

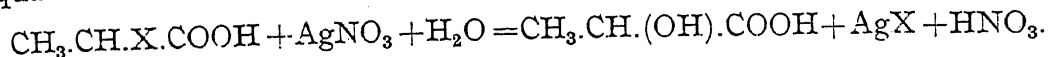
# KINETICS OF THE REACTION BETWEEN *α* BROMPROPIONATE AND SILVER IONS.

A Heterogeneous Reaction taking place on the Surface of Silver Bromide.

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BECKERTS AND ODDO<sup>1</sup> showed that halogen-substituted propionic acids react with silver nitrate quantitatively in the manner indicated by the equation



In the course of his investigations on the reactivity of halogens in substituted fatty acids, Senter<sup>2</sup> made a brief study of the reaction between *α* brompropionate and silver ions and obtained very interesting kinetic data. He found, in fairly dilute solutions, that the bimolecular velocity constants gradually increased as the reaction progressed and the initial velocity constant was found to be dependent upon the dilution of the solutions. Senter attributed the increase in velocity constant with the progress of the reaction to the catalytic effect of the silver halide formed during the course of the reaction and the greater initial velocity in the more dilute solutions to the greater electrolytic dissociation of the reacting salts.

The reaction presents interesting features viewed from different standpoints. First, here we have a reaction which is essentially a hydrolytic one. Senter<sup>3</sup> has shown that sodium brompropionate does not very readily undergo the hydrolytic change in pure aqueous solutions even at fairly high temperatures. In mixtures of sodium brompropionate and silver nitrate, however, the reaction proceeds with great rapidity even at ordinary temperatures. The accelerating effect of silver nitrate in such halogen replacements appears to be quite well known<sup>4</sup> but its mechanism has not been elucidated. Secondly, if, as has been observed by Senter,<sup>2</sup> the silver bromide formed in the course of the reaction exerts a catalytic effect also, the rapid hydrolytic reaction is probably the result of a composite catalytic action—homogeneous and heterogeneous. The present investigation was undertaken with a view to elucidate the probable mechanism of the reaction, by a detailed kinetic study.

*Experimental.*

Senter pointed out that during the course of the reaction, the silver bromide formed, which remains in suspension for some time, coagulates after a while and settles down at the bottom or floats at the top of the solutions. The conditions of experiment will not, therefore, be uniform and this difficulty prevents a systematic treatment of the data. Preliminary experiments showed that in solutions much more dilute than the ones employed by Senter the silver bromide suspension could remain quite stable for some hours, without coagulation, if the silver bromide is formed in presence of excess of silver nitrate. Since in the present investigation, silver nitrate happens to be one of the reacting components and always remains in excess during the progress of the reaction, it is possible to test the catalytic effect of silver bromide under fairly reproducible conditions.

Senter's study was confined to two dilutions; the concentrations of silver nitrate and sodium brompropionate were N/30 each in one case and N/60 each in the other. He followed the reaction by titrating portions of the reaction mixture against N/50 ammonium thiocyanate solution, thus determining the amount of silver nitrate remaining in the mixture at any given time. In the present work this method has been adopted only in a few cases, where the concentration of silver nitrate in the reaction mixture was in the neighbourhood of N/50. In all other cases the reaction has been followed by estimating the amount of acid liberated in the reaction at different intervals in the following way. At intervals a definite quantity of the reaction mixture was pipetted out and excess of potassium iodide was added to it to arrest the reaction immediately; potassium iodate was next added to the mixture. Potassium iodide and iodate together quantitatively react with the hydrogen ion formed in the reaction and liberate an equivalent amount of iodine. The iodine thus liberated was titrated against standard N/100 or N/200 thiosulphate solution. This procedure has the double advantage of enabling us to arrest the reaction at any desired moment and to study the reaction in very dilute solutions.

The experiments were all carried out in bottles covered with black paint on the outside, to prevent the silver bromide from being acted upon, as far as possible, by the diffuse light of the laboratory. It may be mentioned, however, that a few experiments carried out in uncovered bottles gave the same results as in covered bottles. The bottles containing the reaction mixtures were kept in an electrically regulated thermostat. All the experiments described in this paper were carried out at 27° C.

The salts used in this study were all purified by recrystallisation and all the solutions were prepared in conductivity water obtained from a Bartley's still.

Tables I and II contain results obtained with the same concentrations of the reactants, 0.03 N sodium bromopropionate and 0.02 N silver nitrate. In the first case (Table I) the reaction was followed by titrating 25 c.c. of the reaction mixture against N/50 potassium thiocyanate and in the second case (Table II) by treating the same volume of the reaction mixture with potassium iodide and iodate mixture and titrating the liberated iodine against N/50 sodium thiosulphate. In both these experiments the first titration was performed two minutes after the reactants were mixed together. The two experiments were carried out at different times to compare the results obtained by adopting the different methods of analysis.

TABLE I.

Time in minutes	c.c. AgNO <sub>3</sub>
0	23.00
5	19.80
10	16.40
15	13.20
20	10.50
25	9.85
30	9.50
35	9.40

TABLE II.

Time in minutes	c.c. Hypo.	c.c. AgNO <sub>3</sub>
0	2.10	22.90
5	5.35	19.65
10	8.55	16.45
15	12.05	12.95
20	14.70	10.30
25	15.25	9.75
30	15.35	9.65
35	15.45	9.55

It will be observed that the figures at different corresponding intervals in the two tables do not differ appreciably from one another. After about twenty minutes it was observed in both the experiments that coagulation of silver bromide commenced, a portion of it sinking to the bottom and a portion rising to the surface. This was accompanied, as will be seen from the tables, by a fall in the velocity of the reaction.

The bimolecular velocity constants calculated from the data in Table I are shown in Table III.

TABLE III.

Time in minutes	c.c. AgNO <sub>3</sub>	c.c. brom-propionate	K <sub>2</sub>
0	23.00	35.50	
5	19.80	32.30	1.104
10	16.40	28.90	1.325
15	13.20	25.70	1.546
20	10.50	22.50	1.638

It is clear from these results that the velocity of reaction increases as the reaction progresses, indicating the existence of an autocatalytic effect. This result is very similar to the one obtained by Senter.<sup>2</sup>

Further experiments were carried out in more dilute solutions to find out the conditions under which the silver bromide formed in the reaction remains as a stable suspension almost upto the end of the reaction, in the reaction mixtures. The results are recorded in the tables below. Figures in column four of the tables are the bimolecular velocity constants calculated from the data in the first three columns.

TABLE IV.

Concentration of sodium brompropionate 0.015 N = *b*  
 Concentration of silver nitrate 0.01 N = *a*  
 25 c.c. titrated each time against N/50 thiosulphate.

Time in minutes	( <i>a</i> - <i>x</i> )	( <i>b</i> - <i>x</i> )	K <sub>2</sub>	( <i>c</i> + <i>x</i> )	K <sub>3</sub>
0	11.65	17.90		0.85	
5	10.90	17.15	0.8496	1.60	9.93 × 10 <sup>2</sup>
10	8.70	14.95	2.2402	3.80	10.34 ,, ,,
15	7.45	13.70	2.3920	5.05	11.15 ,, ,,
20	6.20	12.45	2.6726	6.30	10.54 ,, ,,
*25	5.05	11.30	3.0038	7.45	10.02 ,, ,,
30	4.65	10.90	2.7516		10.39 ,, ,, mean value
40	4.55	10.80	2.1758		

\* Coagulation became perceptible at this stage.

TABLE V.

Concentration of sodium brompropionate  $0.006 N = b$   
 Concentration of silver nitrate  $0.004 N = a$   
 25 c.c. titrated each time against N/100 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	$K_2$	$(c+x)$	$K_3$
0	9.30	14.30		0.70	
5	8.85	13.85	1.7940	1.15	$4.59 \times 10^3$
10	8.15	13.15	2.4035	1.85	3.49 ,, ,,
15	7.35	12.35	2.9510	2.65	4.84 ,, ,,
20	6.60	11.60	3.3465	3.40	4.56 ,, ,,
25	5.85	10.85	3.7490	4.15	4.36 ,, ,,
30	5.20	10.20	4.0560	4.80	4.14 ,, ,,
40	3.75	8.75	5.2095	6.25	4.10 ,, ,,
50	2.75	7.75	6.0536	7.25	3.99 ,, ,,
60	1.85	6.85	7.3151	8.15	4.26 ,, ,, mean value

At the dilutions in the last three cases (Tables V-VII) the silver bromide formed during the course of the reaction remained as a fine suspension and no coagulation was observable during the time the experiments were in progress.

Experiments carried out at greater dilutions showed that the initial formation of silver bromide was very slow and that during the first five or six hours even ten per cent. of the silver nitrate in the reaction mixture had not reacted with the brompropionate.

The results in the above tables show that the initial velocity of the reaction is much faster in solutions in which the reactants are present in greater concentrations. These results, therefore, do not support Senter's inference<sup>2</sup> (based on only two experiments) that the initial velocity is greater at greater dilutions in this reaction.

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TABLE VI.

Concentration of sodium bromopropionate  $0.003 N = b$

Concentration of silver nitrate  $0.002 N = a$

25 c.c. titrated each time against N/200 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	$K_2$	$(c+x)$	$K_3$
0	9.65	14.65		0.35	
10	9.25	14.25	0.1900	0.75	$1.384 \times 10^4$
20	8.65	13.65	0.2415	1.35	1.278 ,, ,,
30	7.70	12.70	0.2789	2.30	1.255 ,, ,,
40	6.55	11.55	0.3772	3.45	1.234 ,, ,,
50	5.45	10.45	0.4683	4.55	1.196 ,, ,,
60	4.35	9.35	0.5784	5.65	1.182 ,, ,,
70	3.20	8.20	0.7461	6.80	1.114 ,, ,,
					<u>1.250</u> ,, ,, mean value

TABLE VII.

Concentration of sodium bromopropionate  $0.0015 N = b$

Concentration of silver nitrate  $0.0010 N = a$

50 c.c. titrated each time against N/200 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	$K_2$	$(c+x)$	$K_3$
0	9.65	14.65		0.35	
30	9.30	14.30	0.1917	0.70	$1.675 \times 10^4$
60	9.00	14.00	0.2319	1.00	1.30 ,, ,,
120	7.80	12.80	0.3191	2.20	1.22 ,, ,,
180	5.70	10.70	0.5865	4.30	1.28 ,, ,,
270	4.30	9.30	0.6610	5.70	1.06 ,, ,,
330	3.30	8.30	0.7658	6.70	1.02 ,, ,,
					<u>1.26</u> ,, ,, mean value

These results at the same time indicate, beyond doubt, that in solutions in which the silver bromide formed in the reaction does not coagulate and settle down, the velocity of reaction, as judged by the bimolecular velocity coefficient  $K_2$ , uniformly increases with the progress of the reaction. It is quite obvious from this that the reaction product or products exert a catalytic effect on the reaction. That the catalyst is the finely suspended silver bromide formed in the reaction is evidenced by the arrest of the reaction, observable from data in Tables I and II and IV when the silver bromide coagulates and settles down, the tremendous slowing down of the reaction rate being due to the large diminution in the surface area of the particles on coagulation.

In very dilute solutions (below 0.001 N) the reaction does not start at all for quite a long time and until some silver bromide is formed the speed of the reaction is immeasurably small; which shows that the reaction in the homogeneous phase is of a negligible order of magnitude. In other words, the reaction appears to proceed almost entirely on the surface of the silver bromide particles. The bimolecular velocity coefficient  $K_2$  in the above tables, therefore, apart from indicating the general dependency of the rate of reaction on the amount of silver bromide in suspension in the reaction mixture, has very little quantitative significance unless it is considered in relation to the surface area of the seat of reaction.

It has been pointed out above that the reaction does not start at all in extremely dilute solutions for quite a long time and that the presence of at least a trace of silver bromide appears to be essential to initiate the reaction. It is important to bear in mind that the hydrolytic process is one that can and does proceed in solutions containing only sodium bromopropionate; but the process is an extremely slow one and the greater the dilution of sodium bromopropionate the slower the hydrolysis. In more concentrated solutions of this salt, the amount of hydrobromic acid formed in the first few seconds or even minutes is probably quite sufficient to produce enough of silver bromide in the heterogeneous phase (on the addition of silver nitrate), to start the rapid catalysed reaction; whereas in very dilute solutions it will take considerable time for enough bromide ion to form from homogeneous hydrolysis before the solubility product of silver bromide is reached and a certain amount of the halide separates in the heterogeneous phase.

A few experiments were carried out, both in moderately concentrated solutions and in dilute solutions, to see if silver bromide prepared as a colloidal solution when added to a solution of sodium bromopropionate (without the addition of any silver nitrate) would accelerate the hydrolytic process. It was found that the amount of hydrolysis brought about was not more

than 2-3 per cent. of the total concentration of the brompropionate in the course of about 24 hours. It was also observed that the suspensions were very unstable and coagulation set in in the first few hours after the mixtures were made. It would therefore appear that silver ions adsorbed on the surface of silver bromide particles are the effective agents in accelerating the reaction; the actual reaction probably takes place between brompropionate and silver ions both held adsorbed on the surface of the silver bromide particles (the water necessary for the reaction being available in abundance all round the particles). We thus arrive at a qualitative picture of the possible mechanism of the reaction.

Since it is observed that in solutions in which silver bromide remains as a stable suspension, the bimolecular velocity constant increases steadily with the progress of the reaction, *i.e.*, with the progressive addition of silver bromide to the reaction system, if we make an assumption that the velocity of reaction is proportional to the amount of silver bromide present in suspension at any interval—which is tantamount to making an assumption, in view of the mechanism of the reaction pictured in the previous paragraph, that the effective surface of silver bromide in suspension is proportional to its concentration expressed in molecules per litre—the rate of reaction could be expressed by the equation

$$dx/dt = K_3 \cdot (a-x) \cdot (b-x) \cdot (c+x)$$

where  $(a-x)$  and  $(b-x)$  represent the concentrations of silver nitrate and sodium brompropionate respectively and  $(c+x)$  the amount of silver bromide in suspension, at any given instant, expressed in terms of molecules of the substance per litre. On integrating the above expression we get

$$K_3 = \frac{2.3 \left( (b-a) \times \log \frac{c+x}{x} + (b+c) \log \frac{a}{(a-x)} - (a+c) \log \frac{b}{(b-x)} \right)}{t \cdot (a+c) (b+c) (b-a)}$$

The figures in column 6 of the Tables IV-VII are obtained by calculating the constants in accordance with the above equation. The constancy of  $K_3$  in each of the tables provides ample proof of the general validity of the assumptions made above.

It will be observed that  $K_3$  in different tables has different values. In the more dilute solutions the value of  $K_3$  is greater than in the comparatively more concentrated solutions.

Further experiments were carried out with the object of elucidating, how, at great dilutions, where the reaction proceeds rather slowly (*e.g.*, Table VII), the initial formation of some silver bromide in suspension at the time of the addition of silver nitrate to the reaction mixture would affect the reaction rate. The procedure adopted in the following experiments was as follows:—



To the brompropionate solution contained in a measuring flask (in which the reaction mixture was prepared so as to adjust the concentrations at the desired value by starting with known amounts of more concentrated solutions and subsequent dilution) any desired amount of a standard solution of potassium bromide solution was added and the mixture diluted leaving enough of room for the addition of silver nitrate. An amount of silver nitrate required for the reaction proper and for reacting with potassium bromide was next added, the mixture being kept continuously shaken during the course of the addition. The mixture was finally made upto the mark by the addition of water. The silver bromide was thus formed in the reaction mixture itself in the presence of excess of silver nitrate. The results of these experiments are shown in Tables VIII to XI. The initial concentrations of the reactants in these experiments were

Silver nitrate .. .. . 0.001 N  
Sodium brompropionate 0.0015 N

The initial amounts of silver bromide present in the different experiments are indicated in the tables. 50 c.c. of the reaction mixture was titrated in each case against N/200 thiosulphate solution.

The concentrations of the reactants in the four experiments were the same as in the experiment the results of which appear in Table VII. It

TABLE VIII.

*Silver bromide initially present 0.00050 mols. per litre.*

Time in minutes	(a-x)	(b-x)	(c+x)	$K_3$
0	8.80	13.80	6.20	
3	7.50	12.50	7.50	$5.052 \times 10^4$
8	6.15	11.15	8.85	4.46 ,, ,,
13	4.90	9.90	10.10	4.50 ,, ,,
18	4.15	9.15	10.85	4.18 ,, ,,
23	3.10	8.10	11.90	4.56 ,, ,,
30	2.40	7.40	12.60	4.40 ,, ,,
40	1.40	6.40	13.60	4.79 ,, ,,
				<u>4.56</u> ,, ,, mean value

TABLE IX.

*Silver bromide initially present 0.00075 mols. per litre.*

Time in minutes	( $a-x$ )	( $b-x$ )	( $c+x$ )	$K_3$
0	9.00	14.00	8.50	
4	7.15	12.15	10.35	$4.71 \times 10^4$
8	5.60	10.60	11.90	4.80 ,, ,,
12	4.55	9.55	12.95	4.60 ,, ,,
16	3.65	8.65	13.85	4.59 ,, ,,
21	3.00	8.00	14.50	4.30 ,, ,,
27	2.25	7.25	15.25	4.30 ,, ,,
35	1.50	6.50	16.00	4.40 ,, ,,
				<u>4.60</u> ,, ,, mean value

TABLE X.

*Silver bromide initially present 0.0010 mols. per litre.*

Time in minutes	( $a-x$ )	( $b-x$ )	( $c+x$ )	$K_3$
0	8.40	13.40	11.60	
3	6.60	11.60	13.40	$5.155 \times 10^4$
7	5.10	10.10	14.90	4.600 ,, ,,
11	4.00	9.00	16.00	4.44 ,, ,,
15	3.30	8.30	16.70	4.14 ,, ,,
20	2.55	7.55	17.45	4.07 ,, ,,
30	1.60	6.60	18.40	3.94 ,, ,,
				<u>4.40</u> ,, ,, mean value

will be seen that while no silver bromide was initially added to the mixture, six to seven hours are required to enable two-thirds of the silver nitrate to

TABLE XI.

*Silver bromide initially present 0.0015 mols. per litre.*

Time in minutes	$(a-x)$	$(b-x)$	$(c+x)$	$K_3$
0	7.55	12.55	17.45	
3	5.70	10.70	19.30	$4.45 \times 10^4$
7	4.15	9.15	20.85	4.20 ,, ,,
11	3.05	8.05	21.95	4.16 ,, ,,
15	2.35	7.35	22.65	4.10 ,, ,,
19	1.90	6.90	23.10	3.91 ,, ,,
25	1.35	6.35	23.65	3.90 ,, ,,
				4.12 ,, ,, mean value

react, the presence of 0.0005 mol. of silver bromide in the reaction mixture at the start of the reaction enables the reaction to go to completion in less than an hour.

It is also noteworthy that in spite of the wide variation in the initial amounts of silver bromide in suspension in these different experiments the value of the velocity constant  $K_3$  in all these cases is sensibly the same. These experiments were repeated very carefully and it was found that the results could be very easily reproduced correct to within 2-3 per cent. The term  $(c+x)$  is introduced into the velocity expression on the assumption—a very arbitrary assumption at the outset—that the surface offered for reaction is proportional to the amount of silver bromide present in the suspension at any instant. It is remarkable that the constancy of  $K_3$  in these different experiments should so amply justify this assumption. It appears quite justifiable to infer from these data that the silver bromide particles formed in these reaction mixtures are probably of such sizes and shapes that their surface areas are proportional to their masses.

From the standpoint of the kinetics of heterogeneous reactions, since we find, in these dilute solutions, that the velocity of reaction is proportional to the concentration of each one of the reactants raised to the power of one, we infer that the reacting ions are both sparsely adsorbed on the surface of the catalyst.

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Experiments were next carried out to see the influence of varying the concentrations of the reactants on the velocity coefficient, when in all the different cases the same amount of silver bromide is generated at the start of the reaction. The results of these experiments are summarised in Table XII. In each one of these experiments very steady constants were obtained almost upto the end of the reaction.

TABLE XII.

*Silver bromide initially present in the reaction mixtures 0.0010 mols. per litre.*

Conc. of brom-propionate	Conc. of silver nitrate	$K_3$
0.0015 N	0.0005 N	$5.7 \times 10^4$
do.	0.0010 N	4.4 ,, ,,
do.	0.0020 N	2.94 ,, ,,
do.	0.0030 N	2.30 ,, ,,
do.	0.0040 N	1.95 ,, ,,
0.00075 N	do.	2.72 ,, ,,
do.	0.0010 N	4.75 ,, ,,
0.00015 N	do.	4.40 ,, ,,
0.0020 N	do.	4.00 ,, ,,
0.0030 N	do.	3.45 ,, ,,
0.0040 N	do.	3.20 ,, ,,
0.0060 N	do.	2.86 ,, ,,

A survey of these data shows that when the concentration of one of the reactants is kept constant and that of the other increased  $K_3$  gradually diminishes in value. Since under all these circumstances, the reaction rate is always found to be proportional to the concentration of each one of the reactants raised to the first power, there can be no doubt that even when the concentrations are varied over the wide range indicated in Table XII, the surface of the catalyst must be only sparsely covered by the reactants in these different cases. The reaction takes place between the two kinds of ions in the adsorbed layer and it can take place only when the two