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 thiosulphate, 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 [9]; the preferred, more rapid displacement appears to be that of thiosulphate, 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

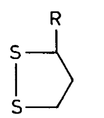
GÖRAN BERGSON

Chemical Institute, University of Uppsala, Sweden

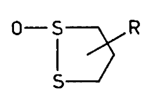
As a result of a number of recent investigations [1] it has been shown that disulphides are oxidized to thiolsulphinates ($R-SO-S-R$) under mild conditions. In addition, Calvin and his co-workers [2] have found that α-lipoic acid (I) is oxidized to the corresponding thiolsulphinate (II) by ammonium persulphate 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 thiolsulphinates generally gives thiolsulphonates ($R-SO_2-S-R$), although it has been supposed that this reaction occurs *via* fission of the sulphur-sulphur bond [3].

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 [4]. The instantaneous conversion of diselenides to seleninic acids by reaction with bromine in aqueous solution has been clearly demonstrated by Fredga [5] 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

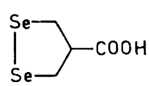


I

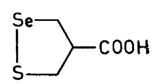


II

$R = -(CH_2)_4-COOH$



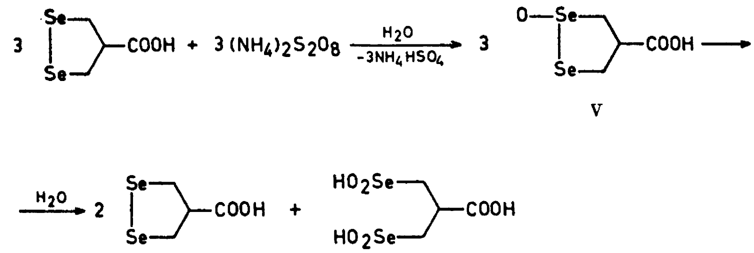
III



IV

present author has made some observations which suggest the existence of lower oxidation products of diselenides and thiolselenenates (R—Se—S—R). The oxidation conditions were analogous to those used by Calvin [2], *i.e.* ammonium persulphate in aqueous ethanol was employed. The molar ratio between ammonium persulphate and diselenide or thiolselenenate was 1:1. The compounds studied were 1,2-diselenolane-4-carboxylic acid (III) and 1-thia-2-selenacyclopentane-4-carboxylic acid (IV).

Figs. 1—3 show the course of oxidation for the compounds I, III, and IV as followed by spectrophotometric techniques. Fig. 1 confirms Calvin's results and demonstrated that after 24 h, the characteristic 1,2-dithiolane peak at 330 mμ has completely disappeared. A peak at 246 mμ due to the thiolsulphinate is then observed. The first noticeable feature in the oxidation of the diselenide (Fig. 2) is the greater speed of this reaction as compared with that for the disulphide. The most remarkable fact is, however, that the optical density of the peak at 440 mμ (characteristic of the 1,2-diselenolane ring) reaches a minimum after about 16 min. The 1,2-diselenolane peak subsequently increases again and finally attains a height approximately two-thirds of the original value. This final height corresponds to the oxidation to seleninic acid, since three oxidation equivalents are required for the oxidation of a diselenide to the corresponding seleninic acid. The pattern of the reaction as outlined above is best explained in terms of the initial formation of a product in a lower oxidation state. This product then undergoes disproportionation to seleninic acid and diselenide. Attempts to isolate the initial oxidation product have failed, presumably owing to its instability. It seems natural to suppose, however, that the reaction proceeds *via* a selenolseleninate (V) as shown in the following scheme:



It is unlikely that the first step would result in fission of the Se—Se bond since a seleninic acid and a selenol would then be

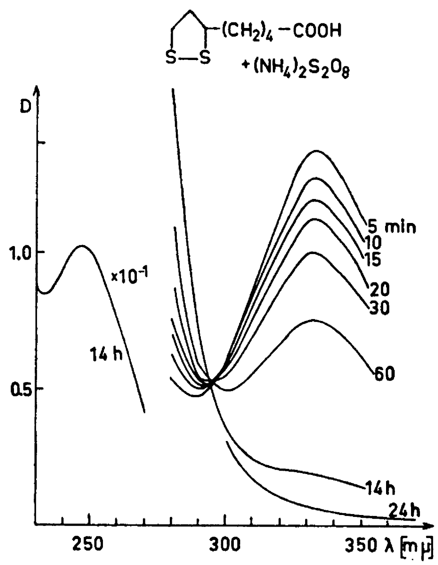


Fig. 1. Oxidation of α-lipoic acid with ammonium persulphate. Initial concentrations of both reactants: 0.01 M. Solvent: 5 parts ethanol and 1 part water. Temperature: 25.0°.

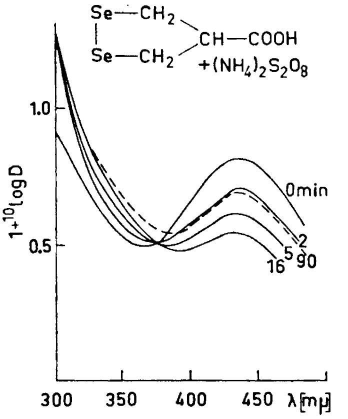


Fig. 2. Oxidation of 1,2-diselenolane-4-carboxylic acid with ammonium persulphate. Initial concentrations of both reactants: 0.005 M. Solvent as in Fig. 1. Temperature: 25.0°.

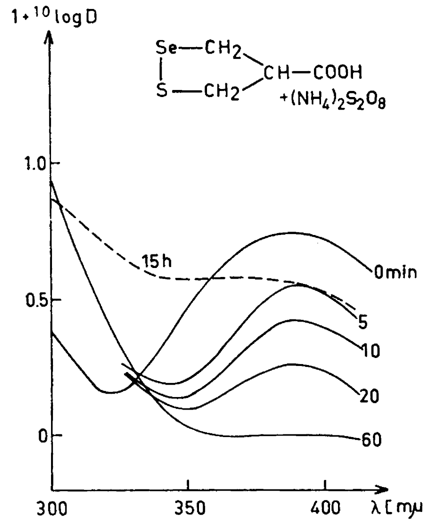


Fig. 3. Oxidation of 1-thia-2-selena-cyclopentane-4-carboxylic acid by ammonium persulphate. Initial concentrations of both reactants: 0.005 M. Solvent as in Fig. 1. Temperature: 25.0°C.

formed, and these products would at once react to form a diselenide.

Fig. 3 shows that the oxidations of the diselenide and the thiolselenenate (IV) follow closely similar paths. The speed of the thiolselenenate oxidation is not as great as that of the diselenide oxidation, but it is much greater than the oxidation of the disulphide. It is probable that in this instance the thiolseleninate is the primary oxidation product.

An investigation of the kinetics of the primary oxidation is in progress, together with a study of non-cyclic diselenides and thiolselenenates.

Experimental. DL-*a-Lipoic acid.* The sample used was synthesized by Hoffmann-La Roche & Co. Ltd, Basle (Switzerland). *1,2-Diselenolane-4-carboxylic acid* was prepared from β,β'-dibromo-isobutyric acid and sodium diselenide [6]; m.p. 148.5—149.5°. The synthesis of *1-Thia-2-selena-cyclopentane-4-carboxylic acid* has been described by Bergson and Biezais [7]; m.p. 105.5—107.5°.

The optical measurements were made with a Beckman Model DU (220—400 mμ) and a Beckman Model B (400—550 mμ) spectrophotometer.

1. Stoll, A. *Helv. Chim. Acta* **31** (1948) 189; Small, D., Bailey, J. H. and Cavallito, C. J. *J. Am. Chem. Soc.* **69** (1947) 1710; Bretschneider, H. and Klötzer, W. *Monatsh.* **81** (1950) 589; Backer, H. J. and Kloosterziel, H. *Rec. trav. chim.* **73** (1954) 129.
2. Barltrop, J. A., Hayes, P. M. and Calvin, M. *J. Am. Chem. Soc.* **76** (1954) 4348; Calvin, M. *Federation Proc.* **13** (1954) 697.
3. Barnard, D. and Percy, E. J. *Chem. & Ind. London* **1960** 1332.
4. Small *et al.* Ref. 1; Fromm, E. and Martin, K. *Ann.* **401** (1913) 184.
5. Fredga, A. *Uppsala Universitets Årsskrift* **1935:5** 134.
6. Bergson, G. *To be published.*
7. Bergson, G. and Biezais, A. *Arkiv Kemi* **18** (1961) 143.

Received October 5, 1961.