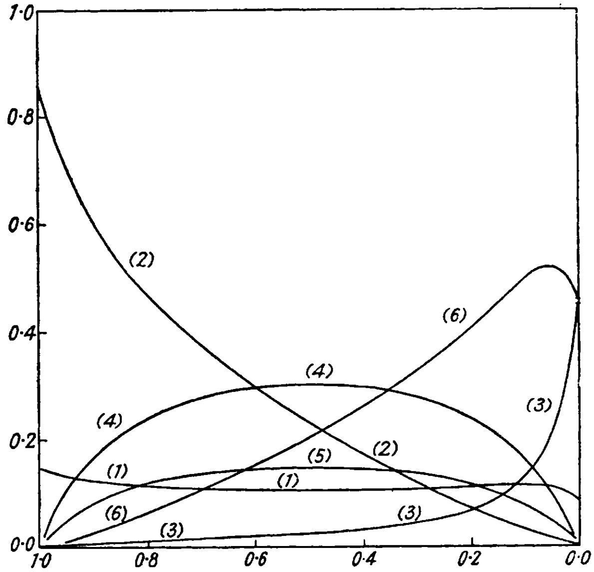
a.	x.	v_1.	v_2.	v_3.	v_4.	v_5.	v_6.	$v_{\text{calc.}}$.	$v_{\text{obs.}}$.
Idealised stages for 0·5M-*sodium bromoacetate.*									
0·50	0	1·60	4·83	—	—	—	—	6·43	6·30
0·45	0·031	1·34	3·37	0·07	0·935	0·455	0·13	6·30	6·25
0·40	0·048	1·13	2·40	0·11	1·21	0·59	0·31	5·75	5·77
0·35	0·058	0·935	1·65	0·13	1·21	0·59	0·45	4·97	5·00
0·30	0·064	0·755	1·08	0·14	1·09	0·525	0·55	4·14	4·14
0·25	0·065	0·59	0·655	0·14	0·86	0·42	0·57	3·24	3·24
0·20	0·064	0·435	0·355	0·14	0·625	0·30	0·55	2·41	2·39
0·15	0·058	0·295	0·165	0·13	0·38	0·185	0·45	1·61	1·58
0·10	0·048	0·165	0·052	0·11	0·18	0·088	0·31	0·905	0·90
0·05	0·031	0·061	0·007	0·068	0·043	0·022	0·13	0·33	0·33
Idealised stages for 1·0M-*sodium bromoacetate.*									
1·0	0	3·20	19·3	—	—	—	—	22·5	22·35
0·95	0·0375	2·92	16·10	0·08	2·47	1·20	0·19	22·95	23·2
0·90	0·0625	2·68	13·55	0·14	3·78	1·84	0·53	22·5	22·9
0·80	0·096	2·25	9·57	0·21	4·86	2·36	1·24	20·5	21·0
0·70	0·116	1·87	6·58	0·26	4·87	2·37	1·83	17·8	18·3
0·60	0·127	1·51	4·32	0·28	4·32	2·10	2·17	14·7	15·0
0·50	0·131	1·18	2·63	0·29	3·48	1·69	2·32	11·6	11·7
0·40	0·127	0·87	1·45	0·28	2·50	1·21	2·17	8·5	8·60
0·30	0·116	0·59	0·66	0·26	1·53	0·75	1·83	5·6	5·50
0·20	0·096	0·33	0·21	0·21	0·72	0·35	1·24	3·05	2·98
0·10	0·0625	0·12	0·03	0·14	0·17	0·08	0·53	1·07	0·99

For the first series the observed and the calculated velocities are in remarkably close agreement, and although the deviations are somewhat greater in the second series, it may justifiably be claimed that the observations give strong support to the view that reactions (1)—(6) are the only ones which play an effective part in the formation of bromide in so far as the intervention of intermediate complex compounds does not call for consideration.

In reference to the trend of the individual partial velocities, it may be noted that v_1

and v_2 diminish continuously as the " idealised " hydrolysis proceeds, but that the others pass through maximum values. For v_3 and v_6, which are proportional to x and x^2 respectively, the maxima are reached at 50% hydrolysis, whilst for v_4 and v_5, which are both proportional to $x(a - x)$, it may be shown that the maximum values correspond with 25% reaction. Further, it is noteworthy that the calculated total velocity for the 1·0M-solution passes through a maximum at about 5% hydrolysis, the decrease in v_1 and v_2 being more than counterbalanced by the increase in velocity attributable to v_3, v_4, v_5, and v_6. The maximum thus indicated by theory is entirely in accord with the experimental data, which show quite definitely that $v_{\text{obs.}}$ passes through a maximum value at about this stage of the reaction.

The relative importance of reactions (1)—(6) in the case of 1M-sodium bromoacetate at successive stages is shown in the figure. The curves show the respective fractions of the total velocity which are attributable to the several component reactions at each stage. It is noteworthy that the curve for (1) is for the most part a horizontal line, which signifies that the contribution of reaction (1) to the total velocity is represented by a nearly constant fraction (*ca.* 0·10) except at the beginning and the end of the change. This possibly affords an explanation of the fact that the actual course of the progressive hydrolysis of sodium bromoacetate conforms approximately to the requirements of the simple unimolecular formula (cf. Table VI). The fraction due to (2) falls rapidly and continuously from a high initial value, whilst the curve for (3) rises continuously and with increasing rapidity as the reaction progresses.



Idealised hydrolysis of 1·0M-*sodium bromoacetate. Curves* (1)—(6) *represent the fractions of the total velocity which are attributable to the several component reactions at successive stages of the hydrolysis. The abscissæ give the molar concentration of the undecomposed bromoacetate.*

Reactions (4) and (5) are represented by curves of cycloidal type with maximum relative contributions at about 50% reaction, whilst the relative importance of (6) rises continuously until reaction has progressed to about 95%, where a maximum is reached.

When more than 90% of the total bromide ion has been liberated, the precise form of the curves cannot, however, be derived without taking into account the hydrogen-ion concentration of the solution.

The Progressive Hydrolysis of Sodium Bromoacetate.—Although the above experiments with idealised synthetic solutions serve to throw considerable light on the mechanism of this kinetically complex reaction, it must be recognised that the sequence of events in the ordinary progressive hydrolysis of sodium bromoacetate is further complicated by the circumstance that the formation of glycollic acid does not keep pace with the formation of bromide. This was attributed by Senter and Ward (J., 1912, **101**, 2534) to the formation of bromoacetoxyacetate, although the corresponding effect in the hydrolysis of sodium monobromosuccinate was supposed by Holmberg (*Ber.*, 1912, **45**, 1713) to be due to the intermediate formation of a lactone. The sum total of the facts now established affords no support for the latter hypothesis, but is quite consistent with the former. Having regard to the constitution of the acid solutions formed in the progressive hydrolysis of sodium bromoacetate, it thus seems probable that the retarded development of acidity is due to the formation of intermediate complexes which, for the reactions (2), (4), (5), and (6) are represented, respectively, by the formulæ

$$\mathrm{CH_2Br{\cdot}CO_2' + CH_2Br{\cdot}CO_2' \longrightarrow CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2' + Br'} \quad . \quad . \quad (2)$$

$$\mathrm{CH_2Br{\cdot}CO_2' + CH_2Br{\cdot}CO_2H \longrightarrow CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2H + Br'} \quad . \quad . \quad (4)$$

$$\mathrm{CH_2(OH){\cdot}CO_2' + CH_2Br{\cdot}CO_2' \longrightarrow CH_2(OH){\cdot}CO_2{\cdot}CH_2{\cdot}CO_2' + Br'} \quad . \quad . \quad (5)$$

$$\mathrm{CH_2(OH){\cdot}CO_2' + CH_2Br{\cdot}CO_2H \longrightarrow CH_2(OH){\cdot}CO_2{\cdot}CH_2{\cdot}CO_2H + Br'} \quad . \quad (6)$$

The rates of formation of these complexes are given by the partial velocities corresponding with v_2, v_4, v_5, and v_6, and the total concentration is measured at each stage of the hydrolysis by the difference between the silver and the alkali titration data if no complexes of higher order are formed. The rates of hydrolysis of the complexes are unknown and the individual concentrations (c_2, c_4, c_5, and c_6) cannot be estimated, but it is apparent that the ratios c_2/c_4 and c_5/c_6 must be controlled by the hydrogen-ion concentration of the solution, and further, that the ratio between the total bromoacetoxyacetate ($c_2 + c_4$) and the total glycolloxyacetate ($c_5 + c_6$) must vary as the reaction progresses. Since the anions of any weak organic acid may take the place of the glycollate ion in reactions (5) and (6), it seems probable that first-order complexes of the type $\mathrm{R{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2'}$ may be directly responsible for the production of bromide by interaction with the bromoacetic ion or molecule to form second-order complexes of the type $\mathrm{R{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2'}$. Such considerations lead to the conclusion that the course of progressive hydrolysis must be appreciably influenced by factors which have been eliminated in the experiments of Table V.

When the hydrolysis of the sodium bromoacetate has reached the stage corresponding with the elimination of 50% of the total bromine, the silver and the alkali titration data for the 1·0*M*-solution indicate that the total concentration of the intermediate complexes is approximately 0·1 mol. per litre. From the slope of the curve connecting the bromide concentration with the time, it is found that the actual rate of bromide formation at this stage in the progressive hydrolysis is $11{\cdot}5 \times 10^{-6}$ mol./l./min. For the idealised reaction the observed rate at the same stage has very nearly the same value, *viz.*, $11{\cdot}7 \times 10^{-6}$ (cf. Table V), although the synthetic solution contains considerably more bromoacetate and glycollic acid than the corresponding solution in the progressive hydrolysis. It thus seems impossible to avoid the conclusion that the intermediate complexes contribute directly to the rate of bromide formation and are not merely responsible for retarding the liberation of glycollic acid.

Having regard to the complexity of the mechanism of the progressive hydrolysis which is thus indicated, it is of interest to recall that Senter's observations on sodium chloroacetate at 102° (J., 1907, **91**, 460) indicate that the rate of hydrolysis, as measured by titration with alkali, is approximately proportional to the chloroacetate concentration until the reaction is more than half complete. In view of this apparent simplicity, the actual course of the reaction for 1·0 and 0·5*M*-solutions of sodium bromoacetate, as measured by both silver and alkali titration, has been examined under "standard" conditions with reference to the unimolecular formula $k' = (1/t)\log_e c_0/c$. The data recorded in Table VI represent the times required for the reaction to proceed 10, 20, 30 . . .% towards completion as measured by silver titration on the one hand, and by alkali titration on the other; these numbers are derived from the large-scale graphs which incorporate the extensive series of actual measurements. The values of k' for the two series of titrations are distinguished by $k_{\mathrm{Br'}}$ and $k_{\mathrm{Ac'}}$.

TABLE VI.

Progressive hydrolysis of 1·0M-*sodium bromoacetate* (25°).

[Bromide], mols./l.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
$t\,.\,10^{-3}$ (mins.)	4·6	9·3	14·6	21·5	29·7	39·8	55·7	82·2
$10^{6}\,.\,k_{Br'}$	22·9	24·0	24·4	23·8	23·3	23·0	21·6	19·6
[Acid], mols./l.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
$t\,.\,10^{-3}$ (mins.)	7·5	13·6	20·7	29·5	40·8	55·2	73·9	106·5
$10^{6}\,.\,k_{Ac'}$	14·1	16·4	17·2	17·3	17·0	16·6	16·3	15·1
[Bromide], mols./l.		0·05	0·1	0·15	0·2	0·25	0·3	0·35
$t\,.\,10^{-3}$ (mins.)		8·3	16·8	26·5	37·8	51·4	69·3	95·0
$10^{6}\,.\,k_{Br'}$		12·7	13·3	13·5	13·5	13·5	13·2	12·7
[Acid], mols./l.		0·05	0·1	0·15	0·2	0·25	0·3	0·35
$t\,.\,10^{-3}$ (mins.)		11·7	22·0	34·3	48·7	66·4	88·5	121·5
$10^{6}\,.\,k_{Ac'}$		9·0	10·1	10·4	10·5	10·4	10·2	9·9

The data in the foregoing table show that the course of the reaction, whether followed by titration with silver or with alkali, can be expressed with fair approximation over a considerable range by the unimolecular formula. The mean values of $k_{Br'}$ and $k_{Ac'}$ show, however, large variations when the concentration of the bromoacetate is increased from 0·5 to 1·0. Having regard to the results previously described, it is apparent that the approximate applicability of the unimolecular formula is devoid of any real significance so far as the real mechanism of the reaction is concerned. The true value of the unimolecular velocity coefficient for the reaction between the bromoacetate ion and the water molecule (reaction 1) is $k_1w = 3{\cdot}2 \times 10^{-6}$ mol./l./min., which of course is quite independent of the concentration. There is no obvious connexion between this and the empirical values of $k_{Br'}$ which are recorded in Table VI.

SUMMARY.

The rate of elimination of bromine as bromide ion in the hydrolysis of sodium bromoacetate is increased in the later stages by effects which are attributable to the glycollic acid formed. The acid itself is not directly responsible for the observed increase in the reaction rate, but the glycollate ion, which is present in accordance with the equilibrium

$$CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H \rightleftharpoons CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2',$$

gives rise to bromide by interaction with the bromoacetate ion and also with the bromoacetic acid molecule. The latter reaction plays a very important part in the liberation of bromide ion in the latest stages of the hydrolysis of sodium bromoacetate.

When effects arising from the formation of complex intermediate compounds are eliminated by the use of synthetic solutions which correspond with idealised stages of the reaction, it is found that the rate of liberation of bromide at all stages of the hydrolysis of sodium bromoacetate can be quantitatively expressed in terms of the velocities of six independent bimolecular processes in which the bromoacetate ion (or the bromoacetic acid molecule) reacts with the bromoacetate ion, the glycollate ion, or the water molecule.

The complexes formed in the actual progressive hydrolysis of sodium bromoacetate are not merely responsible for retarding the formation of glycollic acid, but are found to contribute appreciably to the rate at which bromide ion is eliminated from the bromoacetate.

Although the course of progressive hydrolysis under the usual conditions can be represented approximately by a unimolecular formula over a considerable part of the complete reaction, it is shown that this is an accidental circumstance which is without significance for the mechanism of this highly complicated reaction.

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