method, gave for the per cent. of U: 53.60, 53.44, 53.52 and 53.32, average 53.47.

Discussion of Results

The results show that uranium can be separated from iron and titanium by electrolysis of a solution containing these elements followed by the precipitation of titanium with cupferron. The uranium then can be determined volumetrically.

The average value of the uranium content found for kolm is slightly higher than that of Wells,[2] 0.462% compared to his average, 0.432%. This value, 0.462, also increases the discrepancy between the chemical analysis and the radioactive analysis of the kolm.

It is of interest to note that the uranium content of the Canadian uraninite found by the above described volumetric method (53.47%) is in close agreement with the value (53.52%) found by Wells, who made a gravimetric analysis on material taken from the same twenty-pound sample.

Summary

1. Large amounts of iron can be separated completely from small amounts of elements such as titanium, vanadium and uranium by electrolysis using a mercury cathode.

2. Uranium cannot be determined accurately in presence of titanium by titration with permanganate after reduction by zinc.

3. The color change of permanganate in cold colored solutions is remarkably intensified by the presence of a little diphenylamine sulfonic acid.

4. Uranium in kolm ash and in a Canadian uraninite was determined volumetrically. Results on both substances agree well with the gravimetric results reported by R. C. Wells.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF KENTUCKY]

Kinetics of the Reaction of the Thiosulfate Ion with the Ions of Brominated Malonic and Succinic Acids

BY M. H. BEDFORD, R. BURGESS MASON AND C. E. MORRELL

The velocities of ionic reactions of the second order have been found to be greatly influenced by the magnitude and sign of the charges on the reacting ions. Also it is well known that there is a marked dependence of the rate of such reactions on the ionic strength of the reaction medium. These effects have been considered in connection with the theory of interionic attraction and have been given a satisfactory explanation by Brönsted,[1] who has proposed the following well-known equation for the specific reaction rate in terms of the ionic charges and the ionic strength of the medium

$$\log k_1 = \log k_0 + Z_A Z_B \sqrt{\mu}$$

This equation has been tested by several investigators[2] and in a number of cases has been found to agree quite closely with experiment for very small values of the ionic strength.

However, reactions that do not conform to the Brönsted equation have been studied and their kinetics reported in the literature.[3] The kinetics of these reactions are of special interest because the anomalies they exhibit are probably due to the superposition on the Brönsted primary salt effect of influences arising from the nature of the structure of one or both of the ions. The kinetic effects due to the relative position within the ion of the ionic charge and the reacting group have been studied by La Mer and Kamner in the case of the bromopropionate ions.

In order to make a further study of such structural effects we have investigated the kinetics of the reaction of the thiosulfate ion with the ions of monobromomalonic acid and monobromosuccinic acid

$$S_2O_3^{=} + {}^{-}OOCHBrCOO^{-} \longrightarrow Br^{-} + {}^{=}OOC(S_2O_3)CHCOO^{-}$$

$$S_2O_3^{=} + {}^{-}OOCHBrCH_2COO^{-} \longrightarrow Br^{-} + {}^{=}OOC(S_2O_3)CHCH_2COO^{-}$$

These reactions were chosen because they involve ions containing a seat of charge at each end and a more or less centrally located reacting group. In order to obtain some information about the reactivity of the bromine atom due to its structural position in the molecule and independent of any interaction of ionic charges, the following

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[1] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[2] (a) J. Brönsted and C. E. Teeter, Jr., *J. Phys. Chem.*, **28**, 579 (1924); (b) J. Brönsted and R. Livingston, THIS JOURNAL, **49**, 435 (1927); (c) Victor K. La Mer, *ibid.*, **51**, 3341 (1929).

[3] (a) Victor K. La Mer and Mildred E. Kamner, *ibid.*, **53**, 2832 (1931); (b) J. B. Conant and W. D. Peterson, *ibid.*, **52**, 1220 (1930).

similar reactions of the esters of these acids were investigated

$$C_2H_5OOCCHBrCOOC_2H_5 + S_2O_3^{=} \longrightarrow Br^- + C_2H_5OOCCH(S_2O_3)^-COOC_2H_5$$

$$CH_3OOCCHBrCH_2COOCH_3 + S_2O_3^{=} \longrightarrow Br^- + CH_3OOCCH(S_2O_3)^-COOCH_3$$

The velocities of the reactions of these brominated ions and esters with water were not determined. However, preliminary experiments showed that such hydrolytic reactions proceed more slowly in the presence of thiosulfate than in water alone. For this reason we believe the errors due to the water reaction are negligible.

Preparation of Materials and Procedure

Ethyl monobromomalonate was prepared by brominating diethyl malonate in carbon tetrachloride according to the directions of Palmer and McWherter.[4] The crude product was washed with a solution of sodium carbonate, dried and purified by repeated distillation under vacuum. Analysis of the product used in the reaction mixtures gave a bromine content of 33.58%, a value which is in good agreement with the theoretical value of 33.44%. Potassium monobromomalonate was prepared from malonic acid by the method of Conrad and Reinbach.[5] Dry bromine was added slowly to an ether solution of recrystallized malonic acid. After the product was freed of ether, it was dissolved in water and the potassium salt precipitated by adding potassium acetate and alcohol. The recrystallized product was found to have a potassium content of 29.53%; the theoretical value is 30.10%.

Monobromosuccinic acid and its dimethyl ester were both prepared according to the directions of J. Volhard.[6] Crude monobromosuccinyl bromide was obtained by the action of dry bromine on a mixture of succinic acid and red phosphorus. The impure acid was prepared from this material by hydrolysis with warm water. Impurities were removed by several crystallizations at 50–60° under diminished pressure. Titrations with standard alkali using phenolphthalein as indicator gave the molecular weight of the pure product to be 196.9; the theoretical value is 197.0. For the preparation of the methyl ester of monobromosuccinic acid, the crude acid bromide was esterified with absolute methyl alcohol and the resulting mixture was diluted with ether. After drying with calcium chloride and distilling off the ether, the ester was purified by distillation under 10–12 mm. pressure. The proper fraction boiling at 110–112° was found to contain about 5% of hydrogen bromide produced by decomposition in the distillation flask. Even by long standing in a vacuum desiccator over sodium hydroxide all the hydrogen bromide could not be removed. The purity of the ester was controlled by determinations of the total bromine content and the free acidity of the mixture. By combining the results of such analyses the ester, except for the hydrogen bromide, was found to be 99% pure. Before starting the ester reactions this free acid was neutralized with standard alkali and the resulting sodium bromide was considered in calculating the ionic strength of the reacting solution.

Except for slight changes the experimental procedure was essentially the same as that employed by La Mer and Kamner[3a] in their work on the bromopropionate–thiosulfate reactions. The velocity constants of the reactions were determined by mixing known amounts of thiosulfate solution with water solutions of known concentrations of the other reagent and determining, at intervals during the course of the reaction, the amount of unchanged thiosulfate. Samples were pipetted from the reaction flask, drained into standard iodine solution and the excess iodine titrated with thiosulfate of the appropriate strength. Weight burets were used in such determinations as well as in standardizations. Volumetric apparatus was calibrated. The reactions were carried out in the presence of air. The reaction flasks were thoroughly cleaned with soap, cleaning solution, and steam and then dried in an oven at 140–150° for several hours.

The precautions recommended by La Mer and Kamner were taken to ensure stability of the thiosulfate solutions. The 0.5% starch solution was made from soluble starch. When made it was transferred immediately to small sterilized bottles and kept tightly sealed until ready for use. All titrations were carried out in the presence of 2–3% potassium iodide. The more dilute thiosulfate solutions were standardized against pure potassium iodate, while for 0.1 normal solutions standard dichromate solutions, previously checked against pure iron wire, were used. The iodine solutions were frequently checked by titration with thiosulfate. All reactions were run at 25.00 ± 0.05°. The values of the specific reaction rates were calculated by means of the following formula for second order reactions

$$k_1 = \frac{1}{(a_1 - b_1)}\,\frac{1}{t}\ln\frac{b_1\,(a_2 - x)}{a_1\,(b_2 - x)}$$

where k_1 is the specific reaction rate; a_1 the initial concentration in moles per liter of the reagent taken in excess; b_1 the initial concentration in moles per liter of the other reagent; a_2 and b_2 the numbers of moles present in a 25-ml. portion of the reaction mixture at the start of the reaction; and x the number of moles of thiosulfate ion that is lost by a 25-ml. portion in t minutes.

Results and Discussion

Since, in the ionic reactions investigated in this work, two divalent ions react to form a monovalent ion and a trivalent ion, it is evident that the ionic strength increases during the course of the reaction. For equivalent quantities of reacting substances this increase would amount to 25% when the reaction is complete. Since however an excess of thiosulfate was used in all the reaction mixtures and all measurements were taken before more than 80% of the other reagent was consumed, the largest change in ionic strength of any solution during the period of measurement amounted to 10–15%. The change in the case

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[4] C. S. Palmer and P. W. McWherter, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 34.

[5] M. Conrad and H. Reinbach, *Ber.*, **35**, 1813 (1902).

[6] J. Volhard, *Ann.*, **242**, 141 (1887).

of the ester reactions was much larger and for equivalent quantities represented at the end of the reaction a decrease to 50% of the original value. We have not taken into account such variations and the values of $\sqrt{\mu}$ given below are the values at the start of the reaction. This change in the ionic strength of the medium caused a drift in the values of the reaction constant during the course of the reaction. The tables show the drifts that were observed in typical runs.

Table I

Potassium Monobromomalonate and Thiosulfate

$\sqrt{\mu} = 0.457$ $a_1 = 57.5 \times 10^{-3}$ $b_1 = 12.03 \times 10^{-3}$

$a_2 = 1.437 \times 10^{-3}$ $b_2 = 0.3008 \times 10^{-3}$

Time, min.	10^5 moles thio. used	$k_1 \times 10^3$
4484	12.96	2.297
8677	19.00	2.171
14997	23.44	1.955
18647	24.95	1.863

Table II

Sodium Monobromosuccinate and Thiosulfate

$\sqrt{\mu} = 0.351$ $a_1 = 26.18 \times 10^{-3}$ $b_1 = 15.00 \times 10^{-3}$

$a_2 = 0.655 \times 10^{-3}$ $b_2 = 0.375 \times 10^{-3}$

Time, min.	10^5 moles thio. used	k_1
1261	28.5	0.0598
1514	29.2	.0541
2140	30.8	.0506
2345	32.7	.0502

Tables III and IV summarize the results obtained in the case of the ionic reactions. The values given for k_1 are averages of four to six determinations.

Table III

Potassium Monobromomalonate and Thiosulfate

$\sqrt{\mu}$	$k_1 \times 10^3$	Log k_1 + 3
0.457	2.24 ± 0.32	0.3516
.436	1.62 ± .18	.2095
.411	3.83 ± .45	.5832
.313	4.42 ± .78	.6454
.278	8.79 ± .76	.9940
.234	2.54 ± .29	.4060 (?)
.227	10.8	1.0334
.138	6.11 ± .29	0.7860
.101	12.97 ± 1.20	1.1132

Table IV

Sodium Monobromosuccinate and Thiosulfate

$\sqrt{\mu}$	k_1	Log k_1 + 2
0.507	0.0280 ± 0.003	0.447
.447	.0243 ± .002	.386
.351	.0541 ± .004	.733
.212	.0679 ± .024	.832
.152	.119 ± .014	1.076
.0918	.211 ± .004	1.324
.0807	.362 ± .018	1.559

Due to its very low solubility in water it was necessary to run the reaction with diethyl monobromosuccinate in 40% alcohol. Under these conditions the reaction proceeded so rapidly that it was impossible to study it with the methods at hand. Several measurements were attempted but in every case the reaction was found to go to completion within a period of five minutes. However, the methyl ester of monobromosuccinic acid was sufficiently soluble in water that its reaction with thiosulfate ion could be studied. The results obtained from this reaction are presented in the following table.

Table V

Dimethyl Monobromosuccinate and Thiosulfate

$\sqrt{\mu}$	Concentration of ester	k_1
0.389	0.009900	0.0736 ± 0.0002
.386	.004781	.0742 ± .0005
.384	.003465	.0755 ± .0005
.300	.003960	.0766 ± .0008
.230	.009900	.0773 ± .0010
.173	.003960	.0782 ± .0020
.123	.002475	.0805 ± .0012

Graphs of the above data are shown in Figs. 1–3.

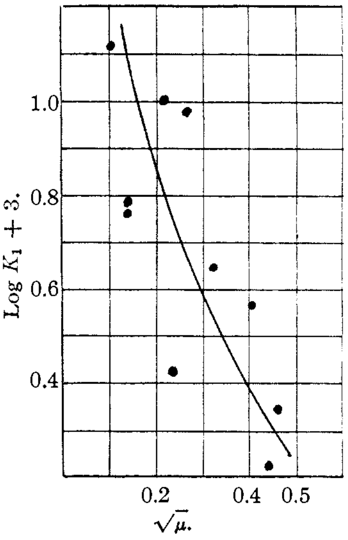

Fig. 1.—Potassium monobromomalonate–thiosulfate reaction.

Although the values of k_1 for the ionic reactions do not fall on smooth curves when plotted against the values of the square root of the ionic strength, they show a very definite increase with decreasing ionic strength. Since the Brönsted theory would predict a limiting slope of four for these curves, the observed effect, which is of the opposite sign to this prediction, must be due to some other influence arising from the nature of the ions themselves. La Mer and Kamner, in accounting for a similar behavior on the part of the β-bromopropionate ion, have suggested that, in the case of ions possessing an aliphatic chain structure, ionic orientation may play the dominant role in regulating the velocity of reaction. Since the ionic chains in this case have excess negative charges at each end, it seems reasonable that, due to electrostatic interaction, such chains must be oriented in a definite manner with respect to negatively charged thiosulfate ions before fruitful collisions can occur. Due to the thermal motion of neighboring ions, the electric field in the vicinity of a given ion should undergo greater fluctuations in solutions of larger ionic strength. Such rapidly changing electric fields would decrease the probability of ideal orientation, and hence, on the basis of such considerations, one would expect the velocity of reaction to decrease with increasing ionic strength.

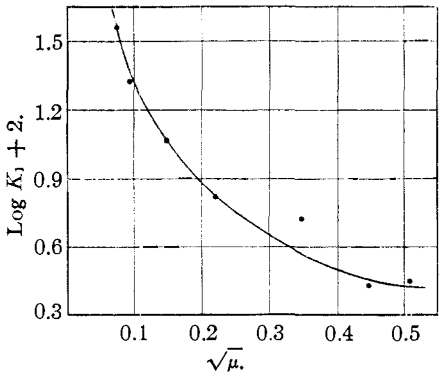

Fig. 2.—Sodium monobromosuccinate and thiosulfate.

A comparison of the velocities of the ester and salt reactions gives some information concerning the chemical reactivity of the bromine atom as related to its position in the molecule. In the case of the ester of monobromomalonic acid, where the bromine atom is in the α-position with respect to the two carboxyl groups, the chemical reactivity is quite large, while in the case of the monobromosuccinic ester the activity is less on account of the greater separation of the bromine atom from the acid groups. Due to the proximity of the bromine atom to the ionic charges the potassium monobromomalonate reaction was very slow, whereas in the case of the monobromosuccinate ion, where the distance between ionic charges and reacting group is larger, the reaction was much faster. These results show the important effect of electrostatic interaction in regulating the speed of such reactions.

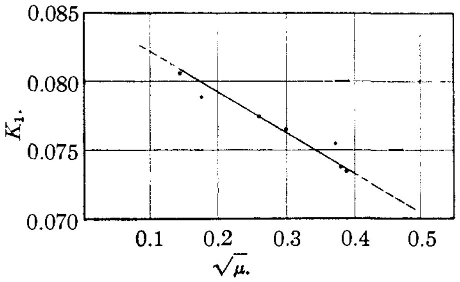

Fig. 3.—Dimethyl succinate and thiosulfate.

Summary

The velocities of the reactions of the esters and the alkali salts of monobromomalonic acid and monobromosuccinic acid with thiosulfate ion have been measured over a range of concentrations. The results cannot be accounted for on the basis of Brönsted's theory alone, but must be explained by means of La Mer and Kamner's theory of oriented ionic collisions.

LEXINGTON, KENTUCKY RECEIVED AUGUST 3, 1933