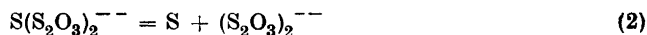
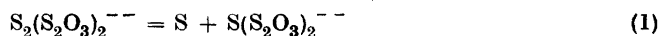


Displacement Equilibria and Catalysis on Thiosulphates, Xanthates and Dithiocarbamates of Divalent Sulphur, Selenium and Tellurium

OLAV FOSS

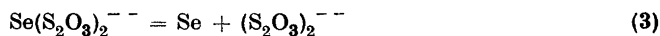
Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

Pentathionate and hexathionate, in reactions with nucleophilic reagents, behave¹ as thiosulphates of divalent sulphur, S^{++} and S_2^{++} . In aqueous solutions, as well as in the solid state, they have a tendency to liberate sulphur, forming tetrathionate²⁻¹¹:

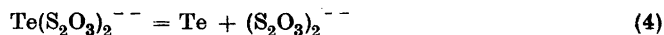


These changes, in solutions, are strongly catalyzed by thiosulphate^{1, 4, 7, 10, 11} and by hydroxyl ions¹⁻¹¹.

In this article, some analogous catalytic reactions are described. Thus, monoselenopentathionate¹², a thiosulphate of divalent selenium, tends to decompose into selenium and tetrathionate:

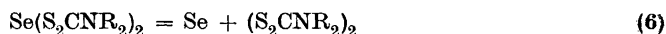
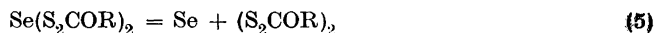


In this case also, thiosulphate^{12, 13} and hydroxyl ions act as catalysts. Likewise, monotelluropentathionate¹⁴, a thiosulphate of divalent tellurium, liberates tellurium, to give tetrathionate:



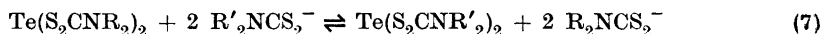
Here, iodide ions, as well as thiosulphate and hydroxyl ions, serve as catalysts.

Thiocarbonyl derivatives of divalent sulphur and selenium undergo the same type of change. In these cases, disulphides are formed, instead of tetrathionate, together with sulphur or selenium. *E. g.*:



These reactions are strongly catalyzed by xanthate and by dithiocarbamate ions.

Xanthates and dithiocarbamates of divalent tellurium are more stable than the corresponding sulphur and selenium compounds. With the tellurium compounds, displacement equilibria of the following type may be demonstrated:



Under special conditions, the selenium compounds react in the same way.

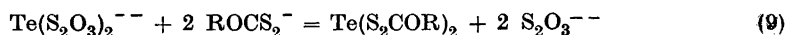
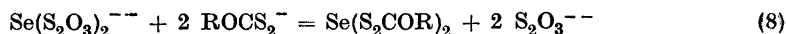
The purpose of this article is, chiefly, to demonstrate the symmetry with respect to catalytic phenomena which is displayed within the class of compounds named in the title. The mechanism of the catalysis is a subject of uncertainty. The experiments are, though, in harmony with a hypothesis, advanced earlier¹, that the catalysis is due, in some way, to ionic displacement equilibria of the type represented by Eq. (7).

XANTHATES AND DITHIOCARBAMATES

Russell¹⁵ reported that selenious acid reacts with sodium dithiocarbamates to give dithiocarbamates of tetravalent selenium. He stated that the product 'frequently, if not usually' appeared as an equimolar mixture of the divalent selenium dithiocarbamate and the corresponding *bis*(thiocarbamyl) disulphide. In the case of the ethyl compounds, the two components could be separated by treatment of the product with cold benzene, giving a selenium *bis*(diethyldithiocarbamate) of m. p. 110° C.

It was shown recently¹² that monoselenopentathionate reacts with sodium diethyldithiocarbamate to give selenium *bis*(diethyldithiocarbamate), m. p. 116° C, in quantitative yield. Likewise¹⁴, monotelluropentathionate reacts with sodium diethyldithiocarbamate and potassium ethylxanthate to give tellurium *bis*(diethyldithiocarbamate) and di(ethylxanthate), respectively.

In this work, xanthates of divalent selenium are described for the first time, together with two new dithiocarbamates, and two new xanthates and dithiocarbamates of divalent tellurium. They were prepared from monoselenopentathionate and monotelluropentathionate, the reactions being, in the case of the xanthates:



with similar equations for the dithiocarbamates. With a slight excess of the thiocarbonyl salt, the reactions are complete in a few minutes:

To 0.01 mole of sodium or potassium monoselenopentathionate or monotelluropentathionate dissolved in 100 ml of water were added, with stirring, 0.025 mole of sodium or potassium xanthate or dithiocarbamate dissolved in the same amount of water. After a few minutes stirring the product had coagulated, leaving the liquid clear. It was filtered off, washed with water and with methanol, and dried *in vacuo* over sulphuric acid. The selenium ethyl- and *iso*-propylxanthates separated out as oils, which were extracted from the aqueous layer by means of ether. The ether extracts were dried over anhydrous sodium sulphate, and the ether subsequently distilled off.

Table 1. Xanthates and dithiocarbamates of divalent selenium and tellurium.

Compound	M. p., °C (uncorr.)	% Se or Te	
		Calc.	Found
$\text{Se}(\text{S}_2\text{COCH}_3)_2$	106 ^a	26.93	26.91
$\text{Se}(\text{S}_2\text{COC}_2\text{H}_5)_2$	Oil	24.57	24.41
$\text{Se}(\text{S}_2\text{COCH}(\text{CH}_3)_2)_2$	Oil	22.60	22.53
$\text{Se}(\text{S}_2\text{CN}(\text{CH}_3)_2)_2$	182—3 ^b	24.72	24.57
$\text{Se}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$	116 ^c	21.03	21.01
$\text{Se}(\text{S}_2\text{CNC}_5\text{H}_{10})_2$	175—6 ^d	19.76	19.70
$\text{Te}(\text{S}_2\text{COCH}_3)_2$	89 ^e	37.31	37.33
$\text{Te}(\text{S}_2\text{COC}_2\text{H}_5)_2$	94 ^f	34.48	34.35
$\text{Te}(\text{S}_2\text{COCH}(\text{CH}_3)_2)_2$	87 ^g	32.05	32.12
$\text{Te}(\text{S}_2\text{CN}(\text{CH}_3)_2)_2$	> 250 ^h	34.67	34.74
$\text{Te}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$	164 ⁱ	30.07	29.89
$\text{Te}(\text{S}_2\text{CNC}_5\text{H}_{10})_2$	> 250 ^h	28.46	28.31

^a Recrystallized from ethylacetate (5 g dissolved in 75 ml at 60°). Plates or prisms.

^b Recrystallized from chloroform (1 g dissolved in about 300 ml at boiling temperature).

Microcrystalline powder.

^c Recrystallized from benzene (5 g dissolved in 80 ml at 60—70°). Plates or leaves.

^d Recrystallized from chloroform (5 g dissolved in about 250 ml at boiling temperature).

Tiny plates.

^e Recrystallized by dissolving 5 g in 20 ml of warm benzene, and adding 50 ml of warm methanol. Flat needles.

^f Recrystallized by dissolving 5 g in 10 ml of warm benzene, and adding 25 ml of warm ethanol. Long needles.

^g Recrystallized by dissolving 5 g in 30 ml of warm ether, and adding 100 ml of methanol. Needles.

^h Too insoluble in ordinary organic solvents to be conveniently recrystallized.

ⁱ Recrystallized by dissolving 5 g in 15 ml of warm carbon disulphide, and adding 25 ml of ether.

In Table 1 the three compounds prepared previously^{12, 14} are included for comparison. For analysis, the selenium compounds were oxidized by means of nitric acid-sulphuric acid, the excess of nitric acid destroyed by means of urea, and the selenious acid determined volumetrically by means of the Norris and Fay method. The tellurium compounds were oxidized by means of nitric acid, and the excess of nitric acid was removed by heating with several portions of concentrated hydrochloric acid. The tellurous acid was reduced by means of hypophosphorous acid, and the tellurium weighed.

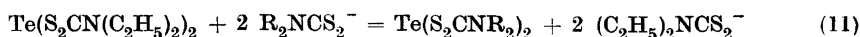
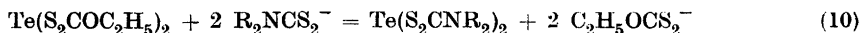
The selenium compounds are greenish yellow, while the tellurium compounds are red. In the solid state, the dithiocarbamates are quite stable, whereas the xanthates may liberate selenium or tellurium after a few days.

The compounds are insoluble in and unaffected by water.

The selenium *bis*(dimethyldithiocarbamate) was proved to be identical with a compound obtained from a commercial sample* of selenium dimethyldithiocarbamate, prepared from selenious acid and sodium dimethyldithiocarbamate.

The tellurium compounds readily exchange their thiocarbonyl groups in reactions with dithiocarbamate ions.

Tellurium *bis*(dimethyldithiocarbamate) and di(piperidyldithiocarbamate) have a very low solubility in ordinary organic solvents. If an excess of sodium dimethyl- or piperidyldithiocarbamate, dissolved in methanol or ethanol, is added to solutions of tellurium *bis*(diethyldithiocarbamate) or a tellurium di(xanthate) in ethylacetate or chloroform, a displacement takes place, and tellurium *bis*(dimethyldithiocarbamate) or tellurium di(piperidyldithiocarbamate) separates out. The reactions of tellurium di(ethylxanthate) and *bis*(diethyldithiocarbamate) were studied in some detail. They may be formulated as follows:



where $\text{R}_2\text{N}-$ is dimethylamino or piperidyl.

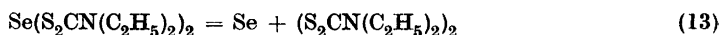
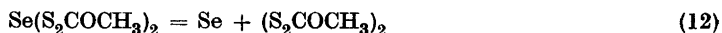
With tellurium di(ethylxanthate) the reactions are quantitative even in the presence of potassium ethylxanthate. In the case of tellurium *bis*(diethyldithiocarbamate) the yields depend upon the excess of sodium dimethyl- or piperidyldithiocarbamate employed. Also, in presence of sodium diethyldithiocarbamate the yields become considerably lower. This shows that an equilibrium is established which is not displaced completely to the right, in

* Sharples Chemicals Inc. The *bis*(dimethylthiocarbamyl) disulphide, present in equimolar proportions, was extracted by means of cold chloroform. The author is indebted to the Airco Export Corp., New York, for samples of Sharples Chemicals Inc.'s sodium and selenium dimethyldithiocarbamate and diethyldithiocarbamate.

spite of the high solubility difference between the tellurium compounds on the left and the right side. Furthermore, it follows that the nucleophilic reactivity of the ethylxanthate ion is markedly lower than that of the dithiocarbamate ions. This difference in nucleophilic reactivity is in accordance with the relative inductive effects of alkoxy and dialkylamino groups, the latter groups having a higher electron releasing power than the former.

No catalytic decompositions were observed in experiments with the tellurium compounds. In the case of the selenium derivatives, a marked catalysis by xanthate and dithiocarbamate ions occurs.

0.01 *M* solutions of selenium di(methylxanthate) and *bis*(diethyldithiocarbamate) in chloroform are stable for over a week. If an equal amount of 0.01 *M* sodium or potassium xanthate or dithiocarbamate in ethanol is added to these yellowish green solutions, red selenium is liberated within one half to four minutes. In the case of selenium *bis*(diethyldithiocarbamate) the second product was identified as *bis*(diethylthiocarbamyl) disulphide, and it may, by analogy, be assumed that di(methylxanthyl) disulphide is formed in the case of selenium di(methylxanthate):



The xanthate liberates selenium more rapidly and completely than the dithiocarbamate. With the xanthate, dithiocarbamate ions are slightly stronger catalysts than are xanthate ions, whereas with the dithiocarbamate, the reverse is the case.

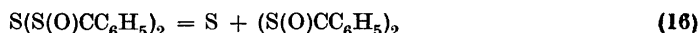
If selenium di(methylxanthate), dissolved in chloroform, is added rapidly to cold methanol solutions of an excess of sodium dimethyl- or piperidylthiocarbamate, a displacement takes place just as in the case of the tellurium compounds:



where $\text{R}_2\text{N}-$ is dimethylamino or piperidyl. The selenium dithiocarbamates separate out so rapidly that only a negligible amount of catalysis has time to take place.

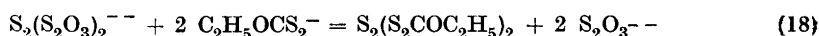
Thiocarbonyl derivatives of divalent sulphur, S^{++} and S_2^{++} , are subject to the same type of catalysis as the xanthates and dithiocarbamates of divalent selenium.

Bloch and Bergmann¹⁶ found that monosulphur and disulphur di(thio-benzoate) readily liberate sulphur, giving dibenzoyl disulphide. The disulphur compound reacted in two stages, first forming the monosulphur compound:



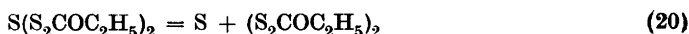
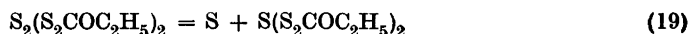
These reactions are catalyzed¹⁶ by dimethylaniline and by potassium thiobenzoate.

In this work, the corresponding reactions of monosulphur and disulphur di(ethylxanthate) have been studied. These compounds^{17, 18}, like the sulphur thiobenzoates¹⁶, were first prepared from the sulphur chlorides and the respective potassium thiocarbonyl salts. They are also formed, in quantitative yields, from aqueous solutions of potassium pentathionate and hexathionate¹:



with similar equations for the thiobenzoates. These reactions are analogous to the reactions of monoselenopentathionate and monotelluropentathionate with thiocarbonyl salts.

Monosulphur and disulphur di(ethylxanthate) are faintly yellowish-green oils, very slightly soluble in ethanol, but miscible with ethylacetate in all proportions. In substance and in ethylacetate solutions they seem to be quite stable. In the presence of potassium ethylxanthate, sulphur is rapidly liberated:



Other alkali xanthates, and dithiocarbamates, also catalyze these reactions.

Experimental

25 millimoles of tellurium di(ethylxanthate) or *bis*(diethyldithiocarbamate) dissolved in 20 ml of chloroform were employed in each experiment. To such solutions were added sodium dimethyl- or piperidylthiocarbamate dissolved in 15 ml of methanol. Addition of 15 ml of methanol alone did not cause any precipitation. The products were filtered off, washed with ether, methanol, and ether, dried *in vacuo* over sulphuric acid, and weighed.

Tellurium di(ethylxanthate). (1) 25 % excess (6.25 millimole) of sodium dimethyldithiocarbamate. Yield 0.9281 g = 100.9 %. (2) As (1) but in presence of 6.25 millimole of potassium ethylxanthate. Yield 0.9255 g = 100.6 %. (3) 25 % excess of sodium piperidylthiocarbamate. Yield 1.1210 g = 100.1 %. (4) As (3) but in presence of 6.25 millimole of potassium ethylxanthate. Yield 1.1182 g = 99.8 %.

For the products from (1) and (2) were found 34.66 % and 34.78 % Te, respectively; calc. for $\text{Te}(\text{S}_2\text{CN}(\text{CH}_3)_2)_2$: 34.67 %. For those from (3) and (4) were found 28.30 % and 28.42 % Te; calc. for $\text{Te}(\text{S}_2\text{CNC}_5\text{H}_{10})_2$: 28.46 %.

Tellurium bis(diethyldithiocarbamate). (5) 100 % excess (10 millimole) of sodium dimethyldithiocarbamate. Yield 0.8756 g = 95.2 %. (6) 25 % excess (6.25 millimole) of sodium dimethyldithiocarbamate. Yield 0.5853 g = 63.6 %. (7) As (6) but in presence of 6.25 millimole of sodium diethyldithiocarbamate. Yield 0.0352 g = 3.8 %. (8) 100 % excess of sodium piperidyldithiocarbamate. Yield 1.1038 g = 98.4 %. (9) 25 % excess of sodium piperidyldithiocarbamate. Yield 0.9464 g = 84.4 %. (10) As (9) but in presence of 6.25 millimole of sodium diethyldithiocarbamate. Yield 0.7344 g = 65.6 %.

For the products from (5) and (6) were found 34.80 % and 34.68 % Te, respectively. For those from (8) and (10) were found 28.51 % and 28.57 % Te, respectively.

No tellurium was liberated in any of the experiments.

Selenium compounds

Catalysis. The following solutions were employed: (a) 0.01 *M* selenium di(methylxanthate) in chloroform, (b) 0.01 *M* selenium *bis*(diethyldithiocarbamate) in chloroform, (c) 0.01 *M* solutions of potassium methyl-, ethyl- and *iso*-propylxanthate, in ethanol, (d) 0.01 *M* solutions of sodium dimethyl-, diethyl- and piperidyldithiocarbamate, in ethanol. The experiments were made at 20° C. Time from mixing till appearance of red selenium:

- 5 ml each of (a) and (c): 45 seconds
- 5 ml each of (a) and (d): 30 seconds
- 5 ml each of (b) and (c): 2 minutes
- 5 ml each of (b) and (d): 4 minutes
- 5 ml of (a) and 2 ml of (c): 4 minutes
- 5 ml of (a) and 2 ml of (d): 2 minutes
- 5 ml of (b) and 10 ml of (c): 45 seconds
- 5 ml of (b) and 10 ml of (d): 1 1/2 minutes

To 5 millimoles of (1) selenium di(methylxanthate) and (2) selenium *bis*(diethyldithiocarbamate) dissolved in 20 ml of chloroform were added 5 millimoles of potassium methylxanthate and sodium diethyldithiocarbamate, respectively, dissolved in 10 ml of methanol. Selenium immediately separated out. After one hour's standing the selenium was filtered off, dried, and weighed: (1) 0.3862 g = 97.8 %. (2) 0.2783 g = 70.5 %.

To 5 millimoles of selenium *bis*(diethyldithiocarbamate) in 20 ml hot ethanol (it did not dissolve completely) were added 5 millimoles of solid sodium diethyldithiocarbamate. The selenium compound dissolved, and selenium separated out. The mixture was filtered while hot: 0.3375 g Se = 85.5 %. The filtrate was cooled to room temperature, and 0.27 g of greenish yellow crystals separated out. They consisted mainly of unchanged selenium *bis*(diethyldithiocarbamate). On addition of 50 ml of water, 1.09 g of faintly greenish crystals were obtained, melting at 69–71° C and containing only a trace of selenium. They were recrystallized from 10 ml of ethanol: Yield 0.70 g of faintly greenish crystals, m. p. 72° C, not depressed in mixture with a sample of *bis*(diethylthiocarbamyl) disulphide obtained from other sources.

Displacements. 2.5 millimoles of selenium di(methylxanthate), dissolved in 15 ml of chloroform, were cooled in ice water and added rapidly to 100 % excess (10 millimoles) of (1) sodium dimethyldithiocarbamate and (2) sodium piperidyldithiocarbamate dissolved in 15 ml of methanol and cooled in ice water (the beakers containing the selenium compound were rinsed with 5 ml of chloroform). Greenish yellow crystals immediately separated out, which after about 30 seconds began to acquire a very faint reddish colour. They were filtered off as rapidly as possible, and washed with methanol and ether: (1) 0.7761 g = 97.2 %. They melted at 179–80° C and were found to contain 24.69 % Se; calc. for $\text{Se}(\text{S}_2\text{CN}(\text{CH}_3)_2)_2$: 24.72 %. (2) 0.9482 g = 95.0 %. They melted at 170–1° C and were found to contain 19.77 % Se; calc. for $\text{Se}(\text{S}_2\text{CNC}_5\text{H}_{10})_2$: 19.70 %.

Sulphur compounds

To 5 millimoles of (1) monosulphur di(ethylxanthate) and (2) disulphur di(ethylxanthate), dissolved in 10 ml of ethylacetate, were added 5 millimoles of potassium ethylxanthate in 10 ml of ethanol. Sulphur immediately separated out. It was filtered off, washed with methanol, dried, and weighed: (1) 0.1037 g = 64.7 %. After 24 hours, more sulphur had crystallized from the filtrate: Total 0.1598 g = 99.3 %. (2) 0.2281 g, corresponding to 1.42 at. S per mole of disulphur di(ethylxanthate). After 24 hours: Total 0.3223 g, corresponding to 2.01 at. S per mole.

THIOSULPHATES: PENTATHIONATE, HEXATHIONATE, MONOSELENO-PENTATHIONATE, AND MONOTELLUROPENTATHIONATE

The properties of these ions as thiosulphates of divalent electropositive sulphur, selenium and tellurium follow from the reactions of pentathionate and hexathionate with piperidine and hydroxide and with ethylxanthate and thiobenzoate ions¹, and of monoselenopentathionate and monotelluropentathionate with hydroxide and with xanthate and dithiocarbamate ions^{12, 14}. In these reactions, the two thiosulphate groups are rapidly and quantitatively displaced by the respective nucleophilic reagents. Thiosulphate itself reacts with sulphur compounds containing groups of a lower nucleophilic reactivity, displacing these groups and forming pentathionate and hexathionate¹.

In presence of small amounts of alkalis, pentathionate and hexathionate rapidly decompose into sulphur and tetrathionate, as mentioned on p. 1385. Hexathionate reacts in two stages, first forming pentathionate¹⁰.

Beside hydroxyl ions, thiosulphate ions catalyze these reactions. The catalytic effect of thiosulphate on pentathionate was first studied by Foerster and Hornig⁴ and Kurtenacker and Kaufmann⁷, and recently by Goehring, Helbing and Appel¹¹. An analogous effect on hexathionate was first reported by Kurtenacker, Mutschin and Stastny¹⁰.

It is shown in this work that thiosulphate and hydroxyl ions have a marked catalytic effect on the corresponding reactions (3) and (4) of monoselenopentathionate and monotelluropentathionate.

That hydroxyl ions act as catalysts, may be concluded from the fact that hydrochloric acid greatly stabilizes the aqueous solutions of these compounds. In the case of monotelluropentathionate, potassium iodide also acts as a catalyst.

The relative stabilities of pentathionate, monoselenopentathionate and monotelluropentathionate in 0.064 *M* neutral aqueous solutions at 25°C are as follows.

Monoselenopentathionate solutions remain unchanged for 10 hours, monotelluropentathionate solutions for 3 hours. Once the monoselenopentathionate solutions have started to decompose, the process proceeds faster than in the case of monotelluropentathionate. According to Goehring, Helbing and Appel¹¹, pentathionate solutions are turbid after 6 hours.

The catalytic effect of thiosulphate increases in the order monotelluropentathionate, pentathionate, and monoselenopentathionate. The catalysis of iodide on monotelluropentathionate is less pronounced than that of thiosulphate.

The reactions are subject to a marked positive salt effect, as demonstrated in this work in the case of monoselenopentathionate and monotelluropentathionate. It seems likely that the salt effect on solutions to which no catalyst, such as thiosulphate or iodide, has been added, is an effect on a hydroxide catalysis. Such an effect on pentathionate was reported earlier¹⁹.

The positive salt effect indicates that the catalysis is due to reactions between ions with similar charge, which, obviously, is negative.

The presence of tetrathionate seems to have no effect on the stability of monoselenopentathionate and monotelluropentathionate solutions, although it is said to decrease the stability of pentathionate solutions²⁰.

The reactions are of the autocatalytic type. The only possible autocatalysts are, beside thiosulphate, selenium and tellurium. Colloidal sulphur has a strong catalytic effect on the corresponding reactions of pentathionate and hexathionate¹⁰. These facts indicate that the release of sulphur, selenium and tellurium is facilitated if the atoms can be deposited directly on a colloidal particle of the same element. This is perhaps part of a nucleus formation effect. Also, the heats of combustion of potassium tetrathionate and pentathionate show²¹ that (in the solid state) the change of pentathionate into tetrathionate and atomic sulphur is endothermic, whereas the change into tetrathionate and monoclinic S₈ is exothermic.

Experimental

Measurements were made in a thermostat at 25°C with 0.064 *M* solutions of sodium monoselenopentathionate and monotelluropentathionate, in 50 ml volumetric flasks. This concentration was chosen in order to allow a comparison with the results of Goehring,

Helbing and Appel¹¹ on potassium pentathionate. For analysis, 5 ml samples were pipetted out, and the selenium or tellurium was filtered off. In the filtrates, the monoselenopentathionate was titrated with bromate as described earlier¹², and the selenious acid determined by means of the Norris and Fay method. In each case, the relative decreases in the bromate and the Norris and Fay titer values corresponded to one mole of tetrathionate formed per mole of monoselenopentathionate consumed. The monoteluropentathionate was titrated directly with iodine¹⁴, and the tetrathionate subsequently determined by means of the sulphite method. The cyanide method^{22, 1} was also used sometimes, to check on a possible rearrangement of the tetrathionate.

No acidity developed in the solutions during the experiments. In the case of monoselenopentathionate, filtered samples were tested with iodine: No thiosulphate was formed, or where it had been added as a catalyst, the amount did not change.

0.064 *M* sodium monoselenopentathionate

(1) In water. Selenium appeared after 10–11 hours. After 24 hours: 4 % decrease. (2) In 2 *M* sodium chloride. Selenium appeared after 2 hours. After 4 hours: 3.1 % decrease; 6 hours: 11.6 %; 8 hours: 20.1 %. (3) In 2 *M* sodium chloride and 0.0013 *M* or 0.064 *M* potassium tetrathionate. As (2). (4) In 2 *M* sodium chloride and 0.06 *N* hydrochloric acid. No change after 12 hours. After 24 hours: 1.8 % decrease. (5) In 0.07 *M* sodium thiosulphate. Selenium appeared after 1 minute. After 15 minutes: 74.8 % decrease; 30 minutes: 87.5 %; 1 hour: 91.8 %; 2 hours: 93.0 %. (6) In 0.01 *M* sodium thiosulphate. Selenium appeared after 10 minutes. After 30 minutes: 20.8 % decrease; 1 hour: 39.3 %; 2 hours: 68.3 %; 3 hours: 79.8 %. (7) In 0.01 *M* sodium thiosulphate and 2 *M* sodium chloride. Selenium appeared after 3 minutes. After 15 minutes: 59.8 % decrease; 30 minutes: 84.8 %; 1 hour: 95.9 %.

0.064 *M* sodium monotelluropentathionate

(8) In water. Tellurium appeared after 3 hours. After 24 hours: 2.1 % decrease. (9) In 2 *M* sodium chloride. Tellurium appeared after 20 minutes. After 4 hours: 0.6 % decrease; 6 hours: 0.9 %; 24 hours: 4.2 %. (10) In 2 *M* sodium chloride and 0.0013 *M* or 0.064 *M* potassium tetrathionate. As (9). (11) In 2 *M* sodium chloride and 0.06 *N* hydrochloric acid. No change after 3 hours. After 9 hours: 0.5 % decrease; 24 hours: 2 %. (12) In 0.07 *M* sodium thiosulphate. Tellurium appeared after 6 minutes. After 30 minutes: 1.7 % decrease; 1 hour: 3.8 %; 2 hours: 7.6 %; 3 hours: 11.6 %; 5 hours: 21.6 %. (13) In 0.07 *M* sodium thiosulphate and 2 *M* sodium chloride. Tellurium appeared after 2 minutes. After 30 minutes: 4.0 % decrease; 2 hour: 10.5 %; 3 hours: 52.3 %. (14) In 0.04 *M* sodium thiosulphate and 2 *M* sodium chloride. Tellurium appeared after 3 minutes. After 30 minutes: 2.5 % decrease; 1 hour: 5.1 %; 2 hours: 15.2 %; 3 hours: 27.4 %. (15) In 0.07 *M* potassium iodide. After 30 minutes: 0.7 % decrease, 1 hour: 1.5 %; 2 hours: 2.3 %; 3 hours: 3.8 %, 16 hours: 18.9 %. (16) In 0.07 *M* potassium iodide and 2 *M* sodium chloride. Tellurium appeared after 1 minute. After 30 minutes: 6.5 % decrease, 1 hour: 10.3 %, 2 hours: 17.4 %, 3 hours: 23.3 %, 4 hours: 28.2 %. (17) In 0.14 *M* potassium iodide. Tellurium appeared after 2 minutes. After 30 minutes: 3.4 % decrease, 1 hour: 5.9 %, 2 hours: 9.2 %, 3 hours: 12.6 %.

The amount of tetrathionate present in the titrated solutions, as determined by means of the sulphite and the cyanide methods, remained constant, except in the experiments with thiosulphate as a catalyst. In Expt. (12), after 5 hours, the amount of tetrathionate had changed as from 0.099 *M* to 0.0949 *M* and that of pentathionate as from zero to 0.0019 *M*. In Expt. (13), after 3 hours, from 0.099 *M* to 0.0923 *M* and from zero to 0.0041 *M*, respectively, and in Expt. (14), after 3 hours, from 0.099 *M* to 0.0962 *M* and from zero to 0.0017 *M*, respectively. These changes correspond roughly to a thio-sulphate-catalyzed rearrangement of some of the tetrathionate, formed from the monoteluro-pentathionate, into trithionate and pentathionate.

The experiments (5) and (12) may be compared with the following experiment of Goehring, Helbing and Appel¹¹: 0.0643 *M* potassium pentathionate, in 0.072 *M* sodium thiosulphate, at 25° C. After 15 minutes: 44.4 % decrease; 1 hour: 51.1 %; 2 ½ hours: 64.5 %; 5 hours: 68.9 %.

Acetate and monohydrogenphosphate ions also bring about an increased instability of monoteluro-pentathionate. These phenomena have not been investigated in any detail.

THE NATURE OF THE CATALYSIS

Reference to the structure of the reacting compounds is pertinent to the succeeding discussion of the mechanism of the catalytic reactions.

There is some controversy in the literature as to whether the pentathionate and hexathionate ions and the organic tri- and tetrasulphides are built up of unbranched, zigzag sulphur chains, or of branched (coordinated) structures. The more recent evidence definitely favours the unbranched chain formulae. A chemical proof of an unbranched structure for polythionic compounds of the pentathionic type (combinations of two thio anions with S⁺⁺) is as follows¹:

In reactions with nucleophilic reagents, such as piperidine and thiocarbonyl anions, these compounds eliminate their thio groups as anions, the reagents, having a higher nucleophilic reactivity, taking their place and becoming linked to S⁺⁺ (*cf.* p. 1392). These ionic displacement reactions show that in each case a divalent sulphur atom forms a bridge between the thio sulphur atoms of two thio groups¹.

The polythionic compounds of the hexathionic type (combinations of two thio anions with S₂⁺⁺) react in an analogous way with piperidine and thiocarbonyl anions, and thus, in these cases a divalent disulphur group forms a bridge between the thio sulphur atoms of two thio groups¹. Here, the disulphur group, as far as the ionic displacement reactions are concerned, may have a branched structure (>S→S or >S=S) or an unbranched chain structure (—S—S—). However, in compounds of divalent sulphur the sulphur atom has in no case been proved able to add sulphur to form bonds of the branched type.

Likewise, structure investigations by physical methods are in favour of unbranched sulphur chains. Particularly, the comprehensive studies by Koch²³ of the ultraviolet absorption spectra of organic disulphides and polysulphides, provide strong evidence on this point.

The chemical reactions of polythionic compounds and analogous sulphur compounds are, predominantly, with nucleophilic reagents. These reactions may be explained in a straight-forward and consistent way on the basis of the electrophilic reactivity of sulphur and formulae with unbranched sulphur chains^{1, 24}.

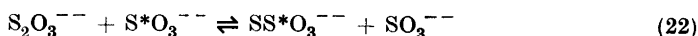
As for the thiosulphates, xanthates and dithiocarbamates of divalent selenium and tellurium, the ionic displacement reactions demonstrated earlier^{12, 14} and in this work prove that these compounds, also, are built up of unbranched chains.

The catalytic effect of thiosulphate on pentathionate was attributed by Kurtenacker and Kaufmann⁷ to the existence of an equilibrium:



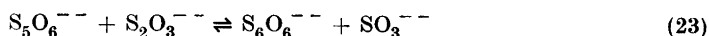
Through the tendency of thiosulphate to liberate sulphur, the corresponding tendency of pentathionate was assumed to be increased.

However, the equilibrium (21) does hardly exist¹. Thus, an exchange:

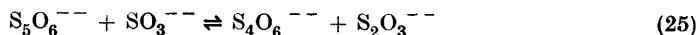


does not take place at ordinary temperatures²⁵.

Goehring, Helbing and Appel¹¹ formulated the thiosulphate catalysis on pentathionate as due to an equilibrium:



followed by



Hexathionate is more unstable than is pentathionate; however, the difference in stability is hardly large enough to account for the marked catalysis on pentathionate as being due to the formation of a relatively small amount of hexathionate. There is a thiosulphate catalysis on hexathionate also, and the acceptance of Goehring, Helbing and Appel's theory would thus merely shift the problem of thiosulphate catalysis from pentathionate to hexathionate.

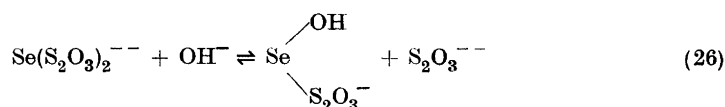
A different mechanism, which has to be considered, is the following. The thiosulphate catalysis on pentathionate, hexathionate, monoselenopentathionate and monotelluropentathionate may be due to a nucleophilic attack by thiosulphate on the thio sulphur atom of one of the two thiosulphate groups of the compounds, with a simultaneous or subsequent release of the other of the thiosulphate groups. Such a displacement would give rise to branched (coordinated) structures, and these would, according to the structural evidence, be unstable and liberate the coordinated sulphur, selenium or tellurium. One might also imagine the thiosulphate group and the sulphur, selenium or tellurium being released simultaneously. A similar picture would apply in

the case of the xanthate and dithiocarbamate catalysis on the xanthates and dithiocarbamates of sulphur, selenium and tellurium, *i. e.*, a nucleophilic attack, not on the central sulphur, selenium or tellurium atoms, but on one of the sulphur atoms linked thereto.

There are, though, two points which argue against such a mechanism. First, it accounts only for the catalysis by thio anions, not for the catalysis by hydroxide or iodide. The catalytic phenomena seem so closely related that a common mechanism must be thought to be responsible. Next, the fact that iodide acts as a catalyst on monotelluropentathionate, but not on pentathionate and monoselenopentathionate, indicates that an attack on tellurium is involved, not on one of the sulphur atoms linked to it.

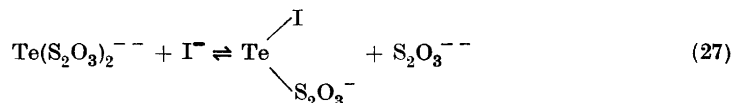
A theory, which avoids these difficulties, was put forward¹ in 1945 to account for the hydroxide and thiosulphate catalysis on pentathionate and hexathionate. The theory is in accordance with the experiments on selenium and tellurium compounds recorded in this work, and is outlined on the remaining pages.

Large amounts of hydroxyl ions rapidly and completely displace the two thiosulphate groups of pentathionate, hexathionate, monoselenopentathionate and monotelluropentathionate^{1, 11, 14}. It seems likely that smaller amounts, such as those which effect the catalytic decompositions, react to displace only one of the thiosulphate groups, like small amounts of sodium diethyldithiocarbamate do in reactions with pentathionate and hexathionate¹. Accordingly, it appears as if the catalysis takes place as a consequence of ionic displacement equilibria such as:

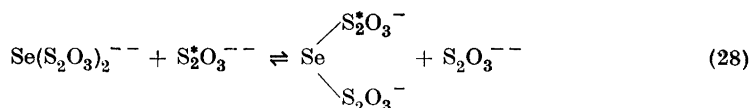


and similar equations with S, S₂ or Te instead of Se.

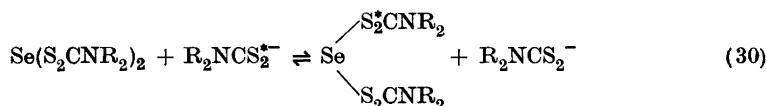
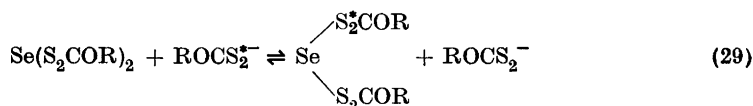
In the same way, a nucleophilic attack by iodide on the tellurium of monotelluropentathionate leads to the following displacement equilibrium:



Furthermore, in view of the properties of pentathionate, hexathionate, monoselenopentathionate and monotelluropentathionate as thiosulphates of divalent sulphur, selenium and tellurium, it seems likely that in the presence of thiosulphate, ionic displacement equilibria are established, of the type:



and likewise with S, S₂ or Te instead of Se. Since catalysis occurs, these equilibria are, possibly, the cause of the catalysis. Analogous considerations apply to the xanthate and dithiocarbamate catalysis on xanthates and dithiocarbamates of divalent sulphur and selenium. The experimental evidence for displacements are the reactions represented by Eqs. (7), (10), (11) and (14). Thus, it appears as if the catalysis is connected with the occurrence of ionic displacements such as:



Especially the experiments made with the selenium compounds, where an excess of sodium dithiocarbamate brings about displacements, while smaller amounts cause decompositions, suggest that there is a link between the displacements and the catalysis.

If the equilibria (26)–(30) are responsible for the catalysis, there is still the problem of why the molecules thereby become unstable. A possibility is the following. The reactions (26)–(30) proceed through a transition state, the energy of which is higher than that of the molecules in the initial state. The molecules are labile even in the initial state, and the increase in energy associated with the passing of the transition state serves to decrease the thermodynamic stability and accelerate the decompositions.

SUMMARY

The decompositions of monoselenopentathionate and monotelluropentathionate into tetrathionate, and selenium and tellurium, respectively, are catalyzed by thiosulphate and hydroxide, the last change also by iodide. There is a positive salt effect on these decompositions.

Some new xanthates and dithiocarbamates of divalent selenium and tellurium are described. The decompositions of the selenium compounds into

the disulphides, and selenium, are catalyzed by xanthate and dithiocarbamate ions. Monosulphur and disulphur di(ethylxanthate) are subject to the same type of catalysis.

Tellurium di(ethylxanthate) and *bis*(diethyldithiocarbamate) react with sodium dimethyl- and piperidyldithiocarbamate to give tellurium *bis*(dimethyldithiocarbamate) and di(piperidyldithiocarbamate). Under special conditions, the selenium compounds react in the same way.

Dithiocarbamate ions have a higher nucleophilic reactivity than xanthate ions, in displacements on tellurium.

The cause of the catalytic decompositions is discussed.

REFERENCES

1. Foss, O. *Kgl. Norske Vid. Selsk. Skrifter* (1945) no. 2.
2. Debus, H. *J. Chem. Soc.* 53 (1888) 278; *Ann.* 244 (1888) 76.
3. Riesenfeld, E. H., and Feld, G. W. *Z. anorg. allg. Chem.* 119 (1921) 225.
4. Foerster, F., and Hornig, A. *Z. anorg. allg. Chem.* 125 (1922) 86.
5. Vogel, I. *Chem. News* 128 (1924) 325, 342, 346, 361, 399.
6. Kurtenacker, A., and Kaufmann, M. *Z. anorg. allg. Chem.* 148 (1925) 43.
7. Kurtenacker, A., and Kaufmann, M. *Z. anorg. allg. Chem.* 148 (1925) 225.
8. Basset, H., and Durrant, R. G. *J. Chem. Soc.* (1927) 1401.
9. Weitz, E., and Achterberg, F. *Ber.* 61 (1928) 399.
10. Kurtenacker, A., Mutschin, A., and Stastny, F. *Z. anorg. allg. Chem.* 224 (1935) 399.
11. Goehring, M., Helbing, W., and Appel, I. *Z. anorg. allg. Chem.* 254 (1947) 185.
12. Foss, O. *Acta Chem. Scand.* 3 (1949) 435.
13. Norris, J. T., and Fay, H. *Am. Chem. Journ.* 23 (1900) 119.
14. Foss, O. *Acta Chem. Scand.* 3 (1949) 708.
15. Russell, W. F. U. S. patent 2 347 128 (1944).
16. Bloch, I., and Bergmann, M. *Ber.* 53 (1920) 961.
17. Twiss, D. *J. Am. Chem. Soc.* 49 (1927) 491.
18. Whitby, G. S. British patent 265 169 (1927).
19. Foss, O. *Kgl. Norske Vid. Selsk. Forh.* 14 (1941) no. 20.
20. Kurtenacker, A., and Fluss, W. *Z. anorg. allg. Chem.* 210 (1933) 125.
21. Martin, F., and Metz, L. *Z. anorg. allg. Chem.* 127 (1923) 83.
22. Kurtenacker, A. *Analytische Chemie der Sauerstoffsäuren des Schwefels*. Stuttgart (1938).
23. Koch, H. P. *J. Chem. Soc.* (1949) 394, 401.
24. Foss, O. *Acta Chem. Scand.* 1 (1947) 307.
25. Voge, H. H. *J. Am. Chem. Soc.* 61 (1939) 1032.

Received October 7, 1949.