mole) of 2,2-diphenylpentanoic acid by refluxing for 7 hours with 25 ml. of thionyl chloride. The excess thionyl chloride was removed *in vacuo*, and the residue was refluxed for 2 hours with 21.2 g. (0.18 mole) of β-diethylaminoethanol, 10 g. of phenol and 40 ml. of dry benzene. The precipitate which formed on cooling was dissolved with more benzene, and a slight excess of dry hydrogen chloride was passed into the solution. Anhydrous ether was added, the resultant precipitate was collected. dissolved in 600 ml. of water, and made alkaline with dilute ammonium hydroxide. The oily amine which formed was extracted with benzene; the benzene layer was washed with water until the extracts were practically neutral to alkacid test paper. The benzene solution was concentrated and dried by distillation. Addition of ether precipitated an oil, which solidified on cooling.

Recrystallization of the amino-ester hydrochloride from acetone-ether gave 11.5 g. of needles; m.p. 122–123° (cor. sealed cap.). A second crop (having the same melting point) of 2.7 g. was obtained by diluting the filtrate with ether; total yield 14.2 g. (40%).

β-Dimethylaminoethyl Ester of 2,2-Diphenyl-4-methyl-4-pentenoic Acid.—This was prepared by the following modification of the Horenstein–Pählicke amino-ester synthesis.[7] A suspension of the potassium salt of 20.0 g. of 2,2-diphenyl-4-methyl-4-pentenoic acid (0.075 mole) in toluene was obtained by dissolving the acid in 75 ml. of 1.0 *N* potassium hydroxide, followed by azeotropic distillation of the water with toluene. A solution of 17.5 g. (0.075 mole) of β-dimethylaminoethyl bromide hydrobromide in 50 ml. of water was neutralized with 1% sodium hydroxide and immediately extracted by two portions of benzene. The benzene solution was dried by distillation of one-half of the solvent. The dry benzene solution was added slowly to the stirred dry suspension of the potassium salt. After stirring the mixture at reflux for 90 minutes, water was added. Acidification of the aqueous layer gave 8.5 g. of recovered starting acid (m.p. 117–119°). The benzene layer was dried by boiling, cooled, and hydrogen chloride was introduced. Addition of the ether gave a precipitate which was recrystallized from ethanol–ether; 12.3 g. (44%, 76% on basis of acid used); m.p. 142–144° (cor. sealed cap.).

2,2-Diphenyl-5-(4′-morpholino)-4-pentanolactone.—A mixture of 14.0 g. (0.423 mole) of 2,2-diphenyl-5-bromo-4-pentanolactone[6] in 42 g. of morpholine (Eastman Kodak Co. practical) was refluxed 2 hours. After 25 g. of morpholine was removed by distillation, ether was added. Filtration gave 7.0 g. of morpholine hydrobromide (theor. 7.9 g.). The filtrate was washed twice with water, and benzene was added to solubilize the product. After three more aqueous extractions, the organic solution was dried over calcium chloride. Addition of dry hydrogen chloride gave a precipitate, which was recrystallized from ethanol and acetone (400 ml. total volume) 12.5 g. (82%) of needles: m.p. 238–240° (open cap. cor.).

2,2-Diphenyl-5-diethylamino-4-pentanolactone.—A mixture of 14.0 g. (0.423 mole) of 2,2-diphenyl-5-bromo-4-pentanolactone[6] and 40 ml. of diethylamine (Eastman Kodak Co., practical) was heated 4 hours at 160° in a sealed bomb. Water was added to the mixture, and the aqueous layer was extracted four times with ether and once with benzene. The combined organic layers were washed with eight portions of water (until a *p*H of eight was obtained for the wash water). The organic solution was dried over calcium chloride, and dry hydrogen chloride was added. The resultant oil solidified readily, and was recrystallized twice from ethanol and ether, using Darco; 8.0 g. (52%) of needles; m.p. 202–204.5° (open cap. cor.).

PHILADELPHIA, PENNA. RECEIVED SEPTEMBER 20, 1950

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[7] H. Horenstein and H. Pählicke, *Ber.*, **71B**, 1644 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Rate Law and Mechanism of the Reaction of Iodine with Thiosulfate Ion: The Formation of the Intermediate $S_2O_3I^-$

BY ALICE D. AWTREY AND ROBERT E. CONNICK

A study has been made of the kinetics of the reactions occurring when thiosulfate and triiodide solutions are mixed. The initial. very rapid reaction results in the formation of $S_2O_3I^-$ and iodide ion. At relatively high iodide concentrations the $S_2O_3I^-$ reacts at a measurable rate to form tetrathionate and triiodide. The following mechanism is consistent with the experimental results

$$S_2O_3I^- + 2I^- \underset{}{\overset{\text{rapid equil.}}{\rightleftarrows}} S_2O_3^{--} + I_3^-$$

$$S_2O_3I^- + S_2O_3^{--} \xrightarrow{\text{slow}} S_4O_6^{--} + I^-$$

where the equilibrium of the first reaction is shifted far to the left.

At low iodide ion concentrations $S_2O_3I^-$ reacts with iodine to give sulfate and iodide. The rate law was determined and possible mechanisms are discussed.

During the mixing a part of the thiosulfate is converted very rapidly to tetrathionate ion by reaction with $S_2O_3I^-$. This reaction is slower than that of thiosulfate with triiodide. yet too fast to measure with the technique available.

Introduction

Visible evidence that the reaction of thiosulfate with iodine is not immeasurably fast, and proceeds in steps, was obtained by the use of a fast mixing device, similar in design to that of Hartridge and Roughton.[1] Solutions of iodine in potassium iodide and of sodium thiosulfate were mixed very rapidly by being forced under pressure from jets into a small circular mixing chamber and thence down a long glass observation tube. The reaction expected is

$$I_3^- + 2S_2O_3^= = S_4O_6^= + 3I^- \qquad (1)$$

which requires two thiosulfate ions for each triiodide. Under certain conditions it was found that the triiodide solution was completely decolorized by the thiosulfate solution at the mixing chamber but that the mixture, while flowing down the observation tube, became colored again. The solution collected at the end of the tube had an easily measurable concentration of triiodide ion.

From the above observation it was apparent that triiodide and thiosulfate can react in a ratio of less than 1 to 2 to form a colorless intermediate.

Assuming the combining ratio to be 1 to 1 (as confirmed by other experiments to be discussed later), the postulated reaction is

$$S_2O_3^= + I^- = S_2O_3I^- + 2I^- \qquad (2)$$

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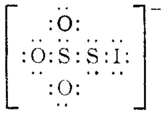
[1] H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.* (*London*), **A104**, 376 (1923).

The electron structure of the intermediate $S_2O_3I^-$ is believed to be



This structure gives complete octets of electrons to all the atoms, and shows no obvious reasons for immediate decomposition or reaction. The iodine atom is most likely attached to the outer sulfur atom of the thiosulfate, in preference to any other position. If it were attached to an oxygen or even to the inner sulfur atom, one might expect sulfate ion to show a similar reaction with iodine, giving the species SO_4I^-, since the oxygen atoms of a sulfate ion must differ chemically only slightly from the oxygen atoms of a thiosulfate ion.

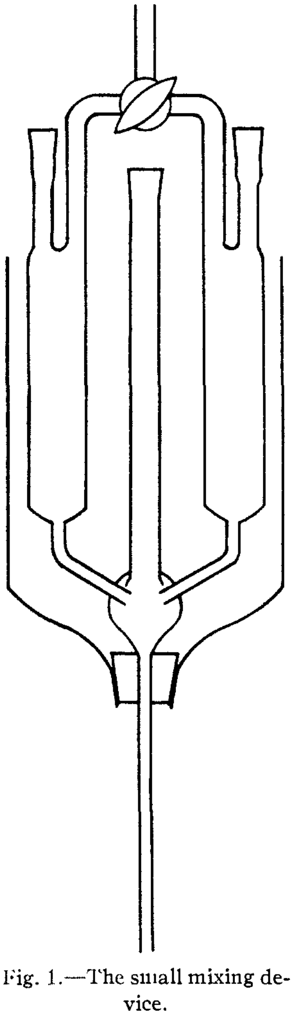


Fig. 1.—The small mixing device.

A search of the literature revealed that Raschig[2] had hypothesized that the reaction of iodine and thiosulfate ion occurs in steps, by way of the intermediate $S_2O_3I^-$, in order to explain the thiosulfate-catalyzed reaction of azide ion with iodine. Kolthoff[3] used the same hypothesis to account for the reappearance of the starch color near the end of a titration of iodine with thiosulfate. While the present work was in progress, a detailed study of the iodine–thiosulfate reaction was published by Dodd and Griffith,[4] who also interpreted their results in terms of $S_2O_3I^-$.

After being formed very rapidly (Eq. 2), $S_2O_3I^-$ reacts at a measurable rate, according to the equation

$$2S_2O_3I^- + I^- = S_4O_6^= + I_3^- \quad (3)$$

thus giving the required stoichiometry (Eq. 1), and accounting for the reappearance of iodine. In writing these equations, of course, no presumptions are made as to the rate laws.

In the above experiments with the fast mixing device the observed ratio of thiosulfate to iodine necessary to give a colorless solution at the point of mixing was greater than unity. This may be explained by postulating that thiosulfate may also react rapidly with $S_2O_3I^-$

$$S_2O_3^= + S_2O_3I^- = S_4O_6^= + I^- \quad (4)$$

This explanation is supported by the rate law found.

Experimental

The large volumes required by the fast mixing device made its use impractical for the determination of the rate law of reaction (3). Instead the reaction was slowed by the use of very dilute solutions of thiosulfate and triiodide, of the order of 10^{-5} M, and its course followed spectrophotometrically as a function of time.

To minimize the mixing time the experiments were started with a small mixing device, shown in Fig. 1. The solutions, propelled by air blown in, as well as by gravity, were forced through capillaries, 1.5 mm. bore, into a funnel-shaped mixing chamber, and were run from this through a narrow tube, 5 mm. bore, into an absorption cell. The flow was started and stopped simply by turning the stopcock controlling the air flow into the solution chambers. Each chamber held about thirty-five ml. A water-bath, equipped with stirrer, surrounded the entire device from below the mixing chamber to the tops of the solution chambers.

The ratio of the volumes delivered by the two chambers of the mixing device was measured accurately by using acid and water and titrating the mixture; the average deviation from the mean in seven trials was 0.2%.

Analytical grade reagents were used for all experiments without further purification. Distilled water was redistilled from alkaline permanganate for use in preparing all solutions. Thiosulfate solutions were not used more than two or three days after preparation. In each experiment the exact concentration of iodine was determined spectrophotometrically.

Two solutions were made up for each run corresponding to the two chambers of the mixing device, one, usually containing the iodine, iodide, acid and in some cases part of the potassium chloride or sodium perchlorate, and the other containing the thiosulfate and the potassium chloride or sodium perchlorate. A few minutes after the run was started, the unused portion of the iodine solution from the mixing device was run out into an absorption cell and the triiodide concentration determined spectrophotometrically.

The reaction was followed by measuring the triiodide concentration by its absorption at 3530 Å., where the molar extinction coefficient is 26,400; those for I_2, I_2Cl^-, $S_4O_6^=$ and $S_2O_3^=$ are 19, 550, 0.5 and 0.2, respectively. In a few cases some other wave length was used when the optical density, log (I_0/I), at 3530 Å. was too high to measure conveniently. No evidence was obtained of absorption by $S_2O_3I^-$, so it is concluded that its molar extinction coefficient is smaller than that of I_3^- from 5000 to 2500 Å.

From the triiodide concentration, the iodide concentration, and the equilibrium constant for triiodide, the total iodine concentration could be calculated. Correction was made for the formation of I_2Cl^-. For fast reactions, or for solutions with an optical density of over 0.9, a Cary recording spectrophotometer was used; its precision was 0.005(log (I_0/I) units), and the accuracy probably about 0.01. For slower runs a Beckman spectrophotometer was employed; the accuracy of these readings of the optical density was about 1% for the log (I_0/I) range of 0.1 to 0.9. The great advantage of the Cary for fast reactions was that it gave a continuous reading, automatically plotting log-(I_0/I) against time.

For reactions where the main part of the reaction was over in a very few minutes, the solutions were at 25.0° when mixed, but no thermostating was attempted. In other runs on the Cary, the experiment was started, and the cell placed in a thermostated holder a few minutes later, after the initial part of the reaction had been measured. All experiments on the Beckman were run in a thermostated holder, with the temperature controlled to within a few hundredths of a degree.

Results

The initial one-to-one reaction of iodine (either molecular iodine, triiodide, or both) and thiosulfate occurs immediately upon mixing; what is observed in all the experiments is the reaction of the $S_2O_3I^-$ formed by this reaction. Some tetrathionate was always formed initially, as far as one could

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(2) F. Raschig, *Ber.*, **48**, 2088 (1915).

(3) I. M. Kolthoff, *Z. anal. Chem.*, **60**, 343 (1921).

(4) G. Dodd and R. O. Griffith, *Trans. Faraday Soc.*, **45**, 546 (1949).

tell; in most cases one-half to two-thirds of the thiosulfate reacted to give $S_2O_3I^-$ while the rest gave tetrathionate immediately.

If $S_2O_3I^-$ reacts with iodide to give tetrathionate, iodine is expected to reappear (eq. 3), and the final iodine concentration can be calculated from the iodine and thiosulfate concentrations used. The experiments performed can be divided into two groups: the first at higher iodide ion concentration, where the $S_2O_3I^-$ apparently all goes to tetrathionate ion, within experimental error, and the second group, at lower iodide, where the final iodine concentration is lower than that expected if tetrathionate alone is formed. For the latter group, some reaction involving the reduction of iodine becomes appreciable or even dominant; a plot of the triiodide ion concentration against time shows a maximum followed by a decrease, or else just a steady disappearance of iodine. This reduction of iodine is not caused by its reaction with tetrathionate, which is much slower.[5] The possible sulfur containing products are $S_3O_6^=$, HSO_3^-, $S_2O_6^=$ and $SO_4^=$. Trithionate can be eliminated because in its formation only one third as many moles of iodine as $S_2O_3I^-$ are consumed and experimentally a larger amount was used up (exp. 33, Table II). Bisulfite ion was shown to be very rapidly oxidized by iodine to sulfate ion under the experimental conditions. Dithionate is difficult to prepare except by oxidation of sulfite and is not formed by iodine oxidation of the latter. Therefore, it seems likely that $SO_4^=$ is the sulfur containing product of the reaction. Additional evidence for this hypothesis was obtained from the rate law (see below). Unfortunately, it was not possible to establish the stoichiometry directly because of the low concentrations.

Corrections for side reactions, *i.e.*, the air oxidation of iodide, the reaction of tetrathionate and iodine, and the volatilization of iodine, were negligible for the experiments at higher iodide, because the time for the main reaction was short.

The experiments at low iodide were corrected for the side reactions by plotting the observed optical density against time on semi-logarithmic paper, and drawing a straight line through the last points, for which the $S_2O_3I^-$ reaction was essentially complete. From the slope of this line the correction to be applied to the observed optical density, in order to eliminate the effect of the side reactions on the observed rate of reaction, could be calculated. The rate of the tetrathionate-iodine reaction is first order with respect to iodine, and the volatilization is probably also, so this seems a reasonable empirical method of correction. The fact that the last points do lie on a straight line, within experimental error, also helps to justify the method. If the loss of iodine from the side reactions is proportional to the iodine concentration, then the correction applied in the early part of the experiment should be larger than that calculated by the method given above, since the iodine concentration is greater at that time than the straight line extrapolation assumes. The error is probably quite small, however.

The Rate Law for the Reaction of $S_2O_3I^-$ to Give Tetrathionate and Triiodide Ions.—In the range of iodide ion concentration 0.07 to 0.007 *M*, the net reaction is

$$2S_2O_3I^- + I^- = S_4O_6^= + I_3^- \qquad (3)$$

with appreciable amounts of I_2 also formed at low iodide ion concentrations. The total iodine concentration, (ΣI_2), which is the sum of the I_2, I_3^- and I_2Cl^- concentrations, is related to the experimentally observed triiodide concentration by[6]

$$(\Sigma I_2) = \{(1 + K_1[1 + K_2(Cl^-)]/(I^-)\}(I_3^-) \qquad (5)$$

where

$$K_1 = \frac{(I_2)(I^-)}{(I_3^-)} \text{ and } K_2 = \frac{(I_2Cl^-)}{(I_2)(Cl^-)} \qquad (6)$$

The value of K_1 was taken to be 1.40×10^{-3} at $25°$[7] and 1.85×10^{-3} at $35°$[8]; that of K_2, 2.1 at both temperatures.[8] The ionic strength effect on both was assumed negligible.

The difference between the iodine which is present when all the $S_2O_3I^-$ has reacted to give tetrathionate, and that present at a given time is proportional to the $S_2O_3I^-$ still unreacted at that time

$$(S_2O_3I^-) = 2[(\Sigma I_2)_f - (\Sigma I_2)] \qquad (7)$$

The experimentally determined rate law is

$$-\frac{1}{2}\frac{d(S_2O_3I^-)}{dt} = \frac{d(\Sigma I_2)}{dt} = k_1\frac{(S_2O_3I^-)^2(I^-)^2}{(I_3^-)} \qquad (8)$$

To determine k_1 for a given experiment Eq. 8 was rewritten in the form

$$\frac{dD}{dt} = k_1'\frac{(D_f - D)^2}{D} \qquad (9)$$

where D and D_f are optical densities at times t and infinity, and

$$k_1' = 4k_1(I^-)^2\frac{(\Sigma I_2)}{(I_3^-)} \qquad (10)$$

The iodide ion concentration was constant during a run because it was in large excess over the other reactants. The integrated form of Eq. 9 is

$$\ln (D_f - D) + D_f/(D_f - D) = k_1't + C \qquad (11)$$

where C is the constant of integration.

The greatest uncertainty in determining the rate constant quantitatively lay in the measurement of the $S_2O_3I^-$ concentration, *i.e.*, in $(D_f - D)$. The value of D_f was known with an accuracy of about 1%, and this uncertainty produced large variations in k_1.

To determine k_1' for a given experiment, the observed data were fitted with a curve calculated from Eq. 11 using two points to determine k_1' and C, and treating D_f as a parameter, varying it within the limits of error of the experimentally determined value. In general the value of k_1' could be fixed with an accuracy of about ±10%.

A typical experimental curve is shown in Fig. 2. The data for all the experiments in this group are given in Table I. The values of (ΣI_2) and $(S_2O_3^=)$ given in the third and fourth columns are the concentrations after mixing if no reaction had occurred. The value of D_0 in the seventh column is the first observed optical density; the rapidity of the reaction prevents an extrapolation to zero time. The zero time point could not be calculated because of

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[5] Alice D. Awtrey and R. E. Connick, to be published.

[6] Parentheses are used throughout to indicate the concentration of the enclosed species in moles per liter of solution.

[7] G. Jones and B. B. Kaplan, This Journal, **50**, 1845 (1928).

[8] A. D. Awtrey and M. S. Tsao, to be published.

TABLE I

EXPERIMENTS AT HIGH IODIDE ION CONCENTRATION

Expt.	(I^-), M	$(\Sigma I_2) \times 10^6 M$	$(S_2O_3^=) \times 10^6 M$	pH	Ionic strength	D_0[c] Obsd.	D_f Obsd.	D_f Theor.	$k_1 \times 10^{-3}$ M^{-2} min.$^{-1}$
1	0.00709	9.30	7.46	3	0.050	0.67	1.18	1.20	5.3
2	.0098	14.9	14.85	3	.050	0.43[d]	0.86	0.865	5.7
3	.0098	22.3	14.85	3	.050	1.22[d]	1.69	1.705	5.2
4	.010	8.54	7.69	3	.050	0.74	1.09	1.10	5.3
5	.010	12.4	11.96	3	.050	0.77	1.45	1.47	4.9
6	.0223	22.4	14.85	3	.051	1.40[d]	1.84	1.84	5.4
7	.0260	~22.4	16.2	4	.050	1.435[d]	1.80	1.810	4.7
8	.0274	~45.0	24.3	4	.050	1.36[e]	1.645	1.65	4.5
9	.0299	9.24	7.45	3	.050	1.042	1.392	1.392	4.1
10	.0299	7.55	7.45	3	.050	0.70	0.96	0.96	4.1
11	.030	12.4	11.96	3	.050	0.65[d]	0.792	0.800	4.3
12	.046	9.25	7.60	4	.050	1.192	1.40	1.395	3.9
13	.0278	9.28	7.60	4	.1007	1.08	1.35	1.355	6.1
14	.046	9.20	7.60	4	.100	1.205	1.363	1.358	6.5
15	.064	9.20	7.60	4	.100	1.26	1.37	1.375	7.2
16[a]	.030	9.33	7.46	3	.050	1.10	1.405	1.405	4.0
17	.01106	14.4	14.93	3	.050[b]	0.89	1.74	1.755	4.1
18	.0263	14.4	14.93	3	.050[b]	1.325	1.93	1.93	4.0
19	.01106	14.4	11.33	3	.100[b]	1.41	2.18	2.19	5.5

[a] Run at 35.0°; all others at 25°. [b] $NaClO_4$ used instead of KCl to make up the required ionic strength. [c] 10-cm. cell unless otherwise indicated. [d] 5-cm. cell. [e] 2-cm. cell.

the unpredictable amount of tetrathionate formed during the mixing (see Eq. 4).

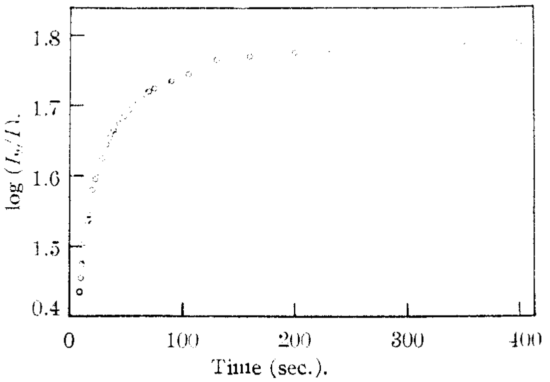


Fig. 2.—An experimental curve at 0.026 M I^-, Expt. 7.

The second power dependence on $(S_2O_3I^-)$ was verified in each run by the fitting procedure described. The triiodide dependence is best checked by comparison of different runs, *e.g.*, 2 and 3 or 8 and 10. There is no effect of hydrogen ion in the range 10^{-3} to 10^{-4} M.

There appears to be a small variation in k_1 with iodide ion concentration when potassium chloride is used to maintain constant ionic strength, *i.e.*, from about 5.4×10^3 at 0.01 M KI, to 3.9×10^3 at 0.046 M KI; the chloride ion concentration changed from 0.04 to 0.004 M. This trend is apparently outside the experimental accuracy: it seems certain that all the experimental curves could not be fitted with the same rate constant. After it was found that chloride ion affected the reaction of $S_2O_3I^-$ with iodine to give sulfate, three experiments were done using sodium perchlorate instead of potassium chloride to maintain constant ionic strength. These are the last three listed in Table I. Experiments 17 and 18 give the same rate constant within experimental error, and the effect of increasing the ionic strength, using sodium perchlorate, is less than that observed with potassium chloride. It seems unlikely, at these relatively low salt concentrations, that this is simply a salt effect; it seems more reasonable to assume that a term involving chloride ion, of minor importance in this region, should be put in the rate law. Doubt may be cast on this hypothesis by the fact that the three experiments, 13, 14 and 15, using sufficient potassium chloride to give an ionic strength of 0.10, show a trend if anything in the opposite direction. These experiments, however, are the most inaccurate, owing to the rapidity of the reaction, and therefore conclusions based on them are most uncertain. In any case, no prediction can be made as to the form of this minor chloride term, and no experimental investigation was undertaken.

The effects of ionic strength and temperature are also shown by the data in Table I. An increase in ionic strength increases the rate. This effect is in the direction expected by theory, but a quantitative prediction cannot be made, because of the high ionic strength. Within the experimental uncertainty, temperature has no effect on the reaction (see experiment 16). Taking a maximum difference in rate of 20%, the maximum heat of activation is calculated to be ±3 kcal. It seems unlikely that $\Delta H^{\ddagger}$ is over half this large.

The Rate Law for the Reaction of $S_2O_3I^-$ with Iodine to Give Sulfate Ion.—At low iodide ion concentrations, 3×10^{-3} to 9×10^{-4} M KI, the stoichiometry no longer corresponds to the formation of tetrathionate alone, but some sulfate ion is also formed

$$S_2O_3I^- + 3I^- + 5H_2O = 2SO_4^= + 10H^+ + 10I^- \quad (12)$$

The reaction must be of lower order than two in $S_2O_3I^-$ concentration, since it becomes more important, relative to the reaction giving tetrathionate, toward the end of an experiment, *i.e.*, as the $S_2O_3I^-$ concentration becomes smaller (see Fig. 3). It was found to be first order in $S_2O_3I^-$ concentration, not zero order, from the shape of the experimental curves. There is no dependence on hydrogen ion, in the *p*H range used: two experiments with 1.37×10^{-3} *M* KI, and at a *p*H of three and four, respectively, gave experimental curves identical within the error of measurement.

Kolthoff[3] reported that, in titrations of 10^{-3} *M* iodine solutions with thiosulfate, the stoichiometry did not correspond to the quantitative production of tetrathionate if the *p*H was greater than five. He attributed this to the reaction of HOI, formed by the hydrolysis of iodine at low acidity, with thiosulfate, giving sulfate ion. The *p*H at which he worked, however, is outside the range studied in this experimental work.

Since two reactions of $S_2O_3I^-$ are occurring at the same time, one producing and the other using up iodine, the measurement of the triiodide ion concentration no longer gives a direct measure of the $S_2O_3I^-$ concentration. Therefore, no rate constants could be calculated graphically, since the $S_2O_3I^-$ concentration at a given point was not known. Instead, the supposed rate law was integrated, and the theoretical curve calculated from it was fitted to the experimental curve at two points. The correctness of the rate law was then judged by the closeness of agreement to the remainder of the curve.

It was found that the following rate laws fitted the data within experimental error for runs at a given iodide concentration

$$\frac{d(\Sigma I_2)}{dt} = k_1 \frac{(S_2O_3I^-)^2(I^-)^2}{(I_3^-)} - 3k_2(S_2O_3I^-) \qquad (13)$$

and

$$\frac{d(S_2O_3I^-)}{dt} = -2k_1 \frac{(S_2O_3I^-)^2(I^-)^2}{(I_3^-)} - k_2(S_2O_3I^-) \qquad (14)$$

The first term on the right is for the reaction of $S_2O_3I^-$ to tetrathionate ion, and the second for that to sulfate ion. The factor of three in the last term of Eq. 13 corresponds to oxidation of the $S_2O_3I^-$ to $SO_4^=$. If HSO_3^- or $S_2O_6^=$ were formed, the factor would be one or two, respectively. Since the experimental data could not be fitted except with the factor of three, it is believed that the product is indeed sulfate ion.

Assuming the iodide to be constant (it varies one to two per cent. during a run) and substituting $u = (I_3^-)/(S_2O_3I^-)$ and $b = (I_3^-)/(\Sigma I_2)$, one can integrate Eq. 13 and 14, obtaining

$$\frac{1}{2}\ln\,(u^2 + (2k - 3b)u + kb) - \frac{k + 3b/2}{\sqrt{\alpha}} \ln\left(\frac{2u + 2k - 3b + \sqrt{\alpha}}{2u + 2k - 3b - \sqrt{\alpha}}\right) = -\ln\,(S_2O_3I^-) + C \qquad (15)$$

and

$$\frac{1}{2}\ln\,[u^2 + (2k - 3b)u + kb] + \frac{k - 3b/2}{\sqrt{\alpha}} \ln \frac{2u + 2k - 3b + \sqrt{\alpha}}{2u + 2k - 3b - \sqrt{\alpha}} = k_2t + C' \qquad (16)$$

where

$$k = k_1(I^-)^2/k_2$$

and

$$\alpha = (2k - 3b)^2 - 4kb \qquad (17)$$

C and *C'* are constants of integration. These equations hold provided α is greater than zero, which is the case in all the experiments except the one at 35°, where trigonometric functions must be used.

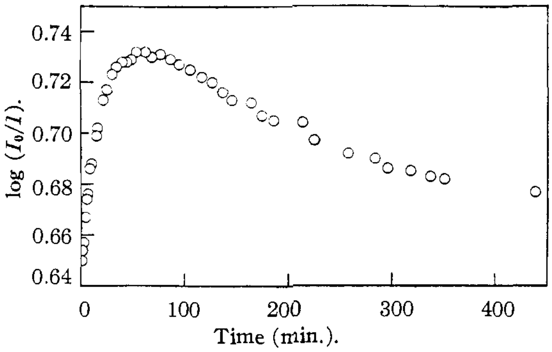


Fig. 3.—An experimental curve at 1.38×10^{-3} *M* I^-, Expt. 26.

For this rate law, it is obvious from Eq. 13 that at the maximum, where $d(\Sigma I_2)/dt = 0$, $u_{max} = k/3$; since $(I_3^-)_{max}$ is known, $(S_2O_3I^-)_{max}$ can be calculated. Using this fact, the experimental curves were fitted at their maxima with curves calculated from Eq. 15, and *C* was thus determined; *C'* was then calculated from the observed time for some point before the maximum. It is interesting to note that the shape of a curve calculated from Eq. 15 and 16 depends only on *k;* the value of u_0 merely determines where on the theoretical curve the experimental observations begin. The initial $S_2O_3I^-$ and I_3^- concentrations together determine the absolute height of the curve. Finally it is noted that *C*, the integration constant in Eq. 15, is equal to the natural logarithm of the final triiodide ion concentration.

The data for all the experiments in this group, using potassium chloride to achieve constant ionic strength, are given in Table II. The second column shows the length of the absorption cell. The values of D_0 in the sixth column are for the first observed point. For experiments at an ionic strength of 0.050, k_1 was taken to be 4.8×10^3 M^{-2} min.$^{-1}$, the arithmetic mean of the values obtained at higher iodide ion concentrations. A value of 5.4×10^3 was tried for some experiments, and had the effect of increasing k_2 about 10%; on the whole the value 4.8×10^3 seemed to give better agreement with the experimental curves. For Run 34, with $\mu = 0.100$, k_1 was taken to be 6.6×10^3 M^{-2} min.$^{-1}$.

The values of k_2 given in Table II show that the rate of the reaction giving sulfate ion is not strictly independent of the iodide ion concentration. Probably the rate law is changing from a zero to an inverse first order dependence with increasing iodide, or *vice versa*.

Experiments at lower iodide ion concentrations, which would aid in finding the form of the iodide dependence, could not be performed, owing to two facts: the correction for volatility and the tetrathionate–iodine reaction becomes so large relative to the reaction rate that an error in the correction makes a significant difference in the shape of the

TABLE II

EXPERIMENTS AT LOW IODIDE ION CONCENTRATIONS USING POTASSIUM CHLORIDE TO MAINTAIN CONSTANT IONIC STRENGTH

Expt.	l, cm.	Concentrations used[a] (I^-) × 10³ M	(ΣI_2) × 10⁵ M	$(S_2O_3^=)$ × 10⁵ M	D_0	D_{max}[b]	D_f[b]	$(I^-)_{av}$ × 10³ M	k_2 × 10³ min.⁻¹
20	10	0.915	1.44	1.11	0.565	0.624	0.449	0.93	2.1
21	5	.93	3.54	1.62	1.123	1.123[c]	0.800	0.96	2.1
22	5	.959	2.77	1.11	0.950	0.950[c]	0.637	0.97	2.1
23	5	0.93	3.54	3.26	0.554	0.658	0.500	0.98	2.0
24	10	1.37	2.3	1.28	1.440	1.557	1.434	1.380	1.7
25	10	1.37	2.16	1.41	1.34	1.511	1.325	1.385	1.6
26	5	1.37	2.1	1.45	0.650	0.732	0.647	1.385	1.6
27	2	1.84	2.88	1.11	0.565	0.585	0.521	1.85	1.6
28	10	2.29	3.76	1.73	3.67	4.01	3.88	2.30	1.3
29	2	2.285	3.64	1.75	0.726	0.800	0.78	2.30	1.3
30	5	2.29	3.69	2.13	1.573	1.806	1.69	2.30	1.3
31	10	2.29	3.75	3.46	1.90	2.88	...	2.30	1.3
32	10	2.32	0.592	0.496	0.260	0.463	0.450	2.30	1.3
33[d]	10	0.916	1.46	1.16	0.515	0.515[c]	0.180	0.94	6.4
34	10	0.916	1.47	1.16	0.485	0.553	0.367	0.93	3.2

[a] All experiments run with 1.0 × 10⁻³ M HClO₄; ionic strength 0.050 except Expt. 34, where μ = 0.100. [b] Corrected for volatility and tetrathionate–iodine reaction. [c] No maximum. [d] Run at 35.0°; all other experiments at 25.0°.

curve; secondly, the fraction of the total iodine which is in the form of triiodide, the measured quantity, becomes too small to measure with the spectrophotometer. If the concentrations of total iodine and thiosulfate used were increased in order to overcome the latter difficulty, the iodide ion concentration would no longer be constant, but would change significantly in the course of a run, and the rate law could not be integrated.

The 50% increase in k_2 shown by Experiment 34, as compared with experiments with the same iodide ion concentration, appears too large to attribute to the twofold increase in ionic strength. It seemed, therefore, that chloride ion, from the potassium chloride used to establish the desired ionic strength, must appear in the rate law.

To check this hypothesis, a few experiments were done using sodium perchlorate instead of potassium chloride. The results are shown in Table III, where the tabulation is similar to that for Table II.

TABLE III

EXPERIMENTS AT LOW IODIDE ION CONCENTRATIONS USING SODIUM PERCHLORATE FOR CONSTANT IONIC STRENGTH

Expt.	Concentrations used[a] (I^-) × 10³ M	(ΣI_2) × 10⁵ M	$(S_2O_3^=)$ × 10⁵ M	D_0[b]	D_{max}[c]	D_f[c]	$(I^-)_{av}$ × 10³ M	k_2[d] × 10³, min.⁻¹
35	2.30	0.733	0.744	0.222	0.532	0.51	2.30	1.0
36	0.915	1.44	1.113	.561	.689	.549	0.93	1.1
37	.915	1.44	1.113	.555	.713	...	.93	1.0[e]
38	.915	1.47	1.23	.427	.458	...	.93	3.2[f]

[a] All experiments with 1.0 × 10⁻³ M HClO₄; ionic strength 0.050 except Expt. 37, where μ = 0.100. [b] 10-cm. cell used for all experiments. [c] Corrected for volatility and tetrathionate–iodine reaction. [d] Calculated with k_1 = 4.1 × 10³ M^{-2} min.⁻¹. [e] Calculated with k_1 = 5.46 × 10³ M^{-2} min.⁻¹. [f] Run at 36.2°; all others at 25.0°.

The rate constant k_2 was calculated for the rate law given in Eq. 13, *i.e.*, assuming no dependence on iodide in the k_2 term. The values calculated for Experiments 35 and 36 seem to indicate that there is no dependence of the rate on iodide ion, in the absence of chloride ion. The data in Tables II and III are consistent with the rate law, for the reaction giving sulfate ion

$$\frac{d(\Sigma I_2)}{dt} = -3k_2'(S_2O_3I^-) - 3k_2'' \frac{(Cl^-)(S_2O_3I^-)}{(I^-)} \qquad (18)$$

with k_2' = 1.0 × 10⁻³ and k_2'' = 2 × 10⁻⁵ min.⁻¹. The dependence on triiodide ion in perchlorate solutions was not investigated, but the results in the presence of potassium chloride show that triiodide ion is most probably not involved in the rate law. Experiments 21 and 20, at the lowest iodide ion concentration, where the second term in Eq. 18 is equal in importance to the first term, give the same value for k_2, while the triiodide ion concentrations differ by almost a factor of four. At 2.3 × 10⁻³ M KI, where the first term of Eq. 18 is more important, Experiments 29 and 32 show the same k_2, while the triiodide concentrations at the maxima differ by a factor of more than eight.

An increase in ionic strength has no effect on k_2', as Experiment 37 shows. This is as expected for the first term of the rate law given in Eq. 18. The effect of temperature was measured, in Experiments 33 and 38. The value of $\Delta H^{\ddagger}$ for the k_2' path is 18 kcal. and correcting for the k_2' path in Experiment 33 one obtains $\Delta H^{\ddagger}$ = 21 kcal. for the k_2'' path.

Mechanisms

The k_1 Rate Law.—The following mechanism, which is that proposed by Dodd and Griffith,[4] conforms to the k_1 rate law

$$S_2O_3I^- + 2I^- \overset{K_3}{=} S_2O_3^= + I_3^- \qquad (19)$$

$$S_2O_3^= + S_2O_3I^- \xrightarrow{k_3} S_4O_6^= + I^- \qquad (20)$$

Equation 19 represents a rapid equilibrium with equilibrium constant K_3 small, and Eq. 20 gives the rate determining step with rate constant k_3. The rate constant k_1 of Eq. 8 equals K_3k_3.

Dodd and Griffith reported the rate law of Eq. 8 but found a drift in their rate constants which they explained by assuming an appreciable amount of $S_2O_3^=$ to be present according to the equilibrium of Eq. 19. Our rate results, however, can only be explained by assuming this equilibrium is displaced far to the left. In some of our experiments the triiodide and iodide concentrations were such that the ratio $(S_2O_3^=)/(S_2O_3I^-)$ was over one hundred-fold greater than in their experiments, yet the rate law of Eq. 8 held.

Further proof that the equilibrium concentration of thiosulfate ion was always very small comes from the fact that thiosulfate ion and $S_2O_3I^-$ react extremely rapidly to form tetrathionate ion during the mixing process.

The values of k_1 reported here are in agreement with those of Dodd and Griffith at 6.67×10^{-3} *M* iodide ion.[9] At lower iodide their rate constant increases. The k_2 term is not great enough to cause this deviation. We see no obvious explanation for this effect unless a new reaction path is becoming important under their experimental conditions, which differ considerably from ours.

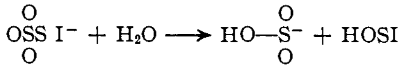
The entropy of activation for k_1 is -50 entropy units. The reaction giving the activated complex

$$2S_2O_3I^- + 2I^- = I_3 + S_4O_6I^{---\ddagger} \qquad (21)$$

should have a large negative entropy of this magnitude because of the charge effect and the change in the number of particles.

It is possible to show that the intermediate $S_2O_3I^-$ does indeed contain iodine. From the k_1 rate law, the activated complex must consist of 2 molecules of the intermediate plus two iodide ions minus one I_3^-. Three iodine atoms have been split out, *i.e.*, I_3^-, and only two put in as I^-; therefore, at least one iodine atom must come from a molecule of the intermediate. This proves the intermediate cannot have the formula $S_2O_5^-$ as hypothesized recently by Abel.[10]

The k_2 Rate Law.—The first term of Eq. 18 corresponds to a unimolecular decomposition of $S_2O_3I^-$ or reaction with water. The initial products are not known but may be those shown below

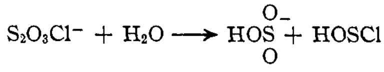


$$\overset{O}{\underset{O}{OSS}}\,I^- + H_2O \longrightarrow HO\!-\!\overset{O}{\underset{O}{S^-}} + HOSI \qquad (22)$$

Rapid follow reactions must convert both sulfur compounds to sulfate ion.

The second term of Eq. 18 could be fitted by the mechanism

$$S_2O_3I^- + Cl^- = S_2O_3Cl^- + I^- \qquad (23)$$



$$S_2O_3Cl^- + H_2O \longrightarrow \overset{O_-}{\underset{O}{HOS}} + HOSCl \qquad (24)$$

where Eq. 23 represents an equilibrium shifted to the left and Eq. 24 the rate determining step. Again the products of Eq. 24 must be rapidly oxidized by iodine to sulfate ion. In equation (23) a Cl^- replaces an iodine in a partially covalent bond. Consideration of the iodine and chlorine oxidation potentials would make this appear to be a highly unfavorable reaction; however, data for the corresponding replacement at a carbon–halogen bond indicate that here chloride ion can replace iodide ion to an appreciable extent. From Pauling's electronegativity values[11] one might expect the sulfur–halogen bond to resemble the carbon–halogen bond.

From the rate constants and heats of activation one calculates activation entropies of -20 and -17 e.u. for the k_2' and k_2'' paths, respectively. These values seem unusually negative for the reaction mechanisms proposed, if it is assumed that the reaction is "adiabatic."[12]

Initial Rapid Reactions.—From the fact that a part of the thiosulfate was oxidized to tetrathionate during the mixing process, it was concluded that thiosulfate reacts very rapidly with both I_3^- and $S_2O_3I^-$ (see Eqs. 2 and 4). Experiments were performed in an attempt to measure the rate of $S_2O_3^=$–I_3^- reaction, using the fast flow apparatus.

The fast mixing device was constructed of glass. Each solution entered the 0.2-ml. mixing chamber through three jets. A piece of square glass tubing of 1.0-cm. inner width was attached to the observation tube 10 cm. below the mixing chamber. The optical density of the solution at this point could be measured by insertion of the tube in the light path of a Beckman spectrophotometer. The volume from the mixing chamber to this point was 7 ml.

The conditions for one experiment are given in Table IV. The optical density observed was 0.003, corresponding to a ΣI_2 concentration of 2×10^{-7} *M*, 2.2×10^{-3} minute after mixing.

TABLE IV

EXPERIMENT TO MEASURE $S_2O_3^{--}$–I_3^- RATE

Concentrations after mixing, assuming no reaction

2.76×10^{-5} *M* $S_2O_3^=$	2.34×10^{-3} *M* I^-
2.54×10^{-5} *M* ΣI_2	1.6×10^{-4} *M* H^+
Flow rate	3.18 liters per min.
Room temperature	*ca.* 20°

If it is assumed that the rate of this initial reaction is given by

$$-\,d(\Sigma I_2)/dt = k_4(S_2O_3^{--})(\Sigma I_2) \qquad (24)$$

and that the reaction of $S_2O_3^{--}$ with $S_2O_3I^-$ does not occur, one calculates a lower limit of 5×10^8 M^{-1} min.$^{-1}$ for k_4.

Chance[13] reported a measurement of the $S_2O_3^{--}$–I_3^- reaction using a much more refined mixing and detection method. Making the same assumptions as above we calculated from his measurements a lower limit of 2×10^9 M^{-1} min.$^{-1}$ for initial ΣI_2 and $S_2O_3^{--}$ concentrations of 2.5×10^{-4} *M* and 5.0×10^{-4} *M*, respectively. There was no added iodide or acid.

In the experiment with the fast mixing device described above, the iodine was almost entirely used up when the molar ratio of thiosulfate to total iodine was 1.10. Therefore, one iodine reacts with one thiosulfate to form $S_2O_3I^-$, as previously assumed. The 10% discrepancy presumably arises from the reaction of some thiosulfate with $S_2O_3I^-$ (Eq. 4).

Under the conditions of the above experiment it is clear that the reaction of thiosulfate with $S_2O_3I^-$ is considerably slower than that of thiosulfate with triiodide. This is required for the establishment of the equilibrium of Eq. 19 of the k_1 mechanism.

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[9] There is a factor of two inconsistency between their definition of k_α and the tabulated values; the latter should be half as great.

[10] E. Abel, *Monatsh.*, **81**, 346 (1950).

[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 65.

[12] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 146.

[13] B. Chance, *J. Franklin Institute*, **229**, 756 (1940).

With the small mixing device, where the mixing was much slower, considerably more tetrathionate was formed during the mixing than in the experiment of Table IV.[14] It is believed that the $S_2O_3^=$–$S_2O_3I^-$ reaction was more important in the former case because of the slowness of mixing, *i.e.*, the rates of the two fast reactions were both comparable with the rate of mixing. There may have been some relative slowness of mixing even in the experiment with the fast mixing device. Therefore, it is not possible to calculate the relative rates of the $S_2O_3^=$–I_3^- and $S_2O_3^=$–$S_2O_3I^-$ reactions; one can conclude only that the former is considerably faster than the latter.

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[14] Dodd and Griffith[4] also observed considerable tetrathionate formation in their experiments in which no special mixing was employed.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

On Cyclic Intermediates in Substitution Reactions. I. The Alkaline Hydrolysis of Some Aliphatic Bromoacids

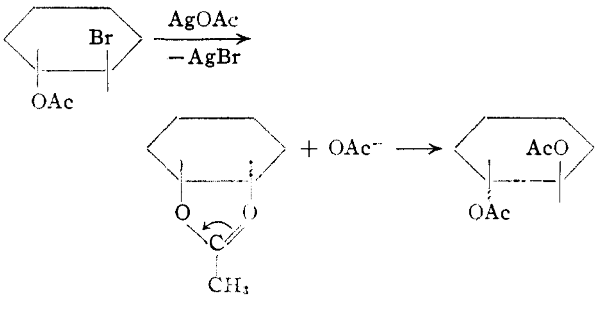
BY JOHN F. LANE AND HAROLD W. HEINE[1]

The rates of aqueous decomposition have been determined for a number of sodium salts of monobromoaliphatic acids in which the position of substitution of the bromine atom ranges from α to γ. It has been established that (1) the rates of decomposition, as measured by the release of bromide ion, are of the first order with respect to the ion of the haloacid; (2) the entropies of activation are positive, and, on the average, about 10 e.u.; (3) the heats of activation decrease in the order $\alpha > \beta > \gamma$.

These results are discussed in terms of a mechanism involving the formation of (increasingly strain-free) cyclic intermediates.

In recent years much evidence[2,3] has been collected to substantiate the idea that certain atoms or groups, capable of donating electrons, which are adjacent to carbon atoms undergoing nucleophilic substitution can, through the formation of cyclic intermediates, exert profound effects not only on the steric course of the displacement reaction, but also on its rate.

Evidence also has been obtained to show that such "neighboring-group" effects are produced by nucleophilic atoms not immediately adjacent to the carbon atom involved in the displacement reaction. Thus, Johannson[4] has reported the isolation of β-butyrolactone as an intermediate in the hydrolysis of β-bromobutyrate ion, and Winstein[3b] has found complete retention of configuration in the displacement of bromine by acetoxyl in the system



where a five-membered cyclic intermediate is postulated. Later investigations[3c] by this author and his co-workers have shown that the tendency of the acetoxyl group to participate in the displacement reaction exceeds by 3–4 kcal. that of methoxyl (which participates by means of a three-membered ring). Freundlich and Salomon[5] have also shown that the rates of formation of cyclic imines from monohalogenoamines are independent of the concentration of added hydroxyl ion and reach a maximum in the formation of a five-membered heterocycle, although their studies leave unanswered the question of whether differences in reactivity are attributable to heat effects or to entropy effects. In general, the information now available in the literature suggests that, other things being equal, the ease of participation of the neighboring nucleophilic atom increases with the strainlessness of the ring formed.

It is the purpose of this series to examine this matter further with quantitative studies on nucleophilic substitution in systems where the distance between the carbon atom on which displacement occurs and the participating neighboring group progressively increases while other variables are substantially constant. In the present study the sodium salts of a number of bromoacids, including the isomeric α-, β- and γ-bromocaproic acids have been chosen for investigation. These substances are soluble in water, and the kinetics of substitution (of oxygen for bromine) are easily followed by measuring the rate of release of the bromide ion. Here, of course, it is the carboxylate ion which plays the role of the neighboring group.

Method of Rate Measurement.—The measurements were carried out in a water-bath in which the temperature was thermostatically controlled to ±0.02°. Ordinarily a quantity of halogen acid sufficient to make the concentration of the sodium salt lie within the range 0.05–0.1 *M* was added to a solution 0.25 *M* in sodium bicarbonate which had been previously brought to the desired temperature. The rate of reaction was then followed by removing aliquot samples at convenient time inter-

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[1] William F. Meredith Fellow in Rutgers University, 1946–1947. Department of Chemistry, Bucknell University, Lewisburg, Penna.

[2] W. A. Cowdrey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1208 (1937).

[3] S. Winstein, *et al.*, THIS JOURNAL, (a) **61**, 1576 (1939); (b) **64**, 2780, 2778 (1942); (c) **70**, 821, 828 (1948).

[4] H. Johannson, *Ber.*, **48**, 1256 (1915); **55**, 647 (1922); *cf.* A. R. Olson and R. J. Miller, THIS JOURNAL, **60**, 2687 (1938).

[5] H. Freundlich and G. Salomon, *Z. physik. Chem.*, **166**, 161 (1933).