Isolation of intermediate products of acidic decomposition of selenopentathionate: the selenopolythionates containing more than four sulfur atoms in the molecule

Vitalijus Janickis* and Virginė Albina Amankavičienė
Faculty of Chemical Technology, Kaunas University of Technology, Radvilienė 19, LT-50254 Kaunas-9, Lithuania.
E-mail: vitalijus.janickis@ktu.lt

The decomposition of potassium monoselenopentathionate under the action of high concentration sulfuric acid (45–75%) proceeding with the liberation of hydrogen sulfide and formation of mono- and polyselenopolythionates, containing more than 4 sulfur atoms in the molecule has been studied. The mono- and diselenopolythionates containing 5–7 sulfur atoms in the molecule are isolated as crystalline salts of trans-dipyridine-bis(dimethylglyoximato)cobalt(III) as the intermediate products of the selenopentathionate decomposition mentioned at the optimal decomposition conditions determined. By this, a new homologous series of the SeS₄O₆²⁻ and Se₂S₅O₆²⁻ (n > 4) types are discovered. The chemical reactions - oxidation by iodine in the acidic and hydrocarbonate medium and under the action of cyanide ions - of the new selenopolythionates are studied. The results confirmed the structure of these compounds to be analogous to the known structure of monoselenopentathionate - a chain of sulfur–selenium atoms with the SO₃⁻ groups on the ends. The mechanism of the formation of more sulfured mono- and diselenopolythionates during the acidic SeS₄O₆²⁻ decomposition is proposed. The main role is attributed to the intermediate compound, monoselenanedisulfonate H–S–Se–S–SO₃H, which forms as a result of the initial hydrolysis of the SeS₄O₆²⁻ anion resulting in the cleavage of a bond between the terminal sulfur atoms.

Key words: potassium selenopentathionate, acidic decomposition, higher mono- and diselenopolythionates

INTRODUCTION

The first data on selenopolythionics – selenotrichionic acid, H₂SeS₂O₆, and monoselenopentathionic acid, H₂SeS₄O₆, were published in 1865 [1] and 1949 [2], respectively.

Since these times numerous studies devoted to the chemistry and technological application of these peculiar sulfur–selenium compounds in the laboratories of various countries (Germany, Norway, Lithuania) was carried out. Three homologous series of the selenopolythionates were known: mono-selenopolythionates, SeS₈O₆²⁻ (n = 2–4), and polyselenopolythionates of two types: the symmetric ones of the general formula SeₙS₂O₆²⁻ (n = 2–7) and the asymmetric ones of the general formula SeₙS₃O₆²⁻ (n = 2–6) [2–11]. Unfortunately, the structure of selenopolythionic acid anions was undoubtedly determined only for the lower selenopolythionates [3, 11–14] - the chains of sulfur–selenium or only selenium atoms with the SO₃⁻ groups on the ends: of the selenotrithionate, O₅S–Se–SO₃⁻, monoselenotetrathionate, O₅S–Se–S–SO₃⁻, diselenotetrathionate, O₅S–Se–Se–SO₃⁻, and monoselenopentathionate, O₅S–S–Se–S–SO₃⁻.

Zelionkaitė and Ūkytė found [7] that monosele-nopentathionic acid, H₂SeS₄O₆, in a con-centrated solution decomposes with the formation of sulfurous,
sulfuric acids and liberation of elemental sulfur and selenium according to the equation:

$$\text{H}_2\text{SeS}_2\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{Se} + + 2\text{S}.$$  \hspace{1cm} (1)

However, the decomposition of barium selenopentathionate, $\text{BaSeS}_2\text{O}_4$, under the action of concentrated sulfuric acid, $\text{H}_2\text{SO}_4$, proceeds with the liberation of hydrogen sulfide, $\text{H}_2\text{S}$ [16]. Since it has been undoubtedly determined that the liberation of hydrogen sulfide occurs during the condensation of sulfanomonosulfonates, $\text{H}_2\text{SeS}_4\text{O}_6^-$, into polythionates [11, 17],

$$2\text{H}_2\text{SeS}_4\text{O}_6^- \rightarrow \text{S}_2\text{O}_7^{2-} + \text{H}_2\text{S}.$$  \hspace{1cm} (2)

Zelionkaite and Dukytë proposed [16] that the hydrolysis of selenopentathionate anion results in the cleavage of a bond between the terminal sulfur atoms and the formation of sulfanomonoselenamono-sulfonate is the first stage during the decomposition of barium selenopentathionate:

$$\text{H}_2\text{O} + \text{S}-\text{Se}-\text{S}-\text{SO}_4^- \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{S}-\text{Se}-\text{S}-\text{SO}_4^-.$$  \hspace{1cm} (3)

This intermediate compound may undergo further decomposition analogously to the decomposition of sulfanomonosulfonates,

$$\text{H}_2\text{S}\text{SeS}_4\text{O}_6^- \rightarrow \text{S}_2\text{SeS}_4\text{O}_6^-$, with the liberation of hydrogen sulfide;

$$\text{H}_2\text{O} + \text{S}-\text{Se}-\text{S}-\text{SO}_4^- \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{S}-\text{Se}-\text{S}-\text{SO}_4^-.$$  \hspace{1cm} (4)

or to condense into a new selenopolythionate ($\text{H}_2\text{SeS}_4\text{O}_6^-$), with the liberation of hydrogen sulfide:

$$\text{H}_2\text{O} + \text{S}-\text{Se}-\text{S}-\text{SO}_4^- \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{S}-\text{Se}-\text{S}-\text{SO}_4^-.$$  \hspace{1cm} (5)

The aim of the present work was isolation of intermediate products of monoselenopentathionate decomposition under the action of concentrated sulfuric acid, i.e. the selenopolythionates containing more than four sulfur atoms in the molecule, and the characterization of these compounds by the chemical reactions typical of selenopolythionates.

**EXPERIMENTAL**

The chemical materials used in the study were chemically and analytically pure commercial (Russia) reagents. Some compounds were prepared using the published procedures: the hydrogen-sulfate of cobalt(III) selenopolythionate decompo-sition products. After the introduction of a portion of the saturated solution of $[\text{Co(DH)}_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$, small crystals of the selenopolythionate of this cation were precipitated. The filtered crystals were washed with water until the rate of temperature increase 5 °C · min⁻¹, etha-nol - $\text{Al}_2\text{O}_3$.

Fractional precipitation was used for the isolation of higher selenopolythionates, potassium selenopentathionate decompo-sition products. After the introduction of a portion of the saturated solution of $[\text{Co(DH)}_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$, small crystals of the selenopolythionate of this cation were precipitated. The filtered crystals were washed with water until disappearance of $\text{SO}_4^{2-}$ ions in the washings and later with acetone. Analogously, the crystals of trans-dipyridine-bis(dimethylglyoximato)cobalt(III) selenopolythionate were analysed determi-ning the contents of cobalt, sulfur, selenium and crystallization water. Cobalt was determined as $\text{Co}_2\text{O}_3$ gravimetrically. For the determination of sulfur, 0.1-0.15 g of a sample was partially dissolved in water, 10 ml of 23% HCl was added and oxidized with bromine. After bromine excess removal by heaning, the sulfate ions were determined gravimetrically as $\text{BaSO}_4$. The amount of selenium was determined by a procedure worked out by us. A about 0.1 g of a sample was dissolved under heating in 20 ml 10 N KOH and heating was continued until the disappearance of the pyridine smell (the presence of pyridine makes the iodometric selenium determination problematic [11]). Then the solution was coo-led 15 ml of 23% HCl and 10 ml of bromine were added for oxidation. After bromine excess removal by heating, selenous acid was determined iodometrically [19]. The amount of crystallization water was determined thermogravimetrically with a derivatog-raph of the F. Paulik, I. Paulik, L. Erdey (Hungary) system in the air atmosphere. The parameters: a 100 mg sample, temperature range up to 1000 °C, the rate of temperature increase 5 °C · min⁻¹, etha-nol - $\text{Al}_2\text{O}_3$. Fractional precipitation was used for the isolation of higher selenopolythionates, potassium selenopentathionate decompo-sition products. After the introduction of a portion of the saturated solution of $[\text{Co(DH)}_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$, small crystals of the selenopolythionate of this cation were precipitated. The filtered crystals were washed with water until disappearance of $\text{SO}_4^{2-}$ ions in the washings and later with acetone. Analogously, the crystals of trans-dipyridine-bis(dimethylglyoximato)cobalt(III) selenopolythionate were analysed.
Isolation of intermediate products of acidic decomposition of selenopentathionate: the selenopolythionates...

The oxidation with iodine in acidic and hydrogencarbonate solution and under the action of cyanide ions characteristic of selenopolythionate reactions was performed for identification of the compounds isolated. To study the reaction of oxidation with iodine in acidic solution, ~0.05 g of the isolated selenopolythionate was dissolved under heating in 50% ethanol (~40 ml) and an excess of the acidified (20 ml 2 N HCl) iodine solution was added. After 5 min the excess of nonreacted iodine was titrated with thiosulfate solution. To study the reaction of oxidation with iodine in the hydrogencarbonate solution, 0.05–0.1 g of K₂Se₅O₆ · 3/2H₂O or trans-dipyridine-bis(dimethylglyoximato)-cobalt(III) selenopolythionate was dissolved in water or 50% ethanol (~30 ml), respectively. Then an excess of the iodine solution and 2 g of K₂CO₃ were added, the reaction mixture left for 5 min, starch and 20 ml 10% CH₃COOH were added and again left for 5 min (to reach a complete consumption of iodine by the complex cation in the acidic medium). Finally, the excess of nonreacted iodine was titrated with thiosulfate solution. To study the reaction with cyanide ions, the sample was partially or completely dissolved in 50% ethanol and 7 ml of 0.5 M KCN was added. The solution soon became clear and was left for 5 min. Then 2 g of KI, 20 ml of 10% acetic acid and an excess of iodine solution were added. The latter was titrated with thiosulfate solution.

RESULTS AND DISCUSSION

The kinetic experiments with the aim to determine the dependence of formation of the final products of selenopentathionate decomposition – H₂S, sulfur and selenium – on the concentration, amount and temperature of sulfuric acid used were performed first.

The rate of hydrogen sulfide liberation increases with an increase in sulfuric acid concentration (Fig. 1). However, this process, when sulfuric acid of a higher concentration (60–70%) was used, slowed down after the liberated amount of H₂S (calculated according to equation (6)) had reached 100%.

The liberation of elemental sulfur does not depend on the concentration of sulfuric acid (Fig. 2), but the minimal amount of selenium after the amount of liberated H₂S (calculated according to equation (6)) had reached 100%.

The liberation of elemental sulfur does not depend on the concentration of sulfuric acid (Fig. 2), but the minimal amount of selenium after the amount of liberated H₂S reached 50% has been found using a 50% solution of sulfuric acid.

The liberation of H₂S slows down with an increase in the amount of sulfuric acid used (Fig. 3), without any effect on the liberation of sulfur and selenium (Fig. 4), except the experiment when the K₂Se₅O₆ solution of the high concentration (~1 M) has been used.

Fig. 1. Liberation of H₂S (% from the amount calculated according to equation (6)) during the decomposition of potassium selenopentathionate with sulfuric acid at a temperature of 50 °C.
The concentration of H₂SO₄ solution, %: 1 – 70, 2 – 65, 3 – 60, 4 – 55, 5 – 50, 6 – 45

Fig. 2. Dependence of liberated amounts of elemental selenium (1) and sulfur (2) during the decomposition of potassium selenopentathionate with sulfuric acid (50% H₂S liberation) on the concentration (%) of H₂SO₄ (10 ml) used
Fig. 3. Liberation of H₂S (% from the amount calculated according to equation (6)) during the decomposition of potassium selenopentathionate with 50% sulfuric acid at a temperature of 50 °C. The concentration of K₂SeS₄O₆ solution, mol/l: 1 – 0.96, 2 – 0.70, 3 – 0.37, 4 – 0.26

Fig. 4. Dependence of amounts of elemental sulfur (a) and selenium (b) liberated during the decomposition of potassium selenopentathionate with sulfuric acid (50% H₂S liberation) on the concentration (mol/l) of K₂SeS₄O₆. The liberation of H₂S, %: 1 – 50, 2 – 100

Fig. 5. Liberation of H₂S (% from the amount calculated according to equation (6)) during the decomposition of potassium selenopentathionate with 50% sulfuric acid. Temperature, °C: 1 – 60, 2 – 50, 3 – 40

Fig. 6. Dependence of amounts of elemental sulfur (a) and selenium (b) liberated during the decomposition of potassium selenopentathionate with 50% sulfuric acid (10 ml) on the temperature. The amount of liberated H₂S, %: 1 – 50, 2 – 100
Table 1. Products of K₂SeS₄O₆ · 3/2H₂O (8 mmol) decomposition with H₂SO₄ (10 ml 50%) at a temperature of 50 °C. The amount of 0.14 M PHSO₄ · 2H₂O solution (ml) used for fractional isolation: 1 - 10, 2 - 30, 3 - 30

<table>
<thead>
<tr>
<th>H₂S, %</th>
<th>No. of fraction</th>
<th>Found, %</th>
<th>Yield**, %</th>
<th>Compound</th>
<th>Calculated, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>Se</td>
<td>S</td>
<td>Se:S</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>8.44</td>
<td>9.60</td>
<td>13.95</td>
<td>2:7.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-</td>
<td>6.52</td>
<td>10.86</td>
<td>1:4.1</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>8.52</td>
<td>11.92</td>
<td>15.30</td>
<td>2:6.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.01</td>
<td>8.75</td>
<td>13.22</td>
<td>1.5:5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.26</td>
<td>11.07</td>
<td>15.73</td>
<td>P₂Se₂S₇O₆ · 3H₂O, Mixture of monodynamolselenopolythionates</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>-</td>
<td>12.35</td>
<td>15.28</td>
<td>2:6.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.52</td>
<td>11.26</td>
<td>15.43</td>
<td>2:6.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.76</td>
<td>8.68</td>
<td>16.05</td>
<td>1.5:6.8</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>8.53</td>
<td>9.95</td>
<td>15.59</td>
<td>2:7.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8.79</td>
<td>6.67</td>
<td>14.40</td>
<td>1.5:5.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-</td>
<td>6.30</td>
<td>10.94</td>
<td>1:4.3</td>
</tr>
<tr>
<td>80</td>
<td>1</td>
<td>-</td>
<td>8.23</td>
<td>15.58</td>
<td>1.5:7.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-</td>
<td>7.53</td>
<td>15.31</td>
<td>1.5:7.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.51</td>
<td>5.82</td>
<td>11.60</td>
<td>1:4.9</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>-</td>
<td>8.23</td>
<td>15.58</td>
<td>1.5:7.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-</td>
<td>7.53</td>
<td>15.31</td>
<td>1.5:7.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-</td>
<td>9.51</td>
<td>5.82</td>
<td>11.60</td>
</tr>
</tbody>
</table>

*P = [Co(DH)₂Py₂]⁺. ** From the amount of Se present in K₂SeS₄O₆ used for decomposition

The rate of H₂S liberation increases with increasing the temperature (Fig. 5), but the lowest amounts of liberated sulfur and selenium were received at a temperature of 50 °C (Fig. 6).

It is worth pointing out that rather small amounts of elemental sulfur, 5–6% (calculated from the sulfur amount in K₂SeS₄O₆ used) after a 50% H₂S liberation and 10–12% after a 100% H₂S liberation were obtained; the minimal amounts of selenium liberated during the decomposition of selenopentathionate with the 50% H₂SO₄ at a temperature of 50 °C were 10% and 30% from the selenium amount in K₂SeS₄O₆ used, respectively.

Thus, the kinetic experiments showed that the smallest amounts of sulfur and selenium liberate (at the same amount of liberated H₂S) when 50–60% sulfuric acid at a temperature of 50 °C was used for the decomposition of selenopentathionate. Therefore it was reasonable to expect that these conditions of decomposition were the most suitable for the isolation of intermediate products of this decomposition.

As mentioned above, a saturated solution of [Co(DH)₂Py₂]HSO₄ was used for the isolation of K₂SeS₄O₆ decomposition intermediate products. The experiments were carried out analogously as during the kinetic studies as described in the experimental part. Fractional crystallization was used for the isolation of intermediate products as described above after the elemental sulfur and selenium were filtered off. The product of each fraction was washed with water, then with acetone before analysis. The analytical data (the average values) are presented in Tables 1–3.

At the beginning of decomposition (20–50% liberation of H₂S) the amount of selenium in the product of the first fraction reaches a maximal value which corresponds to the diselenopolythionates. But later (with an increased degree of selenopentathionate decomposition – after a higher amount of H₂S is liberated) the amount of selenium in the products isolated gradually reduces. The amount of sulfur in the products at the beginning of decomposition increases too, but later it does not reduce. As a result, at a lower degree of selenopentathionate decomposition (up to 40–50% of H₂S liberation) the composition of the products isolated in the first fractions corresponds to diselenopolythionates containing 6–8 sulfur atoms in the molecule. Selenopolythionates of a higher degree of sulfurisation (Se₆S₄O₆⁻², Se₂S₈O₆⁻²) form when 60% H₂SO₄ is used for selenopentathionate decomposition (Table 2). At a higher degree of decomposition (80–100% of H₂S liberation), the monoselenopolythionates containing 6–8 sulfur atoms in the molecule are isolated from the reaction mixture. The highest yield of diseleno-
Vitalijus Janickis and Virginė Albina Amankavičienė

Table 2. Products of $K_2SeS_4O_6 \cdot 3/2H_2O$ (16 mmol) decomposition with $H_2SO_4$ (20 ml 60%) at a temperature of 50 °C. The amount of 0.14 M $PHSO_4 \cdot 2H_2O$ solution (ml) used for fractional isolation: 1 - 15, 2 - 20, 3 - 20

<table>
<thead>
<tr>
<th>H$_2$S, %</th>
<th>No. of fraction</th>
<th>Yield, %</th>
<th>Compound</th>
<th>Calculated, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.91</td>
<td>10.90</td>
<td>15.21</td>
<td>2.69</td>
</tr>
<tr>
<td>2</td>
<td>8.49</td>
<td>12.35</td>
<td>16.86</td>
<td>2.67</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>9.48</td>
<td>5.47</td>
<td>11.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.74</td>
<td>11.35</td>
<td>17.66</td>
<td>2.77</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>11.62</td>
<td>16.26</td>
<td>2.69</td>
</tr>
<tr>
<td>2</td>
<td>8.94</td>
<td>10.00</td>
<td>15.21</td>
<td>2.75</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>8.74</td>
<td>7.61</td>
<td>17.04</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>7.70</td>
<td>15.84</td>
<td>1.57</td>
</tr>
<tr>
<td>80</td>
<td>2</td>
<td>8.85</td>
<td>5.19</td>
<td>16.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>8.86</td>
<td>5.43</td>
<td>17.89</td>
</tr>
<tr>
<td>2</td>
<td>9.18</td>
<td>5.31</td>
<td>17.12</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Table 3. Products of $K_2SeS_4O_6 \cdot 3/2H_2O$ (16 mmol) decomposition with $H_2SO_4$ (20 ml 50%) at a temperature of 60 °C. The amount of 0.14 M $PHSO_4 \cdot 2H_2O$ solution (ml) used for fractional isolation: 1 - 15, 2 - 20, 3 - 20

<table>
<thead>
<tr>
<th>H$_2$S, %</th>
<th>No. of fraction</th>
<th>Yield, %</th>
<th>Compound</th>
<th>Calculated, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.67</td>
<td>11.72</td>
<td>13.86</td>
<td>2.58</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>7.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>8.59</td>
<td>11.35</td>
<td>15.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.47</td>
<td>9.26</td>
<td>15.36</td>
<td>1.56</td>
</tr>
<tr>
<td>50</td>
<td>2</td>
<td>8.97</td>
<td>5.82</td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.77</td>
<td>8.12</td>
<td>13.99</td>
<td>1.56</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>-</td>
<td>9.71</td>
<td>15.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.94</td>
<td>7.02</td>
<td>16.51</td>
<td>1.58</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>9.03</td>
<td>6.38</td>
<td>16.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.50</td>
<td>5.43</td>
<td>14.68</td>
<td>1.67</td>
</tr>
</tbody>
</table>

poly-thionates (% from the selenium taken in the initial $K_2SeS_4O_6$) was received after the liberation of 40% of $H_2S$. The yields calculated according to the amount of $[Co(DH)2Py2]HSO_4$ used for the isolation are 63—76%, indicating a low solubility of the higher monoselenopoly-thionates of this complex cation isolated. The content of selenium found in a number of products exceeds its content in diselenopoly-thionates (for example, Table 2, experiment 2; Table 3, experiment 1) implying the presence of anions $Se_xS_yO_6^{2-}$ with a value of $x > 2$ in the reaction mixture. Thus, during the decomposition of monoseleno-pentathionate with a high concentration sulfuric acid, using fractional precipitation employing trans-dipyridine-bis(dimethylglyoximato)cobalt(III) cation we succeeded in isolation of a series of monoselenopoly-thionates containing 5 to 7 sulfur atoms in the molecule. The reproduction of isolation of monoselenopoly-thionates containing 8 sulfur atoms in the molecule is complicated.
We succeeded in the recrystallisation of new monoselenopolythionates from the mixtures of ethanol with 2N HCl (1:1) after which their composition did approach the corresponding formulas. For example, analysis of freshly isolated \([\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_5\text{O}_6\cdot 6\text{H}_2\text{O}\) showed Se = 5.37%, S = 12.08% and of the recrystallized one Se = 5.30%, S = 17.00% and in the recrystallized one Se = 5.99%, S = 16.76%.

The reactions characteristic of selenopolythionates for the new compounds were performed looking for the data concerning the structure of monoo and diselenopolythionates containing 5 to 7 sulfur atoms in the molecule.

**Oxidation with iodine in acidic medium.** It is known [5, 6, 11] that the consumption of iodine during the oxidation of selenopolythionates in an acidic medium depends on the presence of sulfite groups in a selenopolythionate anion. The selenopolythionates of \(\text{Se}_n\text{S}_2\text{O}_6^{2–}\) type, the structure of which is \(\text{O}_3\text{S}\cdot\text{Se}\cdot\text{SO}_3^{–}\) [11–13, 20], i.e. containing two sulfite groups, undergo oxidation in these conditions according to the equation

\[
\text{Se}_n\text{S}_2\text{O}_6^{2–} + \text{I}_2 + 2\text{H}_2\text{O} \rightarrow n\text{Se} + 2\text{HSO}_4^{–} + + 2\text{HI},
\]

(7)

consuming 2 equiv. \(\text{I}_2\) per 1 mol of the selenopolythionate; the selenopolythionates of \(\text{Se}_n\text{S}_3\text{O}_6^{2–}\) type, the structure of which is \(\text{O}_3\text{S}\cdot\text{Se}\cdot\text{S}_2\text{O}_3^{–}\) [11, 14, 20], i.e. containing 1 sulfite group, undergo an analogous oxidation according to the equation

\[
2\text{Se}_n\text{S}_3\text{O}_6^{2–} + \text{I}_2 + 2\text{H}_2\text{O} \rightarrow 2n\text{Se} + 2\text{HSO}_4^{–} + + \text{S}_4\text{O}_6^{2–} + 2\text{HI},
\]

(8)

consuming 1 equiv. \(\text{I}_2\) per 1 mol of the selenopolythionate. Monoselenopentathionate, \(\text{O}_3\text{S}\cdot\text{Se}\cdot\text{S}_2\text{O}_3^{–}\), [3, 10] is not oxidized by iodine in acidic medium. Thus, according to the results of oxidation with iodine in an acidic medium one can receive an information concerning the nature of the groups that terminate the chain of Se–S atoms of the selenopolythionate anion.

The consumption of iodine in the case of compounds isolated in the present study are close to 4 equiv. \(\text{I}_2\), per 1mol of the selenopolythionate, i.e. is exactly equal to the amount of iodine consumed by two 2 trans-dipyridine-bis(dimethylglyoximato)cobalt(III) cations [11].

**Oxidation with iodine in hydrogen carbonate medium.** Selenopolythionates of \(\text{Se}_n\text{S}_2\text{O}_6^{2–}\) type undergo oxidation in a hydrogen-carbonate medium [4, 6, 11] according to the equation

\[
\text{Se}_n\text{S}_2\text{O}_6^{2–} + (1+2n)\text{I}_2 + (4+6n)\text{HO}^{–} \rightarrow \rightarrow n\text{SeO}_3^{2–} + 2\text{SO}_4^{2–} + (2+4n)\text{I}^{–} + + (2+3n)\text{H}_3\text{O}^{+},
\]

(9)

i.e. all selenium of the selenopolythionate oxidizes into a selenite and the sulfite groups into a sulfate. No data concerning oxidation in these conditions of selenopolythionates of other types are available. But on the basis of the study [21] we could expect that the pure sulfur polythionates may undergo partial oxidation by iodine in a weakly alkaline solution. We firstly studied this reaction on potassium selenopentathionate, \(\text{K}_2\text{SeS}_4\text{O}_6 \cdot 3\text{H}_2\text{O}\), and trans-dipyridine-bis(dimethylglyoximato)cobalt(III) selenopentathionate, \([\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_4\text{O}_6 \cdot 6\text{H}_2\text{O}\). The latter was synthesized by the method described in [22]. The consumption of iodine in the case of potassium salt was found to be 6 equiv. / mol and in the case of cobalt complex cation selenopentathionate...
Vitalijus Janickis and Virginė Albina Amankavičienė

10 equiv./mol (Table 4). All selenium after the oxidation of potassium seleno-pentathionate was found in a selenite form (found 19.31%, calculated 19.35%), two sulfur atoms – as SO₄²⁻ ions (found S₁5.39, 15.63%, calculated for the four sulfur atoms of K₂SeS₄O₆ 31.44%), the turbidity of sulfur was observed in the solution. All that indicates that the selenopentathionate anion undergoes the oxidation in the hydrogencarbonate medium according to the equation:

\[
\text{–O₃S–S–Se–S–SO₃}⁺ + 10\text{HO}⁻ + 3\text{I}_₂ \rightarrow \text{SeO}₃²⁻ + + 2\text{SO}₄²⁻ + 2\text{S} + 6\text{I}⁻ + 5\text{H}_₂\text{O}. \quad (10)
\]

Consumption of iodine in the iodine oxidation reaction of selenopolythionates richer in sulfur in the hydrogencarbonate medium was found higher, exceeding 10 equiv. of I₂ per mol of the selenopolythionate (Table 4). It was an indication that like in the case of pure sulfur polythionates, some amounts of iodine are consumed by the central divalent sulfur atoms of a higher selenopolythionate for oxidation in these conditions. In the case of the simplest selenopolythionate of Se⁡₂S⁡₆O₆²⁻ (y ≥ 4) type (hypothetic diselenohexathionate, Se⁡₂S⁡₆O₆²⁻) of the cation which does not consume iodine for the oxidation, on analogy with K₄SeS₄O₆ one could expect the reaction to proceed according to the equation:

\[
\text{–O₃S–S–Se–Se–S–SO₃}⁺ + 16\text{HO}⁻ + 5\text{I}_₂ \rightarrow 2\text{SeO}₃²⁻ + + 2\text{SO}₄²⁻ + 2\text{S} + 10\text{I}⁻ + 8\text{H}_₂\text{O}. \quad (10)
\]

i.e. with the consumption of 10 equiv. of I₂ per 1 mol of the compound and in the case of \([\text{Co(DH)}₂\text{Py}₂]₂\text{Se}_x\text{S}_y\text{O}_6 \) 14 equiv. of I₂ per mol, i.e. additional four equiv. of I₂ should be consumed by the second selenium atom.

The diselenopolythionates \([\text{Co(DH)}₂\text{Py}₂]₂\text{Se}_x\text{S}_y\text{O}_6 \) isolated in the present study consume a little more of iodine (~15 equiv./mol) for the oxidation. These compounds are less soluble compared to the selenopentathionate of the same cation, therefore for the study of this reaction the dissolution of samples in 50% ethanol with heating was used. The consumption of iodine was found to depend on the temperature of a solution. If a solution was not cooled before adding it into the iodine solution, a higher consumption of the latter was observed (obviously because of the easier oxidation of the central divalent sulfur atoms): about 12 and 14 equiv. of I₂ per mol of \([\text{Co(DH)}₂\text{Py}₂]₂\text{SeS}_5\text{O}_6 \) and \([\text{Co(DH)}₂\text{Py}₂]₂\text{SeS}_7\text{O}_6 \), respectively. The difference between the consumptions during the oxidation of warm solutions of \([\text{Co(DH)}₂\text{Py}₂]₂\text{SeS}_7\text{O}_6 \) and \([\text{Co(DH)}₂\text{Py}₂]₂\text{SeS}_5\text{O}_6 \) was (as expected) ~4 equiv. of I₂ per mol, since the additional selenium atom consumes four equiv. of I₂ for the oxidation into a selenite.

Decomposition under the action of cyanide ions.

The monoselenopentathionate form 1 mol of a thiosulfate during the cyanide decomposition reaction [23]:

\[
\text{SeS}_6²⁻ + 2\text{CN}⁻ + 2\text{HO}⁻ \rightarrow \text{SeCN}⁻ + \text{SCN}⁻ + + \text{SO}_4²⁻ + \text{S}_2\text{O}_3²⁻ + \text{H}_2\text{O}. \quad (11)
\]

i.e. the consumption of iodine after cyanide decomposition is 1 equiv. per mol of a compound. The consumption of iodine during a study of cyanide decomposition reaction of the mono- and diselenopolythionates isolated in the present work was equal to 1 equiv. of I₂ per anion, too (Table 4), i.e. the reaction proceeds according to the overall equations:
Isolation of intermediate products of acidic decompoision of selenopentathionate: the selenopolythionates...

\[ \text{SeS}_2\text{O}_6^{2-} + (n-2)\text{CN}^- + 2\text{H}_2\text{O} \rightarrow \text{SeCN}^- + (n-3)\text{SCN}^- + \text{SO}_4^{2-} + \text{SO}_3^{2-} + \text{H}_2\text{O}, \quad (12) \]
\[ \text{SeS}_2\text{O}_6^{2-} + (n-1)\text{CN}^- + 2\text{H}_2\text{O} \rightarrow 2\text{SeCN}^- + + (n-3)\text{SCN}^- + \text{SO}_4^{2-} + \text{SO}_3^{2-} + \text{H}_2\text{O}. \quad (13) \]

Thus, the desired above reactions of the newly isolated mono- and diselenopolythionates indicate that the structure of these compounds should be analogous to the structure of selenopentathionate and pure sulfur polythionates [3, 10], i.e. a chain of sulfur-selenium atoms with the thiiosulfate groups on the ends.

**On the mechanism of \( \text{SeS}_2\text{O}_6^{2-} \) (\( y > 4 \)) type selenopolythionation formation from selenopentathionate.** The first stage of acidic selenopentathionate decomposition undoubtedly must be hydrolysis. The liberation of hydrogen sulfide and the known condensation of sulfanemonosulfonates into the polythionates [11, 17] (equation (2)) show that the cleavage of a bond between the terminal sul-fur atoms and formation of sulfanemonoselenanemonosulfonate, \( \text{H–Se–S–SO}_2\text{H} \), according to equation (3) occurs at first as proposed by Zelionkaitë ir Ðukytë [16]. The resulting monoselenanedisulfane-monosulfonate may not only condense into a new diselenoheptathionate, \( \text{H}_2\text{Se}_2\text{S}_5\text{O}_6^- \), with the liberation of hydrogen sulfide according to equation (5) but also to react with the not yet decomposed monoselenopentathionate with the formation of diselenoctathionate, \( \text{SeS}_2\text{O}_6^{2-} \):

\[ \text{O}_2\text{S}^- - \text{S} - \text{Se} - \text{S} - \text{SO}_3^- + \text{H} - \text{Se} - \text{S} - \text{S} - \text{Se} - \text{S} - \text{SO}_3^- \rightarrow \text{H}_2\text{SO}_3^- + \text{O}_2\text{S}^- - \text{S} - \text{Se} - \text{S} - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{SO}_3^-. \quad (14) \]

or later - with the diselenoheptathionate formed according to equation (5), furnishing even higher poly-selenopolythionates (e.g., triselenodecathionate, \( \text{SeS}_3\text{O}_6^{2-} \)):

\[ \text{O}_2\text{S}^- - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{SO}_3^- + \text{H} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{SO}_3^- \rightarrow \text{H}_2\text{SO}_3^- + \text{O}_2\text{S}^- - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{S} - \text{Se} - \text{SO}_3^- -. \quad (15) \]

Polyselenopolythionates were isolated from the reaction mixture exactly at the beginning of the decomposition. The liberation of sulfur and selenium occurs probably during the partial decomposition of monoselenanedisulfanemonosulfonate according to equation (4). The liberation of \( S \) may also result from \( H_S \) interaction with \( H_2\text{SO}_3^- \) in the conditions of a very high acidity (45-75% \( H_2\text{SO}_4 \)):

\[ 2\text{H}_2\text{S} + 2\text{H}_2\text{SO}_3^- \rightarrow 3\text{H}_2\text{SO}_4^- + 3\text{S}. \quad (16) \]

**CONCLUSIONS**

1. The decomposition of potassium monoselenopentathionate in the medium of sulfuric acid of high concentration (45-75%) proceeds with the liberation of hydrogen sulfide and formation of monoa- and polyselenopolythionates containing more than four sulfur atoms in the molecule studied.

2. Kinetic experiments have shown that the lowest amounts of elemental sulfur and selenium at the same degree of selenopentathionate decompoision are liberated when a 50-60% \( H_2\text{SO}_4 \) at a temperature of 50 °C is used.

3. The mono- and diselenopolythionates containing 5–7 sulfur atoms in the molecule are isolated as crystalline salts of trans-dipyridine-bis(dimethylglyoximidato)cobalt(III) as intermediate products of selenopentathionate decomposition. The new type \( \text{SeS}_2\text{O}_6^{2-} \) and \( \text{SeS}_3\text{O}_6^{2-} \) homologous series \( (n > 4) \) have been discovered.

4. The chemical reactions of the new selenopolythionates, such as oxidation by iodine in acidic and hydrocarbonate medium and under the action of cyanide ions, have been studied. The results confirmed the structure of these compounds as analogous to the known structure of monoselenopentathionate, a chain of sulfur–selenium atoms with the thiiosulfate groups on the ends.

5. The mechanism of the formation of more sulfured mono- and diselenopolythionates during acidic selenopentathionate decomposition is proposed. The main role is attributed to the intermediate compound monoselenanedisulfanemonosulfonate, \( \text{H–Se–S–SO}_2\text{H} \), formed as a result of the initial hydrolysis of the selenopentathionate anion, leading to the cleavage of a bond between the terminal sulfur atoms.

Received 21 December 2004
Accepted 2 February 2005

**References**

Vitalijus Janickis and Virginė Albina Amankavičienė

SELENOPENTATIONATO RŪGDŽINIO SKILIMO TARPINIO PRODUKTO IDSKYRIMAS: SELENOPOLITIONATAI, TURINTYS DAUGIAU NEI 4 SIEROS ATOMUS MOLEKULĖJE

Santrauka


Raktai: kalio selenopentationatas, rūgštėjo skilimas, aukštesnės molekulo, diselenopolitionatai