

29. *The Kinetics of the Aqueous Hydrolysis of Sodium Phenylbromoacetate and Sodium Phenylchloroacetate.*

By W. R. BULCRAIG and (the late) H. M. DAWSON.

The kinetics of the aqueous hydrolysis of the phenylbromoacetate ion have been investigated over a wide range of conditions at 25°. It is shown that the hydrolysis is unaffected by excess of alkali or by the products, and that the reaction is accurately unimolecular in presence of excess of alkali. Equations are derived for the expected deviation from the unimolecular equation in neutral solution. Evidence of the formation of intermediate compounds in weakly alkaline and in neutral solutions is given, and the mechanism of the hydrolysis is discussed. A reaction between silver nitrate and sodium phenylbromoacetate was found to be autocatalytic. The hydrolysis of the phenylbromoacetate ion was also studied at 0°, and the energy of activation calculated. The hydrolysis of the phenylchloroacetate ion was studied briefly, similar results being obtained.

THE hydrolysis of sodium phenylbromoacetate was first studied by McKenzie and Walker (J., 1915, **107**, 1685), the first kinetic measurements being made by Senter and Tucker (J., 1916, **109**, 690). The latter showed that the rate of hydrolysis of the neutral salt did not conform accurately to a unimolecular equation, that it was not appreciably increased by the presence of excess of alkali, remaining unimolecular throughout since acid could not accumulate, and that it was independent of the amount of alkali present, but the results are not sufficiently accurate to allow critical examination of this point. Phenylbromoacetic acid was hydrolysed much more slowly than the sodium salt, and addition of hydrobromic acid made its hydrolysis still slower. Young and Olson (*J. Amer. Chem. Soc.*, 1936, **58**, 1157) studied the action of halide ions on phenylbromoacetic acid by a polarimetric method, and postulated a lactone mechanism for the hydrolysis.

Dawson and Dyson (J., 1933, **49**, 1133) showed that the hydrolysis of sodium bromoacetate and bromoacetic acid could be elucidated by adopting standard salt conditions and measuring initial velocities of reaction, thus eliminating the effects of varying salt concentration and the interference of reaction products. It was decided to apply similar methods to a study of phenylbromoacetic acid and its sodium salt, in view of the use of this acid in experiments on the Walden inversion, and the interest attaching to reaction mechanism and the effects of substitution on reaction velocity.

Method of Analysis.—Preliminary experiments with sodium phenylbromoacetate, the reaction being followed by estimation of the resulting bromide with standard silver nitrate solution, gave irreproducible results and corresponded to abnormally high rates of reaction. This was found to be due to a reaction between silver nitrate and phenylbromoacetate ions during the titration of bromide, even in presence of considerable amounts of nitric acid. The kinetics of this reaction were studied directly, and will be described elsewhere. It was found that a heterogeneous autocatalytic reaction occurs between silver ions and phenylbromoacetate ions, taking place on the surface of the precipitated silver bromide, which therefore catalyses the reaction. It is thus very similar to that of the α -bromopropionate ion (Senter, J., 1910, **97**, 346; Kappanna, *Proc. Ind. Acad. Sci.*, 1935, **2**, 512), but is considerably faster and does not appear to have been noted before. No reaction was found between undissociated phenylbromoacetic acid and silver ions, and as the dissociation constant of the acid is about 0.004, the reaction of silver ions on phenylbromoacetate ions is reduced considerably by the addition of nitric acid, and by adoption of a special method was eliminated during the titration of bromide. The hydrolysis was also followed by estimation of the acid formed in the reaction, by titration of the excess alkali present, or by direct titration of acid formed in the case of solutions initially neutral.

At 25°, since the unimolecular velocity coefficients for the hydrolysis of the phenylbromoacetate ion are of the order of 0.02 min.⁻¹, it is impossible to measure the initial velocity as in the case of bromoacetate (Dawson and Dyson, *loc. cit.*), and the whole course of the reaction was therefore studied. In presence of excess of alkali the hydrolysis is clearly unimolecular.

Unimolecular coefficients were obtained graphically by plotting $\log_{10}(a - x)$ against time, and are normally based on the first 80% of the reaction. All concentrations are in g.-mols./l., time is in minutes, and experiments are at 25° unless otherwise stated; a is the initial concentration of sodium phenylbromoacetate, and x the concentration of reaction products at time t .

EXPERIMENTAL.

The special method of titration of bromide was as follows. The sample of the reaction mixture from the thermostat at 25°, containing phenylbromoacetate and bromide, was run into 100 c.c. of 6*N*-nitric acid in a conical flask at about

—10°, containing slightly more than the amount of silver nitrate needed to precipitate all the bromide. The flask was shaken to assist coagulation of precipitated silver bromide, and the excess silver nitrate back-titrated rapidly with standard potassium thiocyanate solution, with ferric indicator; with these precautions reproducible results were obtained.

(a) *Hydrolysis in Excess of Alkali*.—The concentration of sodium phenylbromoacetate was varied from 0.30 to 0.01, and the total salt concentration was maintained at 1.0 mol./l. by addition of sodium nitrate. Two series of experiments were made, with solutions containing severally $2a$ and a mols. of excess alkali per l. In both series the reaction, when followed by titration of bromide formed, is accurately unimolecular, as shown in Table II, and the following coefficients (k_{Br}) were obtained from bromide estimations.

$a\text{CHPhBr}\cdot\text{CO}_2\text{Na} + 2a\text{NaOH} + (1-3a)\text{NaNO}_3$						$a\text{CHPhBr}\cdot\text{CO}_2\text{Na} + a\text{NaOH} + (1-2a)\text{NaNO}_3$				
a	0.30	0.10	0.050	0.025	0.010	0.30	0.10	0.050	0.025	0.010
k_{Br}	0.0205	0.0209	0.0209	0.0207	0.0205	0.0207	0.0209	0.0211	0.0207	0.0206

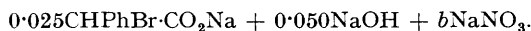
The same series were repeated, the reaction being followed, however, by titration of acid. The results are recorded below. For the series containing $2a$ mols./l. of excess alkali the results are in good agreement, but in that with half this excess certain small differences were noted, and the acid formation was found to deviate from the unimolecular equation in the late stages of the reaction, particularly when a is small. The coefficients for the latter series therefore only apply to the first 50% of the reaction, during which k is constant.

$a\text{CHPhBr}\cdot\text{CO}_2\text{Na} + 2a\text{NaOH} + (1-3a)\text{NaNO}_3$						$a\text{CHPhBr}\cdot\text{CO}_2\text{Na} + a\text{NaOH} + (1-2a)\text{NaNO}_3$				
a	0.30	0.10	0.050	0.025	0.010	0.30	0.10	0.050	0.025	0.010
k_H	0.0208	0.0206	0.0206	0.0200	0.0193	0.0208	0.0202	0.0196	0.0195	0.0191

The differences between k_{Br} and k_H are therefore negligible in presence of appreciable concentrations of excess alkali. More information was obtained in neutral solutions (see below) of the differences between the bromide and the acid titration results.

The rate of hydrolysis of the phenylbromoacetate ion was next studied in presence of various concentrations of sodium nitrate; this has a simple salt effect on the velocity, and the rate, either for bromide or for acid formation, remains strictly unimolecular (see Table I).

TABLE I.



b	Nil	0.425	0.925	1.425	1.925
k_{Br}	0.0180	0.0195	0.0207	0.0225	0.0242
k_H	0.0181	0.0192	0.0200	0.0217	0.0229

This indicates that (i) the primary salt effect of sodium nitrate on the unimolecular ionisation of bromine is linear up to an ionic strength of $\mu = 2.0$, (ii) in absence of sodium nitrate the rates of bromide and acid formation are identical, and (iii) the differences between k_{Br} and k_H increase with increasing concentration of sodium nitrate.

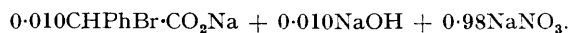
Late stages of hydrolysis in excess of alkali. If in certain cases the rate of acid formation is less than that of bromide formation, as, e.g., if an intermediate compound is formed during the hydrolysis, then the late stages of the hydrolysis should show that bromide formation reaches completion while the acidity is still incomplete. To investigate this, a dilute solution with one equiv. of excess alkali present initially was studied right through to 100% reaction. The rate of bromide formation is strictly unimolecular throughout and is virtually complete after 300 mins. At this time there is still 7% of the original concentration of 0.010M-alkali present (see Table III), indicating that only 93% of the theoretical amount of mandelic acid has been formed. The concentration of acid increases slowly and is only complete after 2000 mins., showing that any intermediate compounds are then fully decomposed.

TABLE II.



t	0	10	15	20	27	35	43	55	70	85	100
$(a-x) \times 10^5$...	2500	2033	1837	1656	1432	1219	1022	809	589	439	324
$k \times 10^4$	—	207	205	206	206	205	208	205	207	205	204

TABLE III.



t .	$[\text{Br}']$ $\times 10^5$.	$[\text{H}']$ $\times 10^5$.	$\{[\text{Br}'] - [\text{H}']\}$ $\times 10^5$.	t .	$[\text{Br}']$ $\times 10^5$.	$[\text{H}']$ $\times 10^5$.	$\{[\text{Br}'] - [\text{H}']\}$ $\times 10^5$.
0	—	—	—	70	763	717	46
10	185	183	2	100	877	809	68
15	266	255	11	200	980	904	76
20	337	322	15	400	1000	940	60
27	426	408	18	1000	1000	968	32
35	520	496	24	2100	1000	991	9
45	608	573	35	5000	1000	1000	—
55	677	639	38				

Temperature coefficient of hydrolysis. In view of the interest attached to the influence of substitution on reaction velocity, the hydrolysis of the phenylbromoacetate ion was studied at 0°, in order to obtain the energy of activation. The experiment was carried out in a thermostat containing water and glycol at 0°, and the solution used was $0.025\text{CHPhBr}\cdot\text{CO}_2\text{Na} + 0.050\text{NaOH} + 0.925\text{NaNO}_3$, which has a unimolecular coefficient of 0.0207 at 25°. The reaction was found to be accurately unimolecular, with a coefficient of 2.36×10^{-4} . The reaction velocity being assumed to obey the Arrhenius equation, the energy of activation is 29,130 cal. The results of Dawson and Dyson (J., 1933, 49) and Dawson and Pycock (J., 1934, 778) show that for bromoacetate and water the unimolecular coefficient is 3.2×10^{-6} at 25° and 4.0×10^{-2} at 45°, whence $E = 24,830$ cal. Hence the great increase in velocity on substitution of the phenyl group into the bromoacetate ion is not due to a decrease in the Arrhenius energy of activation.

Hydrolysis of phenylchloroacetate. A number of experiments was made with sodium phenylchloroacetate for comparison purposes. The hydrolysis was followed by two methods, titration of the chloride by the Volhard method as modified by Rothmund and Burgstaller (*Z. anorg. Chem.*, 1909, **63**, 330), and titration of the acid formed. The hydrolysis of a solution containing $0.025\text{CHPhCl}\cdot\text{CO}_2\text{Na} + 0.050\text{NaOH} + 0.925\text{NaNO}_3$ was found to be accurately unimolecular, coefficients being 0.00167 by chloride estimation and 0.00169 by acid estimation. At 0° the coefficient was 1.75×10^{-5} ; hence $E = 29,680$ cal. In absence of sodium nitrate, the coefficients for the same reaction at 25° were 0.00134 for chloride formation and 0.00136 for acid formation.

(b) *Hydrolysis in Neutral Solution.*—In neutral solution the mandelic acid produced sets up an equilibrium with the phenylbromoacetate present: $\text{CHPh(OH)}\cdot\text{CO}_2\text{H} + \text{CHPhBr}\cdot\text{CO}_2' \rightleftharpoons \text{CHPh(OH)}\cdot\text{CO}_2' + \text{CHPhBr}\cdot\text{CO}_2\text{H}$. The undissociated phenylbromoacetic acid is inert relative to the hydrolysis of the ion; therefore the rate of hydrolysis becomes slower as more mandelic acid is formed, and the reaction cannot conform to the simple unimolecular equation. The extent to which it deviates depends on the above equilibrium, and the concentration of phenylbromoacetate ions present at any stage can be calculated if the dissociation constants of the two acids are known. It is therefore possible to obtain an equation which will give the kinetics of the hydrolysis in neutral solution. For mandelic acid $K = 0.00043$ at 25° (Landolt-Börnstein). For phenylbromoacetic acid the only value known is 0.0035 (given by Senter), owing to the difficulty of determining it in a solution which is hydrolysing rapidly. From the above equilibrium, if K_1 and K_2 are the above values of K , respectively,

$$\frac{[\text{CHPh(OH)}\cdot\text{CO}_2\text{H}][\text{CHPhBr}\cdot\text{CO}_2']}{[\text{CHPh(OH)}\cdot\text{CO}_2'][\text{CHPhBr}\cdot\text{CO}_2\text{H}]} = K' = \frac{[\text{CHPh(OH)}\cdot\text{CO}_2\text{H}]}{[\text{CHPh(OH)}\cdot\text{CO}_2'][\text{H}^+]} \times \frac{[\text{CHPhBr}\cdot\text{CO}_2'][\text{H}^+]}{[\text{CHPhBr}\cdot\text{CO}_2\text{H}]} = \frac{K_2}{K_1} = \frac{0.0035}{0.00043} = 8.0$$

Let x = concentration of reaction products at time t , and y = that of undissociated phenylbromoacetic acid present; then the concentrations of phenylbromoacetate ions, mandelate ions, and undissociated mandelic acid are respectively $(a - x - y)$, y , and $(x - y)$. Substitution in the above equation for K' gives

$$K' = (x - y)(a - x - y)/y^2 = 8.0 \text{ and } y = [-a + \sqrt{a^2 + 28(ax - x^2)}]/14$$

This cannot be incorporated in the velocity equation directly, owing to integration difficulties; hence an approximation was made as follows:

$$y = [-a + \sqrt{(a + 14x)^2 - 224x^2}]/14 = [-a + (a + 14x)\{1 - 224x^2/(a + 14x)^2\}^{1/2}]/14$$

Expansion of the surd to three terms and rearrangement then give, as a first approximation,

$$y = (a^2x + 6ax^2 - 7.2x^3)/(a^2 + 14ax)$$

whence

$$[\text{CHPhBr}\cdot\text{CO}_2'] = a - x - y = (a^3 + 12a^2x - 20ax^2 + 7.2x^3)/(a^2 + 14ax)$$

The rate equation for the formation of bromide is

$$dx/dt = k[\text{CHPhBr}\cdot\text{CO}_2'] = k(a - x - y)$$

therefore

$$kt = \int_0^x \frac{a^2 + 14ax}{a^3 + 12a^2x - 20ax^2 + 7.2x^3} dx$$

To integrate this, the cubic equation is solved, factorised, and resolved into partial fractions:

$$kt = \int_0^x \left(\frac{2.386}{a - 0.9695x} - \frac{0.03190}{a + 13.52x} - \frac{1.354}{a - 0.5496x} \right) dx$$

$$\text{and } k = \frac{2.303}{t} \left[2.461 \log_{10} \frac{a}{(a - 0.9695x)} + 0.00236 \log_{10} \frac{a}{(a + 13.52x)} + 2.463 \log_{10} \frac{a}{(a - 0.5496x)} \right] \dots \dots (1)$$

It was found that the middle term of this equation is small enough to be neglected, also the numerical coefficients of the other two terms are very nearly equal, and the equation is simplified to

$$k = (5.67/t) \log_{10}(a - 0.5496x)/(a - 0.9695x) \dots \dots (2)$$

The observed rate of bromide formation obeyed this equation, and it is therefore much more satisfactory for neutral hydrolysis than the simple unimolecular equation which always gives falling coefficients. The method used was to plot the logarithmic term against time, the resulting line giving the value of $k_{(2)}$. The application of equation (2) to the

TABLE IV.

$0.050\text{CHPhBr}\cdot\text{CO}_2\text{Na} + 0.950\text{NaNO}_3$. (Bromide formation.)

t	15	20	35	45	55	70	85
$10^5 x$	1314	1615	1954	2391	2789	3111	3479
$10^5 (a - 0.9695x)$	3726	3435	3106	2682	2296	1984	1628
$10^5 (a - 0.5496x)$	4278	4112	3926	3686	3467	3290	3088
Ratio	0.8710	0.8354	0.7911	0.7276	0.6622	0.6032	0.5271
$10^4 k_{(2)}$	—	233	231	230	231	231	229

hydrolysis of $0.050\text{CHPhBr}\cdot\text{CO}_2\text{Na} + 0.950\text{NaNO}_3$ is shown in Table IV. Values of $k_{(2)}$ obtained with various concentrations of sodium phenylbromoacetate are as follows (for the two methods of estimation):

a	$a\text{CHPhBr}\cdot\text{CO}_2\text{Na} + (1-a)\text{NaNO}_3$.							
	(Bromide estimation.)				(Acid estimation.)			
a	0.10	0.050	0.025	0.010	0.10	0.050	0.025	0.010
k_2	0.0216	0.0229	0.0239	0.0239	0.017	0.0174	0.0174	0.0177

The coefficients found by estimation of the acid formed in the reaction are constant for the first 70% of the reaction.

There are clearly large differences between the rates of bromide and acid formation, and these are much greater than those found in weakly alkaline solutions. The differences in neutral solution were then analysed, and it was found that

during the course of the reaction the acidity always represented a constant fraction of the bromide, *i.e.*, the bromide-acidity difference is a constant fraction of the reaction products. This is shown in Table V(a), for one typical run.

TABLE V.

0.025CHPhBr·CO₂Na + 0.975NaNO₃. (Bromide and acidity.)

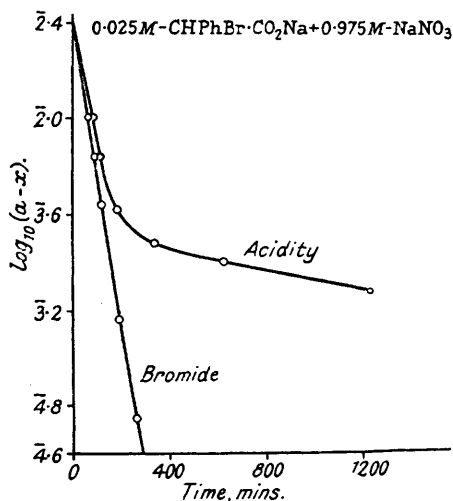
<i>t.</i>	[Br'] × 10 ⁵ .	[H'] × 10 ⁵ .	{[Br'] - [H']} × 10 ⁵ .	$\frac{[\text{Br}'] - [\text{H}']}{[\text{Br}']}$	<i>t.</i>	[Br'] × 10 ⁵ .	[H'] × 10 ⁵ .	{[Br'] - [H']} × 10 ⁵ .	$\frac{[\text{Br}'] - [\text{H}']}{[\text{Br}]}$.
(a) 0 to 100 mins.									
10	404	356	48	0.12	45	1401	1198	203	0.15
15	592	512	80	0.14	55	1568	1343	225	0.14
20	779	664	115	0.15	70	1752	1521	231	0.13
27	977	833	144	0.15	85	1908	1656	252	0.13
35	1182	1014	168	0.14	100	2036	1782	254	0.13
(b) 0 to 7000 mins.									
10	404	356	48	0.12	600	2498	2249	249	0.10
35	1182	1014	168	0.14	1000	2500	2291	209	0.08
70	1752	1521	231	0.13	2000	2500	2355	145	0.06
100	2036	1782	254	0.13	5000	2500	2432	68	0.03
150	2271	2010	261	0.12	7000	2500	2460	40	0.01
300	2460	2190	270	0.11					

The amount of acid present is always about 86% of the bromide, suggesting that a stable intermediate is being formed as a uniform product.

As these differences in alkaline solution appeared to be related to the amount of sodium nitrate present (Table I), the hydrolysis in neutral solution was also studied in absence of sodium nitrate. Using a solution of 0.025M-sodium phenylbromoacetate alone, and applying equation (2), it was found that the bromide-acidity differences were only one-sixth of those in Table V(a). The coefficients obtained were *k*_{Br} = 0.0190, and *k*_H = 0.0183.

Late stages of neutral hydrolysis. Confirmatory evidence for the formation of intermediate compounds was obtained by following the late stages of the hydrolysis as in the excess alkali experiments. A solution of 0.025CHPhBr·CO₂Na + 0.975NaNO₃ was followed by both bromide and acid estimation to completion. Bromide formation follows equation (2) throughout, reaching 99.9% after 520 mins. At this stage the acidity is only 90% of the theoretical, indicating that 10% of intermediate compounds is present. The acidity increases slowly over several days, as these compounds hydrolyse. The diagram shows log₁₀ (a - x) plotted against time for bromide and for acid formation, and illustrates the striking change in the rate of acid formation which occurs as bromide formation nears completion. Table V(b) gives details of the amounts present throughout the reaction.

Effects of inert salts on neutral hydrolysis. A series of experiments was made to find the effect of replacing the sodium nitrate by other uni-univalent sodium salts. Rate of bromide formation gives the normal salt effect, and the bromide-acid difference indicates the extent of intermediate compound formation. Velocity coefficients are calculated from equation (2), except in the case of sodium mandelate (NaM), for in presence of this salt the hydrolysis is strictly unimolecular owing to displacement of the equilibrium between mandelate and phenylbromoacetate ions.



0.025CHPhBr·CO₂Na + 0.975NaX.

Salt, NaX	Nil	NaNO ₃	NaBr	NaClO ₄	NaM
<i>k</i> _{Br}	0.0190	0.0238	—	0.0250	0.0191
<i>k</i> _H	0.0183	0.0176	0.0184	0.0238	0.0176
% intermediate corresponding to <i>k</i> _{Br} - <i>k</i> _H	2	14		3	4

The hydrolysis of the phenylchloroacetate ion in neutral solution is exactly analogous to that of the bromine compound. With a solution of 0.025CHPhCl·CO₂Na + 0.975NaNO₃, the usual fall in the unimolecular coefficient was found. The dissociation constant of phenylchloroacetic acid is given by Senter as 0.0043; hence an equation analogous to (1) was derived, and simplified in the same manner to give

$$k = (7.09/t) \log_{10} (a - 0.561x) / (a - 0.894x) \dots \dots \dots (3)$$

This equation was applied to the results for the above solution, and *k*₍₃₎ = 0.00171 (Table VI). The late stages of hydrolysis of sodium phenylchloroacetate were examined. Chloride formation is not complete until about 3500 mins., and at this stage only 3.5% of the theoretical acidity is withheld.

Discussion.—It has been shown that unimolecular coefficients for the hydrolysis of the phenylbromoacetate ion in presence of excess alkali remain constant with varying initial concentration of sodium phenylbromoacetate. This shows that there is no reaction between two phenylbromoacetate ions or between one phenylbromoacetate ion and a hydroxyl ion, in marked contrast to the case of the bromoacetate ion, where the ion-ion reaction is often dominant (Dawson and Dyson, *loc. cit.*). The reaction must therefore consist either of a bimolecular reaction between a phenylbromoacetate ion and water, or of a unimolecular ionisation reaction, and since the hydrolysis is unaffected by excess alkali the latter is more probable. It is noteworthy that the

TABLE VI.

0.025CHPhCl·CO₂Na + 0.975NaNO₃. (Chloride estimation.)

<i>t</i>	10	50	100	180	370	540	720	1450
[Cl] × 10 ⁵	25	188	369	604	1065	1355	1597	2133
(<i>a</i> - 0.561 <i>x</i>) × 10 ⁵	2486	2395	2293	2161	1902	1740	1604	1303
(<i>a</i> - 0.894 <i>x</i>) × 10 ⁵	2478	2332	2170	1960	1548	1288	1072	594
Ratio	1.003	1.027	1.056	1.103	1.228	1.351	1.496	2.194
10 ⁵ <i>k</i> ₍₃₎	—	170	173	169	172	172	173	167

hydrolysis is much faster than that of bromoacetate, the unimolecular velocity coefficients being 0.0207 and 3.2×10^{-6} respectively at 25°, but that the Arrhenius energy of activation is greater, 29,130 and 24,830 cal., respectively; hence the higher rate is due to some other factor. For phenylbromoacetate, if $k = PZe^{-E/RT}$, where *Z* is the collision frequency, calculated by Bradley's formula (J., 1934, 1910) as $Z = 4.2 \times 10^{12}$ sec.⁻¹ at 25°, *E* becomes 30,020 cal. and $P = 1.1 \times 10^4$. Thus the number of solute-solvent collisions with the observed energy of activation is much less than corresponds to the observed rate of reaction, confirming the view that the reaction is not a simple bimolecular reaction with water, and is probably a true unimolecular reaction. The reaction is therefore of the same type as the aqueous hydrolysis of *tert.*-butyl chloride (Hughes, J., 1935, 225), hydrolysis of α -chloroethylbenzene (Ward, J., 1927, 445), and the decomposition of γ -bromobutyrate (Caldin and Wolfenden, J., 1936, 1239).

Closer examination of the hydrolysis shows that, although bromide formation is strictly unimolecular, acid formation shows a slight lag in certain cases, particularly in neutral solutions containing a high concentration of sodium nitrate. This shows that, despite the apparent simplicity of the hydrolysis and the absence of an ion-ion reaction, some intermediate compound formation can occur under certain conditions. The presence of this intermediate compound is confirmed by the late-stage experiments, which show the slow hydrolysis of this intermediate after bromide formation is complete. The following reaction mechanism is suggested to account for its presence.

The first stage of the reaction is unimolecular ionisation, giving a bromide ion and a carbonium ion, $C_6H_5^+CH\cdot CO_2'$, which reacts immediately with hydroxyl ions if present, and with water, and also with any additional ions present such as the nitrate ion. Water and hydroxyl ions yield mandelic acid, the normal product of hydrolysis, and it is suggested that nitrate ions give $C_6H_5\cdot CH(NO_3)\cdot CO_2'$, which on subsequent hydrolysis gives mandelic acid and regenerates the nitrate ion. The intermediate compound is decomposed rapidly by hydroxyl ions and only hydrolyses slowly in neutral solution. Hence, in presence of excess alkali it cannot accumulate, and acid formation will follow bromide formation closely, but in neutral solutions containing sodium nitrate the conditions favour its formation and stability, and acid formation will lag behind bromide formation throughout. Formation of this intermediate compound has no effect on the rate of bromide formation since ionisation of bromine is the primary stage of the reaction. The experimental results confirm that bromide formation is strictly unimolecular under all conditions.