268. *Mechanism of Substitution in Organic Compounds. Elimination of Bromine from Bromoacetic Acid and the Bromoacetates.*

By H. M. Dawson and N. B. Dyson.

In a previous paper (this vol., p. 49) it has been shown that the elimination of bromine from the alkali bromoacetates in neutral aqueous solution is due to two simultaneous reactions, one of which is apparently unimolecular and a single-stage reaction represented by

$$CH_2Br{\cdot}CO_2' + H_2O \longrightarrow CH_2(OH){\cdot}CO_2H + Br' \quad . \quad . \quad . \quad . \quad (I)$$

The second reaction is bimolecular with respect to the bromoacetate and involves two stages corresponding with

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

$$CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2' + H_2O \longrightarrow CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H \quad . \quad (IIb)$$

The second stage does not keep pace with the first, and as a consequence the alkali required for the titration of the glycollic acid is always less than the silver required for the titration of the bromide.

In both reactions silver titration affords a means of determining the rate at which bromine is eliminated from the bromoacetate, and when the reaction velocities are measured under conditions in which the disturbing influence of effects due to the reaction products and the varying salt content of the solutions is avoided, it is found that the velocity varies with the concentration (x) of the bromoacetate in accordance with the equation

$$v = v_1 + v_2 = k_1x + k_2x^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k_1 is the velocity coefficient for (I), and k_2 that for (II*a*).

Since bromoacetic acid in pure aqueous solution is appreciably ionised, it is apparent that the elimination of bromine from the free acid will be due to some extent to the above reactions. In comparison with the actually observed rate, the velocity calculated from (1) is, however, quite small, and it is apparent that a very considerable part of the measured velocity is due to one or more reactions in which the un-ionised bromoacetic acid is concerned. The facts show clearly that the bromoacetic acid molecule is involved in a reaction which may be formulated in accordance with the usually accepted mechanism as

$$CH_2Br{\cdot}CO_2H + H_2O \longrightarrow CH_2(OH){\cdot}CO_2H + H^{\bullet} + Br' \quad . \quad . \quad (III)$$

but this alone is not sufficient to account for the observed velocity in solutions of the free acid and, more particularly, for the data which have been obtained as a result of the more general investigation of solutions containing both bromoacetic acid and the bromoacetates. These observations lead indubitably to the conclusion that a further reaction is involved in which the bromoacetic acid molecule reacts with the bromoacetate ion. This bimolecular reaction is probably similar to (II) in that two stages are involved which for our purpose may be formulated as

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

$$CH_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CO_2H + H_2O \longrightarrow CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2H \quad . \quad (IVb)$$

The relative rates of the successive stages in reaction (IV) are not known, and for the present purpose are not required. It suffices in this connexion to realise that the progress of the reactions represented by (III) and (IV*a*), in which bromine is eliminated from the CH_2Br radical, can be followed by titration with silver solution. There is obviously a close analogy between reactions (I) and (III) and between reactions (II*a*) and (IV*a*), and the silver titration data obviously afford a means of measuring the joint rate of the reactions (I)—(IV) in so far as the liberation of the bromine atom and the production of the bromide ion are concerned. For a solution which contains both bromoacetic molecules and bromoacetate ions, the reaction velocity, in the absence of disturbing effects, should therefore be given by the equation

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

in which v_1, v_2, v_3, and v_4 are the separate velocities of (I), (II*a*), (III), and (IV*a*) respectively and k_1, k_2, k_3, and k_4 are the corresponding velocity coefficients.

In conjunction with the results obtained in the study of neutral solutions of the bromoacetates (*loc. cit.*), the experiments to be described would seem to justify the conclusion that equation (2) includes all the processes by which the halogen can be eliminated from halogen-substituted aliphatic acids and salts in the absence of reaction products or added foreign substances.

As in the previous experiments with neutral bromoacetates, the velocities recorded in the present paper are, for the most part, the values of $v = \Delta[Br']/\Delta t$ for a small initial stage representing 2% of the complete reaction. An important exception will be noted in due course. This method of experimentation is an essential feature of the enquiry and is necessitated partly by the complex nature of the change which involves reactions of different orders, and partly by the circumstance that the velocity in the later stages is very considerably affected by the products of reaction. The effects of these differ both in nature and in magnitude according to whether the measurements relate to solutions of bromoacetic acid or to neutral bromoacetate solutions. The measurements were made at 25° unless otherwise specified, and to save space the velocities (mols./litre/min.) and velocity coefficients have been multiplied by 10^6. In some cases, the recorded data have reference to pure aqueous solutions, but more frequently, the solutions contain sodium nitrate in such quantity as to give a total salt concentration of 1 mol. per litre. Such solutions, the use of which is intended to eliminate as far as possible the so-called inert-salt effects, will be referred to as solutions providing " standard conditions."

The first experiments with free bromoacetic acid in salt-free solution showed that the specific velocity v/x increases continuously from 2·2 to 4·0 when the concentration x is raised from 0·02 to 1·0 mol. per litre, but no simple interpretation of the observations could be found. Since the relations are complex, the results for free bromoacetic acid solutions will be discussed later. On the other hand, the behaviour of bromoacetic acid in presence of excess of a strong acid appears to be quite simple, and consideration will therefore be given in the first instance to the behaviour of the acid in solutions of large hydrogen-ion concentration.

Elimination of Bromine from Bromoacetic Acid in Presence of a Strong Acid.—In previous experiments by Senter (J., 1907, **91**, 460) evidence was obtained that the rate of hydrolysis of halogen-substituted aliphatic acids is reduced by the addition of the corresponding halogen acid. The rate of the reaction was measured by titration with standard alkali and the results expressed in terms of $k = 1/t \, . \log_e c_0/(c_0 - x)$, the diminution of k in presence of the strong acid being attributed to the formation of less reactive bromoacetic acid molecules from the corresponding ions. It will presently become clear that this explanation is quite inadequate, but the particular point to be noted at the moment is that our experiments show that the course of the reaction is modified very considerably by the addition of strong acid. Table I gives results obtained with 0·2*M*-bromoacetic acid under standard conditions (*a*) in the absence of strong acid, (*b*) in presence of 0·5*M*-nitric acid. The recorded data are *t*, *x*, and *k*. Since the reaction is slow at 25°, these observations were made at 45°.

TABLE I.

(*a*) 0·198*M*-$CH_2Br \cdot CO_2H$ + 1*M*-$NaNO_3$ (45°).

t (mins.)	582	1720	2950	6140	10,020	16,230	25,910
x	0·0051	0·0142	0·0231	0·0436	0·0641	0·0890	0·1180
k	45·1	43·3	42·2	40·5	39·0	36·8	35·0

(*b*) 0·198*M*-$CH_2Br \cdot CO_2H$ + 1*M*-$NaNO_3$ + 0·5*M*-HNO_3 (45°).

t (mins.)	1105	2603	6925	11,330	17,050
x	0·0064	0·0147	0·0368	0·0564	0·0785
k	30·0	29·6	29·7	29·6	29·6

In the presence of 0·5*M*-nitric acid the reaction proceeds in close agreement with the unimolecular formula. This does not apply, however, when the strong acid is absent, and in these circumstances it is apparent that the initially higher value of *k* falls continuously as the reaction progresses.

Similar results have been obtained in corresponding experiments with chloroacetic acid, and the difference in behaviour under conditions (*a*) and (*b*) is without doubt connected with the fact that the halogen acid produced by the reaction has practically no influence on the ionisation of the halogen-substituted acid when a considerable amount of strong acid is already present, whereas this effect is considerable when the strong acid is absent.

Measurements of the initial velocities for 0·2*M*-bromoacetic acid in the presence of varying amounts of nitric acid afford substantial support for this explanation of the difference between the two series of data in Table I. The results obtained in salt-free solutions and also under standard conditions (see above) are shown in Table II.

TABLE II.

$0{\cdot}2M\text{-CH}_2\text{Br}{\cdot}\text{CO}_2\text{H} + xM\text{-HNO}_3$.

x	0	0·02	0·05	0·1	0·2	0·3	0·5
v	0·59	0·515	0·46	0·415	0·39	0·38	0·375

$0{\cdot}2M\text{-CH}_2\text{Br}{\cdot}\text{CO}_2\text{H} + 1M\text{-NaNO}_3 + xM\text{-HNO}_3$.

x	0	0·02	0·05	0·1	0·2	0·3	0·5
v	0·73	0·635	0·565	0·52	0·48	0·46	0·45

The nature of the relations is the same in both series, and from the trend of the v–x curves (cf. Fig. 1) it would seem that the velocity approaches a lower limiting value as the concentration of the bromoacetate ion is gradually reduced. In so far as secondary effects resulting from the gradual change in the nature of the reaction medium by the addition of nitric acid can be neglected, this limiting velocity should afford a measure of the velocity of reaction (III).

From consideration of the results in later tables, it is apparent that the determination of k_3 from the data for bromoacetic acid solutions to which a strong acid has been added can only be justified if the concentration of the bromoacetate ion is strictly limited. Since larger additions of nitric acid not only change the character of the reaction medium but give rise to small quantities of free bromine, it follows that the concentration of the bromoacetic acid in these solutions must be restricted. This point has been kept in view in the two series of experiments recorded in Table III, which show that in presence of 0·5M-nitric acid the reaction velocity is proportional to the concentration of the bromoacetic acid.

TABLE III.

$xM\text{-CH}_2\text{Br}{\cdot}\text{CO}_2\text{H} + 0{\cdot}5M\text{-HNO}_3$.

x	0·02	0·03	0·05	0·07	0·10	0·15	0·20
v	0·037	0·0545	0·093	0·128	0·191	0·280	0·375
v/x	1·85	1·82	1·86	1·83	1·91	1·87	1·88

$xM\text{-CH}_2\text{Br}{\cdot}\text{CO}_2\text{H} + 1M\text{-NaNO}_3 + 0{\cdot}5M\text{-HNO}_3$.

x	0·02	0·03	0·05	0·07	0·10	0·15	0·20
v	0·044	0·066	0·110	0·154	0·223	0·333	0·450
v/x	2·20	2·20	2·20	2·20	2·23	2·22	2·25

The measurements under standard conditions thus lead to $v/x = k_3 = 2{\cdot}2$. Since k_1 and k_2 are also known (previous paper, *loc. cit.*), it is possible to enquire to what extent the measured velocities for solutions of free bromoacetic acid (cf. Table IX) under standard conditions can be interpreted in terms of reactions (I), (II), and (III). The result shows that the measured velocities are considerably greater than those given by $v = v_1 + v_2 + v_3 = 3{\cdot}4[\text{A}'] + 19{\cdot}3[\text{A}']^2 + 2{\cdot}2[\text{HA}]$, and that the divergence increases with the concentration of the acid. The relations thus disclosed lead to the conclusion that some reaction other than (I), (II), and (III) is responsible in considerable measure for the observed rate of the reaction in solutions of free bromoacetic acid.

The supposition that this is the bimolecular change in which the bromoacetic acid molecule and the bromoacetate ion are the reactants is fully borne out by the results which have been obtained in experiments with solutions containing both bromoacetic acid and sodium bromoacetate. Certain selected series of such solutions show simple relations which have greatly facilitated the investigation of the general problem.

Elimination of Bromine from Mixtures of Bromoacetic Acid and Sodium Bromoacetate.—Preliminary experiments showed that the velocity (v_m) for a solution which contains equivalent quantities of the acid and salt (x mols. of each per litre) is very much greater than the sum of the velocities for the two separate solutions each containing x mols. of the acid or salt per litre. Table IV shows the results for a series of pure aqueous solutions which are related in this way. The velocities under v_a refer to solutions of bromoacetic acid, and those under v_s to solutions of sodium bromoacetate.

TABLE IV.

x.	v_a.	v_s.	$(v_a + v_s)$.	v_m.	$v_m/(v_a + v_s)$.
0·05	0·116	0·145	0·261	0·416	1·60
0·10	0·264	0·369	0·633	1·26	1·99
0·25	0·77	1·50	2·27	6·40	2·84
0·50	1·74	5·12	6·86	24·1	3·51

The last column shows that the ratio $v_m/(v_a + v_s)$ increases markedly with the concentration, and also that the reaction which involves both the bromoacetic acid molecule and the bromoacetate ion is responsible for the greater part of the observed velocity in the mixed solutions at the highest concentrations. Having regard to the fact that the salt content of the solutions is variable and that the acid is appreciably ionised in the solutions of the free acid but only to a very small extent in the mixed solutions, it is, however, not possible to make any precise quantitative comparison of the above data.

FIG. 1.

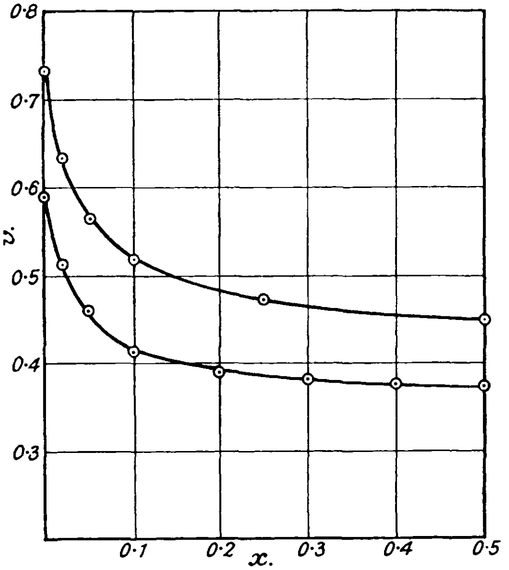


FIG. 2.

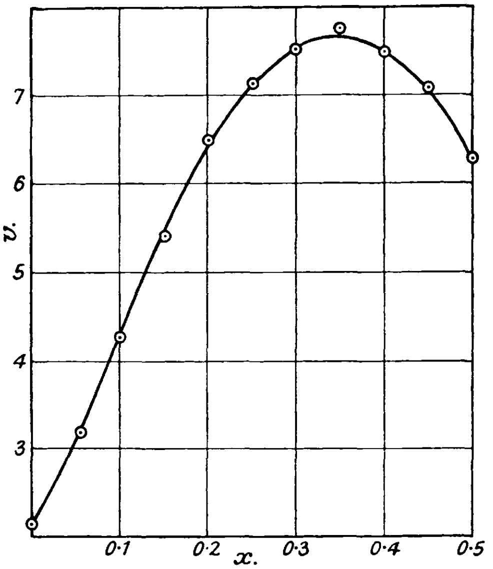


FIG. 1.—*Influence of strong acid* (xM-HNO_3) *on the reaction velocity* (v) *for* $0{\cdot}2M$-$CH_2Br{\cdot}CO_2H$. *Upper curve refers to standard solutions and lower curve to salt-free solutions.*

FIG. 2.—v—x *Graph for the series* xM-$CH_2Br{\cdot}CO_2Na + (0{\cdot}5 - x)M$-$CH_2Br{\cdot}CO_2H$ *under standard conditions.*

Experiments have accordingly been made with a series of solutions (A) which contain equivalent quantities of acid and salt under standard conditions. These solutions are represented by the general formula xM-$CH_2Br{\cdot}CO_2H + xM$-$CH_2Br{\cdot}CO_2Na + (1 - x)M$-$NaNO_3$. For values of x such that it is possible to measure the initial reaction velocity ($x > 0{\cdot}02$), the concentrations of the bromoacetic acid molecule and of the bromoacetate ion are given with very close approximation by $[HA] = x - [H^{\cdot}] = x - K$ and $[A'] = x + [H^{\cdot}] = x + K$, where K is the ionisation constant of the acid in the standard salt solution. On substitution of these values in equation (2), this takes the form

$$v = k_1(x + K) + k_2(x + K)^2 + k_3(x - K) + k_4(x^2 - K^2), \text{ whence}$$
$$v = (k_1 + k_3 + 2k_2K)x + (k_2 + k_4)x^2 + (k_1 - k_3)K - (k_4 - k_2)K^2$$

in which, having regard to the values of k_1, k_2, k_3, k_4, and K, the constant terms are negligible if x is not very small. Since, further, the value of $2k_2K$ is only about 1% of $(k_1 + k_3)$, it follows that the previous equation reduces with a close degree of approximation to the simple form

$$v = (k_1 + k_3)x + (k_2 + k_4)x^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

According to this, the plot of v/x against x should yield a straight line, the intercept of which on the zero ordinate affords a measure of $k_1 + k_3$, whilst the slope of the line gives $k_2 + k_4$.

Close agreement with this linear relation is shown by the actual velocities for solutions of this series ($x = 0{\cdot}05$—$1{\cdot}0$), and the data lead to $k_1 + k_3 = 5{\cdot}6$ and $k_2 + k_4 = 90{\cdot}8$. By introducing $k_1 = 3{\cdot}4$ and $k_2 = 19{\cdot}3$ (the values given by neutral sodium bromoacetate solutions), we obtain $k_3 = 2{\cdot}2$ and $k_4 = 71{\cdot}5$. The value thus derived for k_3 is identical with that afforded by the experiments with bromoacetic acid in presence of $0{\cdot}5M$-nitric acid.

Confirmation of the value of k_4 has been obtained from the data afforded by an independent series of mixed solutions (*B*) represented by the general formula $cM\text{-}CH_2Br{\cdot}CO_2Na + xM\text{-}CH_2Br{\cdot}CO_2H + (1 - c)M\text{-}NaNO_3$, where c is constant and x is variable. If the ratio x/c is suitably restricted, the application of equation (2) to this series of solutions (under standard conditions) leads to

$$v = k_1c + k_2c^2 + k_3x + k_4cx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

according to which v should vary linearly with the concentration (x) of the bromoacetic acid. The v–x graph for this series with $c = 0{\cdot}1$ is, apparently, strictly linear, and leads to $k_3 + k_4c = 9{\cdot}50$, from which, if $k_3 = 2{\cdot}2$, we obtain $k_4 = 73$, which is in good agreement with the value 71·5 given by the previous series of solutions (*A*).

The above measurements, in combination with those of the previous paper (this vol., p. 49), have thus enabled us to evaluate the velocity coefficients for the reactions (I), (II*a*), (III), and (IV*a*) under standard conditions. These coefficients, *viz.*, $k_1 = 3{\cdot}4$, $k_2 = 19{\cdot}3$, $k_3 = 2{\cdot}2$, and $k_4 = 72$, may now be used to calculate the reaction velocities for solutions containing bromoacetic ions and molecules. Table V shows the results for solutions which contain equivalent quantities of bromoacetic acid and sodium bromoacetate, and Table VI the results for solutions which contain a fixed quantity of the salt and a variable amount of the acid. The numbers recorded are the partial velocities v_1, v_2, v_3, and v_4, together with the calculated total velocity ($v_{\text{calc.}}$) and the observed velocity ($v_{\text{obs.}}$).

TABLE V.

(*A*) $xM\text{-}CH_2Br{\cdot}CO_2H + xM\text{-}CH_2Br{\cdot}CO_2Na + (1 - x)M\text{-}NaNO_3$.

x.	v_1.	v_2.	v_3.	v_4.	$v_{\text{calc.}}$	$v_{\text{obs.}}$	x.	v_1.	v_2.	v_3.	v_4.	$v_{\text{calc.}}$	$v_{\text{obs.}}$
0·02	0·068	0·004	0·044	0·029	0·145	0·147	0·10	0·340	0·193	0·220	0·720	1·47	1·46
0·03	0·102	0·017	0·066	0·065	0·250	0·254	0·30	1·02	1·74	0·66	6·48	9·90	9·75
0·05	0·170	0·048	0·110	0·180	0·508	0·502	0·50	1·70	4·82	1·10	18·00	25·6	25·6
0·06	0·204	0·069	0·132	0·259	0·664	0·666	0·70	2·40	9·45	1·55	35·3	48·7	48·2
0·08	0·272	0·123	0·176	0·461	1·03	1·05	1·00	3·40	19·3	2·20	72·0	96·9	97·2

TABLE VI.

(*B*) $0{\cdot}1M\text{-}CH_2Br{\cdot}CO_2Na + xM\text{-}CH_2Br{\cdot}CO_2H + 0{\cdot}9M\text{-}NaNO_3$.

0·02	0·340	0·193	0·044	0·144	0·72	0·695	0·10	0·340	0·193	0·220	0·720	1·47	1·46
0·04	0·340	0·193	0·088	0·288	0·91	0·89	0·15	0·340	0·193	0·330	1·08	1·94	1·97
0·06	0·340	0·193	0·136	0·432	1·10	1·08	0·20	0·340	0·193	0·440	1·44	2·41	2·40
0·08	0·340	0·193	0·176	0·576	1·285	1·28							

The close agreement between the observed and calculated velocities in the above tables affords very strong evidence for the validity of equation (2) as a basis for the interpretation of the experimental facts. The measured velocities cover a wide range, and the relative contributions of the several component reactions to the total effect also vary very considerably.

A further interesting series (*C*) of solutions which contain both acid and salt is that represented by the general formula $xCH_2Br{\cdot}CO_2Na + (c - x)CH_2Br{\cdot}CO_2H$, in which the total concentration (acid and salt) remains constant and equal to c. If the solutions at the extreme acid end of this series are excepted, the ionisation of the acid may be neglected without serious error, and equation (2) applied to this series takes the form

$$\begin{aligned} v &= k_1x + k_2x^2 + k_3(c - x) + k_4x(c - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2c) \\ &= k_3c + (k_1 + k_4c - k_3)x - (k_4 - k_2)x^2 \end{aligned}$$

whence $\quad dv/dx = (k_1 + k_4c - k_3) - 2(k_4 - k_2)x,$

from which it follows that the velocity should pass through a maximum when

$$x/c = k_4/2(k_4 - k_2) + (k_1 - k_3)/2c(k_4 - k_2) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where x/c represents the molar fraction of the sodium bromoacetate in the acid–salt mixture.

Preliminary experiments with pure aqueous solutions and with solutions under standard conditions in which the total bromoacetate (acid and salt) is equal to $0{\cdot}2M$, showed that the initial velocity for a series of this type passes through a maximum value. This is evident from Table VII, which gives the initial velocities for mixtures dissolved in water (*a*) and for the same mixtures under standard conditions (*b*). The curve which is obtained by plotting the velocity for the standard series against x is rather flat in the neighbourhood of the maximum-velocity mixture, and the composition of this is not very precisely indicated. From theoretical considerations it appeared that the conditions would be more favourable if the total concentration (*c*) were increased, and experiments were therefore made with $c = 0{\cdot}5$ under standard conditions. The results for this series are recorded in Table VIII, which gives the calculated partial and total velocities as well as the observed velocity.

TABLE VII.

(*a*) $xM\text{-}CH_2Br{\cdot}CO_2Na + (0{\cdot}2 - x)M\text{-}CH_2Br{\cdot}CO_2H$.

x ……………………	0	0·025	0·05	0·075	0·10	0·125	0·15	0·175	0·20
$v_{obs.}$ …………………	0·59	0·79	1·02	1·16	1·29	1·31	1·27	1·15	1·05

(*b*) $xM\text{-}CH_2Br{\cdot}CO_2Na + (0{\cdot}2 - x)M\text{-}CH_2Br{\cdot}CO_2H + (1 - x)M\text{-}NaNO_3$.

x ……………………	0	0·025	0·05	0·075	0·10	0·125	0·15	0·175	0·20
$v_{obs.}$ …………………	0·73	0·91	1·12	1·29	1·46	1·54	1·53	1·48	1·43

TABLE VIII.

(*c*)' $xM\text{-}CH_2Br{\cdot}CO_2Na + (0{\cdot}5 - x)M\text{-}CH_2Br{\cdot}CO_2H + (1 - x)M\text{-}NaNO_3$.

x.	v_1.	v_2.	v_3.	v_4.	$v_{calc.}$	$v_{obs.}$	x.	v_1.	v_2.	v_3.	v_4.	$v_{calc.}$	$v_{obs.}$
0·15	0·51	0·43	0·77	3·78	5·49	5·40	0·35	1·19	2·36	0·33	3·78	7·66	7·76
0·20	0·68	0·77	0·66	4·32	6·43	6·49	0·40	1·36	3·09	0·22	2·88	7·55	7·50
0·25	0·85	1·21	0·55	4·50	7·11	7·13	0·45	1·53	3·91	0·11	1·62	7·17	7·09
0·30	1·02	1·74	0·44	4·32	7·52	7·52	0·50	1·70	4·82	—	—	6·52	6·30

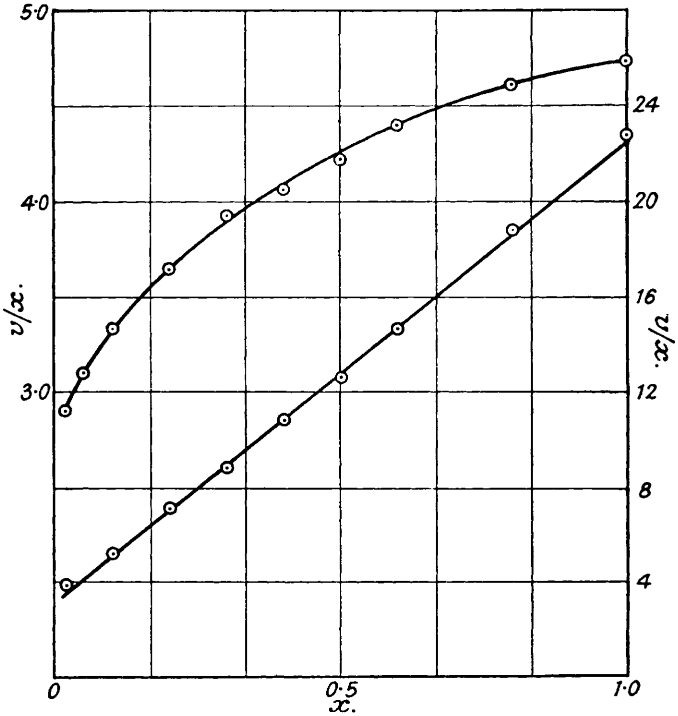
From the $v_{obs.}$–x graph shown in Fig. 2, it is apparent that the velocity passes through a maximum when x/c is approximately 0·70, which agrees closely with the molar fraction given by equation (3). This may be written in the form $x/c = 0{\cdot}683 + 0{\cdot}0114/c$, and for $c = 0{\cdot}5$, this gives $x/c = 0{\cdot}705$. According to the general relation, the fraction of the salt in the maximum-velocity mixture increases as c diminishes and becomes equal to 1·0 when $c = 0{\cdot}036$. For such values of c as can be effectively examined in this connexion, the variation of the composition of the maximum-velocity mixture is, however, not large enough to be determined with accuracy. The solutions in the above series may be supposed to be produced either by the mixing of equivalent solutions of the acid and salt in varying proportions or by the gradual addition of nitric acid (without change of volume) to a solution of sodium bromoacetate. In either case the maximum velocity is of particular interest, and its occurrence is to be attributed to the relatively high value of the coefficient for the reaction between the bromoacetic acid molecule and the bromoacetate ion. The velocity of this component change is given by $v_4 = k_4x(c - x)$, which for all values of c reaches a maximum when $x/c = 0{\cdot}5$, and the fact that the observed maximum velocity occurs at $x/c = 0{\cdot}70$ when $c = 0{\cdot}5$ is, of course, to be attributed to the superimposed effects of the three other simultaneous reactions.

Elimination of Bromine from Free Bromoacetic Acid.—The usual method for the determination of the initial velocity cannot be applied to the more concentrated solutions of free bromoacetic acid on account of the pronounced retarding effect of the resulting hydrobromic acid, and an extrapolation method (see p. **1143**) has been used. The results obtained in this way show that the variation of the velocity with the concentration of the acid is quite different from that shown by neutral solutions of the bromoacetate, as may be seen from Fig. 3, in which the specific velocity is plotted against the concentration. The graph for the neutral salt is a straight line, but the free acid shows no such simple behaviour.

Since the degree of ionisation of the acid varies with its concentration, it will be readily understood that the relations exhibited by solutions of free bromoacetic acid are more complex than those which are peculiar to solutions of the neutral salt or to solutions containing both acid and salt in which the ionisation of the acid is negligibly small.

The measured velocities for bromoacetic acid solutions under standard conditions are recorded in Table IX, which shows also the calculated partial and total velocities. The calculated values are based on concentrations of the reactant ions and molecules derived from $[A'] = \sqrt{Kx + (K/2)^2} - K/2$ and $[HA] = x - [A']$, where x is the concentration, and $K = 2{\cdot}2 \times 10^{-3}$ the ionisation constant of the acid under standard conditions. The latter is the value given by the method of Dawson, Hall, and Key (J., 1928, 2844) from kinetic data relating to the acetone–iodine reaction in $1M$-sodium nitrate solution with bromoacetic acid ($0{\cdot}02$—$0{\cdot}2M$) as a catalyst. The corresponding values for salt-free solutions are $1{\cdot}38 \times 10^{-3}$ at 25° (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 178) and $1{\cdot}56 \times 10^{-3}$ at 0° (Kortright, *Amer. Chem. J.*, 1896, **18**, 365). The influence of the inert salt is of the expected order.

FIG. 3.



Plot of specific velocity v/x *against* x. *Upper curve refers to bromoacetic acid* (v/x *scale on left*) *and lower curve to sodium bromoacetate* (v/x *scale on right*).

TABLE IX.

xM-$CH_2Br{\cdot}CO_2H + 1{\cdot}0M$-$NaNO_3$.

x.	v_1.	v_2.	v_3.	v_4.	$v_{calc.}$	$v_{obs.}$
0·02	0·0185	0·0005	0·032	0·006	0·057	0·058
0·05	0·031	0·002	0·090	0·027	0·150	0·155
0·10	0·045	0·003	0·191	0·083	0·322	0·332
0·20	0·065	0·007	0·398	0·250	0·720	0·730
0·30	0·081	0·011	0·607	0·473	1·17	1·18
0·40	0·094	0·015	0·82	0·74	1·67	1·62
0·50	0·105	0·018	1·03	1·05	2·20	2·07
0·60	0·115	0·022	1·245	1·39	2·77	2·64
0·70	0·125	0·026	1·46	1·76	3·37	3·12
0·80	0·135	0·030	1·67	2·16	3·99	3·69
1·00	0·150	0·038	2·10	3·05	5·34	4·73

For the more dilute solutions the observed and calculated velocities are in close agreement, but for the more concentrated the observed values are definitely smaller than the calculated and the divergence increases with the concentration. In the $1M$-solution the calculated velocity is about 12% greater than the observed.

In this connexion it is to be noted that the velocity in the more concentrated solutions is mainly determined by $v_3 = k_3[\mathrm{HA}]$ and $v_4 = k_4[\mathrm{HA}][\mathrm{A}']$, and since the degree of ionisation of the acid in these solutions is small, it follows that v_3 would only be affected by a change in k_3, whereas v_4 would be affected by changes in either k_4 or K.

Evidence of the diminution of k_3 in the more concentrated bromoacetic acid solutions is afforded by the experimental data for such solutions in the presence of $0{\cdot}5M$-nitric acid. In the standard series of solutions represented by the formula $xM\text{-}CH_2Br{\cdot}CO_2H + 0{\cdot}5M\text{-}HNO_3 + 1M\text{-}NaNO_3$, the concentration of the bromoacetate ion is given approximately by $[\mathrm{A}'] = K[\mathrm{HA}]/[\mathrm{H}^{\cdot}] = 2Kx = 0{\cdot}0041x$, and by substitution in equation (2) it may be shown that this takes the form $v = v_3 + v_4 = 2{\cdot}20x + 0{\cdot}30x^2$, according to which the velocity for $x = 1{\cdot}0$ should be 2·50, whereas experiment gives 2·19. Since v_3 is mainly responsible for the observed rate of change in this solution, this result seems to indicate that k_3 diminishes as the concentration of the bromoacetic acid increases.

Although the results in Table V afford no evidence for a diminution of k_4, it seems probable that v_4 will be reduced in the more concentrated acid solutions as a consequence of a diminution in the ionisation constant of the acid. A quantitative explanation of the differences between $v_{\mathrm{calc.}}$ and $v_{\mathrm{obs.}}$ for the more concentrated solutions in Table IX is, however, not possible.

From the results in this and the previous paper (*loc. cit.*) it is apparent that the elimination of bromine from the $\cdot CH_2Br$ group in solutions which contain bromoacetate ions and bromoacetic acid molecules is, in general, the result of four independent reactions. Under conditions which provide for the elimination of the accelerating or retarding effects which are caused by the products of reaction, the observed velocity at 25° can be represented very satisfactorily by equation (2). When the total salt concentration is kept constant, this equation may be written

$$v = v_1 + v_2 + v_3 + v_4 = 3{\cdot}4[\mathrm{A}'] + 19{\cdot}3[\mathrm{A}']^2 + 2{\cdot}2[\mathrm{HA}] + 72[\mathrm{HA}][\mathrm{A}'].$$

By appropriate variation of the composition of the solution, any one of the four reactions may assume the dominant rôle in the bromine-elimination process. In very dilute solutions of neutral bromoacetate, the observed change is almost entirely due to the first reaction, whilst the second is the chief factor in the change in concentrated neutral solutions. For solutions of bromoacetic acid to which an excess of a strong acid has been added, the observed velocity is almost exclusively due to the third reaction, whilst the fourth is by far the most important in fairly concentrated solutions which contain equivalent quantities of bromoacetic acid and bromoacetate. These reactions, it may be noted, include all but one of the possible reactions of the first and second order. The fifth would be represented by the interaction of two molecules of bromoacetic acid, but no evidence for the occurrence of this reaction has been obtained.

With regard to the relative magnitudes of the four velocity coefficients, it is not possible to compare directly the coefficients for reactions of different orders. On theoretical grounds, it is, however, probable that the first-order reactions (v_1 and v_3) are not really unimolecular, but involve collisions in which the water molecule is the second reactant. Since the " standard " solutions contain approximately 54 mols. of water per litre, the coefficients k_1 and k_3 should be divided by 54 for comparison with the coefficients k_2 and k_4. The relative values of the bimolecular velocity coefficients for the four (five) reactions are then represented by the following numbers :

Reactants	Mol.–H_2O.	Ion–H_2O.	Ion–Ion.	Mol.–Ion.	(Mol.–Mol.).
Relative vel. coeffs.	1·0	1·55	475	1770	(0)

In so far as the elimination of bromine from the halogen-substituted radical $\cdot CH_2Br$ is concerned, the above numbers indicate that collisions between two ions or between a molecule and an ion are vastly more effective than are collisions in which the water molecule is involved. In collisions with the water molecule, bromine is eliminated more readily from the bromoacetate ion than from the bromoacetic molecule, but the difference between these is not nearly so striking as the differences between the results of collisions between pairs of bromoacetic entities. The data have obviously some considerable bearing on recent speculations relative to the mechanism of substitution reactions, but this will not be discussed in the present paper.

Influence of Reaction Products on the Course of the Reaction.—In solutions of free bromoacetic acid, the rate of change at the outset is jointly due to the four reactions which correspond with v_1, v_2, v_3, and v_4. As the reaction proceeds, the hydrogen ion increases continuously as the result of the formation of hydrobromic and glycollic acid. At the same time, the concentration of the bromoacetate ion decreases, with the result that v_1, v_2, and v_4 diminish and approximate to zero, whilst v_3 increases to a constant limiting value. If c is the concentration of the acid and α its degree of ionisation in the original solution, the ratio of the constant limiting value to the initial value of v_3 is given by $c/c(1 - \alpha) = 1/(1 - \alpha)$. In the solutions in which the hydrogen-ion concentration has risen considerably, the glycollic acid is also practically un-ionised, and since experiments with bromoacetic acid in the presence of $0{\cdot}5M$-nitric acid have shown that the reaction velocity is not appreciably altered by the addition of glycollic acid, it may be inferred that bromine is not liberated by the interaction of the glycollic acid formed with the residual bromoacetic acid. In these circumstances, it is clear that the course of the reaction will be such as to approximate to a condition in which v_3 is the only effective component (cf. Tables I and II). The reaction which is complicated at the outset thus tends to become a simple unimolecular change.

With solutions of sodium bromoacetate, the course of the reaction is more complicated. If at different stages of the reaction the actual values of the velocity $v' = \Delta[\mathrm{Br}']/\Delta t$ are compared with those (v) which correspond with the concentration of the residual bromoacetate, it is found that v'/v increases very considerably as the reaction proceeds (cf. Table I, this vol., p. 49). The reaction products are mainly sodium bromide and undissociated glycollic acid, but as a consequence of the equilibrium $CH_2Br{\cdot}CO_2' + CH_2(OH){\cdot}CO_2H \rightleftharpoons CH_2Br{\cdot}CO_2H + CH_2(OH){\cdot}CO_2'$, it is evident that bromoacetic acid molecules and glycollate ions must be present together with bromoacetic ions and glycollic acid molecules.

At the outset, the velocity is given by $v = v_1 + v_2$ (equation 1), but it is clear that reactions (III) and (IV), corresponding with v_3 and v_4, must begin to play a part as the reaction proceeds. The effects corresponding with these partial reactions are, however, not by any means sufficient to account for the observed acceleration, and there can be little doubt that other reactions, in which the glycollic acid is more directly concerned, contribute towards the accelerating effects which correspond with the increasing values of v'/v. The possible reactions involving glycollic acid are those in which the reactant pairs are (*a*) bromoacetate ion and glycollate ion (V), (*b*) bromoacetate ion and glycollic acid molecule (VI), (*c*) bromoacetic acid molecule and glycollate ion (VII), (*d*) bromoacetic acid molecule and glycollic acid molecule (VIII). The velocity coefficient ($k = 35$) for reaction (V) has already been determined (previous paper, p. 54), whilst reaction (VIII) appears to be extremely slow. Since (V) alone does not account for the observed effects, it would seem that (VI) and/or (VII) are partially responsible for the accelerated course of the reaction. The reactants in (VI) and (VII) are, however, the reciprocal pairs involved in the above equilibrium, and it does not seem possible to distinguish between these two partial reactions. Notwithstanding this limitation, the facts justify the conclusion that six (possibly seven) different reactions are involved in the later stages of the experimentally observed change for solutions of sodium bromoacetate.

EXPERIMENTAL.

In general, the measurement of the initial velocity was made by the method previously described. For the more concentrated solutions of free bromoacetic acid, this method is, however, not satisfactory on account of the rapid diminution which occurs in the early stages. To meet these special circumstances, the mean velocities for successive short stages were determined. When these are plotted against the mean hydrogen bromide concentrations, a straight line is obtained, and by extrapolation to [HBr] = 0, a value for the initial velocity may be derived. The data in question for 1·0*M*-$CH_2Br\cdot CO_2H$ under standard conditions are :

Mean [HBr]	0·00443	0·00920	0·0149	0·0193	0·0241
Mean v	4·60	4·48	4·32	4·21	4·08

which lead to $v = 4{\cdot}73$ for the initial velocity.

Summary.

The kinetic study of the substitution of bromine by the hydroxyl group in solutions which contain bromoacetate ions (A′) and bromoacetic acid molecules (HA) has shown that four simultaneous reactions are involved.

In each of these reactions the bromide ion is liberated in the primary stage, and the observed rate of this process can be represented very closely by the equation

$$v = v_1 + v_2 + v_3 + v_4 = k_1[A'] + k_2[A']^2 + k_3[HA] + k_4[HA][A']$$

when the very considerable disturbing effects due to the reaction products and to variations in the nature of the reaction medium are eliminated.

When the composition of the reacting solution is suitably varied, any one of the four component reactions may be made the dominant factor in the observed rate of change.

Under certain conditions the general velocity equation reduces to very simple forms which have facilitated the determination of the several velocity coefficients.

When equivalent solutions of bromoacetic acid and of sodium bromoacetate are mixed in various proportions, the velocity–composition curve shows a well-defined maximum.

The retardation effects observed with solutions of bromoacetic acid are mainly due to the gradual elimination of the molecule–ion reaction (v_4) as the result of the formation of hydrobromic acid and consequent fall in the concentration of the bromoacetate ion.

The progressive acceleration effects observed with solutions of sodium bromoacetate are due to the intervention of other reactions in which glycollic acid is directly or indirectly concerned.

The authors thank Imperial Chemical Industries Ltd. for grants received.