17. *The Hydrolysis of Salts of the Halogen-substituted Aliphatic Acids in Aqueous Solution.*

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Measurements of the rate of hydrolysis of salts of chloro- and bromo-acetic acid by Kastle and Keiser (*Amer. Chem. J.*, 1893, **15**, 471) are mainly of interest in the evidence they afford that under comparable conditions the various salts of each acid are hydrolysed at the same rate and that the reaction velocity increases with the concentration but much more rapidly. Much greater significance must be ascribed to the work of Senter and his co-workers, whose experiments with the free acids and their salts suggest that there is a difference between the reactivities of the un-ionised molecules and the corresponding anions.

The results of Senter's earlier experiments (J., 1907, **91**, 460; 1909, **95**, 1827), in which the progress of hydrolysis was followed by titration with alkali, were said to indicate that the hydrolysis of the salts in dilute solution is almost entirely due to reaction between the anion and water, but that the undissociated salt plays an increasingly important part as the concentration of the solution increases. In the case of solutions of the free acids, the observed rates of reaction were supposed to be mainly due to the hydrolysis of the un-ionised molecules.

Further investigations (Senter and Bulle, J., 1912, **101**, 2523), in which the influence of foreign salts was examined, showed that the hydrolysis of the bromoacetates is accelerated to an abnormally large extent by the addition of sodium acetate (or formate), and that the reaction, when followed by titration with silver solution, appears to take place more rapidly than is suggested by the alkali-titration data. This is explained by the formation of acetoxyacetate (formoxyacetate) as an intermediate stage in the ultimate production of glycollic acid. The correctness of this interpretation is established by the experiments of Senter and Ward (J., 1912, **101**, 2534), which show also that the hydrolysis of sodium bromoacetate, in the absence of acetate (or formate), is similarly associated with the intermediate formation of bromoacetoxyacetate, and that the special features which characterise the two-stage reaction become more pronounced as the concentration of the bromoacetate solution increases.

The work of Senter represents an important contribution towards the elucidation of the mechanism of the hydrolysis of halogen-substituted carbon compounds, but in the light of the observations recorded in the present paper, it is apparent that the methods of investigation previously used have given results which in many respects are of uncertain value, and that the interpretation given to these observations requires very considerable modification. In so far as Senter's theory involves the view that undissociated molecules are involved in the hydrolysis of the salts of the halogen-substituted acids, it may be noted, incidentally, that modern conceptions relative to the degree of ionisation of salts in solution render this view very much less acceptable.

The observations recorded in this paper are concerned only with the hydrolysis of the salts, the behaviour of which is relatively simple in comparison with that of the corresponding acids.

Having regard to the simultaneous and successive changes which are involved in the hydrolytic process, the question of the actual procedure which has been followed in the kinetic investigation of the mechanism must be given adequate consideration.

From the results it is apparent that the bromoacetate ion takes part in two reactions, the relative importance of which varies with the concentration of the solution. One of these reactions is unimolecular with respect to the bromoacetate ion and may for our purpose be represented by

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

whilst the second is bimolecular with reference to the bromoacetate ion and takes place in two stages (cf. Senter and Ward, *loc. cit.*), which may be represented by

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

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

According to the above equations it is apparent that the disappearance of the bromoacetate as a result of the hydrolysis represented by (I) can be followed either by titration of the bromide ion with a silver solution or of the glycollic acid with alkali. On the other hand, since the hydrolysis of the bromoacetoxyacetate ion (II*b*) does not keep pace with its rate of formation, it is apparent that the rate of disappearance of bromoacetate in accordance with (II*a*) may be measured by titration with silver but not with alkali. The difference between the titration values at any stage affords a measure of the concentration of the intermediate complex $R{\cdot}CH_2{\cdot}CO_2'$, and this difference is found to pass through a maximum value.

The precise relation between the rates of the reactions (II*a*) and (II*b*) is not a matter of any importance in the present investigation, which is primarily concerned with the rate of disappearance of the hydrolyte in accordance with (I) and (II*a*), and in this connexion the essential point to note is that the silver-titration data afford a measure of the combined rates of these reactions. Since the relative rates of (I) and (II*a*) vary very widely with the concentration of the bromoacetate, it will be readily understood that the progress of the hydrolysis as determined by titration with silver solution does not conform to the requirements of a kinetic formula based on the assumption that the reaction is either uni- or bi-molecular. Such formulæ will have still less significance when considered with reference to the alkali-titration data.

The occurrence of simultaneous reactions is by no means the only circumstance which tends to complicate the interpretation of the titration data, for it has been found that the glycollic acid formed in (I) and (II*b*) has a very considerable influence on the measured reaction velocity. The influence of the reaction products may be shown by a comparison of the actual velocities (v') at various stages in the hydrolysis of a bromoacetate solution with the velocities (v) for solutions which contain the same amounts of bromoacetate but are devoid of the reaction products (glycollic acid and sodium bromide) which are necessarily associated with the bromoacetate in the former case. Pairs of velocity values corresponding with 25, 50, 75, and 90% hydrolysis of 0·2*M*-bromoacetate solution are shown in Table I, the velocities being expressed in mols. per litre per minute.

TABLE I.

Influence of reaction products on rate of hydrolysis of sodium bromoacetate at 25°.

Bromoacetate concn.	0·2	0·15	0·10	0·05	0·02
$10^6 . v'$	(1·05)	0·875	0·553	0·244	0·171
$10^6 . v$	1·05	0·660	0·369	0·145	0·049
v'/v	1	1·33	1·50	1·68	3·50

In the measurement of v' the several solutions were prepared synthetically by the addition of the required amounts of the reaction products. For convenience and accuracy of titration, the sodium bromide was replaced by sodium nitrate but this can scarcely have any measurable influence on the relation between v' and v, which is mainly determined by the glycollic acid. As the values of v'/v indicate, the influence of the reaction products on the velocity is very large and increases continuously as the reaction proceeds.

In these circumstances the question of the dependence of the reaction velocity on the concentration of the sodium bromoacetate can only be studied satisfactorily by measurement of the initial velocities, and in accordance with this conclusion the data recorded in this paper represent the actual velocities for a very small fraction (2%) of the total reaction. In order to make allowance for the variations of concentration within this small interval, the determination of the velocity for concentration c was actually carried out with an original concentration of $c + 0{\cdot}01c$ and a final concentration of $c - 0{\cdot}01c$.

When the concentration of the bromoacetate is increased from 0·02 to 1·0 mol. per litre, the initial velocity $v = \Delta[\mathrm{Br}']/\Delta t$ (mols./litre/min.) at 25° increases from 0·049 to 22·9. The velocity ratio is thus nearly ten times as large as the concentration ratio. The results are presented later in Table IV.

On the assumption that the simultaneous reactions (I) and (II*a*) are responsible for the disappearance of the bromoacetate, the initial reaction velocity should be given by

$$v = v_1 + v_2 = k_1c + k_2c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which k_1 and k_2 are the velocity coefficients for the two reactions. According to this equation, v/c should be a linear function of the concentration of the bromoacetate, but the actual results show that the velocity in pure aqueous solution increases with the concentration more rapidly than this. Since reactions (I) and (II*a*) are both accelerated by the addition of inert salts, it may be taken for granted that the bromoacetate will itself be responsible for an inert-salt effect expressible in terms of gradually increasing values of k_1 and k_2 as the concentration of the bromoacetate solution increases.

In order to obviate this disturbing factor, a parallel series of experiments has been made with bromoacetate solutions in which the total salt concentration is maintained constant at 1·0 mol. per litre by the addition of the appropriate quantities of sodium nitrate. The assumption hereby involved is that the inert-salt effects of the bromoacetate and the nitrate are equal. Since this effect varies to an appreciable extent with the nature of the salt, this equality may not be exact, but it seems probable that the disturbing influence of the neutral-salt effect will be largely eliminated by this procedure. The experimental results support this conclusion in that the data for this series give a straight line when v/c is plotted against c.

Since, according to (1), $v/c = k_1 + k_2c$, the intercept of this line on the ordinate $c = 0$ gives the value of $k_1 = 3{\cdot}4 \times 10^{-6}$, and the slope of the line gives the value of $k_2 = 19{\cdot}3 \times 10^{-6}$. The reaction velocities calculated from (1) by the introduction of these values of k_1 and k_2 are in close agreement with the actually measured velocities over the entire concentration range, as may be seen from Table II, in which col. 1 gives the concentration of the bromoacetate, cols. 2, 3, and 4 show respectively the calculated partial velocities v_1 and v_2 and the total velocity $v_{\text{calc.}}$, whilst col. 5 records the observed velocity $v_{\text{obs.}}$.

TABLE II.

Hydrolysis of sodium bromoacetate in aqueous solution with constant total salt concentration = 1·0 mol. per litre.

$c\text{CH}_2\text{Br}{\cdot}\text{CO}_2\text{Na} + (1 - c)\text{NaNO}_3$.

c.	$10^6 . v_1$.	$10^6 . v_2$.	$10^6 . v_{\text{calc.}}$.	$10^6 . v_{\text{obs.}}$.	c.	$10^6 . v_1$.	$10^6 . v_2$.	$10^6 . v_{\text{calc.}}$.	$10^6 . v_{\text{obs.}}$.
0·02	0·068	0·008	0·076	0·077	0·30	1·02	1·70	2·72	2·65
0·03	0·102	0·017	0·119	0·120	0·40	1·36	3·09	4·45	4·33
0·04	0·136	0·031	0·167	0·169	0·50	1·70	4·82	6·52	6·30
0·05	0·170	0·048	0·218	0·220	0·60	2·04	6·95	8·99	8·80
0·07	0·238	0·094	0·332	0·331	0·80	2·72	12·35	15·05	15·0
0·10	0·340	0·193	0·533	0·522	1·00	3·40	19·30	22·7	22·9
0·20	0·680	0·772	1·45	1·43					

Apart from the close agreement between the observed and calculated velocities which Table II shows, it may be noted that the values of v_1 and v_2 indicate that about 90% of the hydrolysis in the most dilute solution is attributable to the unimolecular reaction, whilst in the most concentrated solution 85% of it is due to the bimolecular reaction. In view of the high reactivity of the hydroxyl ion (cf. p. 55), it is desirable to point out that the initial reaction velocities recorded in the above and later tables for originally neutral solutions of sodium bromoacetate are not measurably affected by this factor. This would be the case even if the solutions remained neutral, but in actual fact the solutions become acid as the result of hydrolysis.

In the interpretation of the results which have been obtained for pure aqueous solutions of the bromoacetate, the variation of k_1 and k_2 with the salt concentration must be taken into account, and the assumption has been made that the variation in question is the same as that produced by the addition of sodium nitrate. This assumption seems to be fully justified by the results recorded in Table II.

In this connexion experiments have been made with 0·05 and with 0·2*M*-solutions of sodium bromoacetate to which various quantities of sodium nitrate were added. The results are shown in Table III.

TABLE III.

$0{\cdot}05\text{CH}_2\text{Br}{\cdot}\text{CO}_2\text{Na} + x\text{NaNO}_3$.

x	0	0·25	0·5	0·75	1·0
$10^6 . v$	0·145	0·163	0·184	0·203	0·224

$0{\cdot}2\text{CH}_2\text{Br}{\cdot}\text{CO}_2\text{Na} + x\text{NaNO}_3$.

x	0	0·25	0·5	0·75	1·0
$10^6 . v$	1·05	1·14	1·28	1·36	1·48

For both series the velocity is a linear function of the nitrate concentration, and if the inert-salt effects of the bromoacetate and the nitrate are equal, it follows that the velocity is a linear function of the total salt concentration (y) corresponding with $v = v_0(1 + \alpha y)$, where α measures the salt effect and v_0 is the hypothetical velocity in the entire absence of salt. The measured velocities can be expressed by $v/v_0 = 1 + 0{\cdot}56y$ for the 0·05*M*-bromoacetate series and by $v/v_0 = 1 + 0{\cdot}47y$ for the 0·2*M*-series. Since the contributions of the uni- and the bi-molecular reaction to the observed velocity vary with the bromoacetate concentration, this difference in the value of α may indicate that the inert-salt effects for the two reactions are unequal in magnitude. No definite answer can be given to this question, and for the present purpose it is assumed that the inert-salt effect can be represented with sufficient accuracy by the mean value of α corresponding with $v/v_0 = 1 + 0{\cdot}52y$. It may then be shown that the values of k_1 and k_2 for pure aqueous solutions of sodium bromoacetate of concentration c are given by $k_1 = 2{\cdot}25 \times 10^{-6}(1 + 0{\cdot}52c)$ and $k_2 = 12{\cdot}7 \times 10^{-6}(1 + 0{\cdot}52c)$, where $2{\cdot}25 \times 10^{-6}$ is the value of k_1 and $12{\cdot}7 \times 10^{-6}$ the value of k_2 in the absence of inert-salt effect. In so far as Brönsted's theory (*Z. physikal. Chem.*, 1922, **102,** 169) is applicable to such relatively concentrated solutions as those in Table III, it might be expected that reaction (II*a*) would be more sensitive than (I) to the influence of added inert salt. Since the relative importance of (II*a*) is greater for 0·2 than for 0·05*M*-bromoacetate, the value of the coefficient α would be expected to be larger for the more concentrated bromoacetate solutions, whereas the experimental data show the opposite effect.

The velocity coefficients derived in the above manner have been used in the calculation from equation (1) of the reaction velocities for pure aqueous solutions of sodium bromoacetate which are recorded in Table IV. Apart from the fact that the values of k_1 and k_2 are given in cols. 2 and 3, the arrangement of this table is the same as that of Table II.

TABLE IV.

Hydrolysis of sodium bromoacetate in pure aqueous solution.

c.	$10^6 . k_1$.	$10^6 . k_2$.	$10^6 . v_1$.	$10^6 . v_2$.	$10^6 . v_{\text{calc.}}$.	$10^6 . v_{\text{obs.}}$.
0·02	2·27	12·8	0·0455	0·005	0·0505	0·049
0·03	2·28	12·9	0·068	0·012	0·080	0·083
0·04	2·29	12·9	0·091	0·021	0·112	0·116
0·05	2·30	13·0	0·115	0·032	0·147	0·145
0·07	2·32	13·1	0·162	0·064	0·226	0·225
0·10	2·36	13·3	0·236	0·133	0·369	0·369
0·20	2·47	14·0	0·495	0·560	1·055	1·05
0·30	2·59	14·7	0·78	1·32	2·10	2·01
0·40	2·72	15·4	1·09	2·46	3·55	3·40
0·50	2·83	16·0	1·41	4·00	5·41	5·12
0·60	2·95	16·6	1·77	5·98	7·75	7·40
0·80	3·17	17·9	2·53	11·45	14·0	13·85
1·00	3·40	19·3	3·40	19·3	22·7	22·9

In reference to the data for pure aqueous solutions, it may be noted that if k_1 and k_2 vary linearly with the bromoacetate concentration in accordance with $k_1 = k_1{}^\circ(1 + \alpha c)$ and $k_2 = k_2{}^\circ(1 + \alpha c)$, then equation (1) takes the form

$$v = k_1{}^\circ(1 + \alpha c)c + k_2{}^\circ(1 + \alpha c)c^2$$

or

$$v/c = k_1{}^\circ + (k_1{}^\circ\alpha + k_2{}^\circ)c + k_2{}^\circ\alpha c^2$$

according to which v/c is a parabolic function of the bromoacetate concentration, as would seem to be indicated by the experimental graph.

The results presented in Tables II and IV are such as to warrant the conclusion that the elimination of bromine from the bromoacetates is due to the simultaneous reactions represented by (I) and (II*a*), and that the velocity of the process is adequately represented by the equation $v = k_1c + k_2c^2$, when the disturbing effects due to the products of reaction or to variations in the salt content of the solutions are eliminated or appropriately taken account of. Since one of the bromoacetate ions which are involved in (II*a*) is regenerated in (II*b*), it is obvious that reaction (II) may be regarded as the autocatalysed form of (I), which in turn may be considered to represent the normal non-accelerated hydrolytic reaction.

In the interpretation of the experimental data, it has been tacitly assumed that the bromoacetate is completely ionised and that the bromoacetate is the only halogen-containing entity which is involved in the reactions. The closeness of the agreement between the calculated and observed velocities would seem to afford ample justification for this assumption. The kinetic data may, indeed, be regarded as affording no evidence for the existence of un-ionised salt molecules in the solutions, for it may be reasonably expected that the reactivity of these would differ appreciably from that of the corresponding anions.

Catalytic Effects produced by Foreign Salts.—Reference has already been made to the accelerated hydrolysis observed in the presence of salts of the fatty acid series and to the interpretation of the increased velocity in terms of reactions corresponding in type with (II). In the light of the preceding observations, further experiments have been made to ascertain the relation of these catalysed reactions to the reactions which are represented kinetically by equation (1), and also to compare the accelerating effects of different anions in so far as the velocity of the first stage (liberation of Br′) in the catalysed reactions is increased.

The experimental results show that the reaction velocity for a mixture represented by the general formula $c\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na} + c'\text{NaA}$, in which A denotes the formate, acetate, glycollate, or other similar anion, exceeds the velocity for $c\mathrm{CH_2Br{\cdot}CO_2Na}$ by an amount which is directly proportional to the product of the concentrations of the bromoacetate and A ions. In these circumstances the equation for the reaction velocity becomes

$$v = v_1 + v_2 + v_3 = k_1c + k_2c^2 + k_3cc' \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which v_1 and v_2 are the same as in equation (1) and v_3 is the partial velocity due to the presence of the salt NaA. This partial velocity corresponds with the reaction represented by

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

which is precisely analogous to (II*a*). The coefficient k_3 thus affords a measure of the accelerating influence of the A ion.

In order to minimise the influence of inert-salt effects, the measurements of the initial reaction velocity were made with solutions of the same total salt concentration (1 mol. per litre). These solutions, with the appropriate addition of sodium nitrate, may thus be represented by the general formula $c\mathrm{CH_2Br{\cdot}CO_2Na} + c'\mathrm{NaA} + (1 - c - c')\mathrm{NaNO_3}$. The value of k_3 in equation (2) is derived from $k_3 = (v - v_1 - v_2)/cc'$, where v is the measured velocity, and v_1 and v_2 are the partial velocities recorded in Table II. Although differences in the inert-salt effects of NaA as compared with those due to sodium nitrate may be expected to have some influence on the values of k_3 obtained when c' is varied, the actual results show that the variations are quite small and that this coefficient may be evaluated with considerable accuracy.

Table V shows the results of experiments with bromoacetate in presence of varying quantities of acetate, formate, and glycollate. The calculated velocities are those derived from equation (2) with $10^6 . k_1 = 3{\cdot}4$, $10^6 . k_2 = 19{\cdot}3$, and $10^6 . k_3 = 50{\cdot}0$ for the acetate, 50·0 for the formate, and 35·0 for the glycollate.

TABLE V.

0·1*M*-Sodium bromoacetate + *c'M*-sodium acetate.

c'	0	0·1	0·2	0·3	0·4	0·5	0·7
$10^6 . v_{\mathrm{obs.}}$	0·52	1·00	1·51	1·98	2·53	3·03	4·12
$10^6 . v_{\mathrm{calc.}}$	0·53	1·03	1·53	2·03	2·53	3·03	4·03

0·05*M*-Sodium bromoacetate + *c'M*-sodium acetate.

c'	0	0·1	0·2	0·3	0·4	0·5	0·7
$10^6 . v_{\mathrm{obs.}}$	0·22	0·45	0·70	0·95	1·22	1·45	1·95
$10^6 . v_{\mathrm{calc.}}$	0·22	0·47	0·72	0·97	1·22	1·47	1·97

0·1*M*-Sodium bromoacetate + *c'M*-sodium formate.

c'	0	0·1	0·2	0·3	0·4	0·5	0·6
$10^6 . v_{\mathrm{obs.}}$	0·52	1·02	1·55	2·04	2·51	3·22	3·55
$10^6 . v_{\mathrm{calc.}}$	0·53	1·03	1·53	2·03	2·53	3·63	3·53

0·05*M*-Sodium bromoacetate + *c'M*-sodium glycollate.

c'	0	0·1	0·2	0·3	0·4	0·5	0·6
$10^6 . v_{\mathrm{obs.}}$	0·22	0·38	0·555	0·73	0·92	1·095	1·28
$10^6 . v_{\mathrm{calc.}}$	0·22	0·395	0·57	0·745	0·92	1·095	1·27

Experiments have also been made with chloroacetate as catalyst, and the conditions in this case are somewhat peculiar in that the catalyst also undergoes hydrolysis. From data which are already available it is quite certain that this hydrolytic process is precisely similar to that for the bromoacetate, although the velocity of the chloroacetate hydrolysis is very much smaller at the same temperature and concentration. The contribution of the chloroacetate to the observed velocity for mixtures of bromo- and chloro-acetate can be readily determined by independent measurements with solutions of sodium chloroacetate at the same total salt concentration.

If this velocity is v'' and that for the mixture with the same concentration of chloroacetate is v, then $v - v''$ represents the velocity of those reactions in which the bromoacetate is involved, and from this the value of k_3 for the accelerating effect of the chloroacetate on the rate of hydrolysis of the bromoacetate is found by the method described above to be $14{\cdot}0 \times 10^{-6}$. Table VI shows the measured velocities for a series of chloroacetate solutions (v'') and for a parallel series in which bromoacetate is present to the extent of 0·2 mol. per litre. The fourth row gives the velocities for the mixed solutions calculated from equation (3), with the addition of the corresponding value of v''. Although v'' is thus regarded as a small experimental correction factor, it may be noted that this could be calculated from $v'' = k_1'c' + k_2'c'^2$ if the coefficients k_1' and k_2' were available. The reaction velocity for the mixtures $c\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na} + c'\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$ would then be expressed by

$$v = k_1c + k_2c^2 + k_3cc' + k_1'c' + k_2'c_2' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

TABLE VI.

0·2*M*-Sodium bromoacetate + *c'M*-sodium chloroacetate.

c'	0	0·1	0·2	0·3	0·4	0·5
$10^6 . v''$	—	0·02	0·05	0·08	0·12	0·17
$10^6 . v_{\text{obs.}}$	1·43	1·75	1·98	2·24	2·64	3·06
$10^6 . v_{\text{calc.}}$	1·45	1·75	2·06	2·37	2·68	3·02

The results in the above table are of particular interest in that they show that the rate of hydrolysis of the bromoacetate is considerably accelerated by the chloroacetate.

Reference may finally be made to the hydrolysis of the bromoacetate in presence of sodium hydroxide. This reaction is usually regarded as being essentially different from the hydrolytic process which occurs in pure aqueous solutions, and the distinction may be justified to some extent by the fact that the alkali hydrolysis conforms closely under certain conditions to the requirements of the bimolecular formula $v = k[\text{bromoacetate}] \times [\text{alkali}]$. It should be pointed out, however, that this velocity formula represents the third term of equation (2) and that the kinetic characteristics of alkaline hydrolysis are solely due to the very large value of k_3 for the hydroxyl ion. This value ($k_3 = 4150 \times 10^{-6}$) is such that v_1 and v_2 are generally negligible in comparison with v_3. When the concentration of the bromoacetate (c) is large compared with that of the hydroxide (c'), the complete equation $v = k_1c + k_2c^2 + k_3cc'$ is, however, necessary to account for the observed course of the reaction. If, for instance, $c = 1{\cdot}0$ and $c' = 0{\cdot}05$, then $v_1 + v_2$ represents about one-tenth of the total velocity and this increases to about one-third when the alkali has been used up to the extent of 80%.

The initial velocities for mixtures of sodium bromoacetate and sodium hydroxide with a total salt ($\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na} + \text{NaOH} + \text{NaNO}_3$) concentration of 1 mol. per litre are shown in Table VII; cols. 1 and 2 give the concentrations of the reactants, col. 3 gives the observed velocity, and col. 4 the velocity calculated from equation (2) with $10^6 . k_3 = 4150$.

TABLE VII.

Alkaline hydrolysis of sodium bromoacetate.

Bromoacetate.	Hydroxide.	$10^6 . v_{\text{obs.}}$	$10^6 . v_{\text{calc.}}$
0·10	0·05	21·35	21·3
0·10	0·10	41·90	42·0
0·20	0·05	43·0	42·95

The applicability of equation (2) to the initial rate of formation of bromide from the bromoacetate with hydroxide as catalyst suggests that alkaline hydrolysis is precisely similar to that which occurs in presence of the acetate, etc. The only difference lies in the fact that the rates of reaction measured by titration with standard silver and with standard acid are identical within very narrow limits in the case of the reaction with hydroxide as catalyst. This suggests that the two stages corresponding with (II*a*) and (II*b*) are replaced by a single-stage reaction in the hydrolysis with alkali or that the second stage is very rapid.

Since the alkaline hydrolysis may be represented stoicheiometrically by $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na} + \text{NaOH} \longrightarrow \text{CH}_2(\text{OH})\cdot\text{CO}_2\text{Na} + \text{NaBr}$, it is clear that the glycollate formed will have an accelerating influence (cf. Table V) on the reaction as measured in the usual way. This autocatalytic effect will of necessity be responsible for additional deviations from the course of the reaction when this is expressed by the simple bimolecular formula $v = k$[bromoacetate][hydroxide].

When the catalysing effects of the various anions measured by k_3 and the autocatalytic effect of the bromoacetate ion measured by k_2 are compared, we obtain the series :

	Chloroacetate.	Bromoacetate.	Glycollate.	Formate.	Acetate.	Hydroxide.
$10^6 . k_3$	14	19·3	35	50	50	4150

from which it is apparent that, in general, the catalytic activity of the anion increases with increase in its basic character. The parallelism is by no means complete, however, and it would seem that the position of the formate ion in the series is somewhat anomalous in that formic acid is considerably stronger than acetic acid.

EXPERIMENTAL.

Carefully purified KBr was employed for the standardisation of the $AgNO_3$ and KNCS solutions used in the velocity measurements. In all cases the titrated solutions were comparable in vol. and in Br content, such conditions being attained in the kinetic expts. by suitable variation of the quantity and the preliminary dilution of the reaction mixture which was subjected to titration. Preliminary expts. indicated approximately the periods of time which were necessary for the production of the required amount of Br′. These precautions have been found to increase appreciably the accuracy of the measurements.

In the expts. with solutions containing chloroacetate, the halide was determined directly by titration with $AgNO_3$ in the presence of K_2CrO_4 as indicator, and in the case of the most dilute solutions the initial stage of hydrolysis was increased from 2 to 4% corresponding with the change from $c + 0{\cdot}02c$ to $c - 0{\cdot}02c$.

SUMMARY.

The kinetic measurements described above show definitely that the formation of bromide from sodium bromoacetate in aqueous solution is the result of simultaneous reactions which can be represented very accurately by the reaction velocity formula $v = k_1c + k_2c^2$ if the velocity is measured under conditions which provide for the elimination of inert-salt effects and for the accelerating influence of the products of the reaction. In this formula the constants k_1 and k_2 are the velocity coefficients for the unimolecular and the bimolecular reaction and c is the concentration of the bromoacetate.

The same equation is applicable to pure aqueous solutions of the bromoacetate if appropriate allowance is made for the influence of the varying salt content ($c = 0{\cdot}02$—$1{\cdot}0$) on the values of the coefficients k_1 and k_2.

In the presence of other salts—acetate, formate, glycollate, chloroacetate—the velocity is given by $v = v_1 + v_2 + v_3 = k_1c + k_2c^2 + k_3cc'$, where c' is the concentration of the catalysing salt and the constant k_3 is the corresponding velocity coefficient. The reactions which correspond with v_2 and v_3 are precisely similar, and k_2 affords a measure of a catalytic effect due to the bromoacetate itself which is analogous in every way to that produced by the other catalytically active salts.

The three-term equation applies also to the hydrolysis of bromoacetate in presence of hydroxide, and the fact that the course of the alkali hydrolysis can usually be expressed with close approximation by a simple bimolecular expression is entirely due to the large value of k_3 in comparison with k_1 and k_2.

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