34. *The Elimination of Bromide Ion from Aqueous Solutions of Phenylbromoacetic Acid.*

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The rate at which bromide ion is liberated from aqueous solutions of phenylbromoacetic acid has been studied in the presence of nitric acid up to a concentration of 1·0M. The course of the reaction is satisfactorily accounted for by a general equation in terms of the acidity of the solution, but under suitable conditions simpler equations are applicable.

The dissociation constant of phenylbromoacetic acid in the presence of M-sodium nitrate has been determined by kinetic measurements and is $6{\cdot}1 \times 10^{-3}$ at 25°.

It is shown that the reactivity of the undissociated phenylbromoacetic acid cannot be greater than about 0·002 of that of the phenylbromoacetate ion.

In a previous paper (Bulcraig and Dawson, J., 1943, 80) observations on the hydrolysis of the group $\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}$ in alkaline and in neutral solutions were reported. Consideration of the kinetic measurements leads to the conclusion that under these conditions the only process leading to the elimination of bromide ion is one involving the phenylbromoacetate ion. In particular, even in the absence of any added alkali, the course of the reaction is completely accounted for on the basis of the reactivity of the anion, although in the later stages of the reaction, considerable proportions of undissociated phenylbromoacetic acid are present in the solution. It follows, therefore, in agreement with Senter and Tucker (J., 1916, **109**, 690), that the reactivity of the undissociated acid must be very small in comparison with that of the ion, and consequently, it is only in solutions of relatively high acidity that the reactivity of the acid itself would be revealed. The kinetic measurements now described refer to the rate of liberation of bromide ion from phenylbromoacetic acid at 25° in the presence of various concentrations of nitric acid under controlled conditions of electrolyte content, and the analysis of the observations is based initially on the tentative assumption that the ion only is undergoing reaction. As in previous papers, concentrations are in g.-mols./l. and time is in minutes.

In the presence of added nitric acid, as in an initially neutral solution, the course of the reaction as followed by the rate of production of bromide ion will not, in general, conform to the simple unimolecular formula, owing to the increase in acidity during the reaction, and indeed, it is not possible to derive any simple rate expression of a general nature in terms of the directly measured quantities. On the other hand, however, it is possible to obtain an equation of general applicability in terms of the acidity of the solution. The derivation of this equation is given below, since Senter's equation (J., 1915, **107**, 908), which refers to an analogous system, is but a special case of the general expression. If a and b are respectively the initial concentrations of phenylbromoacetic acid and of nitric acid, and x and y are respectively the concentrations of bromide ions and hydrions at any instant, then, account being taken of the processes

$$\mathrm{CHPhBr{\cdot}CO_2H \rightleftharpoons CHPhBr{\cdot}\overset{-}{CO_2} + \overset{+}{H}}$$

and

$$\mathrm{CHPhBr{\cdot}\overset{-}{CO_2} \rightarrow \overset{-}{Br}} + \text{reaction products}$$

it follows that $a = [\mathrm{CHPhBr{\cdot}CO_2H}] + [\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}] + x$ and, if the contribution to the acidity made by the reaction products is neglected,

$$y = [\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}] + b + x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Hence, since

$$K = [\mathrm{H^+}][\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}]/[\mathrm{CHPhBr{\cdot}CO_2H}] = y(y - b - x)/(a + b - y) \quad . \quad . \quad . \quad (2)$$

then

$$x = y - b + K - K(a + b)/y$$

and

$$\mathrm{d}x/\mathrm{d}y = 1 + K(a + b)/y^2$$

If only the phenylbromoacetate ion is reacting

$$\mathrm{d}x/\mathrm{d}t = k_3[\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}] = k_3(y - b - x)$$

and consequently

$$\mathrm{d}y/\mathrm{d}t = (\mathrm{d}y/\mathrm{d}x)(\mathrm{d}x/\mathrm{d}t) = k_3y^2(y - b - x)/[y^2 + (a + b)K] = k_3Ky(a + b - y)/[y^2 + (a + b)K]$$

which on integration gives

$$k_3 = \frac{1}{Kt}\left\{K \ln\frac{y}{y_0} - (a + b + K) \ln\frac{a + b - y}{a + b - y_0} + y_0 - y\right\} \quad . \quad . \quad . \quad . \quad (3)$$

where y_0 is the value of y when $t = 0$.

The application of equation (3) to the experimental data, which is shown in Table I, involves the tedious calculation from each value of x of the corresponding value of y, by means of the equation

$$y = \tfrac{1}{2}\left\{x + b - K + \sqrt{(K - x - b)^2 + 4K(a + b)}\right\}$$

For this reason a series of equations in terms of x have been developed, which are more convenient to handle, although each of these equations, in contrast to equation (3), is valid over only a restricted range of acidities. It follows from (1) and (2) that

$$[\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}] = K(a - x)/(K + b + x + [\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}]).$$

Now when $b =$ or $>a$, $b>[\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}]$, and hence as a first approximation,

$$K + b + x + [\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}] = K + b + x + K(a - x)/(K + b + x)$$

from which it follows that

$$[\mathrm{CHPhBr{\cdot}\overset{-}{CO_2}}] = K(a - x)(K + b + x)/[(K + b + x)^2 + K(a - x)]$$

Hence

$$dx/dt = k_4K(a - x)(K + b + x)/[(K + b + x)^2 + K(a - x)]$$

which on integration gives

$$k_4 = \frac{1}{t}\left\{\frac{a + b + K}{K}\ln\frac{a}{a - x} + \ln\frac{K + b + x}{K + b} - \frac{x}{K}\right\} \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

When b is much greater than a, a further simplification is possible, for it may then be assumed that

$$[\mathrm{CHPhBr{\cdot}C\overline{O}_2}] = K(a - x)/(K + b + x)$$

from which it follows that

$$k_5 = \frac{1}{t}\left\{\frac{a + b + K}{K}\ln\frac{a}{a - x} - \frac{x}{K}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Finally, when b is very large, equation (5) reduces to the pseudo-unimolecular formula

$$k_6 = [(a + b + K)/Kt]\ln a/(a - x) \; . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

The evaluation of the velocity coefficient of the reaction by means of equations (3)—(6) involves a knowledge of the dissociation constant of phenylbromoacetic acid. The recorded value of this constant at 25° is $3{\cdot}5 \times 10^{-3}$ (Senter and Tucker, *loc. cit.*) but this was determined by means of conductivity measurements on the acid solution which was undergoing hydrolysis, and moreover, it relates to a dilute aqueous solution of the acid, so it is not only suspect but is also not applicable to the strong salt solutions used in the present experiments. It has therefore been necessary, by means of kinetic experiments, to determine the dissociation constant of the acid under the prevailing salt conditions. The velocity measurements used for this purpose refer to solutions of low acidity, where, as already pointed out, it is evident that only the phenylbromoacetate ion undergoes reaction. Equation (3) alone is valid under these conditions. The application of this equation, together with a knowledge of k_3, as evaluated from measurements in alkaline solutions (Bulcraig and Dawson, *loc. cit.*), then allows of the determination of K. The data for two experiments are given in (*a*) and (*b*) of Table I. In each case, in the second line are given the bromide-ion concentrations (x), as determined by silver titration, and in the third line the hydrion concentrations (y) derived therefrom on the assumption that $K = 6{\cdot}06 \times 10^{-3}$ in (*a*) and $6{\cdot}15 \times 10^{-3}$ in (*b*); these numbers lead to the previously determined value for 10^4k_3, *viz.*, 207. The approximate constancy of the values of k_3, given in the last line, shows that the premises on which the calculation is based are substantially correct. It may therefore be taken that K has the value $6{\cdot}1 \times 10^{-3}$ in these solutions, and this value has been adopted in all subsequent experiments.

TABLE I.

(*a*) $0{\cdot}025\text{M-CHPhBr{\cdot}CO}_2\text{H} + 1{\cdot}0\text{M-NaNO}_3$; $K = 6{\cdot}06 \times 10^{-3}$

t	0	30	45	60	85	100	122	150	180	240
10^3x	0	4·63	6·67	8·33	10·68	12·00	13·42	15·03	16·57	18·58
10^3y	9·68	11·65	12·65	13·53	14·85	15·66	16·55	17·61	18·65	20·08
10^4k_3	—	204	208	208	205	210	206	207	207	205

(*b*) $0{\cdot}025\text{M-CHPhBr{\cdot}CO}_2\text{H} + 0{\cdot}01\text{M-HNO}_3 + 0{\cdot}99\text{M-NaNO}_3$; $K = 6{\cdot}15 \times 10^{-3}$.

t	0	15	30	45	60	90	121	150	180	210	270	360
10^3x	0	1·47	3·18	4·76	6·17	8·62	10·74	12·52	13·86	15·08	16·96	19·21
10^3y	16·71	17·55	18·59	19·58	20·50	22·17	23·67	24·98	25·99	26·92	28·39	30·19
10^4k_3	—	—	206	204	204	205	207	211	208	207	205	206

Two series of experiments were carried out. In the first series (A) where the solutions were of composition $0{\cdot}025\text{M-CHPhBr{\cdot}CO}_2\text{H} + b\text{M-HNO}_3 + (1 - b)\text{M-NaNO}_3$, the total electrolyte concentration remained constant at 1 g.-mol./l. In the second series (B) a constant concentration of sodium nitrate was maintained, the solutions having compositions given by $0{\cdot}025\text{M-CHPhBr{\cdot}CO}_2\text{H} + b\text{M-HNO}_3 + 1{\cdot}0\text{M-NaNO}_3$. In such solutions, as b is progressively increased, equations (4), (5), and (6) become successively applicable. When $b =$ or $> 0{\cdot}025$, equation (4) accounts satisfactorily for the course of the reaction, as is shown by the constancy of the coefficients given in the last line of Table II (*a*) as an example.

TABLE II.

(*a*) $0{\cdot}025\text{M-CHPhBr{\cdot}CO}_2\text{H} + 0{\cdot}050\text{M-HNO}_3 + 1{\cdot}0\text{M-NaNO}_3$.

t	30	60	100	160	240	300	420	550	660
$\ln 10^3(b + K + x)/(b + K)$	24	50	80	116	158	182	222	255	276
$[(a + b + K)/K]\ln a/(a - x)$	0·75	1·61	2·73	4·31	6·40	7·87	10·86	13·97	16·61
$10^3x/K$	224	469	759	1134	1564	1830	2284	2662	2924
10^4k_4	210	213	213	211	212	210	211	212	213

(*b*) $0{\cdot}025\text{M-CHPhBr{\cdot}CO}_2\text{H} + 1{\cdot}0\text{M-HNO}_3$.

t	782	1445	2287	2920	3700	5100	6670	9450
10^3x	2·872	4·961	7·452	9·036	10·90	13·57	15·93	19·05
$[(a + b + K)/K]\ln a/(a - x)$	20·52	37·27	59·62	75·56	96·47	131·8	170·8	241·8
x/K	0·47	0·81	1·22	1·48	1·78	2·22	2·60	3·11
10^4k_5	256	252	255	254	256	254	252	253
10^4k_6	268	263	266	264	266	264	262	262

When $b \nless$ *ca.* 0·2, equation (5) becomes applicable, and when b has reached 1·0, the course of the reaction approximates to the pseudo-unimolecular. In the last two lines of Table II(b) are given the coefficients as calculated from equations (5) and (6) respectively. For this reaction mixture it will be noted that, although the course of the reaction is accounted for by a pseudo-unimolecular formula, the resulting coefficients are considerably greater than the true values obtained by means of equation (5).

The results given above are typical of those obtained throughout the experiments, and the remainder are therefore given in summarised form. In Table III, section A (cols. 2, 3, 4) and section B (col. 5), are given respectively the velocity coefficients for the first and the second series of experiments. Section C is discussed later. Inspection of the figures in sections A and B shows that the value of k_4 remains constant over only a limited range of b values, and thereafter increases steadily with increase in b. Since k is derived on the assumption that only the phenylbromoacetate ion is undergoing hydrolysis, the increase in k in solutions of high acidity might be taken as indicating that under these conditions the hydrolysis of the undissociated acid is no longer negligible in comparison with that of the ion. It is shown below, however, that such a conclusion does not necessarily follow if due regard is paid to the possible influence of other factors.

TABLE III.

0·025M-$CHPhBr{\cdot}CO_2H$ + bM-HNO_3 with added $NaNO_3$.

b.	A.			B.	C.
	$[NaNO_3] = 1 - b$.			$[NaNO_3]$ = 1.	
	10^4k_3.	10^4k_4.	10^4k_5.	10^4k_4.	$10^4k_{corr.}$
0	205	—	—	—	—
0·0100	207	—	—	—	—
0·0250	—	206	—	—	—
0·0500	—	207	—	211	209
0·100	—	209	—	213	212
0·200	—	214	213	222	220
0·300	—	221	221	228	230
0·500	—	232	232	240	247
1·00	—	254	254	266	285

In this connection it will be noted that in section A, where the total concentration of electrolyte remains practically constant throughout the series, there is a gradual replacement of sodium nitrate by nitric acid as b increases, whereas in section B the total electrolyte content of the solution increases continuously with the addition of nitric acid. Hence, in both cases, account must be taken of the possibility that the velocity of reaction will be modified by intervention of inert-salt effects. These effects may be expected to be two-fold: (i) there is the primary salt effect which influences the velocity of reaction directly, and (ii), since the apparent specific reaction rate is here a function of the equilibrium constant K, account must also be taken of the possible secondary salt effect.

Evidence as to the magnitude of the primary salt effect is provided by the figures given below, which refer to conditions under which secondary salt effects can play no part (Bulcraig and Dawson, *loc. cit.*). The numbers given in the last line of the table are obtained by means of the equation $10^4k_{calc.} = 181 + 31C$. It is thus clear that the primary salt effect is linear up to an ionic strength, μ, of about 2·0. The systematic differences which are found between the velocity coefficients for corresponding solutions in series A and B must be due, at least in part, to the primary salt effect of sodium nitrate, since the compositions of the two series of solutions differ only in respect of sodium nitrate content. On the basis of the above data an allowance for this difference in primary salt effect can be made. The correction is made by adding to each of the velocity coefficients given in Table III,A the quantity $31\Delta[NaNO_3]$, where $\Delta[NaNO_3]$ is the difference in sodium nitrate concentration between corresponding solutions (*i.e.*, identical b values) in the two series. The resulting values of $k_{corr.}$ are given in section C of Table III. A comparison of these numbers with the corresponding ones in section B shows that the two are in substantial agreement up to a value for b of nearly 0·5. It may be recalled that the velocity coefficients are a function of K, from which it is apparent that the agreement noted above implies that K has the same value in both series A and B; *i.e.*, the secondary salt effects do not differ appreciably in the two series. If it is borne in mind that as between the two series of solutions very considerable differences in total electrolyte concentration may exist, it becomes clear that, in the range of high electrolyte concentrations employed in these experiments, the value of K is relatively insensitive to quite large changes in ionic environment. The assumption of a constant value for K appears, therefore, to be amply justified over the greater part of the concentration range.

0·025M-$CHPhBr{\cdot}CO_2Na$ + 0·050M-NaOH + CM-$NaNO_3$.

C	0	0·425	0·925	1·425	1·925
$10^4k_{obs.}$	180	195	207	225	242
$10^4k_{calc.}$	181	194	210	224	241

This conclusion is also suggested by the evidence recorded by Dawson and Lowson (J., 1929, 1217) and it is pertinent that in the presence of a sufficiently large concentration of electrolyte, K will decrease with the addition of further electrolyte. It might reasonably be supposed that this stage is reached when μ has attained the value of 2·0, as in the last experiment in series B. The velocity coefficient for this mixture ($10^4k = 266$) is appreciably smaller than that for the corresponding solution in series A ($10^4k_{corr.} = 285$). It seems probable that this difference is due to a decrease in K in the solution of higher electrolyte content.

From the foregoing discussion it is clear that, with the exception of the solutions just noted, the increase in k with increase in concentration of nitric acid is real, and is therefore due either to the hydrolysis of the acid itself or to the primary salt effect on the specific reaction rate of the ion, brought about by the gradual increase in nitric acid concentration. If the latter be the case, the results given in B and C of Table III would require that the salt effect due to nitric acid should be about 2·6 times that due to sodium nitrate. No data on this point are available, but the figures given below for the effect on k of four different electrolytes (sodium salts or hydroxide) show the strongly specific nature of these effects :

Electrolyte.	Nitrate.	Perchlorate.	Hydroxide.	Mandelate.
Increase, %, in k for 0·925M-electrolyte	15·0	26·1	12·2	6·7

In view of these figures it would clearly be unsafe to reject the possibility that the observed changes in k are due entirely to the primary salt effect of the nitric acid and that the phenylbromoacetic acid is completely unreactive. It is therefore not possible to give a definite value for the specific velocity for the undissociated acid. On the other hand, a reliable estimate can be made of the maximum value that this coefficient can have.

The minimum value that can be assigned to the primary salt effect caused by nitric acid is obviously zero. On this supposition the increases in k in B and C of Table III will represent partial velocities due to the hydrolysis of the phenylbromoacetic acid. These partial velocities (Δk) are given in l. 3 of Table IV and are in each case the difference between the observed velocity coefficient (mean of values under B and C) and that for the phenylbromoacetate ion which is 207×10^{-4}.

Table IV.

$0{\cdot}025\text{M-CHPhBr}{\cdot}\text{CO}_2\text{H} + b\text{M-HNO}_3 + 1\text{M-NaNO}_3$.

b	0·050	0·100	0·200	0·300	0·500
$10^4 k_{\text{obs.}}$	210	213	221	229	244
$10^4 \Delta k$	3	6	14	22	37
$[\text{H}^+]$	—	0·11	0·21	0·31	0·51
$10^5 k$	—	3·3	4·1	4·3	4·4

The values for the specific velocity for the acid, k_m, are then obtained from $k_m = \Delta k/[\text{CHPhBr}{\cdot}\text{CO}_2\text{H}] = \Delta k{\cdot}K/[\text{H}^+]$ on taking for $[\text{H}^+]$ the mean of the initial and the final value for each experiment. The maximum value for k_m is thus about 4×10^{-5}. It can, therefore, be asserted that the reactivity of phenylbromoacetic acid, if indeed this is admitted at all, cannot be greater than about 0·002 of that of the phenylbromoacetate ion.

Experimental.—The reaction was started by dissolving the phenylbromoacetic acid in the appropriate aqueous solution, and followed by estimating the liberated bromide, as previously described. In the absence of free alkali the dissolution of the acid is slow and hence it is not possible to assess directly an exact time for the commencement of the reaction. This was obtained as follows. For each of the velocity equations a straight line is obtained when a function of x or y is plotted against time. The intercept of the line on the time axis gives the error in the estimated zero time which is used in making the plot. This correction, which is usually 1—4 minutes, is added or substracted to give the true zero time of the reaction.

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