[Contribution from the Department of Chemistry, University of Kentucky]

Rates of Reaction of Brominated Malonic and Succinic Acid Salts with the Thiosulfate Ion at Two Temperatures[1]

By M. H. Bedford, R. J. Austin and W. L. Webb

During the past few years the reaction rates of both brominated fatty acids and brominated dibasic acids with the thiosulfate ion have been determined.[2,3,4] These reactions were carried out in a variety of media and the effects of the position of the bromine atom in the carbon chain and the length of the chain have been studied. Some investigators have found that the rates of reaction vary with the ionic strength in accordance with the well-known Brönsted equation[5]

$$\log k_1 = \log k_0 + Z_1Z_2\sqrt{\mu}$$

while others found an inverse relation between the two variables (k_1, $\sqrt{\mu}$). These discrepancies with the Brönsted equation have been explained by the orientation hypothesis of La Mer and Kamner.[3]

In order to make a further study of such structural effects the reaction rates of the following reactions have been studied at two temperatures

$$S_2O_3^{=} + {}^{-}OOCCHBrCOO^{-} \longrightarrow {}^{-}OOCCH(S_2O_3)COO^{=} + Br^{-}$$

$$S_2O_3^{=} + {}^{-}OOCCHBrCH_2COO^{-} \longrightarrow {}^{-}OOCCH(S_2O_3)CH_2COO^{=} + Br^{-}$$

An attempt was also made to determine the energies of activation of these two reactions from the equation[6]

$$\ln k = (-E/RT) + B$$

where k is the specific reaction rate, E the energy of activation, R the gas constant, T the absolute temperature and B the constant of integration.

Preparation of Materials and Procedure

Potassium monobromomalonate was prepared by brominating malonic acid according to the directions of Erdmann.[7] The crude acid was prepared from c. p. monochloroacetic acid.[8] This method of preparation gave a salt which showed a potassium content of 30.05%, and a bromine content of 30.31%. The theoretical values are 30.18 and 30.84%, respectively. A purity of 98.28% was used in all calculations. Monobromosuccinic acid was prepared according to the directions of J. Volhard.[9] The bromine content of this acid was found to be 41.25% against a theoretical value of 40.62%. A molecular weight of 199.2 was calculated from the acid titration value whereas the theoretical value is 196.9. On the assumption that the impurity was dibromosuccinic acid, the bromide analysis yielded a purity of 95.96% and the acid–base titration gave a purity of 95.23%. The average purity of 95.6% was used in all calculations.

Thiosulfate solutions were prepared and standardized against standard iodate solutions. Iodine solutions, which were standardized against the thiosulfate solutions, were also prepared. The starch solution was made according to the directions of Treadwell and Hall.[10] The strengths of all solutions were expressed in weight normality and all thiosulfate–iodine titrations were carried out in 4% potassium iodide solution to utilize the maximum sensitivity of the starch–iodine end-point. Weight burets were used throughout the work. A 0.1 N sodium hydroxide solution was prepared for the neutralization of the monobromosuccinic acid solutions.

All glass apparatus was cleaned with sulfuric acid–chromic acid cleaning solution and distilled water, and finally treated for one-half hour with live steam. The volumetric apparatus was standardized at the temperatures of the runs.

The reaction mixtures were made as follows: a weighed amount of 0.1 N thiosulfate solution was diluted almost to 250 cc. in a volumetric flask and placed in the thermostat. The correct weight of salt was then washed into another 250-cc. volumetric flask, diluted nearly to the mark and placed in the thermostat. (In the monobromosuccinate runs the correct weight of acid was placed in the flask, exactly neutralized with 0.1 N sodium hydroxide, diluted nearly to the mark, etc.) When the contents of the two flasks had

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(1) Presented at the Cleveland Meeting of the American Chemical Society, September, 1934.

(2) Arthur Slator, *J. Chem. Soc.*, **85**, 1286 (1904).

(3) Victor K. La Mer, This Journal, **51**, 3341 (1929); Victor K. La Mer and Mildred E. Kamner, *ibid.*, **53**, 2832 (1931).

(4) M. H. Bedford, R. Burgess Mason and C. E. Morrell, *ibid.*, **56**, 280 (1934).

(5) J. N. Brönsted and Robert Livingston, *ibid.*, **49**, 435 (1927).

(6) Victor K. La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

(7) Hugo Erdmann, "Anleitung zur Darstellung organischer chemischer Präparate," p. 231.

(8) Roger Adams and C. S. Marvel, University of Illinois Bulletin, **19**, 12–14 (1921).

(9) J. Volhard, *Ann.*, **242**, 141 (1887).

(10) Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 7th ed., Vol. II, p. 556.

come to the correct temperature they were diluted to exactly 250 cc. and then poured into a 600-cc. Kjeldahl flask. The 250-cc. flasks were allowed to drain for two minutes. The reaction velocity for each run was determined by withdrawing 25-cc. portions (exactly one-twentieth of the reaction mixture) at various times, running them into weighed amounts of iodine solution and titrating with thiosulfate solution to a colorless starch end-point. A thermostat which varied less than 0.1° was used for the 35 and 50° runs. The runs at 0° were carried out in tubs containing cracked ice. The values of the specific reaction rate were calculated from the formula

$$K = \frac{1}{a-b}\,\frac{1}{t}\ln\frac{b\,(a'-x)}{a\,(b'-x)} \qquad a > b$$

in which K is the specific reaction rate, a is the concentration of the thiosulfate at the beginning of the reaction, b is the concentration of the salt at the beginning of the reaction, a' and b' are the equivalents present in any single portion (25 cc.) at the beginning of the reaction and x is the equivalents of the resultant product, which is identical with the equivalents of the thiosulfate used.

Results and Discussion

Tables I and II show data taken on typical runs of the monobromomalonate–thiosulfate reaction and monobromosuccinate–thiosulfate reaction at 0°.

TABLE I

POTASSIUM MONOBROMOMALONATE AND SODIUM THIOSULFATE REACTION AT 0°

Run 3

$\mu = 0.03748$ $\sqrt{\mu} = 0.1936$	$c = 84.96 \times 10^{-4}$ $a' = 2.127 \times 10^{-4}$	$b = 39.43 \times 10^{-4}$ $b' = 0.9858 \times 10^{-4}$
Time, min.	Equiv. thio. in 25 cc.	$K \times 10^3$
4,249	2.057×10^{-4}	1.022
19,029	1.948	1.299
31,942	1.879	1.137
42,277	1.843	1.139
		Average, 1.149

TABLE II

SODIUM MONOBROMOSUCCINATE AND SODIUM THIOSULFATE REACTION AT 0°

Run 1

$\sqrt{\mu} = 0.325$ $c = 0.0014$	$a = 20.42 \times 10^{-3}$ $a' = 0.5105 \times 10^{-3}$	$b = 14.29 \times 10^{-3}$ $b' = 0.3572 \times 10^{-3}$
Time, min.	Equiv. thio. in 25 cc.	$K \times 10^2$
7,374	0.4486×10^{-3}	0.136
10,158	.4279	.136
13,236	.4091	.135
20,178	.3748	.137
		Average, .136

A slight drift will be observed in the values of K in the first table. This drift can be attributed to experimental error or more probably to the decomposition of the thiosulfate. As data were taken over a time interval of thirty days, it is not at all unlikely that a small part of the thiosulfate would be changed to the sulfite. The strengths of the thiosulfate standards showed a slight change over this period of time and their normalities were corrected for the various times assuming a linear change. At the end of this time interval the reactions were from 10 to 20% complete. A calculation using the observed reaction rate showed that in the most concentrated run (1) the reaction would have been 95% complete in thirty-nine weeks. Due to the fact that this reaction is so extremely slow, other errors of a mathematical nature would be introduced. It can be seen that the value of the term $b(a'-x)/a(b'-x)$ in the mathematical equation of the reaction rate approaches 1 as x approaches 0. In this range the logarithm changes very rapidly. As, in this work, x is of the order of 1 or 2% of b, the slightest error in x would cause a much larger one in the logarithmic term. This could account for the discrepancy in the first few values for the reaction rates in each run.

Tables III and IV show the summaries of the data taken at 0°.

TABLE III

SUMMARY OF POTASSIUM MONOBROMOMALONATE AND SODIUM THIOSULFATE REACTION AT 0°

Run	$\sqrt{\mu}$	Average $K \times 10^3$
1	0.2852	0.5498
2	.2076	.7752
3	.1936	1.149
4	.1869	1.434
5	.1584	1.513
6	.1325	2.286
7	.1170	3.286

TABLE IV

SUMMARY OF SODIUM MONOBROMOSUCCINATE AND SODIUM THIOSULFATE REACTION AT 0°

Run	$\sqrt{\mu}$	Average $K \times 10^2$
1	0.325	0.136
2	.221	.179
3	.210	.306
4	.191	.240
5	.186	.422
6	.151	.318
7	.141	.458
8	.068	4.10

When log K is plotted against $\sqrt{\mu}$ (Fig. 1) the curves obtained have slopes of the order of -5. This is in disagreement with the Brönsted

Equation[6] as it predicts a slope of +4. This disagreement can be explained by the orientation hypothesis of La Mer and Kamner.[3] In the case of the more concentrated solution more resistance would be offered to the orientation of the molecules than in the weaker solution and therefore the rate should increase rapidly with decreasing concentration.

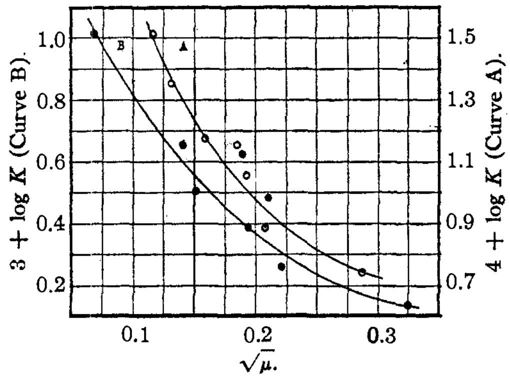

Fig. 1.—Reactions at 0°: ○, potassium monobromomalonate reaction (Curve A); ●, sodium monobromosuccinate reaction (Curve B). Curve B was first drawn with respect to all points but interpolated points from this curve (marked with a superscript *a* in Table VI) did not give good values for the energy of activation. The curve was then drawn with respect to the lower points, giving values which are in better agreement.

Table V shows a summary of the data for the monobromosuccinate–thiosulfate runs at 35°.

Table V

Summary of Sodium Monobromosuccinate and Sodium Thiosulfate Reaction at 35°

Run	$\sqrt{\mu}$	K_1
1	0.325	No average
2	.238	0.298
3	.221	No average
4	.219	0.323
5	.205	.320
6	.192	.335

By comparing these data (Tables IV and V) with the data taken by Morrell[4] for the same reaction at 25°, the energies of activation can be calculated for three temperature intervals. These are given in Table VI.

Table VI

Activation Energy and Temperature Coefficient for the Succinate–Thiosulfate Reaction

Range, 0 – 25°

K (25°)	$\sqrt{\mu}$ (25°)	K (0°)	$\sqrt{\mu}$ (0°)	Temp. coeff.	E act. (Cal.)	B (min.)
0.0541	0.351	0.00136	0.325	4.36	23,880	16.2
.0679	.212	.00179	.221	4.29	23,570	16.1
.0679	.212	.00306	.210	3.50	20,080	17.3
.119	.152	.00318	.151	4.26	23,470	16.3

Range, 25–35°

K (35°)	$\sqrt{\mu}$ (35°)	K (25°)	$\sqrt{\mu}$ (25°)	Temp. coeff.	E act. (Cal.)	B (min.)
0.298	0.238	0.0597[a]	0.238	4.99	29,090	20.1
.323	.219	.0679	.212	4.76	28,220	19.5
.320	.205	.0679	.212	4.72	28,050	19.4
.335	.192	.0714[a]	.192	4.69	27,970	19.3

Range, 0–35°

K (35°)	$\sqrt{\mu}$ (35°)	K (0°)	$\sqrt{\mu}$ (0°)	Temp. coeff.	E act. (Cal.)	B (min.)
0.323	0.210	0.00179	0.221	4.42	24,820	17.1
.335	.192	.00246	.191	4.08	23,480	16.6

The data taken for the monobromomalonate–thiosulfate runs at 50° show a decided drift which is probably due to one or more simultaneous reactions. The reaction mixtures showed the same *p*H after a week as at the beginning of the reaction, indicating that there was very little hydrolysis of the salt at 50°. The most probable reaction is the decomposition of the thiosulfate. In fact, in a controlled run on the thiosulfate at 50°, the reducing power of the solution was found to be considerably greater after a time interval of forty hours. Also the reaction mixture showed a considerable quantity of sulfite at the end of the reaction. Practically no sulfate was found to be present at the end of the runs, indicating that the products of the reaction were not hydrolyzed to form mercaptans. As the drift in the data at this temperature was so pronounced no attempt was made to average the various values of K and no one value was taken as the reaction rate.

By combining the data in Table III with those reported by Mason[4] for the same reaction at 25°, the temperature coefficient was found to be 3.7 to 3.9 for the 25° temperature interval and therefore the energy of activation is of the order of 10,000 calories. Unfortunately, the amount of comparable data in the two investigations is so meager that nothing more than a very crude approximation of the activation energy can be made. This value, 10,000 calories, seems entirely too low in view of the values reported for the monobromosuccinate–thiosulfate reaction and the value of 24,000 ± 1000 calories reported by La Mer[11] for the β-propionate–thiosulfate reaction. This discrepancy can be attributed to the fact that the two reaction rate constants were determined by different persons using different salts. Even when the same salt is used for the determination

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(11) Victor K. La Mer, This Journal, 55, 1739 (1933).

of both values of K, a considerable variation in the energy of activation is found.

Summary

The velocities of the monobromomalonate–thiosulfate reaction and the monobromosuccinate–thiosulfate reaction have been measured at various concentrations and temperatures. The results cannot be accounted for on the basis of the Brönsted theory, but must be explained by means of the La Mer and Kamner theory of orientation. The values of the energies of activation of these two reactions have been calculated. However, the value for the former reaction is so low that little significance can be attached to it.

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The Constitution of Isosucrose

BY JAMES COLQUHOUN IRVINE AND DONALD ROUTLEDGE

It is now recognized that despite many attempts to control and modify the reaction, the condensation of tetraacetylglucose with tetraacetyl-γ-fructose does not lead to the formation of sucrose octaacetate but gives the corresponding derivative of an isosucrose as the only definite product. Faulty manipulation during the condensation or in the course of isolating the products cannot be held responsible for this result as isosucrose is much less stable to hydrolysis than is sucrose and the capacity of the isosucrose octaacetate to crystallize is no more pronounced than is that of sucrose octaacetate. Several explanations may be put forward to account for the failure of the reaction to yield sucrose and among them must be included the possibility that despite the evidence of methylation the accepted constitution of sucrose is incorrect, but the simplest view is that in the synthesis of isosucrose the fructose component reacts as the β-stereoisomeride in place of the α-form. In such an event, sucrose and isosucrose may be regarded as isomeric disaccharides constituted on the same structural model and differing merely in the configuration of the glucosidic-fructosidic linking. If this view be correct, the hydrolysis of a fully methylated isosucrose should give the same products as are obtained from octamethylsucrose, *viz.*: (a) normal tetramethylglucose and (b) tetramethyl-γ-fructose. This we have ascertained to be the case.

While the reactions involved—methylation, hydrolysis and separation of the scission sugars—are simple in theory, the practical execution is in this instance beset with difficulties. Isosucrose is not readily available in the quantities required, the sugar is much more liable to undergo molecular rupture than is sucrose and the methylation is more tedious. Moreover, when the methylation is conducted by either of the two standard methods, it is arrested sharply at the heptamethyl stage and although as in the case of sucrose itself the hydrolysis of this derivative gives valid evidence of the structure of the parent disaccharide, it was not considered advisable to rely on such a method in the present instance and it became necessary to find a route to octamethylisosucrose.

Our preparations of isosucrose octaacetate have of necessity been carried out on a scale considerably larger than any hitherto attempted. In all, 0.75 kg. of the mixed glucose and fructose tetraacetates was brought into reaction and the fact that no trace of sucrose was found in the product speaks for itself sufficiently. The isosucrose octaacetate was methylated in the first series of experiments by the silver oxide process following the method originally applied by Purdie and Irvine to sucrose.[1] As stated, the methylation could not be extended beyond the heptamethyl stage and the eighth alkyl group could not be introduced. Precisely the same result was obtained when the methyl sulfate method of alkylation was employed either alone or in conjunction with the silver oxide method. This heptamethylisosucrose is not, however, a uniform chemical individual, as hydrolysis revealed that the steric hindrance to methylation was shared to approximately an equal extent by both the glucose and the fructose components. Complete methylation was, however, effected by dissolving the heptamethylate in liquid ammonia and converting it

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[1] Purdie and Irvine, *J. Chem. Soc.*, **83**, 1036 (1903).