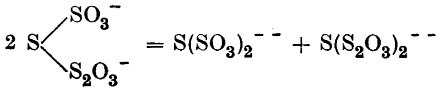
ACTA CHEMICA SCANDINAVICA 4 (1950) 866–869

Thiosulphate Catalysis on Mixtures of Tetrathionate and Monoselenotrithionate

OLAV FOSS

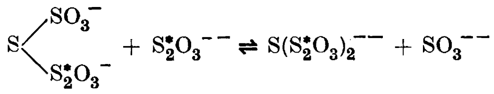
Universitetets Kjemiske Institutt, Blindern—Oslo, Norway

In neutral, weakly alkaline and weakly acid solutions tetrathionate undergoes a slow rearrangement into trithionate and pentathionate:

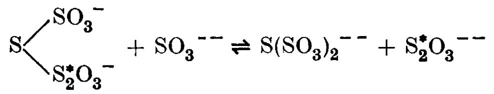


$$2\,S\begin{cases}SO_3^-\\S_2O_3^-\end{cases} = S(SO_3)_2^{--} + S(S_2O_3)_2^{--} \qquad (1)$$

This change is strongly catalyzed by thiosulphate [1-4]. The catalysis is due to the following equilibria [1-3]:



$$S\begin{cases}SO_3^-\\S^*_2O_3^-\end{cases} + S^*_2O_3^{--} \rightleftharpoons S(S^*_2O_3)_2^{--} + SO_3^{--} \qquad (2)$$



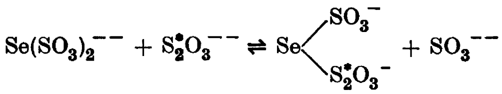
$$S\begin{cases}SO_3^-\\S^*_2O_3^-\end{cases} + SO_3^{--} \rightleftharpoons S(SO_3)_2^{--} + S^*_2O_3^{--} \qquad (3)$$

In presence of a slight excess of sulphite, the equilibria are displaced completely to the side of thiosulphate. If sulphite is removed as hydrogen sulphite [2, 5], or by use of formaldehyde in buffered solutions [6], the equilibria are displaced slowly to the side of sulphite. The reactions with sulphite are nucleophilic displacements of thiosulphate by sulphite [7, 8], as indicated through stars in Eqs. (2) and (3) above. By analogy, the reverse reactions can hardly be anything else than displacements also, *viz.*, of sulphite by thiosulphate.

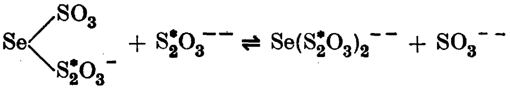
Monoselenotrithionate reacts more readily with thiosulphate than do trithionate and tetrathionate [9]:

$$Se(SO_3)_2^{--} + 2\ S^*_2O_3^{--} \rightleftharpoons Se(S^*_2O_3)_2^{--} + 2\ SO_3^{--} \qquad (4)$$

and this equilibrium is displaced farther to the side of sulphite than are the equilibria (2) and (3). It is, presumably, composed of two separate equilibria, in analogy with (2) and (3):



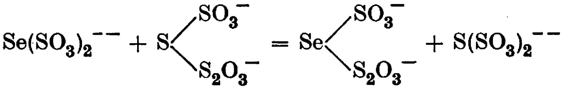
$$Se(SO_3)_2^{--} + S^*_2O_3^{--} \rightleftharpoons Se\left\langle\begin{matrix}SO_3^-\\ S^*_2O_3^-\end{matrix}\right. + SO_3^{--} \qquad (5)$$



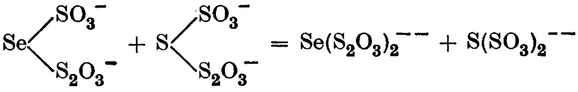
$$Se\left\langle\begin{matrix}SO_3\\ S^*_2O_3^-\end{matrix}\right. + S^*_2O_3^{--} \rightleftharpoons Se(S^*_2O_3)_2^{--} + SO_3^{--} \qquad (6)$$

The intermediate, monoselenotetrathionate, has not been isolated in a pure state, although Heuer[10] stated to have obtained the potassium salt in mixture with potassium tetrathionate.

In a mixture of tetrathionate or pentathionate with monoselenotrithionate or monoselenotetrathionate, in presence of thiosulphate, there should, as a result of the equilibria (5) and (6) which are displaced to the side of sulphite, and the equilibria (2) and (3) which are displaced to the side of thiosulphate, take place a rearrangement, with a decrease of the sulphur content of the polythionate and an increase of the sulphur content of the monoselenopolythionate. *E. g.*, thiosulphate should catalyze the changes:



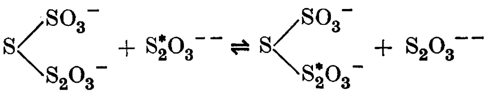
$$Se(SO_3)_2^{--} + S\left\langle\begin{matrix}SO_3^-\\ S_2O_3^-\end{matrix}\right. = Se\left\langle\begin{matrix}SO_3^-\\ S_2O_3^-\end{matrix}\right. + S(SO_3)_2^{--} \qquad (7)$$



$$Se\left\langle\begin{matrix}SO_3^-\\ S_2O_3^-\end{matrix}\right. + S\left\langle\begin{matrix}SO_3^-\\ S_2O_3^-\end{matrix}\right. = Se(S_2O_3)_2^{--} + S(SO_3)_2^{--} \qquad (8)$$

In fact, in a mixture of tetrathionate and monoselenotrithionate, in presence of thiosulphate, the content of monoselenotrithionate gradually decreases. This decrease is, presumably, due to the processes (7) and (8) or, depending on the relative amounts of tetrathionate and monoselenotrithionate present, to (7) alone. Of these processes, (8) bears a close resemblance with the rearrangement (1) of tetrathionate into trithionate and pentathionate.

In an earlier paper[7] it was suggested that a different equilibrium:



$$S\left\langle\begin{matrix}SO_3^-\\ S_2O_3^-\end{matrix}\right. + S^*_2O_3^{--} \rightleftharpoons S\left\langle\begin{matrix}SO_3^-\\ S^*_2O_3^-\end{matrix}\right. + S_2O_3^{--} \qquad (9)$$

might be responsible for the thiosulphate catalysis on the rearrangement (1) of tetrathionate, in analogy with the catalysis of thiosulphate on the decompositions of pentathionate and hexathionate[7, 11]. Such an equilibrium probably exists; however, it now seems more likely that it proceeds simultaneously with and independently of the catalyzed rearrangement. If so, there are two modes of interaction of thiosulphate with tetrathionate, corresponding to Eqs. (2) and (9). Both reactions involve a nucleophilic attack by thiosulphate on one of the divalent sulphur atoms of tetrathionate, but in different directions. Each of the divalent sulphur atoms of tetrathionate forms a bridge between a sulphite and a thiosulphate group. In (2) the sulphite group is displaced by thiosulphate, whereas in (9) the thiosulphate group is displaced, also by thiosulphate. The nucleophilic reactivity of sulphite is higher than that of thiosulphate, in displacements on sulphur, as evidenced by the fact that the equilibria (2) and (3) are displaced far to the side of thiosulphate. If other effects do not enter, thiosulphate should thus displace the thiosulphate group (Eq. 9) markedly faster than it displaces the sulphite group (Eq. 2).

EXPERIMENTAL

5 millimole each of potassium tetrathionate and potassium monoselenotrithionate were used in each experiment, and 25 ml of a buffer, being 0.5 M with respect to dihydrogenphosphate and 0.1 M with respect to monohydrogenphosphate. Thiosulphate was added as a catalyst, and the volume adjusted to 100 ml. For analysis, 20 ml samples were pipetted out, into a mixture of 20 ml of the phosphate buffer described above, 20—25 ml of 0.1 N sodium thiosulphate, 1 ml of 40 % formaldehyde, and 100 ml of water. After standing for 5 minutes, 20 ml of 10 % acetic acid were added, and the excess of thiosulphate was back-titrated with 0.1 N iodine. This procedure[9] gives the content of monoselenotrithionate according to Eq. (4) and, presumably, the content of monoselenotetrathionate according to Eq. (6). Tetrathionate has no effect on this analysis, because the formaldehyde removes the sulphite before it can react with tetrathionate[9].

Table 1. Per cent decrease in amount of thiosulphate consumed (originally 20 ml of 0.1 N thiosulphate).

Thiosulphate added as a catalyst	Time of standing 30 min	 1 hour	 2 hours
None	1.25	2.15	2.50
1 ml 0.1 N	5.10	8.00	11.95
5 » 0.1 »	14.25	20.75	29.35
10 » 0.1 »	21.50	29.50	41.10

The catalysis manifested itself through the gradual appearance of a greenish colour in the solutions. During the analyses, in the cases where the decrease in titer value was more than about 20 %, a red selenium colour developed one or two minutes after the thiosulphate had been added; however, the end points in the titrations were sharp.

SUMMARY

Thiosulphate exerts a catalytic effect on mixtures of tetrathionate and monoselenotrithionate. The mechanism of the catalysis is analogous to that of the thiosulphate catalysis on tetrathionate alone.

The author is indebted to *Styret for Nansenfondet og de dermed forbundne fond* for a grant.

REFERENCES

1. Colefax, M. A. *J. Chem. Soc.* **93** (1908) 798.
2. Foerster, F., and Centner, K. *Z. anorg. allg. Chem.* **157** (1926) 45.
3. Goehring, M., Helbing, W., and Appel, I. *Z. anorg. allg. Chem.* **254** (1947) 185.
4. Kurtenacker, A., Mutschin, A., and Stastny, F. *Z. anorg. allg. Chem.* **224** (1935) 399.
5. Stamm, H., Seipold, O., and Goehring, M. *Z. anorg. allg. Chem.* **247** (1941) 277.
6. Foss, O. Unpublished results.
7. Foss, O. *Kgl. Norske Vid. Selsk. Skrifter* (1945) no. 2.
8. Christiansen, J. A., and Drost-Hansen, W. *Nature* **164** (1949) 759.
9. Foss, O. *Acta Chem. Scand.* **3** (1949) 435.
10. Heuer, O. Thesis. Technische Hochschule, Hannover (1926).
11. Foss, O. *Acta Chem. Scand.* **3** (1949) 1385.

Received May 25, 1950.