In solutions of essentially constant acidity, a condition which is attained when the reaction is carried out in solutions with a fixed buffer ratio, equation 13 could be considered to indicate general acid catalysis. However, our results in both water and methanol indicate that the molar catalytic constant for acetic acid is zero. Therefore, one must conclude that the reaction is subject to general base catalysis only.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY, UNIVERSITY OF PADOVA]

Kinetics of the Catalytic Rearrangement of Tetrathionate

BY ANTONINO FAVA[1] AND SILVANO BRESADOLA

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The catalytic effect of thiosulfate on the rearrangement of tetrathionate in tri- and pentathionate, has been investigated kinetically. The rate of disappearance of tetrathionate has been determined by titration with the cyanide method. The initial rate was extrapolated graphically and found to be proportional to the initial concentration of tetrathionate and thiosulfate. An equation has been derived based on the assumption that the rearrangement is due to the reaction between a molecule of tetrathionate and one of thiosulfate giving one molecule of pentathionate and one of sulfite. The latter, whose concentration is always very small, may in turn react (specific rate k_2) with the tetrathionate in excess giving trithionate and thiosulfate, or with the pentathionate formed in the mean time going back to tetrathionate and thiosulfate (specific rate k_{-1}). The experimental values are found to fit the equation. Moreover the ratio k_{-1}/k_2 given by the equation closely agrees with that obtained from the values of k_{-1} and k_2 found in literature. The influence of different electrolytes at constant ionic strength is shown, and the strong catalysis of polyvalent positive ions is pointed out.

Higher polythionates in neutral solution decompose under the action of thiosulfate ions according to the equations

$$2S_4O_6^{--} \longrightarrow S_3O_6^{--} + S_5O_6^{--} \qquad (1)$$

$$S_5O_6^{--} \longrightarrow S_4O_6^{--} + S \qquad (2)$$

$$S_6O_6^{--} \longrightarrow S_5O_6^{--} + S \qquad (3)$$

Catalysis of thiosulfate ions has been known for a long time and studied by several workers. A complete bibliography on the argument may be found in papers of Foss[2a] and Goehring.[2b]

The most studied of these reactions is the tetrathionate rearrangement. The reaction occurs according to equation (1) only initially because when the concentration of pentathionate becomes high, other side reactions take place, sulfur separates, and concentration of pentathionate is no longer equal to that of trithionate. This paper deals only with the first part of the reaction, that is up to the point where tri- and pentathionate cease to be formed in equimolecular amounts. Though several authors have put forward hypotheses about the probable mechanism and the literature reports approximate values of velocity, no kinetic work has been done as yet, so that no unambiguous mechanism can be suggested.

We have, therefore, studied kinetically this reaction with the purpose of deciding between the proposed mechanisms.

Some authors[3-6] have suggested that thiosulfate catalysis is due to the dissociation of thiosulfate, according to

$$S_2O_3^{--} \longrightarrow SO_3^{--} + S \qquad (4)$$

followed by

$$S_4O_6^{--} + S \longrightarrow S_5O_6^{--} \qquad (5)$$

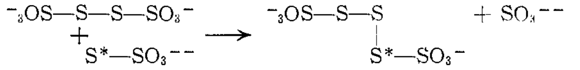
$$S_4O_6^{--} + SO_3^{--} \longrightarrow S_3O_6^{--} + S_2O_3^{--} \qquad (6)$$

However this point of view has been criticized by Foss[7-9] and by Goehring, Helbing and Appel,[10] who suggested that rearrangement of tetrathionate is due to the reactions

$$S_4O_6^{--} + S_2O_3^{--} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} S_5O_6^{--} + SO_3^{--} \qquad (7)$$

$$S_4O_6^{--} + SO_3^{--} \xrightarrow{k_2} S_3O_6^{--} + S_2O_3^{--} \qquad (8)$$

This interpretation is more consistent with the chemical behavior of polythionates. According to this hypothesis the first step is the nucleophilic attack on the chain of sulfur atoms of tetrathionate by a thiosulfate ion, with displacement of sulfite according to the scheme



$$^{-}{}_3OS{-}S{-}S{-}SO_3^{-} + S^*{-}SO_3^{--} \longrightarrow {}^{-}{}_3OS{-}S{-}\underset{\displaystyle S^*{-}SO_3^{-}}{S} + SO_3^{--}$$

This view seems very likely since Foss' hypothesis concerning the exchange of thiosulfuric groups between thiosulfate ion and polythionates has been experimentally confirmed[11] by exchange experiments with isotopically labeled thiosulfate and polythionates.

Our reasoning is therefore based on reactions (7) and (8): one molecule of tetrathionate reacts with one molecule of thiosulfate, with specific rate k_1, giving one molecule of pentathionate and one molecule of sulfite. The latter may now react either with tetrathionate in excess giving thiosulfate and trithionate according to (8) with specific rate k_2, or with the pentathionate formed simultaneously, giv-

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[1] Department of Chemistry, University of Utah, Salt Lake City Utah.

[2] (a) O. Foss, *Kgl. Norske Videnskabers Selskab. Skrifter*, 1945 NR 2 (1947). (b) M. Goehring, *Fortschr. Chem. Forsch.*, **2**, 444 (1952).

[3] A. Kurtenacker, *Z. anorg. Chem.*, **148**, 225 (1925).

[4] A. Colefax, *J. Chem. Soc.*, **93**, 708 (1908).

[5] F. Foerster and A. Hornig, *Z. anorg. Chem.*, **126**, 86 (1922).

[6] F. Foerster and K. Centner, *ibid.*, **157**, 45 (1926).

[7] See reference 2a, p. 117.

[8] O. Foss, *Acta Chem. Scand.*, **3**, 1385 (1949).

[9] O. Foss, *ibid.*, **4**, 866 (1950).

[10] M. Goehring, W. Helbing and I. Appel, *Z. anorg. Chem.*, **254**, 185 (1947).

[11] A. Fava, *Gazz. chim. ital.*, **83**, 87 (1953).

ing thiosulfate and tetrathionate, with specific rate k_{-1}.

According to these views the rate of disappearance of tetrathionate is

$$-\frac{\mathrm{d}S_4}{\mathrm{d}t} = k_1S_4S_2 + k_2S_4S - k_{-1}S_5S \qquad (9)$$

and the rate of formation of sulfite is[12]

$$\frac{\mathrm{d}S}{\mathrm{d}t} = k_1S_4S_2 - k_2S_4S_2 - k_{-1}S_5S \qquad (10)$$

Since the sulfite concentration is practically zero, we can apply the steady-state approximation and put

$$\mathrm{d}S/\mathrm{d}t = 0 \qquad (11)$$

This leads to

$$S = \frac{k_1S_4S_2}{k_2S_4 + k_{-1}S_5} \qquad (12)$$

Substituting (12) in (9) we obtain

$$-\frac{\mathrm{d}S_4}{\mathrm{d}t} = \frac{2k_1k_2S_4{}^2S_2}{k_2S_4 + k_{-1}S_5} \qquad (13)$$

Because of the stoichiometry of reactions (7) and (8), the concentration of pentathionate is equal to one-half that of the transformed tetrathionate. Therefore, calling a the initial concentration of tetrathionate, we have

$$S_5 = \frac{1}{2}(a - S_4) \qquad (14)$$

Putting (14) in (13) we obtain

$$-\frac{\mathrm{d}S_4}{\mathrm{d}t} = 2k_1k_2S_2\frac{S_4{}^2}{S_4\left(k_2 - \frac{1}{2}k_{-1}\right) + \frac{1}{2}k_{-1}a} \qquad (15)$$

Since S_2 acts as catalyst its concentration is constant with time, so that (15) may be integrated. Integration between times zero and t gives

$$\frac{k_{-1}}{k_2} = \frac{4tk_1S_2 - 2\ln(a/S_4)}{a/S_4 - \ln(a/S_4) - 1} \qquad (16)$$

The specific rate k_1 may be obtained by direct measurement of the initial rate of disappearance of tetrathionate. At the beginning, when the concentration of S_5 is exceedingly small, equation 13 becomes

$$-\left(\frac{\mathrm{d}S_4}{\mathrm{d}t}\right)_{t=0} = 2k_1S_4S_2 \qquad (17)$$

Therefore, if the hypotheses on which equation 16 is based are correct, putting the experimentally determined values of k_1, t and S_4 into it, it should give constant values.

Experimental

The reaction has been followed by determining tetra- and pentathionate at the same time according to Kurtenacker's[13] cyanide method as improved by Foss.[14]

Pure tetrathionate, prepared according to the method of Stamm, Goehring and Feldmann,[15] and commercial pure thiosulfate were used.

Since one of the most important pieces of data is the initial rate, we used a Y-shaped vessel by means of which the solutions can be mixed when the desired temperature is attained. Therefore, the initial sample is withdrawn practically at zero time. For each time three 5-cc. samples are withdrawn: one is titrated with iodine in order to obtain the value of the thiosulfate concentration; both of the others are titrated by the cyanide method in order to have two values for the tetra- plus pentathionate concentrations.

$^1/_{50}$ N iodine solution standardized against As_2O_3, was used. The reaction was studied in a buffered solution at a pH 7.15 using a KH_2PO_4/Na_2HPO_4 buffer. Except for some experiments on the influence of electrolytes on rate, the ionic strength was kept constant at 0.94, and adjusted with sodium sulfate. The temperature was 50.0 ± 0.1° in all runs.

In Table I the results for a typical run are given.

TABLE I

VARIATION OF CONCENTRATION OF TETRATHIONATE WITH TIME

$(K_2S_4O_6) = 3.87 \times 10^{-2}$; $(Na_2S_2O_3) = 2.38 \times 10^{-2}$; $(Na_2SO_4) = 2.5 \times 10^{-1}$. a = cc. of $^1/_{50}$ N iodine per 5 cc. of soln. (= thiosulfate). b = cc. of $^1/_{50}$ N iodine per 5 cc. of soln. after reaction with cyanide (= thiosulfate + tetra- + pentathionate). $b - a$ = tetra- + pentathionate.

t, min.	a	b	$S_4 \times 10^2$	$\frac{4tk_1S_2 - 2\ln(a/S_4)}{a/S_4 - \ln(a/S_4) - 1}$
0	5.95	15.62	3.868	..
6	5.95	15.39	3.684	(25.7)
15	5.95	15.19	3.536	(29.4)
30	5.96	14.92	3.300	(21.9)
50	6.00	14.63	3.036	16.5
75	6.05	14.44	2.844	17.0
105	6.08	14.23	2.532	17.0
140	6.11	14.03	2.468	16.3
180	6.19	13.90	2.300	16.0
225	6.26	13.78	2.148	15.8
275	6.30	13.72	2.068	17.6

It can be seen that thiosulfate concentration is not strictly constant, but increases slightly with time. However for short time it is practically constant and does not interfere with the measurement of initial rate.

The increase in concentration of thiosulfate is very likely due to the hydrolysis of the trithionate,[5] according to

$$S_3O_6{}^{--} + H_2O \longrightarrow S_2O_3{}^{--} + 2H^+ + SO_4{}^{--} \qquad (18)$$

In order to evaluate k_1, we determined the initial rate of disappearance of tetrathionate for a number of concentrations of tetrathionate and thiosulfate. Results are collected in Table II.

TABLE II

INITIAL RATE OF DISAPPEARANCE OF TETRATHIONATE IN MOLE L.$^{-1}$ MIN.$^{-1}$ FOR VARIOUS CONCENTRATIONS OF TETRATHIONATE AND THIOSULFATE

$S_4 \times 10^2$	$S_2 \times 10^2$	$\left(\frac{-\mathrm{d}S_4}{\mathrm{d}t}\right)_{t=0} \times 10^4$	$2k_1$	k_{-1}/k_2
1.33	0.428	0.38	0.670	19.6
1.98	0.496	.53	.535	20.5
1.95	1.00	.62	.318	20.0
4.48	0.448	.97	.484	14.6
3.87	.984	2.3	.591	13.5
7.77	.836	3.7	.565	13.4
3.72	2.00	2.2	.297	19.3
3.87	2.38	4.0	.434	16.6
3.86	2.96	4.8	.423	18.3
3.78	3.96	5.1	.341	16.9
7.90	3.05	11.0	.471	14.7
		Av.	0.466	17.04

The value of k_1 (obtained assuming the reaction being first order with respect to both reagents) varies in wide limits, but it does not show any trend. The large variations are due to the poor approximations introduced by the graphical evaluation of the initial rate. Orders of reaction, calculated with the least square method, are: for tetrathionate

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[12] S, S_2, S_3, S_4, S_5, S_6 stand for sulfite, thiosulfate, tri-, tetra-, penta- and hexathionate concentrations, respectively.

[13] A. Kurtenacker, "Analytische Chemie der Sauerstoffsauren der Schwefels," Ferdinand Enke, Stuttgart, 1938, p. 165.

[14] See reference 2a, p. 20.

[15] H. Stamm, M. Goehring and U. Feldmann, *Z. anorg. Chem.*, **250**, 226 (1942).

0.99 ± 0.16; for thiosulfate 0.89 ± 0.12. The average value of k_1 is 0.233 l. mol.$^{-1}$ min.$^{-1}$.

Introducing this value into (16) we can see if the right member remains constant when the experimental values of S_4 and t are introduced in it. As an example this has been made for the run reported in Table I. In the last column are the values calculated from equation (16) and we see that these values are practically constant. It must be pointed out that since the first values are concerned with small ratios a/S_4, small errors in determining S_4 lead to large deviations. This is verified almost in all runs: first values deviate more than the average (being either larger or smaller). Thereafter the right member of (16) remains virtually constant and we can assume that its value gives the ratio k_{-1}/k_2.

For all runs the value k_{-1}/k_2 has been calculated and the mean value obtained in each run is reported in the last column of Table II. It can be seen that by varying the concentrations of tetrathionate and thiosulfate this ratio remains constant. The average of the mean values is 17.0 but the weighted average (*i.e.*, taking into account the number of values from which each mean value has been calculated) is slightly higher: 18.1.

One set of experiments deals with the effect of electrolytes on the reaction rate. Foss[16] observed that sodium chloride strongly affects the rate of the tetrathionate rearrangement, and an analogous observation was made by Goehring, Helbing and Appel.[10] We noticed this effect also. However, we would like to point out that this is not simply due to the increase in ionic strength of the solution. As one of us pointed out in a previous paper dealing with the trithionate–thiosulfate exchange,[17] the most important factor is not the ionic strength but rather the concentration and charge of ions whose charge sign is opposite from that of the reactants. This is also in accord with the findings of Olson and Simonson.[18]

We determined the specific rate k_1 by adjusting the ionic strength at a constant value (0.2) with different electrolytes. In these experiments k_1 has not been calculated graphically, but rather from the equation 16 by introducing the value 18.1 for k_{-1}/k_2, the assumption being made that this ratio is not affected by varying the ionic strength. This seems reasonable in view of the close similarities between reactions (7) backwards, and (8). The results of this analysis are given in Table III and the strong catalytic effect of the polyvalent positive ions is evident.

TABLE III

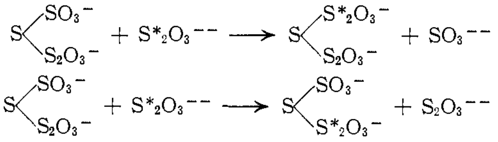
INFLUENCE OF DIFFERENT ELECTROLYTES ON RATE OF REACTION (7) FORWARD, AT CONSTANT IONIC STRENGTH

$Na_2S_2O_3$ = 1.17 × 10^{-2}, $K_2S_4O_6$ = 1.17 × 10^{-2}, μ = 0.2, *p*H 5.8, buffered with sodium acetate/acetic acid.

Electrolyte	Concn., mole/l.	$k(= 2k_1)$
$La(NO_3)_3$	0.0166	3.97 ± 0.38
$Mg(NO_3)_2$	.0335	.385 ± .036
$NaNO_3$	.1	.195 ± .025
Na_2SO_4	.033	.184 ± .023
$K_3Co(CN)_6$	.0166	.164 ± .040

Discussion of Results

The constancy of equation (16) when experimental results are substituted into it shows that the hypotheses on which it is based are correct. Moreover the dependence of initial velocity on concentration of tetrathionate and thiosulfate shows that the first step is the reaction between one molecule of tetrathionate and one of thiosulfate to give pentathionate and sulfite. In a paper on catalysis of thiosulfate on mixtures of tetrathionate and seleniumtrithionate,[9] Foss suggested "there are two modes of interaction of thiosulfate with tetrathionate, corresponding to the equations



$$\mathrm{S}\begin{matrix}\diagup\mathrm{SO_3^-}\\ \diagdown\mathrm{S_2O_3^-}\end{matrix} + \mathrm{S^*{}_2O_3^{--}} \longrightarrow \mathrm{S}\begin{matrix}\diagup\mathrm{S^*{}_2O_3^-}\\ \diagdown\mathrm{S_2O_3^-}\end{matrix} + \mathrm{SO_3^{--}} \quad (a)$$

$$\mathrm{S}\begin{matrix}\diagup\mathrm{SO_3^-}\\ \diagdown\mathrm{S_2O_3^-}\end{matrix} + \mathrm{S^*{}_2O_3^{--}} \longrightarrow \mathrm{S}\begin{matrix}\diagup\mathrm{SO_3^-}\\ \diagdown\mathrm{S^*{}_2O_3^-}\end{matrix} + \mathrm{S_2O_3^{--}} \quad (b)$$

Both reactions involve a nucleophilic attack by thiosulfate on one of the divalent sulfur atoms of tetrathionate, but in different directions. Each of the divalent sulfur atoms of tetrathionate forms a bridge between a sulfite and a thiosulfate group. In (a) sulfite group is displaced by thiosulfate, whereas in (b) the thiosulfate group is displaced also by thiosulfate."

Our present results, together with the isotopic exchanges studied between thiosulfate and polythionates, form an experimental test for this hypothesis.

Sulfite formed according to (7) may in turn react in two ways: either with tetrathionate or pentathionate according to the reverse of (7) or (8), respectively. When (8) occurs the over-all result is that two molecules of tetrathionate give one molecule of pentathionate and one of trithionate.

In addition to reactions (7) and (8) which we have taken into account to deduce equation 16, others could take place, *viz.*, the following

$$S_5O_6^{--} + S_2O_3^{--} \rightleftarrows S_6O_6^{--} + SO_3^{--} \quad (19)$$

$$S_3O_6^{--} + S_2O_3^{--} \longrightarrow S_4O_6^{--} + SO_3^{--} \quad (20)$$

Equation (20) is nothing but the reverse of (8). It probably can be neglected in the deduction of (16) because it is very slow (as is shown by the rate of exchange between thiosulfate and trithionate).[17] However, reaction (19) in the forward direction could have about the same velocity as (7) forward.[19] If it is possible to neglect it in the deduction of (16) it may be because the backward reaction is so fast that the concentration of hexathionate is practically zero even at fairly high concentrations of pentathionate.

In conclusion our results completely confirm Foss's point of view: rearrangement of tetrathionate occurs through a nucleophilic displacement of a sulfite group by a thiosulfate ion, followed by a nucleophilic displacement of thiosulfate by means of sulfite. The latter displacement may occur either on the tetrathionate in excess or on the pentathionate formed in the mean time.

It is remarkable that the value of the ratio k_{-1}/k_2 found by us is in good accord with that deduced by the direct measurement of k_{-1} and k_2 separately: Foerster and Centner[6] who measured the rate of the reactions between sulfite and polythionates, found that the reaction with pentathionate is about 22 times faster than that with tetrathionate. Our value is about 18.

The influence of electrolytes on the specific rate shows that an intermediate complex is not formed with free ions, but more likely by ionic complexes, either of thiosulfate or tetrathionate, or perhaps of both. The existence of ionic complexes for thiosulfate is well known from conductivity data[20] and from spectrophotometry.[21] For polythionates the existence of such complexes has not been investigated as yet.

In any case it seems that the intermediate complex is associated with positive ions.

SALT LAKE CITY, UTAH

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[16] See reference 2a, p. 120.

[17] A. Fava and G. Pajaro, *J. chim. phys.*, **51**, 594 (1954).

[18] A. Olson and T. Simonson, *J. Chem. Phys.*, **17**, 1167 (1947).

[19] Foss obtained some evidence supporting this view (private communication).

[20] T. O. Denney and T. B. Monk, *Trans. Faraday Soc.*, **47**, 922 (1951).

[21] D. P. Ames and J. Willard, THIS JOURNAL, **75**, 3267 (1953).