

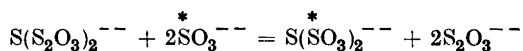
## The Interrelationship between Monoseleno Polythionates \*

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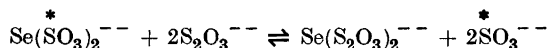
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The polythionate series, trithionate, tetrathionate, pentathionate and hexathionate, has no selenium counterpart, containing oxygen and selenium, only, in the anions. This article is concerned with trithionate and pentathionate, in which only one of the sulphur atoms is substituted by selenium. Sodium selenopentathionate, or sodium selenium di(thiosulphate),  $\text{Na}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$ , and also the potassium salt,  $\text{K}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , have been isolated in a pure state, as the first salts of selenopentathionic acid.

There is a striking difference between the polythionates and the monoseleno polythionates as regards their behaviour towards sulphite and thiosulphate. Tetrathionate, pentathionate and hexathionate react rapidly and quantitatively with sulphite, to give trithionate and thiosulphate. *E. g.*:



These reactions probably are ionic displacement reactions<sup>2</sup>, as indicated through the stars. In the case of the monoseleno polythionates, an equilibrium exists:



In presence of formaldehyde, as a sulphite acceptor, in buffered solutions, the equilibrium goes quantitatively to the right. Thus, sulphite is displaced by thiosulphate, whereas in the case of the polythionates, thiosulphate is displaced by sulphite.

Trithionate, tetrathionate and pentathionate are derivatives<sup>2</sup> of divalent electropositive sulphur,  $\text{S}^{++}$ . In reactions with nucleophilic reagents, pentathionate acts as a monosulphur di(thiosulphate),  $\text{S}(\text{S}_2\text{O}_3)_2^{--}$ . The compounds

\* This is the second in a series of papers on selenium sulphur compounds. First paper: Ref. 1.

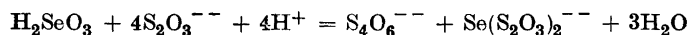
discussed in this article are derivatives of divalent electropositive selenium,  $\text{Se}^{++}$ . Selenopentathionate is a selenium di(thiosulphate),  $\text{Se}(\text{S}_2\text{O}_3)_2^{--}$ , its thiosulphate groups being displaceable by diethyldithiocarbamate. Selenotri-thionate, in the equilibrium with thiosulphate, behaves as a selenium disulphite,  $\text{Se}(\text{SO}_3)_2^{--}$ .

#### PREVIOUS WORK

Rathke<sup>3</sup> discovered selenotri-thionic acid,  $\text{Se}(\text{SO}_3\text{H})_2$ . He prepared the potassium salt,  $\text{K}_2\text{Se}(\text{SO}_3)_2$ , by adding aqueous selenious acid to a concentrated mixture of potassium sulphite and potassium selenosulphate. Schulze<sup>4</sup> reported the formation of selenotri-thionic acid in a mixture of aqueous selenious acid and excess sulphurous acid. Foerster, Lange, Drossbach and Seidel<sup>5</sup> prepared the salt by means of Rathke's method, and so did Heuer<sup>6</sup>. According to Rathke, selenotri-thionate is also formed, in small yields, when selenium is treated with aqueous potassium sulphite or hydrogen sulphite.

Morgan and Smith<sup>7</sup> found that selenium acetylacetonate reacts with hydrogen sulphites, to give selenotri-thionates in quantitative yields. In this way, they prepared the lithium, sodium, rubidium, cesium, ammonium and barium salts. The free acid, formed from selenium acetylacetonate and sulphurous acid, could not be obtained in an anhydrous state, since selenium was liberated as soon as the concentration of the aqueous solutions reached about 50 %.

The existence of selenopentathionic acid, in aqueous solutions, was first ascertained by Norris and Fay<sup>8</sup>. They found that selenious acid, in acid solutions, reacts with sodium thiosulphate, to give a mixture of tetrathionate and selenopentathionate:



The acid reaction mixtures are first clear, but, gradually, red selenium is liberated. If alkalis are added, the same process takes place immediately. Norris and Fay pointed out the analogy with pentathionate, which liberates sulphur when acted upon by small amounts of alkalis. The observations of Norris and Fay were confirmed by Foerster, Lange, Drossbach and Seidel<sup>5</sup>.

The above-mentioned reaction forms the basis for the so-called Norris and Fay method<sup>8,9</sup> for the iodometric analysis of selenious acid, and has been used as such by various workers<sup>10-13</sup>. Excess of thiosulphate is back-titrated with iodine. According to the critical study by Coleman and McCrosky<sup>14</sup>, the accuracy of the method is between 1 and 2 parts per 1000.

Norris and Fay<sup>8</sup> reported that »An effort was made to isolate the selenopentathionate, but without success, as selenium was always precipitated

when the solutions were concentrated by heat or in a vacuum». Unsuccessful attempts to isolate the selenopentathionate were also made by Heuer <sup>6</sup>.

#### SODIUM AND POTASSIUM SELENOPENTATHIONATE

These salts have been prepared by means of the Norris and Fay reaction between selenious acid and thiosulphate. Their isolation, without any liberation of selenium, has been achieved by use of (a) an excess of selenious acid at every stage of the process (b) concentrated acetic acid as a solvent for the selenious acid. The excess of selenious acid is necessary, because thiosulphate acts as a catalyst in the decomposition of selenopentathionate, as already observed by Norris and Fay <sup>6</sup>.

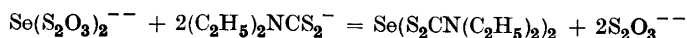
Sodium selenopentathionate forms small, shiny, pale yellowish green leaves (thin plates), the mass of crystals being fairly voluminous. It is very soluble in water, and is also appreciably soluble in methanol, insoluble in ethanol. It crystallizes with three moles of water.

Potassium selenopentathionate is in most cases obtained as needles or prisms, which may be more than 5 mm in length and 1 mm in thickness. The colour is yellowish green. It is less soluble in water than is the sodium salt, and insoluble in methanol. It crystallizes with one and a half mole of water, as does potassium pentathionate. The crystal water is kept very firmly, and is not given off *in vacuo* over sulphuric acid.

The salts are stable, though in the case of the potassium salt, spots of selenium have a tendency to develop inside some of the larger crystals after two or three days.

Aqueous solutions of the selenopentathionates are yellowish green. Even in 0.02 *M* solutions a pale green colour is observable. In neutral and acid solutions, selenopentathionate seems to be at least as stable as are corresponding solutions of pentathionate. The solutions are very sensitive to alkalies, as are pentathionate solutions. According to Foerster and Hornig <sup>15, 16</sup> 1 millimole of pentathionate dissolved in 1 liter of water can be detected, when 1 drop of 2 *N* sodium hydroxide is added to 10 ml of the pentathionate. The corresponding reaction of selenopentathionate is at least 10 times as sensitive. 10 ml of a 10<sup>-4</sup> *M* solution of selenopentathionate, to which is added 1 drop of 2 *N* sodium hydroxide, gives immediately a distinct brownish red colour (selenium).

Selenopentathionate reacts rapidly and quantitatively with excess diethyldithiocarbamate, to give selenium bis(diethyldithiocarbamate), and thiosulphate:



Since the diethyldithiocarbamate, with little doubt, acts as a nucleophilic reagent, the reaction is an ionic displacement on  $\text{Se}^{++}$ . The thiosulphate groups are displaced by diethyldithiocarbamate. Selenopentathionate is thereby characterized as being a selenium di(thiosulphate).

It contains two thiosulphate groups bonded to a selenium atom. Since the thio sulphur atom of the thiosulphate group has a higher polarizability and hence a higher reactivity towards electrophilic centres than have the oxygen atoms, it is the thio sulphur atom of thiosulphate which is linked to the selenium, and not any of the oxygen atoms.

The selenium-sulphur bonds are covalent; though, presumably they possess a definite amount of ionic character, with excess electropositivity on the selenium. In reactions with nucleophilic reagents, the bonding electron pairs of the selenium-sulphur bonds are released to the thiosulphate groups, which thereby become liberated as thiosulphate anions.

In pentathionate, a monosulphur di(thiosulphate), two thiosulphate groups are bonded to a sulphur atom, through the thio sulphur atoms of the thiosulphate groups<sup>2</sup>. The polarity of the selenium-sulphur bonds in selenopentathionate is, presumably, more pronounced than the polarity of the corresponding sulphur-sulphur bonds in pentathionate, because of the slightly higher electropositivity of selenium as compared with sulphur.

#### EXPERIMENTAL

*Sodium selenopentathionate*,  $\text{Na}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$ . To 20 g of selenious acid dissolved in 20 ml of water and 100 ml of glacial acetic acid are added dropwise, in the course of about 20 minutes, under mechanical stirring and cooling with ice-sodium chloride freezing mixture, 130 g of sodium thiosulphate pentahydrate in 40 ml of water (dissolved by heating, and cooled to room temperature). The temperature of the reaction mixture should be kept at about 0° C. To the clear, viscous, yellowish green solution of sodium tetrathionate and sodium selenopentathionate, containing an excess of selenious acid, are then added 150 ml of ethanol and, after the crystallization has begun, 50 ml of ether. The cooling and stirring are continued for 15 minutes, the product is then filtered off, drained well, washed with ethanol and with ether, and dried for a short time *in vacuo* over sulphuric acid.

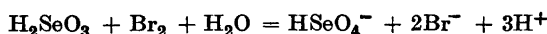
The product, a yellowish green, voluminous mass of crystals, contains about 40 g  $\text{Na}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$  with about 4 mole % of tetrathionate.

It is dissolved in 50 ml of 0.2 *N* hydrochloric acid at about 30° C, and the solution filtered with suction through a fine sintered glass filter. 100 ml of methanol are added, and the mixture cooled in ice-sodium chloride freezing mixture. The product, consisting of about 25 g pure sodium selenopentathionate trihydrate, is washed with ethanol and dried *in vacuo* over sulphuric acid.

For analysis, 0.5 millimole is dissolved in 25 ml of water. 10 ml of 6 *N* hydrochloric acid and 10 ml of a saturated solution of potassium bromide are added, and the solution is titrated with approx. 0.45 *N* potassium bromate. Toward the end of the titration the temperature of the solution is kept at about 40 or 50° C. The end point is observed by the appearance of a stable bromine colour, or by the use of 1 drop of a 0.2 per cent solution of methyl red as an indicator. The selenopentathionate is oxidized to selenious acid, and sulphate:



0.5 millimole of selenopentathionate corresponds to 20 ml of 0.45 *N* potassium bromate. The high acidity and the large amount of potassium bromide serve to prevent<sup>14</sup> the further oxidation of selenious acid:



The selenious acid formed may be determined by means of the Norris and Fay method. A few drops of a saturated alcoholic solution of acetanilide are added<sup>14</sup> to the titrated solution in order to discharge the slight excess of bromine. The solution is covered and heated just to boiling, cooled to below 20° C, and diluted to a volume of 200 ml. Then 0.1 *N* sodium thiosulphate is added, and the excess of thiosulphate is back-titrated with 0.1 *N* iodine. 0.5 millimole of selenious acid (or selenopentathionate) corresponds to 20 ml of 0.1 *N* thiosulphate (or iodine).

If tetrathionate is present, the amount of 0.45 *N* potassium bromate consumed is higher than the amount of 0.1 *N* thiosulphate. Tetrathionate is oxidized by bromine to sulphate<sup>16</sup>:



0.1927 g substance: 21.50 ml of 0.4012 *N* potassium bromate (corresponding to 19.16 ml of 0.45 *N* bromate). 19.88 ml — 0.86 ml = 19.02 ml of 0.1006 *N* iodine (corresponding to 19.14 ml of 0.1 *N* iodine).

$\text{Na}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$  (403.3) Calc. Se 19.58 Found Se 19.60

*Potassium selenopentathionate*,  $\text{K}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ . This salt is best prepared from the sodium salt by metathesis with potassium acetate. To the filtered solution of the crude sodium selenopentathionate in 50 ml 0.2 *N* hydrochloric acid (p. 438) is added in portions, under mechanical stirring and cooling with ice-sodium chloride freezing mixture, a suspension of potassium acetate prepared as follows: 25 g of potassium acetate are dissolved by heating in 50 ml of ethanol, 25 ml of glacial acetic acid are added, and the mixture is cooled to room temperature. The crystals of potassium selenopentathionate are filtered off, and washed with ethanol and with ether. Yield about 34 g of almost pure product (containing 1 mole %, or less, of tetrathionate). It is dissolved in a double amount of 0.2 *N* hydrochloric acid at 45—50° C, the solution is filtered with suction through a fine sintered glass filter, and the filtrate is cooled in an ice-sodium chloride freezing mixture. Yield, about 25 g of pure product.

0.1995 g substance: 21.88 ml of 0.4012 *N* potassium bromate (corresponding to 19.51 ml of 0.45 *N* bromate). 19.88 ml — 0.48 ml = 19.40 ml of 0.1006 *N* iodine (corresponding to 19.52 ml of 0.1 *N* iodine).



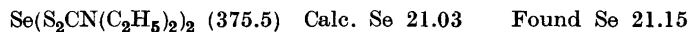
Potassium selenopentathionate may also be prepared directly from potassium thiosulphate. If 20 g of selenious acid dissolved in 40 ml of water and 80 ml of glacial acetic acid are reacted with 100 g of potassium thiosulphate (anhydrous) in 80 ml of water, under the same conditions as in the case of sodium thiosulphate, crystals begin to separate after about one third of the thiosulphate solution has been added. When the addition of thiosulphate is complete, the product is filtered off without any addition of ethanol or ether. In this way about 90 g of a yellowish green product is obtained, which, however, contains about 48 mole % of tetrathionate, as compared with only about 4 mole % in the case of the sodium salts. To remove the tetrathionate, the product is dissolved in 150 ml of 0.2 *N* hydrochloric acid at 45–50° C, the solution is filtered with suction through a fine sintered glass filter, and the filtrate is allowed to cool slowly to about 15° C. If the mixture is cooled further down, white tetrathionate crystals begin to separate out rather suddenly. The liquid is decanted from the crystals, and the crystals are brought on to the filter by means of a little water. Yield, about 18 g of a product which contains about 2 mole % of tetrathionate. It is finally recrystallized from a double amount of 0.2 *N* hydrochloric acid as described p. 439. The yield of the pure salt is thus about onehalf of that obtained by use of sodium thiosulphate.

*Selenopentathionate and diethyldithiocarbamate.* To 50 ml of 0.3 *M* sodium diethyldithiocarbamate were added, under stirring, 2.051 g  $\text{K}_2\text{Se}(\text{S}_2\text{O}_3)_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  dissolved in 50 ml of water. A light brown product immediately separated out. After 10 minutes stirring, the product was filtered off, washed with water, and dried *in vacuo* over sulphuric acid: 1.89 g (theoretically, 1.88 g  $\text{Se}(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_2$ ). To the filtrate was added, in order to remove the excess of diethyldithiocarbamate, a suspension of cadmium carbonate, freshly prepared by mixing 20 ml of 10 %  $\text{Na}_2\text{CO}_3$  with an equal volume of 15 %  $\text{CdSO}_4$  solution. The mixture was made up to 250 ml in a volumetric flask, and filtered through a dry filter. 50 ml of the filtrate, to which had been added 20 ml of 10 % acetic acid, consumed 20.29 ml of 0.09917 *N* iodine (theoretically, 20.25 ml).

The selenium *bis*(diethyldithiocarbamate) was recrystallized from carbon disulphide-ether, and thus obtained as yellowish green crystals, m. p. 116° C. It may also be recrystallized from carbon tetrachloride. When potassium hydroxide is added to its alcoholic solutions, red selenium is deposited.

For analysis, the compound was oxidized with nitric acid-sulphuric acid, the nitric acid was destroyed by means of urea, and the selenious acid was determined volumetrically by means of the Norris and Fay method.

0.2074 g substance: 24.85 ml – 2.75 ml = 22.10 ml 0.1006 *N* iodine.



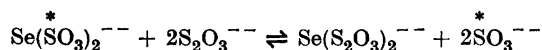
*The optical transmittance of selenopentathionate solutions* was measured by means of a Beckman quartz spectrophotometer, model DU (1 cm cells). 0.01 *N* hydrochloric acid was used as a solvent and as a blank. The results, for wave lengths from 360  $\mu$  to 460  $\mu$ , are listed in Table 1. A slow change of transmittance took place during the measurements. Beer's law is seen to hold.

Table 1. Molar extinction coefficient,  $\epsilon$ , for potassium selenopentathionate dissolved in 0.01 N hydrochloric acid, as a function of wave length.

$m\mu$	Molarity				Average
	0.02	0.05	0.1	0.2	
360	41.2	40.9			41.1
370	24.2	24.3			24.3
380	14.2	14.4			14.3
390	8.56	8.50			8.5
400	5.01	5.06			5.0
410	2.75	2.68	2.73	2.71	2.7
420	1.55	1.52	1.51	1.51	1.5
430	0.86	0.83	0.80	0.82	0.83
440	0.48	0.44	0.44	0.45	0.45
450		0.26	0.23	0.25	0.25
460		0.14	0.12	0.14	0.13

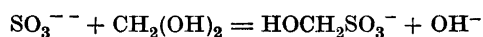
THE EQUILIBRIUM OF SELENOTRITHIONATE AND SELENO-PENTATHIONATE WITH THIOSULPHATE AND SULPHITE

Selenotrithionate gives the following equilibrium with thiosulphate:



The equilibrium probably involves ionic displacements of sulphite by thiosulphate, and vice versa, as indicated through the stars, and not transfers of sulphur from thiosulphate to selenotrithionate, or from selenopentathionate to sulphite.

In buffered solutions, in presence of formaldehyde and excess thiosulphate, the equilibrium is displaced quantitatively to the right. Formaldehyde ties up sulphite as hydroxymethanesulphonate:

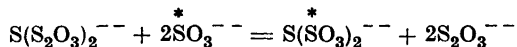


The buffer serves to keep the solutions slightly acid and thus to prevent the liberation of selenium from selenopentathionate.

Under such conditions, the reaction may be employed for the iodometric analysis of selenotrithionate (see the experimental part). Excess of thiosulphate is back-titrated with iodine, hydroxymethanesulphonate<sup>16,17</sup> and also selenopentathionate being indifferent to iodine in acid solutions.

The equilibrium may be demonstrated from both sides, *i. e.*, also from selenopentathionate and sulphite.

In the case of trithionate and pentathionate, no such measurable equilibrium exists. Pentathionate reacts quantitatively with sulphite, to give trithionate, and thiosulphate\*:



The reaction of pentathionate with sulphite proceeds in two steps: First one thiosulphate group is displaced, to give tetrathionate. Analogously, the displacement of sulphite in selenotrithionate by thiosulphate probably involves two steps, with a selenium sulphite-thiosulphate, *i. e.*, selenotetrathionate,  $SeS_3O_6^{--}$ , as an intermediate.

#### EXPERIMENTAL

*Potassium selenotrithionate* was prepared by means of Rathke's method<sup>3</sup>. The procedure differs in some details from that used by Foerster, Lange, Drossbach and Seidel<sup>5</sup> and by Heuer<sup>6</sup>.

8 g of selenium (red or grey) are dissolved by heating in 20 ml of water containing 12 g of potassium hydroxide. To the dark red solution is added, cautiously, a hot solution of 72 g of potassium hydrogen sulphite in 100 ml water. The resulting solution is filtered, if necessary, and cooled to 30—40° C. Then 13 g selenious acid dissolved in 20 ml water are added. The mixture becomes hot, and crystals of potassium selenotrithionate begin to separate out. After cooling in water to 20° C, the crystals are filtered off, and washed with 50 % ethanol. Yield, about 52 g, being about 94 % pure. It is dissolved in 150 ml water at 45—50° C, the solution is filtered, if necessary, and cooled in ice-sodium chloride freezing mixture. Yield, about 36 g of pure potassium selenotrithionate,  $K_2Se(SO_3)_2$ .

It may be analyzed iodometrically as follows:

To 25 ml of 0.01 *M* selenotrithionate are added 2 g of sodium hydrogen carbonate and then 20 ml of 0.1 *N* iodine. After standing for 5 minutes in stoppered flask, 20 ml 10 % acetic acid are added, and the excess of iodine is back-titrated with 0.1 *N* thiosulphate.

The selenotrithionate is oxidized to selenite, and sulphate:  $Se(SO_3)_2^{--} + 3I_2 + 10 OH^- = SeO_3^{--} + 2SO_4^{--} + 6I^- + 5H_2O$ . Selenite is indifferent to iodide in acetate buffers, therefore acetic acid can be used for back-titration of the excess iodine. The method is analogous to that worked out for the analysis of di-*o*-alkylmonoselenophosphates<sup>18</sup>.

The following experiment shows the merit of the method:

0.7929 g of  $K_2Se(SO_3)_2$  was dissolved to 250 ml, and 25 ml samples were pipetted out. Time of standing between the addition of iodine and acetic acid: 3, 5, 15, 20 minutes. Amounts of 0.1073 *N* thiosulphate consumed: 18.86 ml (by the 20 ml iodine employed) — 5.08 ml, 4.92 ml, 4.92 ml, 4.92 ml, respectively. 10 times 13.94 ml of 0.1073 *N* thiosulphate corresponds to 0.7911 g of  $K_2Se(SO_3)_2$ , *i. e.*, 99.77 %.

\* For literature references, see Ref. 2.



In neutral and acid solutions, selenotriethionate is oxidized by iodine to selenium and sulphate, as stated by Heuer<sup>6</sup>. Selenopentathionate, however, is indifferent to iodine in acid solutions, as shown by the accuracy and consistency of the Norris and Fay method.

*Selenotriethionate and thiosulphate.* If thiosulphate and formaldehyde are added to a solution of selenotriethionate, the mixture immediately becomes alkaline (to phenolphthalein). If an excess of thiosulphate is present, selenium is rapidly liberated.

In buffered solutions, the pale green colour of selenopentathionate gradually develops.

Thus, selenotriethionate may be analyzed iodometrically as follows:

1 millimole selenotriethionate is dissolved in 100–150 ml of water, and 25 ml of a buffer is added, being 0.5 *M* with respect to dihydrogen phosphate and 0.1 *M* with respect to monohydrogen phosphate (68.07 g  $\text{KH}_2\text{PO}_4$  and 35.82 g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  dissolved to 1 liter). Next 1 ml of 40 % formaldehyde and 25 ml of 0.1 *N* thiosulphate are added. After standing for 5 minutes, 20 ml of 10 % acetic acid are added, and the excess of thiosulphate is back-titrated with 0.1 *N* iodine.

The following experiment illustrates the method:

3.986 g of  $\text{K}_2\text{Se}(\text{SO}_3)_2$  (the same specimen that was analyzed by means of the iodine-sodium hydrogen carbonate method) was dissolved to 250 ml, and 20 ml samples were pipetted out, and diluted to 120 ml. Time of standing between the addition of formaldehyde-thiosulphate and acetic acid: 5, 10, 15, 15 minutes. Amounts of 0.1013 *N* iodine consumed: 26.51 ml (by the 25 ml thiosulphate employed) — 6.70 ml, 6.70 ml, 6.70 ml, 6.71 ml, respectively. 12.5 times 19.81 ml of 0.1013 *N* iodine corresponds to 3.980 g of  $\text{K}_2\text{Se}(\text{SO}_3)_2$ , *i. e.*, 99.84 %.

In presence of 10 ml of 0.05 *M* tetrathionate: 6.69 ml of iodine. Thus, tetrathionate does not affect the results. If, however, the thiosulphate is added before the formaldehyde is added, too low results are obtained. This is because the sulphite formed reacts with tetrathionate to give thiosulphate, which thus becomes regenerated.

The buffer employed has a pH = 6.5. After the formation of 20 ml of 0.1 *M* hydroxymethanesulphonate the solutions will have approx. pH = 6.9. The solutions should not stand for more than 15 minutes before they are titrated, since after about 20 minutes a selenium colour begins to appear. The titrated solutions, the catalyzing thiosulphate having been removed, are stable for several hours. On addition of an appropriate amount of potassium hydroxide, selenium is liberated.

Selenotriethionate solutions are not very stable. In the approx. 0.05 *M* solution employed above (3.986 g of  $\text{K}_2\text{Se}(\text{SO}_3)_2$  in 250 ml), the content of selenotriethionate, 14 hours after the preparation of the solution, had decreased by 2 % (determined by means of the formaldehyde-thiosulphate method).

*Selenopentathionate and sulphite.* To 50 ml of 0.02 *M* potassium selenopentathionate were added 10 ml of buffer solution (0.5 *M*  $\text{H}_2\text{PO}_4^-$  and 0.1 *M*  $\text{HPO}_4^{2-}$ ) and 5 ml of 0.1 *M* sodium sulphite (in 20 % ethanol, as a stabilizer). The sulphite, in blind runs, consumed 9.92 ml of 0.1 *N* iodine. After standing, the mixture was titrated with 0.1 *N* iodine. Time of standing: 1, 2, 5 minutes. Amounts of 0.1 *N* iodine consumed: 6.42 ml, 6.31 ml, 6.30 ml, respectively. Thus selenopentathionate reacts with sulphite to give thiosulphate, though not quantitatively (would require a consumption of only 4.96 ml of iodine).

To a mixture of 50 ml of 0.02 *M* selenopentathionate, 10 ml buffer solution, and 5 ml 0.1 *M* sulphite, after standing, were added 100 ml water, 1 ml of 40 % formaldehyde, and 5 ml of 0.1 *N* thiosulphate (to displace the equilibrium more quantitatively towards selenopentathionate). The thiosulphate consumed, in blind runs, 5.02 ml of 0.1 *N* iodine.

After standing for 5 minutes, 20 ml of 10 % acetic acid were added, and the solution titrated with 0.1 N iodine. Time of standing between the addition of sulphite and formaldehyde-thiosulphate: 1, 2, 5 minutes. Amounts of 0.1 N iodine consumed: 5.06 ml, 5.10 ml, 5.16 ml, respectively. The experiment shows that although selenopentathionate reacts partly with sulphite, to give thiosulphate, the reaction is reversed on addition of formaldehyde and thiosulphate. Theoretical consumption of 0.1 N iodine in the last titrations, for quantitative displacement, would be 5.02 ml.\* The small discrepancy, increasing on standing, is probably due to hydrolysis of lower selenopolythionates formed by the action of sulphite.

No selenium was liberated in the solutions at any stage of the experiments.

#### SUMMARY

Sodium and potassium selenopentathionate have been prepared in a pure state, as the first salts of selenopentathionic acid. Selenopentathionate is a selenium di(thiosulphate).

It is shown that an equilibrium exists between selenotrithionate and thio-sulphate, on one side, and selenopentathionate and sulphite, on the other side. This equilibrium has been utilized for the iodometric analysis of selenotrithionate.

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The work on selenopolythionates and analogous selenium sulphur compounds is being continued. Also the corresponding tellurium sulphur compounds are being investigated.

#### REFERENCES

1. Foss, O. *J. Am. Chem. Soc.* **69** (1947) 2236.
2. Foss, O. *Kgl. Norske Vid. Selsk. Skrifter* (1945) no. 2.
3. Rathke, B. *J. prakt. Chem.* **95** (1865) 1.
4. Schulze, H. *J. prakt. Chem.* [2] **32** (1885) 390.
5. Foerster, F., Lange, F., Drossbach, O., and Seidel, W. *Z. anorg. allg. Chem.* **128** (1923) 245.
6. Heuer, O. Thesis, Technische Hochschule Hannover (1926).
7. Morgan, G. T., and Smith, J. D. M. *J. Chem. Soc.* **119** (1921) 1066.
8. Norris, J. T., and Fay, H. *Am. Chem. Journ.* **23** (1900) 119.
9. Norris, J. T., and Fay, H. *Am. Chem. Journ.* **18** (1895) 703.
10. Norton, J. T. *Z. anorg. allg. Chem.* **20** (1899) 221.
11. Moser, L., and Prinz, W. *Z. anal. Chem.* **57** (1918) 277.
12. Berg, R., and Teitelbaum, M. *Chem.-Ztg.* **52** (1928) 142.
13. Someya, K. *Z. anorg. allg. Chem.* **187** (1930) 337.
14. Coleman, W. C., and McCrosky, C. R. *Ind. Eng. Chem., Anal. Ed.* **9** (1937) 431.
15. Foerster, F., and Hornig, A. *Z. anorg. allg. Chem.* **125** (1922) 86.
16. Kurtenacker, A. *Analytische Chemie der Sauerstoffsäuren des Schwefels*. Stuttgart (1938).
17. Kurtenacker, A. *Z. anal. Chem.* **64** (1924) 56.
18. Foss, O. *Acta Chem. Scand.* **1** (1947) 8.

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