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CHEMICAL KINETICS. II. THE INFLUENCE OF RELATIVE POSITION OF ELECTRIC CHARGE AND REACTING GROUP ON THE VELOCITY OF THE BROMOPROPIONATE-THIOSULFATE REACTION

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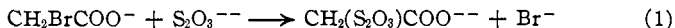
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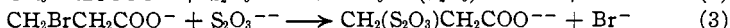
I. Introduction

It is well known that the velocities of bimolecular ionic reactions are markedly influenced by the number of ions present as well as by the sign and magnitude of the excess charge upon them. These kinetic effects designated by Brönsted as primary salt effects are the result of the relatively greater opportunity for collision between ions of opposite sign than between ions of the same sign. They have been accounted for successfully in dilute solutions by the theory of inter-ionic attraction.

Except for two papers¹ (which will be considered later), giving relevant but not complete data, no measurements exist for a consideration of the more detailed problem of the possible kinetic effect arising from the structural position of the charge of the ion in relation to the structural position, within the ion, of the specific group which reacts chemically with the second ion. Except for a remark by Bjerrum² that the problem is not without interest and a brief discussion by Christiansen, no one appears to have even considered this possibility. The reactions between thiosulfate ion and the various brominated fatty acids furnish a type of reactions capable of answering this question. Thus, if we consider the reaction



which has been studied, previously, in this Laboratory,³ and elsewhere,⁴ and the analogous reactions



it is evident that the chemical reaction involves the exchange of bromine for thiosulfate in each case. From electrostatic considerations, (3) should be more rapid than (2) because the electrical field of force repelling the entering negative thiosulfate ion is less intense in the beta position than in the alpha position. Chemical theory, alone, without electrostatic considerations would predict the opposite effect.

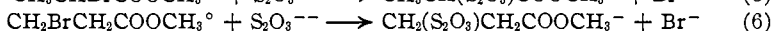
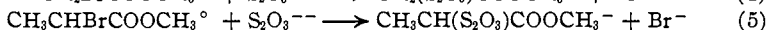
¹ (a) H. Euler, *Ber.*, **39**, 2726 (1906); (b) H. J. Backer and W. H. Van Mels, *Rec. trav. chim.*, **49**, 177 (1930).

² N. Bjerrum, *Z. physik. Chem.*, **113**, 82 (1924); J. A. Christiansen, *ibid.*, **113**, 35 (1924).

³ Victor K. La Mer, *THIS JOURNAL*, **51**, 3341 (1929); Paper No. 1 of this series.

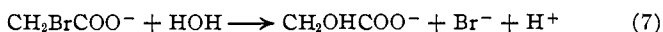
⁴ (a) A. Slator, *J. Chem. Soc.*, **87**, 481 (1905); (b) S. Krapiwins, *Z. physik. Chem.*, **82**, 439 (1913); (c) A. N. Kappana, *J. Indian Chem. Soc.*, **6**, 45 (1929); **6**, 419 (1929).

In order to determine quantitatively the role which relative position of charge and reacting group plays, it is necessary to eliminate the various influences upon the reactivity of the bromine atom which are dependent upon its structural position but independent of the presence of a neighboring charge. This can be accomplished by determining the rates of reaction of thiosulfate with the corresponding esters of the brominated fatty acids.

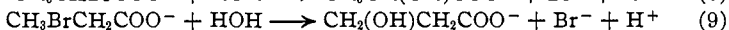
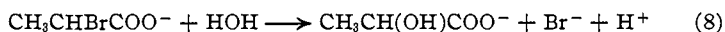


Then, by comparing the ratios of ion rate/ester rate in each case, we measure the influence which the electric charge exercises in determining the rate of reaction.⁵

As the investigation proceeded, it became apparent that reactions (2) and (3) are not as simple as represented. Although the rate of the simultaneous water reaction



is quite negligible as compared with the thiosulfate reaction (1), when bromoacetate ion is employed, this simplicity does not obtain in the spontaneous water reactions of the homologous acids—the water reactions being sufficiently rapid, in the case of the propionates, to be appreciable. These two reactions to be discussed later are⁶



II. Preparation and Purification of Reagents

For an investigation of this kind purity of reagents is important. A redistilled sample of Kahlbaum's bromoacetic acid, m. p. 50.6–50.9° (Beilstein 50–51°), yielded kinetic results almost identical with those obtained with the bromoacetic acid used in the previous investigation. The propionic acids were Eastman's products and were redistilled at 10 mm. pressure before use. The esters were prepared according to the directions of Lepercq,⁷ Lederer,⁸ and Drushel and Hill,⁹ by heating on a sand-bath a mixture of the brominated acid with an excess of methyl alcohol and refluxing for two hours. The product was neutralized with sodium carbonate, poured into a large volume of water and after washing was

⁵ Except for one value of Slator's, *J. Chem. Soc.*, **87**, 481 (1905), for the rate of reaction between methyl bromoacetate and thiosulfate, there are no data in the literature for these last three reactions.

⁶ Reactions (8) and (9) have been studied by Senter [*ibid.*, **91**, 460 (1907)], but only at 52.4 and 79°, and the results of Simpson [*THIS JOURNAL*, **40**, 674 (1918)] were obtained at 70°.

⁷ M. G. Lepercq, *Bull. soc. chim.*, [3] **11**, 297 (1894).

⁸ L. Lederer, *J. prakt. Chem.*, **42**, 384 (1890).

⁹ W. A. Drushel and J. W. Hill, *Am. J. Sci.*, **180**, 72 (1910).

dried over calcium chloride and fractionated. The esters of bromoacetic and bromopropionic acids were distilled at reduced pressure to prevent decomposition. Table I gives a summary of the properties indicating the purity of the compounds used. The figures for bromine content were determined by the micro Carius method.¹⁰

TABLE I
PURITY OF COMPOUNDS

Compound	Final purification	Bromine content, %	
		Calcd.	Found
Bromoacetic acid	Distn., 79° 10 mm.	57.52	56.58 ± 0.02
α-Bromopropionic acid	Distn., 73-75° 10 mm.	52.24	53.12 ± 0.03
β-Bromopropionic acid	Distn., 94-95° 10 mm.	52.24	52.26 ± 0.01
Me ester bromoacetic acid	Distn., reduced pressure	52.24	53.09 ± 0.08
Me ester α-bromopropionic acid	Distn., 147-150°	47.86	48.94 ± 0.06
Me ester β-bromopropionic acid	Distn., reduced pressure	47.86	48.10 ± 0.10
Sodium hydroxide	Concentrated solution of Kahlbaum product was filtered according to directions of Clark ¹¹		
Sodium thiosulfate	c. p. salt was recrystallized and air dried		

It has been found by Slator and Twiss¹² and by La Mer¹³ that one equivalent of sodium bromoacetate reacts with one equivalent of sodium thiosulfate, and in the present investigation that one equivalent of sodium β-bromopropionate reacts with 0.98 equivalent of sodium thiosulfate when the latter is in excess. Under the same conditions one equivalent of sodium α-bromopropionate was found to react with not more than 0.935 equivalent of sodium thiosulfate before the solution showed signs of decomposition, due to the exceedingly long time (more than thirty days) required for the completion of the reaction. There is no valid reason to doubt that the results would have been similar to those for the salt of the β-acid had it not been for this interference.

In the case of the esters it was observed by Slator that one equivalent of methyl bromoacetate reacts with one equivalent of sodium thiosulfate^{4a} and that the ethyl ester of α bromopropionate reacts with only 0.93 equivalent of sodium thiosulfate.¹²

III. Experimental

All experiments were made at $25 \pm 0.01^\circ$. Volumetric apparatus was calibrated. Distilled water, freed from carbon dioxide by boiling, was used in the reaction mixtures.

For thiosulfate reactions (1), (2) and (3) the required amount of bromi-

¹⁰ These bromine determinations were made in duplicate by the Research Service Laboratories, 37 East 28th Street, New York City.

¹¹ W. M. Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, p. 195.

¹² A. Slator and D. F. Twiss, *J. Chem. Soc.*, 95, 93 (1909).

¹³ Victor K. La Mer, *THIS JOURNAL*, 51, 3341 (1929).

nated acid was weighed out, neutralized with sodium hydroxide solution, using phenolphthalein, and, in some cases, brom thymol blue as an indicator, and made up to volume. The desired amount of sodium thiosulfate solution was pipetted into each reaction flask (200-cc. capacity, fitted with ground-glass stopper and trough for potassium iodide solution when needed to prevent loss of vapor if the flask contained iodine solution). With both salt and thiosulfate solutions at 25° the former was added to the latter in the reaction flask, taking into account the time of delivery of the pipets. The stopwatch was frequently checked against Naval Observatory Time. The reaction was stopped by adding an excess of iodine solution. The excess (approximately 0.01 *N*) was back titrated at once with dilute sodium thiosulfate solution.

For reactions (4), (5) and (6) the procedure was the same, the ester solution replacing the salt solution.

To study reactions (7), (8) and (9) solutions of the sodium salts of the brominated acids were kept in the thermostat and portions removed for titration with standard sodium hydroxide solution.

In a second series of experiments, to avoid the catalytic effect of the hydrogen ion liberated, the standard base was added at frequent intervals to a large volume of the solution to keep the solution neutral to brom thymol blue as an internal indicator—that is, the hydrogen ion was titrated as soon as it was liberated.

IV. Analytical

The iodine solutions containing 4% of potassium iodide were kept in dark bottles. They were standardized against Kahlbaum's arsenious oxide according to the directions of Washburn.¹⁴

Sodium thiosulfate was made up in 0.1 *M* solutions from which more dilute solutions were prepared and standardized against iodine. The use of stock bottles which had been dried at a high temperature, boiled water, and a minimum time of contact of solutions with air made possible quite stable solutions of thiosulfate, although frequent restandardizations were performed as a check. We have many data to show that 0.01 *N* thiosulfate solutions when so prepared retain their titer to within one part per thousand for at least a week. With weight burets a precision of one part per thousand is easily obtained.

The 0.5% starch solutions were prepared from potato starch by boiling for two hours, filtering through cotton and sterilizing at eighteen pounds' pressure in cotton stoppered tubes. Under the conditions of our experiments we find that $6 \cdot 10^{-7}$ equivalent of iodine is sufficient to produce a detectable color. This correction is negligible except for the most dilute solutions; the blank correction was applied whenever it was significant.

¹⁴ E. W. Washburn, *THIS JOURNAL*, 30, 31 (1908).

The stability of the very dilute thiosulfate solutions under the exact conditions of the experiments was controlled by blank experiments. After four thousand minutes we recovered 99.99% at P_H 6.5 and 99.96% at P_H 4.5. In the more acid solutions necessary for studying the rate of reaction of the undissociated brominated fatty acid, the instability of thiosulfate becomes important and the necessary corrections for blanks were made in these cases. These data for very acid solutions, however, are used only in a qualitative sense.

Although the P_H of the brominated ion plus thiosulfate ion reactions was initially 7, owing to access of carbon dioxide from the air and the liberation of traces of hydrogen bromide, the P_H at the time of titration was more often 6 than 7. Moreover, even at P_H 7 recovery of thiosulfate from 0.002 N thiosulfate solutions (by adding excess iodine and back titrating with thiosulfate) was 100.9%, the initial amount present having been determined by a 0.01 N thiosulfate, 0.03 N iodine standardization.

We have been unable to detect any perceptible difference in the velocity constants when the reaction is stopped by titrating the residual thiosulfate with standard iodine as against the method of adding excess iodine and back titrating with thiosulfate. It is important to note that any minute error due to the course of the iodine-thiosulfate reaction in 0.01 N solution is canceled out since the thiosulfate was always standardized by the same iodine solution at the time of making the experiment.

It has been shown that the constants for the β -bromopropionate-thiosulfate reaction, in the most dilute region, obtained when the reaction was carried on under nitrogen and with the reaction mixture brought to a P_H of approximately 5, immediately before the addition of iodine (run number 83), show no significant difference from those obtained in the other runs.

For the second order reactions (1), (2), (3), (4), (5), (6)

$$k = \frac{1}{(a-b)} \cdot \frac{1}{t} \cdot \ln \frac{b \left(\frac{a''}{b''} - x \right)}{a \left(\frac{a''}{b''} - x \right)} \quad \text{when } a > b$$

$$k = \frac{1}{t} \frac{1}{a} \frac{x}{(a-x)} \quad \text{when } a = b$$

where k is velocity constant: a is initial concentration in moles per liter of thiosulfate; b is initial concentration in moles per liter of salt, or ester; x is equivalents of b converted = equivalents of thiosulfate used; " a'' " and " b'' " are equivalents present, at beginning of reaction; t is time in minutes. For the first order reactions (7), (8) and (9), $k = (1/t) \ln [a/(a-x)]$, where a is equivalents of salt present, at beginning of reaction; x is equivalents of H^+ titrated with alkali = equivalents of salt converted by water reaction.

Since so far as we are aware no one has worked out the kinetics of first and second order reactions proceeding independently and simultaneously

in a solution, we give the following development by R. W. Fessenden of this Laboratory.¹⁵ Let k_1 be velocity constant for first order reaction; k_2 , velocity constant for second order reaction; a , substance disappearing by two reactions; b , substance disappearing by second order reaction only; dx/dt be rate of first order reaction; dy/dt be rate of second order reaction; then

$$\frac{dx}{dt} = k_1(a - x - y) \quad (10)$$

$$\frac{dy}{dt} = k_2(a - x - y)(b - y) \quad (11)$$

where a is concentration of salt in moles per liter; b is concentration of thiosulfate in moles per liter; x is moles per liter of salt transformed by water reaction; and y is moles per liter of salt transformed by thiosulfate reaction. Dividing (10) by (11) we obtain

$$\frac{dx}{dy} = \frac{k_1}{k_2(b - y)} \quad (12)$$

which gives

$$-x = \frac{k_1}{k_2} \ln(b - y) + C \quad (13)$$

When $x = 0$ and $y = 0$, then $C = -(k_1/k_2) \ln b$, or

$$x = \frac{k_1}{k_2} \ln \frac{b}{(b - y)} \quad (14)$$

Substituting this value of x in (11) we obtain

$$\frac{dy}{dt} = k_2 \left[a - y - \left(\frac{k_1}{k_2} \ln \frac{b}{(b - y)} \right) \right] (b - y) \quad (15)$$

By use of the calculus of finite differences, dy/dt can be evaluated for any given time, t . All other quantities except k_2 are known, and the equation is solved for k_2 . This formula applied to the β -bromopropionate-thiosulfate runs in the dilute region gives a corrected bimolecular constant greater than the uncorrected constant. The correction is negligible in concentrated solutions. Evidence will be given later to show that the assumption that the two simultaneous reactions are proceeding independently is not warranted and that the k_1 values obtained in the absence of thiosulfate are much larger than those obtained in its presence. The correction consequently becomes negligible even in dilute solution. It is important, however, to note that this water reaction correction is of the wrong sign to account for the anomalous results for the β -ion to be discussed later.

¹⁵ The formula of Brönsted, Kilpatrick and Kilpatrick, [THIS JOURNAL, 51, 428 (1929)], for the disappearance of epichlorohydrin in a buffer solution, by two paths—that is, by reaction with water and with an anion—was developed for a case in which the concentration of anion remains constant. This cannot be applied to reactions in which brominated fatty acid ion reacts with water and with thiosulfate, since the concentration of the thiosulfate ion does not remain constant throughout the reaction.

V. Typical Runs

TABLE II

RUN 8. SODIUM BROMOACETATE AND THIOSULFATE

$\sqrt{\mu} = 0.493$ "a" = 2.094×10^{-3} $a = 0.0698$
 $\mu = \text{ionic strength}$ "b" = 1.000×10^{-3} $b = 0.0333$

Time, min.	10^3 Equiv. thio. used	k
8	0.294	0.674
12	.399	.680
16	.488	.692
23	.602	.694

Av. $k = 0.685 \pm 0.008$

TABLE III

RUN 81. SODIUM α -BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.408$ "a" = 2.102×10^{-3} $a = 0.04204$
"b" = 2.000×10^{-3} $b = 0.04000$

Time, min.	10^3 Equiv. thio. used	$10^3 k$
1529	0.494	5.03
1652	.515	4.92
2618	.708	4.92
2973	.771	4.94
3355	.832	4.98
4081	.931	4.98

Av. $k = 4.96 \pm 0.035 \times 10^{-3}$

TABLE IV

RUN 33. SODIUM α -BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.237$ "a" = 2.108×10^{-3} $a = 0.01622$
"b" = 1.000×10^{-3} $b = 0.00769$

Time, min.	10^3 Equiv. thio. used	$10^3 k$
4036	0.231	4.25
5489	.299	4.31
6894	.357	4.35
9753	.455	4.38
12,738	.534	4.35

Av. $k = 4.33 \pm 0.04 \times 10^{-3}$

TABLE V

RUN 79. SODIUM α -BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.153$ "a" = 2.018×10^{-4} $a = 0.006727$
"b" = 1.000×10^{-4} $b = 0.003333$

Time, min.	10^4 Equiv. thio. used	$10^3 k$
3928	0.093	3.78
12,905	.3222	4.91
13,227	.3249	4.84
13,925	.3503	5.09
16,906	.3961	4.98
21,180	.4625	5.02

Extrapolated $k = 3.23 \times 10^{-3}$

TABLE VI

RUN 30. SODIUM β -BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.494$	"a" = 2.108×10^{-3}	a = 0.0703
	"b" = 1.000×10^{-3}	b = 0.0333
Time, min.	10^3 Equiv. thio. used	$10^2 k$
248	0.205	1.38
285	.236	1.43
468	.346	1.42
597	.412	1.42
1336	.663	1.44
1404	.677	1.43
1682	.730	1.42

$$\text{Av. } k = 1.42 \pm 0.01 \times 10^{-2}$$

TABLE VII

RUN 31. SODIUM β -BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.237$	"a" = 2.108×10^{-3}	a = 0.01622
	"b" = 1.000×10^{-3}	b = 0.00769
Time, min.	10^3 Equiv. thio. used	$10^2 k$
617	0.192	2.22
1288	.348	2.24
1404	.375	2.28
1668	.419	2.25
2742	.581	2.33
3117	.621	2.34

TABLE VIII

RUN 74. SODIUM β -BROMOPROPIONATE AND THIOSULFATE

$\sqrt{\mu} = 0.0937$	"a" = 2.010×10^{-4}	a = 0.002512
	"b" = 1.000×10^{-4}	b = 0.00125
Time, min.	10^4 Equiv. thio. used	$10^2 k$
1148	0.212	8.77
1529	.260	8.44
2574	.386	8.46
5464	.612	8.47
6932	.663	7.86

$$\text{Av. } k = 8.40 \pm 0.27 \times 10^{-2}$$

TABLE IX

SUMMARY OF VELOCITY CONSTANTS OF THIOSULFATE AND BROMINATED ION (IN THE PRESENCE OF Na^+) AS A FUNCTION OF THE SQUARE ROOT OF IONIC STRENGTH

Run	$\sqrt{\mu}$	k	Log k + 1
Bromoacetate			
27 ^a	0.0447	0.298 \pm 0.001	0.474
26 ^a	.0516	.304 \pm 0.0008	.483
25 ^a	.0632	.371 \pm 0.003	.501
22 ^a	.0816	.325 \pm 0.004	.512
20 ^a , 21 ^a	.1000	.354 \pm 0.003	.549
23 ^a , 19 ^a , 6, 4 ^a	.1414	.385 \pm 0.005	.585
2 ^a , 5 ^a	.2000	.445 \pm 0.002	.648
7	.493	.690 \pm 0.006	.839
8	.493	.685 \pm 0.008	.836

TABLE IX (Concluded)

α -Bromopropionate			
Run	$\sqrt{\mu}$	k	$\log k + 3$
18	0.495	$5.12 \pm 0.06 \times 10^{-3}$	0.709
29	.494	$4.86 \pm 0.09 \times 10^{-3}$.687
81	.408	$4.96 \pm 0.04 \times 10^{-3}$.695
33	.237	$4.33 \pm 0.04 \times 10^{-3}$.636
80	.182	3.75×10^{-3} (extrap.)	.574 (?)
79, 38	.154	3.23×10^{-3} (extrap.)	.509
78, 82	.0939	2.64×10^{-3} (extrap.)	.422 (?)

β -Bromopropionate			
	$\sqrt{\mu}$	k	$\log k + 2$
72	0.526	$1.59 \pm 0.08 \times 10^{-2}$	0.201
30	.494	$1.42 \pm 0.01 \times 10^{-2}$.152
35	.462	$1.63 \pm 0.05 \times 10^{-2}$.212
31	.237	$2.28 \pm 0.04 \times 10^{-2}$.358
36	.189	$3.79 \pm 0.12 \times 10^{-2}$.579
83	.0961	$8.01 \pm 0.21 \times 10^{-2}$.904
32	.0937	9.05×10^{-2} (extrap.)	.957 (?)
74	.0937	$8.40 \pm 0.27 \times 10^{-2}$.924
37	.078	13.2×10^{-2} (extrap.)	1.121 (?)
77	.0759	$13.5 \pm 0.5 \times 10^{-2}$	1.130

^a Victor K. La Mer, THIS JOURNAL, 51, 3341 (1929): see correction, page 3678.

The plots of these data are shown in Figs. 1, 2 and 3. The following tables show typical runs for thiosulfate-ester reactions.

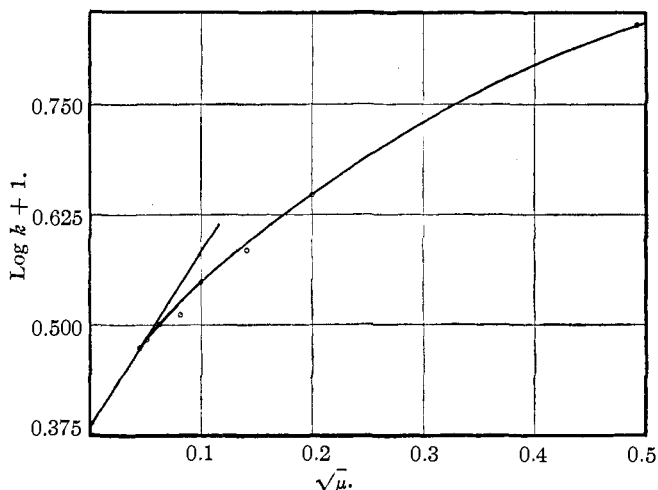


Fig. 1.—Bromoacetate ion and thiosulfate ion.

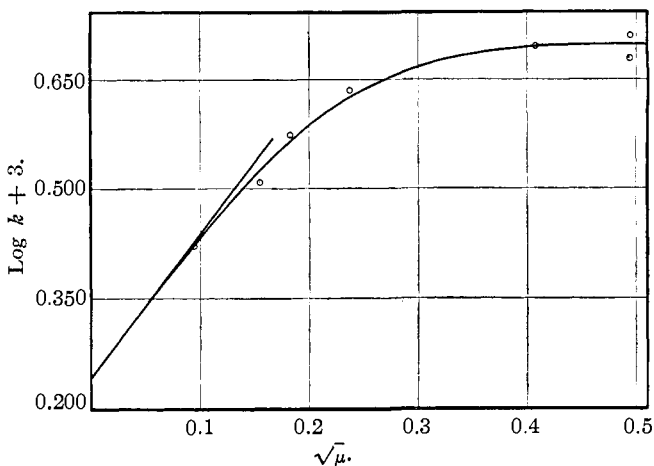


Fig. 2.— α -Bromopropionate ion and thiosulfate ion.

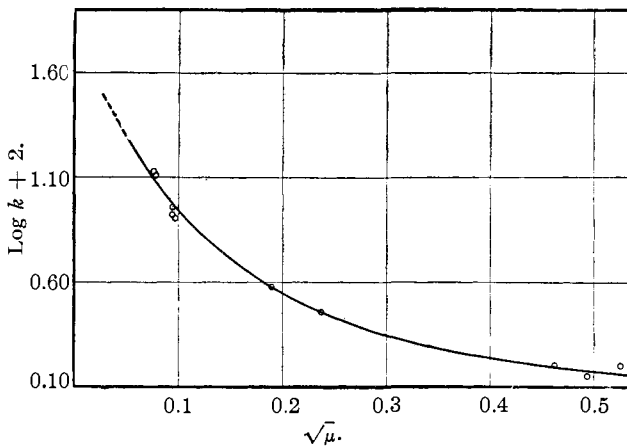


Fig. 3.— β -Bromopropionate ion and thiosulfate ion.

TABLE X

RUN 50. METHYL ESTER OF BROMOACETIC ACID AND THIOSULFATE
 $\sqrt{\mu} = 0.0580$ Concentration of ester, mole per liter = 0.000416

Time, min.	10^4 Equiv. thio. used	k
18	0.092	13.8
27	.126	13.5
36	.153	13.2
47	.190	13.8
60	.226	14.4

Av. $k = 13.7 \pm 0.3$

TABLE XI

RUN 53. METHYL ESTER OF α -BROMOPROPIONIC ACID AND THIOSULFATE
 $\sqrt{\mu} = 0.399$ Concentration of ester, mole per liter = 0.00912

Time, min.	10^3 Equiv. thio. used	k
15	0.026	0.197
32	.049	.190
51	.069	.183
73	.088	.179
81	.092	.172

Extrapolated $k = 0.202$

The graph for this extrapolation is shown in Fig. 4.

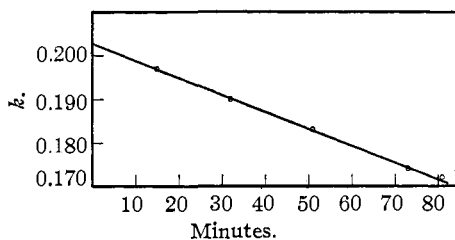


Fig. 4.—Extrapolation for run No. 53.

TABLE XII

RUN 59. METHYL ESTER OF β -BROMOPROPIONIC ACID AND THIOSULFATE
 $\sqrt{\mu} = 0.163$ Concentration of ester in mole per liter = 0.002245

Time, min.	10^4 Equiv. thio. used	k
1023	0.297	0.0282
1313	.398	.0312
1464	.437	.0315
2494	.619	.0297
2879	.673	.0292

Av. $k = 0.030 \pm 0.001$

TABLE XIII

SUMMARY OF ESTER-THIOSULFATE RUNS

Run	$\sqrt{\mu}$	Concentration of ester in moles per liter	Average k
Methyl Ester of Bromoacetic Acid			
42	0.0669	0.00078	13.2 \pm 0.2
43	.0674	.00085	14.6 \pm 0.65
44	.0674	.00083	13.8 \pm 0.8
45	.0677	.00052	15.3 \pm 0.3
48	.0675	.00043	14.0 \pm 0.3
49	.0580	.00055	12.9 \pm 0.3
50	.0580	.00042	13.7 \pm 0.3
51	.0516	.00029	13.8 \pm 0.3
52	.0469	.00042	14.1 \pm 0.2

TABLE XIII (Concluded)

Run	$\sqrt{\mu}$	Concentration of ester in moles per liter		Average k
		Methyl Ester of α -Bromopropionic Acid	Methyl Ester of β -Bromopropionic Acid	
53	0.399	0.00912		0.203 (extrap.)
58	.399	.00334		.166 (extrap.)
71	.301	.00368		.178 \pm 0.008
21 (a)	.229	.0111		.169 (extrap.)
54	.146	.00367		.233 (extrap.)
24	.145	.00554		.217 (extrap.)
55	.066	.00369		.218 (extrap.)
Methyl Ester of β -Bromopropionic Acid				
57	0.461	0.00449		0.0297 \pm 0.0015
60	.461	.00197		.0387 \pm 0.002
20	.460	.00741		.036 \pm 0.000
21 (b)	.224	.00741		.0266 \pm 0.0007
59	.163	.00225		.0300 \pm 0.001
62	.070	.00098		.0306 \pm 0.0003
63	.070	.00171		.0299 (one value)

The plots of these data are shown in Fig. 5.

TABLE XIV
TYPICAL "SPONTANEOUS WATER REACTION" RUNS

Time, min.	Salt converted according to NaOH titration, %		k
	Run 13.	0.05 M Na Bromoacetate	
..... ^a			
60, 544		15.2	2.71×10^{-6}
.....			
86, 116		21.2	2.76×10^{-6}
149, 510		34.1	2.79×10^{-6}
207, 060		45.1	2.90×10^{-6}
Run 14. 0.1 M Na α -Bromopropionate			
9, 793		11.8	1.29×10^{-5}
.....			
18, 770		21.1	1.26×10^{-5}
.....			
24, 442		26.3	1.24×10^{-5}
76, 335		58.8	1.16×10^{-5}
Run 26. ^b 0.1 M Na β -Bromopropionate			
.....			
1, 329		16.5	1.35×10^{-4}
.....			
1, 823		22.2	1.38×10^{-4}
2, 815		31.5	1.34×10^{-4}
.....			
3, 150		34.2	1.33×10^{-4}
4, 585		42.8	1.22×10^{-4}

^a indicates that a number of determinations were made at these times but are omitted here to save space.

^b Alkali was added at short time intervals to maintain the P_{H} at approximately 7.0.

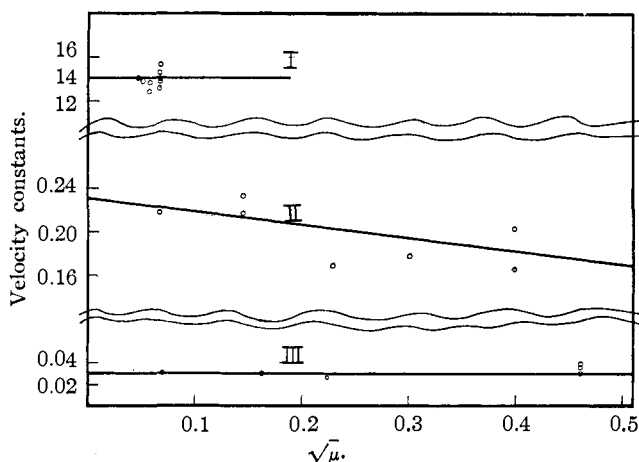


Fig. 5.—Data for reaction of thiosulfate with methyl esters of: I, bromoacetic acid; II, α -bromopropionic acid; III, β -bromopropionic acid.

TABLE XV
SUMMARY OF "SPONTANEOUS WATER REACTION" RUNS

Run	Salt	$\sqrt{\mu}$	k
12	0.1 M Na bromoacetate	0.316	$3.37 \pm 0.14 \times 10^{-6}$
13	0.05 M Na bromoacetate	.224	$2.78 \pm 0.06 \times 10^{-6}$
14	0.1 M Na α -bromopropionate	.316	$1.27 \pm 0.03 \times 10^{-5}$
15	0.05 M Na α -bromopropionate	.224	$1.24 \pm 0.04 \times 10^{-5}$
73 ^a	0.3 M Na β -bromopropionate	.548	1.21×10^{-4}
25 ^a	0.1 M Na β -bromopropionate	.316	1.53×10^{-4}
26 ^a	0.1 M Na β -bromopropionate	.316	1.35×10^{-4}
27 ^a	0.1 M Na β -bromopropionate	.316	1.27×10^{-4}
28 ^a	0.1 M Na β -bromopropionate	.316	1.24×10^{-4}
16	0.1 M Na β -bromopropionate	.316	1.42×10^{-4} (extrap.)
17	0.05 M Na β -bromopropionate	.224	1.59×10^{-4} (extrap.)

^a Alkali was added at short time intervals to maintain the P_{H} at approximately 7.0.

TABLE XVI

		SUMMARY							
		$\sqrt{\mu}$	0.00	0.05	0.10	0.20	0.30	0.40	0.50
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$	Bromoacetate	(58)	46	40	32	26	23	20	
	α -Bromopropionate	(131)	102	81	53	42	36	34	
	β -Bromopropionate	0.4	0.9	1.4	1.9	2.2	
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$	α -Bromopropionate	218	58.5	28.9	19.7	15.7	
$\frac{k_{\text{ester}}}{k_{\text{salt}}}$	β -Bromopropionate	32.2	9.1	4.8	3.5	3.0	
$\frac{k_{\text{salt}}}{k_{\text{salt}}}$	α -Bromopropionate	0.25	0.08	0.04	0.03	0.02	
$\frac{k_{\text{salt}}}{k_{\text{salt}}}$	β -Bromopropionate	0.25	0.08	0.04	0.03	0.02	
$\frac{k_{\text{salt}}}{k_{\text{salt}}}$	Bromoacetate	0.25	0.08	0.04	0.03	0.02	

^a A plot of these data is shown in Fig. 6.

VI. Discussion

Position of Charge in Relation to Velocity.—From Table XVI and Fig. 6, where the value of k for the methyl ester is compared with that for the salt, we find in the case of bromoacetate and α -bromopropionate that the rate of reaction of the negative thiosulfate ion is twenty to a hundred and thirty-fold faster with the ester than with the ion, depending upon the concentration of the reactants. When the bromine is in the β -position, thiosulfate ion reacts about as rapidly with the ester as with the salt, since in this case the number of impacts of the thiosulfate upon the bromine is less influenced by the presence or absence of a charge on the carboxyl group.

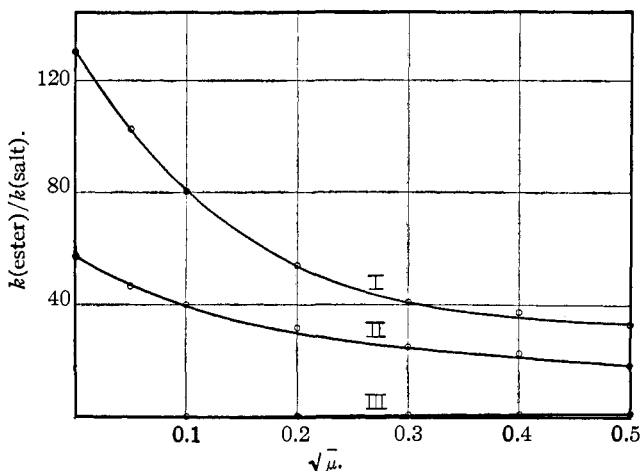


Fig. 6.—I, α -Bromopropionic acid; II, bromoacetic acid; III, β -bromopropionic acid.

Although the α -ester reacts five to seven times faster than the β -ester in harmony with the rule that the α -position is more reactive than the β -position, the velocity of reaction of the β -bromopropionate ion greatly exceeds that for the α -bromopropionate ion. The recent data of Backer and Van Mels^{1b} on the rate of reaction of the negative sulfite ion with the β -bromopropionate ion show it to be double that for the corresponding α -ion at the 0.1 M concentration used. These data, consequently, support our view that the electrostatic interaction is the dominant factor in regulating the rates of ionic reactions.

With reactions between ions of opposite sign, a reverse result should be obtained. Euler,^{1a} studying the reaction $\text{ClCH}_2\text{COO}^- + \text{H}_2\text{O} + \text{Ag}^+ \rightarrow \text{AgCl} + (\text{OH})\text{CH}_2\text{COOH}$, actually found that the rate of reaction of the corresponding ester of chloroacetic acid is only about one-eighth that for the sodium salt. Here the presence of the negative charge in-

creases the probability that a positive silver ion will collide with the chlorine atom and react. Euler's data show also that sodium thiosulfate reacts fourteen times as rapidly with the ester as with the sodium salt of chloroacetic acid.

Concentration Dependence of the Ratios in Table XVI.—We had hoped to determine the values of k_0 for each reaction, *i. e.*, k , freed from interionic effects, by extrapolating the values of $\log k$ plotted against $\sqrt{\mu}$ to infinite dilution in accordance with the limiting slope predicted by the Debye-Hückel limiting theory; namely, $\log k_{\text{obs.}} = \log k_0 + Z_A Z_B \sqrt{\mu}$. This limiting slope of $Z_A Z_B = 2$ is approached in the case of bromoacetate and also by the α -bromopropionate reaction as shown in Figs. 1 and 2. Much to our surprise, however, we found that the observed values for k for the β -bromopropionate salt, instead of decreasing with concentration, actually increased! The β -bromopropionate-thiosulfate reaction is the only one in dilute solution which, to our knowledge, is in direct contradiction to this prediction of the Brönsted theory. The cause of the discrepancy is, consequently, a matter of considerable theoretical interest.

Several factors which might be relevant have been investigated. Experiments to detect errors in procedure were first carried out. The data have been confirmed in a second series of experiments performed nine months after the first. Reaction flasks, scrupulously cleaned with soap and chromic acid, before rinsing with distilled water and finally steamed, showed no difference in reaction rate for their contents as compared with the rate in cases where flasks had been merely cleaned with cleaning mixture and rinsed with distilled water. The possibility of traces of catalyst from the glass affecting the dilute solutions is not likely. Results no different from the others were obtained when the reactants were protected from the action of light.

In those experiments extending over several days where perceptible drifts in k occurred with time, the possibility was considered that the liberation of hydrogen bromide from concurrent water reaction might produce an analytical error in the iodine-thiosulfate titration. Some experiments were therefore made in which the reaction mixture was brought to a P_{H} of 7 using brom thymol blue as indicator, immediately before the iodine was added to stop the progress of the reaction. This did not eliminate the drifts in the case of α -salts (which will be discussed later) but gave for the β -bromopropionate-thiosulfate reaction values which showed no drift with time and *were not appreciably different* (Nos. 32, 74 and 37, 77) from the extrapolated values of the earlier runs in which neutralization of the hydrogen bromide before addition of iodine was omitted. This precaution is unnecessary for the runs at higher $\sqrt{\mu}$ values, since in the more concentrated solutions the iodine-thiosulfate reaction is less sensitive to acidity, and the reaction time being less there is a quite negligible

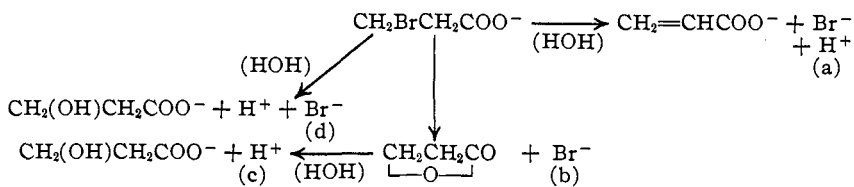
accumulation of hydrogen ion. Moreover, the rate of development of acidity in the concentrated β -bromopropionate-thiosulfate reaction mixtures is enough less than the rate in the dilute mixtures that the actual titratable hydrogen ion formed is less in the former solutions, for a given period of time.

It has been found that the rate of formation of hydrogen ion in water solution by sodium β -bromopropionate in the absence of thiosulfate is considerably greater than the rate for the same concentration of salt in the presence of sodium thiosulfate. For instance, Run 72 shows that after 1523 minutes in the presence of thiosulfate of about twice its concentration, titratable hydrogen ion equivalent to only 0.2% of the original salt present (0.0375 M) has been formed, while in the absence of thiosulfate about one hundred times this amount would be formed. This can hardly be considered a salt effect in the ordinary sense. It would appear that the bromine atoms in the activated state react preferentially with thiosulfate rather than with water. Another fact pointing to this conclusion is that we found that 98% of the sodium β -bromopropionate present in a 0.0333 M solution reacted with thiosulfate as calculated from the disappearance of the latter. Reaction 9 therefore proceeds more slowly in the presence of Reaction 3 than in its absence. *These observations cast considerable doubt upon the validity of corrections for side reactions based upon the rate of the side reaction in the absence of the main reaction.* Therefore, the previously mentioned correction of the bimolecular reaction due to the monomolecular side reaction (water reaction) has not been used.

Since owing to its monomolecular character the rate of the water reaction is relatively greater than the bimolecular thiosulfate reaction in the dilute solutions of sodium β -bromopropionate, and it is these same solutions which show the unusually large value of k for the thiosulfate reaction, the question arises as to whether the accumulation of the hydrolysis products, either by catalytic action or by reaction with the thiosulfate, can cause this increase in velocity. Run 74, with concentration of thiosulfate 0.002512 M and sodium β -bromopropionate 0.00125 M ($\sqrt{\mu} = 0.0937$), performed by adding thiosulfate to salt immediately after its preparation and making up to volume, gave a velocity constant of $8.40 \pm 0.27 \times 10^{-2}$. A portion of the same salt solution was kept in the thermostat until the water reaction had converted 74.6% of the original salt (as determined by titration of hydrogen ion formed). To this neutralized solution, thiosulfate to give the same final concentration as above was added, and the mixture made up to the same volume. The velocity constant of this run was $6.61 \pm 0.39 \times 10^{-2}$ (calculated on the basis of concentration of salt remaining unchanged by water reaction). A similar experiment using more concentrated solutions also showed that the presence of the water reaction products *decreases* the rate of the reaction of sodium

β -bromopropionate with thiosulfate and, therefore, their presence (which even in the runs of greatest dilution and longest time never approaches the large concentration, here) can be eliminated as the cause of the increase in velocity constants in the dilute region.

Possible courses of the water reaction of sodium β -bromopropionate are



The velocity of the water reaction as determined by the titration of hydrogen ion indicates how much salt has been converted to (a), (c) or (d) but if (b \rightarrow c) is slower than (salt \rightarrow b), this fact is not detected by acid titration, alone. Difference in concentration of bromide ion and hydrogen ion would be an index of whether more of (b) than (c) exists, but since silver nitrate reacts to some extent with the salt itself this does not promise to be a very satisfactory procedure. It has been found,¹⁶ however, that at 70° solutions of α -bromopropionate and of β -bromopropionate show a negligible excess of bromide ion over hydrogen ion. We found in Run 11 that 0.98 equivalent of thiosulfate disappeared per equivalent of sodium β -bromopropionate present originally. It appears, then, that whatever water reaction products had accumulated, reacted (within two parts per hundred) with thiosulfate in the same ratio as postulated for the original salt. Whether the reaction took place through the intermediate step of lactone, hydroxy compound or even unsaturated compound should not influence the interpretation of the results since one equivalent of each is formed from one equivalent of salt. If the (b \rightarrow c) conversion is slower than the formation of (b), then lactone accumulates and the water reaction products mixture should contain enough to make the velocity constant exceed that of the usual runs if the lactone reacted very rapidly with thiosulfate. That no appreciable thiosulfate was used up as soon (after a few minutes) as the reactants were mixed is evidence that the water reaction mixture contains no very reactive substance which could account for the increase in velocity of the dilute β -bromopropionate-thiosulfate runs.

In order to isolate the reaction product, equivalent amounts of sodium β -bromopropionate and thiosulfate were allowed to react for a sufficient time to approach completion of the reaction (adding sodium hydroxide occasionally to neutralize acidity). After proceeding according to the directions of Purgotti¹⁷ for preparation of the barium salt of the thio deriva-

¹⁶ G. S. Simpson, *THIS JOURNAL*, **40**, 674 (1918).

¹⁷ A. Purgotti, *Gazz. chim. ital.*, **22**, 416 (1892).

tive of chloroacetic acid, a fine, white crystalline substance was obtained. After recrystallization, analysis¹⁸ showed 19.60% sulfur. The theoretical sulfur content of $\text{CH}_2(\text{S}_2\text{O}_3)\overline{\text{CH}_2\text{COOBa}}$ is 19.94%. The corresponding sodium salt has been postulated as the reaction product in the thiosulfate reactions studied in this paper. A solution of the barium salt prepared had no perceptible action on an iodine solution.

The dissociation constant of α -bromopropionic acid is 108×10^{-5} , that of β -bromopropionic acid is 9.8×10^{-5} . Can the acidity resulting from hydrogen ion liberated by the reaction of the salt with water, by repressing the ionization of these rather weak acids, particularly the latter, cause thiosulfate to react with undissociated acid molecules as well as with the ion? By the use of citric acid-phosphate buffer solutions, the reacting mixtures for salts of the above acids were maintained at various P_{H} values and the rate of thiosulfate reaction determined. In the more acid solutions the stability of the thiosulfate was determined by "recovering" it by iodine titration in control experiments from buffer mixtures of the same P_{H} value and these values were used as the initial concentration of thiosulfate in calculating the velocity constant. With sodium β -bromopropionate 0.00125 M and thiosulfate 0.0027 M , the velocity constant decreased rapidly as the solutions became more acid than P_{H} 4.5 and at 3.5 had fallen to a value but slightly more than half that at P_{H} 6.5. The plot of these results has the form of a titration curve and shows that the undissociated molecule of β -bromopropionic acid reacts more slowly than does the ion with thiosulfate. This possibility of explaining the anomalous rise in velocity constant with decreasing $\sqrt{\mu}$ value is thus eliminated.

In the case of α -bromopropionate in buffered solutions (salt 0.0125 M , thio controls, varying slightly about the value 0.0266 M), the velocity constant is increased markedly with increasing acidity and at P_{H} 4.0 has more than doubled its value at P_{H} 6.5. The plot of these results also takes the form of a titration curve. The upward drift of the constants in runs of low concentrations of the α -salt can be accounted for by the increasing acidity which occurs during the many days required for a run. On this basis, then, it seems justifiable to extrapolate the results to determine the α -bromopropionate-thiosulfate velocity constant at zero time, for any run which shows a drift with time.

The fact that repression of the ionization of the acid increases more markedly the velocity of the reaction of the α -acid with thiosulfate than it decreases the velocity of the β -acid is in harmony with what we have found in comparing the effect of removal of charge in forming a methyl ester.

¹⁸ Analysis by Research Service Laboratories, 37 East 28th Street, New York, N. Y.

An Orientation Theory of Reaction Velocity.¹⁹—Having exhausted the possible chemical explanations, we present a physical explanation which is in harmony with the known facts and at the same time does not entail rejection of the Brönsted–Debye theory. In order to test Brönsted's theory it is necessary to introduce the Debye–Hückel limiting law. This law is derived on the simplifying assumption that the charges on the ions may be considered as symmetrically distributed upon a sphere of radius "b" so that the distance of closest approach of their centers equals the parameter "a." This assumption appears to be sufficiently valid to account for the bromoacetate–thiosulfate data and for the α -bromopropionate–thiosulfate data but can hardly be considered valid for β -bromopropionate if we are to consider the formulas of structural organic chemistry as representing even the approximate positions of the bromine atom and the charge on the carboxyl group. Since a reaction occurs only when a thiosulfate ion collides with the bromine in the β -position, our molecular model should be revised to take the form of one spherical ion (thiosulfate) and a long chain ion with a negative charge at one end and reacting bromine atom at the opposite end. From this model of structural organic chemistry, we contend that an orientation effect should be superimposed upon the effect predicted for spherical ions on the basis of the Brönsted–Debye equation.

Although the influence upon the activity coefficient produced by superimposing a dipole upon an excess charge has never been worked out quantitatively, it is generally recognized that the contribution of the dipole to the free energy should be small and vanish more rapidly with dilution than the contribution of the excess charge.²⁰ The influence of the dipole upon the reaction velocity, however, is not exactly comparable, for in reaction velocity we measure only the frequency of those collisions which occur between a thiosulfate ion and a β -bromopropionate chain when the chain is oriented within a given critical solid angle such that a chemical reaction will occur. Thus, the comparatively minute contribution to

¹⁹ In his important paper on reaction kinetics, Christiansen [*Z. physik. Chem.*, 113, 35 (1924)], in a carefully worded sentence, considers the possibility of orientation but expresses the opinion that it is of less importance than that of deactivating collisions. Christiansen, however, was, apparently, drawing primarily on his experience with gaseous reactions where the possibility of the orienting effect of the net charge of one ion upon another ion is remote as contrasted with the case of aqueous ionic solutions. We do not believe his analogy applicable in the present case. He does mention, however, the importance of attention to electrical forces in calculating concentration dependence of the velocity constant especially in treating a reaction in which large organic molecules are concerned, representing the organic molecule as being a chain and burdened with a charge at one place and at a proportionally great distance from the center of reaction. His reference to Holmberg's acetylglycolic acid experiments does not make clear, however, his point as we would interpret it.

²⁰ Discussion of one of us with Professor Debye in 1926.

the activity coefficient arising from the orientation due to dissymmetry of the charge in the β -bromopropionate ion may become the predominant factor in such a specific process as the oriented collision necessary for a chemical reaction.

That the molecular model, spherical ion and non-spherical ion with the point of attack at a great distance from the excess charge, should lead to a decreased velocity on increasing ionic concentration, may be shown as follows. Consider the extreme case of a volume of solution containing only one thiosulfate ion and one β -bromopropionate ion. Collisions will be very infrequent but, when they do occur, the bromine end will collide with the thiosulfate owing to the repulsive effect of the negative charges on the two ions. Every collision having a velocity sufficient to exceed the critical increment should, therefore, be fruitful. As we pass to slightly more concentrated solutions, the rapidly fluctuating fields produced by the thermal movement of the neighboring ions, will disturb the ideal orientation of the collisions that prevails at extreme dilution. Many of the collisions predicted by the term $C_A \cdot C_B$ in the rate equation $dx/dt = k \cdot C_A \cdot C_B$ will no longer occur with an orientation represented as lying within the critical solid angle necessary for chemical reaction. The result will be a decrease in the value of the velocity constant with increasing concentration which will be most pronounced in the highly dilute region. Since this effect will be superimposed upon the Debye-Hückel effect arising from the net charges on the ions, it is clear that we have a plausible explanation of the anomaly which does not conflict with the Brönsted theory.

It is hoped that theoretical physicists will essay a solution of this problem suitable for numerical evaluation. In the meantime, we are testing the idea by studying the rates of reaction in a homologous series of brominated compounds. Our theory requires a greater change in the temperature coefficient for the β -reaction as compared with the α -reaction, with variation in concentration, since an orientation effect should be more sensitive to temperature changes than is the Brönsted-Debye effect.

VII. Summary

1. Data are given for the rates of reaction of bromoacetate, α -bromopropionate and β -bromopropionate ions, and of their methyl esters, with sodium thiosulfate over a wide range of concentrations. The rates of the corresponding spontaneous water reactions have been investigated.

2. At all concentrations the velocity constant for the reaction of negatively charged thiosulfate ion with bromine in the β -position to a negatively charged carboxyl group greatly exceeds that for the reaction with bromine in the α -position to the carboxyl group. The converse is true when the esters are used in place of the salts.

3. Removal of the negative charge on the brominated ion either by

ester formation or by repression of ionization increases the velocity constant over a hundred fold when the bromine is in the α -position to the group bearing the charge, but has little effect when the bromine is in the β -position. All of these facts are in accord with the predictions of the electrostatic theory of reaction velocity.

4. For the α -bromopropionate-thiosulfate reaction, the limiting slope predicted by the Brönsted-Debye theory is approached for concentrations less than $\sqrt{\mu} = 0.06$. For the β -bromopropionate-thiosulfate reaction the velocity constant contrary to this theory *increases* with decreasing $\sqrt{\mu}$ values, the effect being most marked in the very dilute region.

5. As an explanation of this anomalous result for the β -bromopropionate, a theory based on the assumption of oriented collision is submitted.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

THE CRYSTALLINE FORM OF SOME NEW COBALTAMMINES¹

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Introduction

The recent work of V. M. Goldschmidt on crystal chemistry has shown that crystal structure is determined by the relative numbers, size and deformability of the constituent particles.³ These results are based largely on x-ray investigation, but deal primarily with relatively simple compounds. The structure of a compound consists of an interpenetration of a definite anion and cation arrangement, whose mutual influence on each other determines the final structure of the compound. A given cation structure is expanded by the introduction of various anions, but this expansion has a limit, at which the fundamental cation arrangement alters. The substitution of various cations similarly influences the structure of the anion.

The cation of a complex cobaltamine must represent the largest and most determining part of the final structure of compounds containing this cation in combination with a simple anion. The structure of compounds of

¹ This paper is a thesis submitted to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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³ V. M. Goldschmidt, *Skrifter Norske Videnskap. Akad. Oslo*, 1926, No. 2; *ibid.*, 1926, No. 8; *Naturwissenschaften*, 14, 477 (1926); *Trans. Faraday Soc.*, 25, 253-83 (1929).