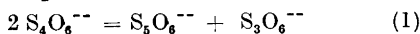


## Thiosulphate Catalysis on Rearrangements of Higher Polythionates

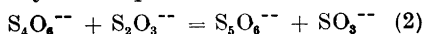
OLAV FOSS

*Chemical Institute, University of Bergen,  
Bergen, Norway*

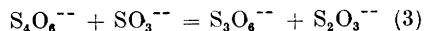
The rearrangement of tetrathionate ion into pentathionate and trithionate:



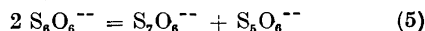
is strongly catalyzed by thiosulphate ion<sup>1</sup>. The catalysis is due to nucleophilic displacements<sup>2,3</sup>, of sulphite group of tetrathionate by thiosulphate:



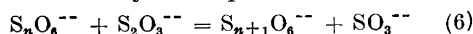
and of thiosulphate group by sulphite:



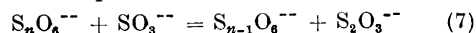
It is the purpose of the present note to point out that thiosulphate ion should catalyze the rearrangement into a higher and a lower polythionate, not only of tetrathionate but also of pentathionate and higher polythionates:



and so forth, through the same two-step nucleophilic displacement mechanism as in the case of tetrathionate. As shown in a previous note<sup>4</sup>, the displacement which would initiate such catalytic rearrangement, *i.e.*, the displacement of a sulphite group of pentathionate and higher polythionates by thiosulphate:



appears to take place with the same or approximately the same rate as for tetrathionate, and the subsequent displacement of a thiosulphate group of another polythionate ion by the sulphite released in the first step:

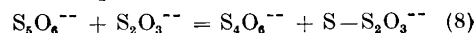


will occur rapidly<sup>1</sup>.

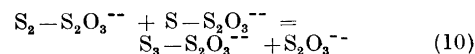
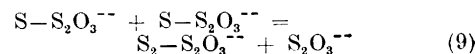
Thiosulphate ion also catalyzes the change of pentathionate and higher polythionates into lower polythionate, and sulphur<sup>1</sup>. Perhaps therefore, the above thiosulphate catalysis on rearrangements which should simultaneously occur, has not been directly observed. However, apparently pure pentathionate has occasionally been found to rearrange into hexa- and tetrathionate<sup>5</sup>,

perhaps because of minute amounts of impurities like thiosulphate, and the formation in a mixture of tetrathionate and thiosulphate, not only of trithionate and pentathionate but also of hexathionate and probably heptathionate, has been demonstrated by Skarżyński and Szczepkowski<sup>6</sup>.

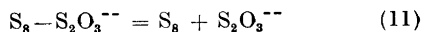
The thiosulphate-catalyzed decomposition of pentathionate and higher polythionates into lower polythionates and sulphur<sup>1</sup> may be due to the displacement, in the case of pentathionate<sup>7-9</sup>:



This is then followed by a building-up of dithio- and polythio-thiosulphate ions  $\text{S}_x-\text{S}_2\text{O}_3^{--}$  from the thio-thiosulphate ion released in the first step, through a series of consecutive nucleophilic displacements of thiosulphate by thio-thiosulphate:

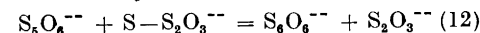


and so forth, with ultimate ring closure to  $\text{S}_8$ :



This building-up process is of the same type as proposed by Davis<sup>10</sup> for the decomposition of acidified thiosulphate (there displacement of sulphite or hydrogensulphite by thiosulphate). The acids corresponding to the species  $\text{S}_x-\text{S}_2\text{O}_3^{--}$ , the so-called sulphane monosulphonic acids  $\text{HS}-\text{S}_x-\text{SO}_3\text{H}$ , have been prepared and studied by Schmidt<sup>11</sup>; they decompose into sulphur in presence of basic substances, probably due to a reaction sequence analogous to the above, *i.e.*, nucleophilic attack of the terminal divalent sulphur atom of an ion  $\text{S}_x-\text{S}_2\text{O}_3^{--}$  on a divalent sulphur atom of another, not necessarily ionized species.

The point is that a thiosulphate-catalyzed rearrangement of pentathionate into tetrathionate and hexathionate may occur also as a result of an initial displacement (8) followed by:



and correspondingly for rearrangements of still higher polythionates. In fact, any species  $\text{S}_x-\text{S}_2\text{O}_3^{--}$ , occurring in the sequence (8)–(11) or released directly from a polythionate, should be expected to attack a polythionate chain to give another polythionate, preferably a higher one since thiosulphate probably is the better leaving group relative to a thio-, dithio- or poly-

thio-thiosulphate group. The  $S_x-S_2O_3^{--}$  ions are probably stronger nucleophiles than thiosulphate ion, in accordance with the lower strength of the corresponding  $-SH$  acids the longer the distance from the sulphonate group.

The above interactions of thiosulphate and polythionate ions, leading to rearrangements or decompositions, involve the displacement of a sulphite group of tetrathionate or higher polythionate by thio-sulphate, eqns. (2) and (6); of a thio-thiosulphate group of pentathionate or higher polythionate, eqn. (8); of a dithio-thiosulphate group of hexathionate or higher polythionate. The various modes of heterolysis of the sulphur-sulphur bonds of the tetra-, penta- and hexathionate ions in reactions with nucleophilic reagents have been discussed<sup>9</sup>; the preferred, more rapid displacement appears to be that of thio-sulphate, as for example in the second step of the rearrangements, eqns. (3), (7) and (12) above.

1. Gmelin's *Handbuch der anorganischen Chemie*, Vol. **9 B 2**, Verlag Chemie, Weinheim/Bergstrasse, 1960, pp. 915—917, 1001—1028.
2. Foss, O. *Acta Chem. Scand.* **4** (1950) 866.
3. Fava, A. and Bresadola, S. *J. Am. Chem. Soc.* **77** (1955) 5792.
4. Foss, O. and Kringlebotn, I. *Acta Chem. Scand.* **15** (1961) 1608.
5. Fehér, F. *Private communication* (1959).
6. Skarżyński, B. and Szczepkowski, T. W. *Nature* **183** (1959) 1413.
7. Foss, O. *Acta Chem. Scand.* **3** (1949) 1385.
8. Fava, A. *Gazz. chim. ital.* **83** (1953) 87.
9. Foss, O. *Acta Chem. Scand.* **12** (1958) 959.
10. Davis, R. E. *J. Am. Chem. Soc.* **80** (1958) 3565.
11. Schmidt, M. *Z. anorg. u. allgem. Chem.* **289** (1957) 158.

Received September 20, 1961.

## On the Oxidation of Diselenides and Related Compounds

GÖRAN BERGSON

*Chemical Institute, University of Uppsala, Sweden*

As a result of a number of recent investigations,<sup>1</sup> it has been shown that disulphides are oxidized to thiosulphinates ( $R-SO-S-R$ ) under mild conditions. In addition, Calvin and his co-workers<sup>2</sup> have found that *a*-lipoic acid (I) is oxidized to the corresponding thiosulphinates (II) by ammonium persulphate under conditions in which non-cyclic disulphides are not attacked; this demonstrates the increased reactivity associated with the 1,2-dithiolane ring. Further oxidation of the thiosulphinates generally gives thiosulphonates ( $R-SO_2-S-R$ ), although it has been supposed that this reaction occurs *via* fission of the sulphur-sulphur bond<sup>3</sup>.

It has been reported that diselenides are oxidized directly to seleninic acids ( $R-SeO_2H$ ), and although several attempts to detect lower oxidation products have been made, none have ever been found<sup>4</sup>. The instantaneous conversion of diselenides to seleninic acids by reaction with bromine in aqueous solution has been clearly demonstrated by Fredga<sup>5</sup> using polarimetric methods.

In a comparative study of the properties and reactions of simple molecules containing the S—S, Se—S, or Se—Se bonds, the

