

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 Amankaviėienė

Faculty of Chemical Technology,
Kaunas University of Technology,
Radvilėnø 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(dimethylglyoximate)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 $\text{SeS}_n\text{O}_6^{2-}$ and $\text{Se}_2\text{S}_n\text{O}_6^{2-}$ ($n > 4$) 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 SO_3^- groups on the ends. The mechanism of the formation of more sulfured mono- and diselenopolythionates during the acidic $\text{SeS}_4\text{O}_6^{2-}$ decomposition is proposed. The main role is attributed to the intermediate compound, monoselenanedisulfanemonosulfonate $\text{H-S-Se-S-SO}_3\text{H}$, which forms as a result of the initial hydrolysis of the $\text{SeS}_4\text{O}_6^{2-}$ 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 selenopolythionic acids - selenotriithionic acid, $\text{H}_2\text{SeS}_2\text{O}_6$, and monoselenopentathionic acid, $\text{H}_2\text{SeS}_4\text{O}_6$, 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, $\text{SeS}_n\text{O}_6^{2-}$ ($n = 2-4$), and polyselenopolythionates of two types: the symmetric ones of the general formula $\text{Se}_n\text{S}_2\text{O}_6^{2-}$ ($n = 2-7$) and the asymmetric ones of the general formula $\text{Se}_n\text{S}_3\text{O}_6^{2-}$ ($n = 2-6$) [2–11]. Unfortunately, the structure of selenopolythionic acid anions was undoubtedly determined only for the lower selenopolythionates [3, 11–

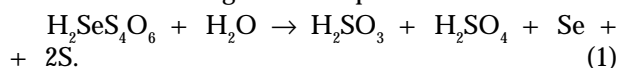
14] - the chains of sulfur-selenium or only selenium atoms with the SO_3^- groups on the ends: of the selenotriithionate, $^-\text{O}_3\text{S-Se-SO}_3^-$, monoselenotettrathionate, $^-\text{O}_3\text{S-Se-S-SO}_3^-$, diselenotettrathionate, $^-\text{O}_3\text{S-Se-Se-SO}_3^-$, and monoselenopentathionate, $^-\text{O}_3\text{S-S-Se-S-SO}_3^-$.

The first indications about the existence of selenopolythionates containing more than four sulfur atoms in the molecule were received studying the interaction of selenous acid, H_2SeO_3 , with the thio-sulfate, $\text{S}_2\text{O}_3^{2-}$, by the method of ionphoresis on paper using the isotopes S^{35} and Se^{75} [15]. The ions of monoselenohexathionate, $\text{SeS}_5\text{O}_6^{2-}$, diselenoheptathionate, $\text{Se}_2\text{S}_5\text{O}_6^{2-}$, and triselenooctathionate, $\text{Se}_3\text{S}_5\text{O}_6^{2-}$, in the mixtures with purely sulfur lower polythionates - trithionate, $\text{S}_3\text{O}_6^{2-}$, tetrathionate, $\text{S}_4\text{O}_6^{2-}$, pentathionate, $\text{S}_5\text{O}_6^{2-}$, and hexathionate, $\text{S}_6\text{O}_6^{2-}$ - were detected in the solution.

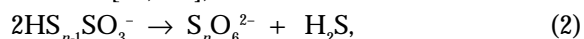
Zelionkaitė and Ėukytė found [7] that monoselenopentathionic acid, $\text{H}_2\text{SeS}_4\text{O}_6$, in a concentrated solution decomposes with the formation of sulfurous,

* Corresponding author.

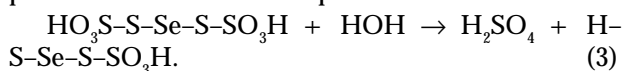
sulfuric acids and liberation of elemental sulfur and selenium according to the equation:



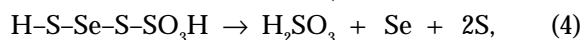
However, the decomposition of barium selenopentathionate, BaSeS_4O_6 , under the action of concentrated sulfuric acid, H_2SO_4 , proceeds with the liberation of hydrogen sulfide, H_2S [16]. Since it has been undoubtedly determined that the liberation of hydrogen sulfide occurs during the condensation of sulfanemonosulfonates, $\text{HS}_{n-1}\text{SO}_3^-$, into polythionates [11, 17],



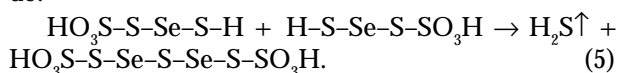
Zelionkaitė and Ėukytė proposed [16] that the hydrolysis of selenopentathionate anion results in the cleavage of a bond between the terminal sulfur atoms and the formation of sulfanemonoselenane-mono-sulfonate is the first stage during the decomposition of barium selenopentathionate:



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



or to condense into a new selenopolythionate ($\text{H}_2\text{Se}_2\text{S}_3\text{O}_6$), with the liberation of hydrogen sulfide:



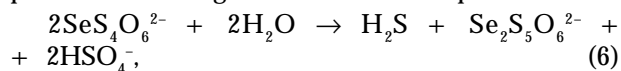
The aim of the present work was isolation of intermediate products of monoselenopentathionate decomposition under the action of concentrated sulfuric acid, *i.e.* the selenopolythionates containing more than four sulfur atoms in the molecule, and the characterization of these compounds by the chemical 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 *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III), $[\text{Co}(\text{DH})_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ as described in [18] and the potassium monoselenopentathionate, $\text{K}_2\text{SeS}_4\text{O}_6 \cdot 3/2\text{H}_2\text{O}$, as described in [2].

The higher *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III) selenopolythionates have been isolated during the decomposition of potassium selenopentathionate under the action of sulfuric acid of a high concentration. A saturated solution (8%) of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ was used for the isolation of selenopolythionates. A crystalline $\text{K}_2\text{SeS}_4\text{O}_6 \cdot 3/2\text{H}_2\text{O}$ and 45–75% sulfuric acid mixture was continuously stirred in a thermostatic vessel. $\text{K}_2\text{SeS}_4\text{O}_6$

$\cdot 3/2\text{H}_2\text{O}$ was dissolved, the solution was gradually acquiring the green and later the yellow colour, and the liberation of elemental sulfur (first) and selenium (later) was gradually beginning. The hydrogen sulfide liberated during decomposition was absorbed by iodine solution, the consumption of which served to determine the degree of $\text{K}_2\text{SeS}_4\text{O}_6$ decomposition according to the assumed equation



which is an overall equation of the reactions (3) and (5).

8 mmol (3.264 g) or 16 mmol of $\text{K}_2\text{SeS}_4\text{O}_6 \cdot 3/2\text{H}_2\text{O}$ was used for every experiment. The reaction mixture after the liberation of a fixed amount of H_2S was diluted with an amount of distilled water equal to the amount of sulfuric acid solution used for the decomposition at the beginning of the experiment. Then it was cooled to 10 °C, the liberated sulfur and selenium filtered off and determined quantitatively after the oxidation with bromine by the gravimetric and iodometric methods, respectively.

The *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III) selenopolythionates were analysed determining the contents of cobalt, sulfur, selenium and crystallization water. Cobalt was determined as Co_3O_4 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 heating, the sulfate ions were determined gravimetrically as BaSO_4 . The amount of selenium was determined by a procedure worked out by us. 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 cooled 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 derivatograph 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, ethanol – Al_2O_3 .

Fractional precipitation was used for the isolation of higher selenopolythionates, potassium selenopentathionate decomposition products. After the introduction of a portion of the saturated solution of $[\text{Co}(\text{DH})_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$, small crystals of the selenopolythionate of this cation were precipitated. The filtered crystals were washed with water until disappearance of SO_4^{2-} ions in the washings and later with acetone. Analogously, the crystals of *trans*-dipyridine-bis(dimethylglyoximato)cobalt(III) seleno-

polythionates in the next fractions of crystallization were isolated from the filtrate after the first precipitate.

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 retitrated with thiosulfate solution. To study the reaction of oxidation with iodine in the hydrogen-carbonate solution, 0.05–0.1 g of $K_2SeS_4O_6 \cdot 3/2H_2O$ or *trans*-dipyridine-bis(dimethylglyoximate)-cobalt(III) selenopolythionate was dissolved in water or 50% ethanol (~30 ml), respectively. Then an excess of the iodine solution and 2 g of $KHCO_3$ were added, the reaction mixture left for 5 min, starch and 20 ml 10% CH_3COOH 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 retitrated 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 retitrated 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 – H_2S , 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 H_2S (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 H_2S reached 50% has been found using a 50% solution of sulfuric acid.

The liberation of H_2S 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 $K_2SeS_4O_6$ solution of the high concentration (~1 M) has been used.

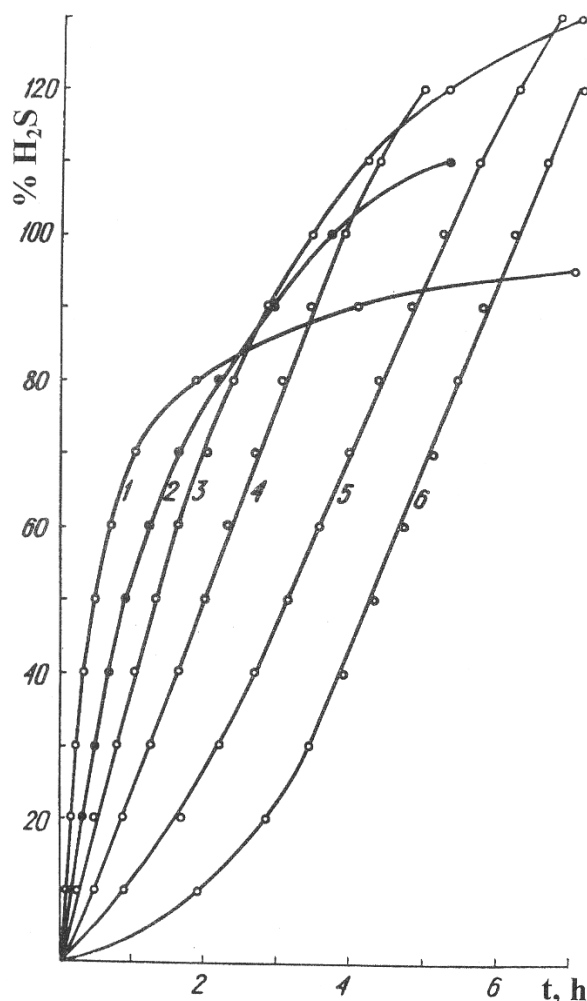


Fig. 1. Liberation of H_2S (% from the amount calculated according to equation (6)) during the decomposition of potassium selenopentathionate with sulfuric acid at a temperature of 50 °C.

The concentration of H_2SO_4 solution, %: 1 – 70, 2 – 65, 3 – 60, 4 – 55, 5 – 50, 6 – 45

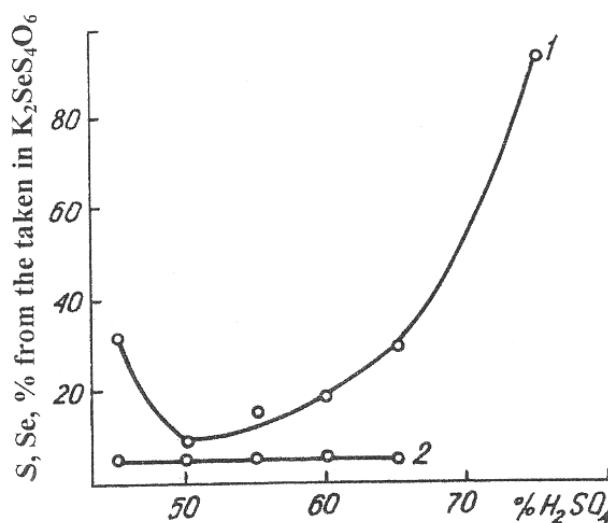


Fig. 2. Dependence of liberated amounts of elemental selenium (1) and sulfur (2) during the decomposition of potassium selenopentathionate with sulfuric acid (50% H_2S liberation) on the concentration (%) of H_2SO_4 (10 ml) used

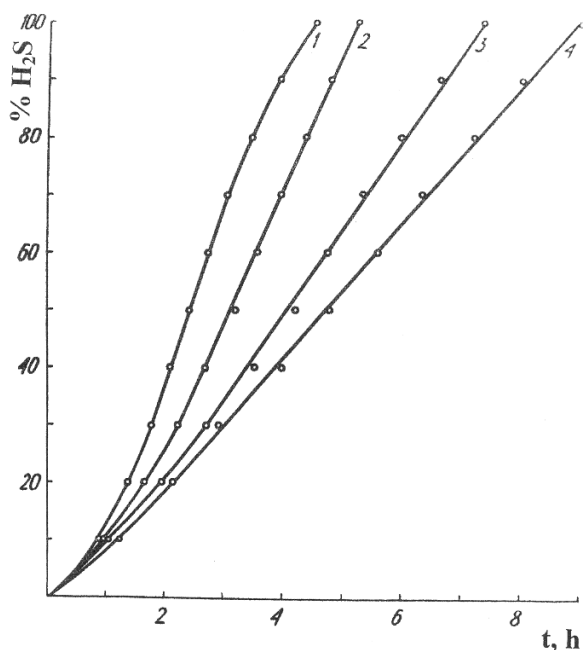


Fig. 3. Liberation of H₂S (% from the amount calculated according to equation (6)) during the decomposition of potassium selenopentathionate with 50% sulfuric acid at a temperature of 50 °C. The concentration of K₂SeS₄O₆ solution, mol/l: 1 - 0.96, 2 - 0.70, 3 - 0.37, 4 - 0.26

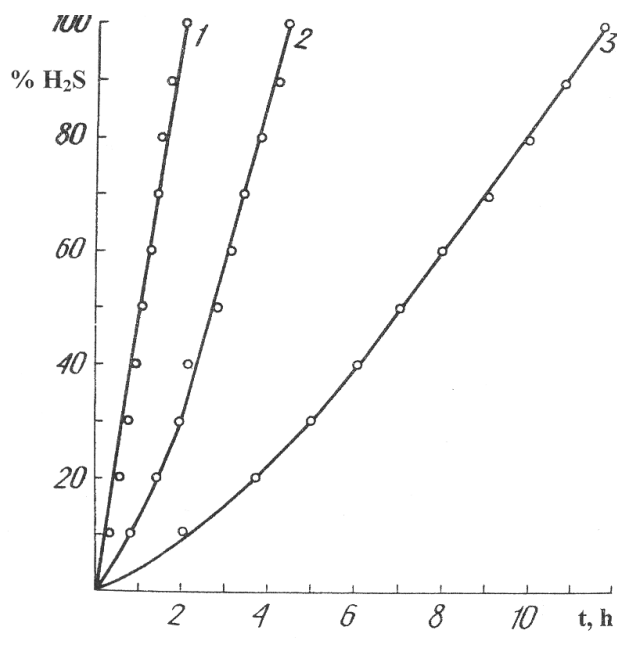


Fig. 5. Liberation of H₂S (% from the amount calculated according to equation (6)) during the decomposition of potassium selenopentathionate with 50% sulfuric acid. Temperature, °C: 1 - 60, 2 - 50, 3 - 40

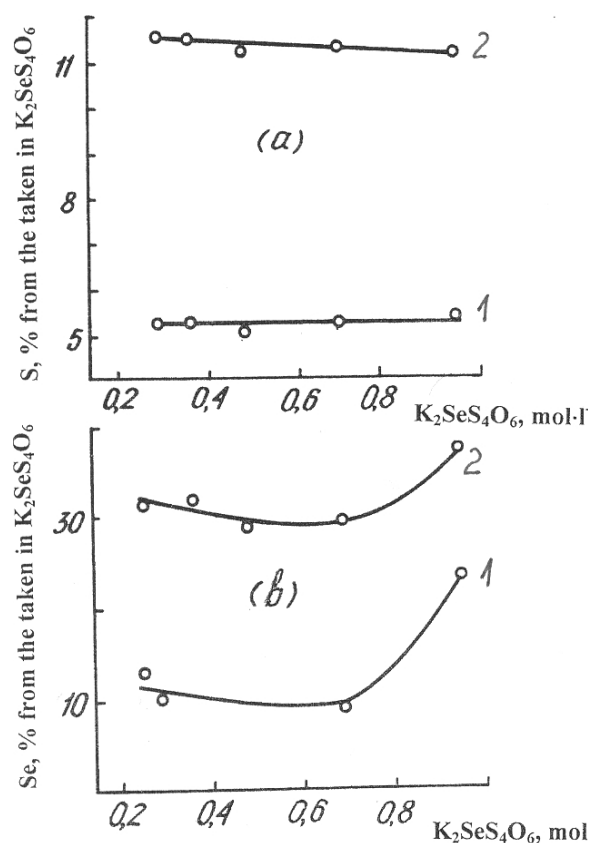


Fig. 4. Dependence of amounts of elemental sulfur (a) and selenium (b) liberated during the decomposition of potassium selenopentathionate with sulfuric acid (50% H₂S liberation) on the concentration (mol/l) of K₂SeS₄O₆. The liberation of H₂S, %: 1 - 50, 2 - 100

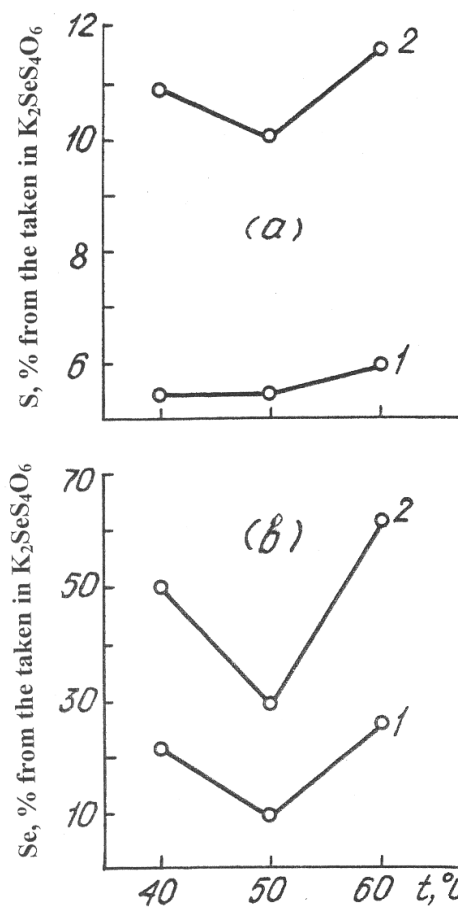


Fig. 6. Dependence of amounts of elemental sulfur (a) and selenium (b) liberated during the decomposition of potassium selenopentathionate with 50% sulfuric acid (10 ml) on the temperature. The amount of liberated H₂S, %: 1 - 50, 2 - 100

Table 1. Products of $K_2SeS_4O_6 \cdot 3/2H_2O$ (8 mmol) decomposition with H_2SO_4 (10 ml 50%) at a temperature of 50 °C. The amount of 0.14 M $P'HSO_4 \cdot 2H_2O$ solution (ml) used for fractional isolation: 1 – 10, 2 – 10, 3 – 30

H ₂ S, %	No. of fraction	Found, %				Yield**, %	Compound	Calculated, %		
		Co	Se	S	Se:S			Co	Se	S
20	1	8.44	9.60	13.95	2:7.2	7.5				
	2	–	6.52	10.86	1:4.1	–				
40	1	8.52	11.92	15.30	2:6.3	11	≈P ₂ Se ₂ S ₇ O ₆ · 3H ₂ O, Mixture of mono- and diselenopolythionates	8.26	11.07	15.73
	2	9.01	8.75	13.22	1.5:5.6	5				
50	1	–	12.35	15.28	2:6.1	11	P ₂ Se ₂ S ₇ O ₆ · 3H ₂ O			
	„	8.52	11.26	15.43	2:6.8	4				
60	1	8.53	9.95	15.59	2:7.7	9	–,–			
80	1	8.76	8.68	16.05	1.5:6.8	9	Mixture of mono- and diselenopolythionates			
	2	8.99	6.67	14.40	1:5.3	6	P ₂ SeS ₆ O ₆ · 3H ₂ O	8.96	6.00	14.62
	3	–	6.30	10.94	1:4.3	–				
100	1	–	8.23	15.58	1.5:7	9	Mixture of mono- and diselenopolythionates P ₂ SeS ₅ O ₆ · 6H ₂ O	8.81	5.90	11.98
	2	–	7.53	15.31	1.5:7.5	8				
	3	9.51	5.82	11.60	1:4.9	5				

*P = [Co(DH)₂Py₂]⁺. ** From the amount of Se present in $K_2SeS_4O_6 \cdot 3/2H_2O$ 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 $K_2SeS_4O_6$ 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 $K_2SeS_4O_6$ 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 $K_2SeS_4O_6$ 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 iso-

lation 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 increase of the 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 (SeS₈O₆²⁻, Se₂S₈O₆²⁻) 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-

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

H ₂ S, %	No. of fraction	Found, %				Yield, %	Compound	Calculated, %		
		Co	Se	S	Se:S			Co	Se	S
20	1	8.91	10.90	15.21	2:6.9	8	$P_2Se_2S_7O_6 \cdot 3H_2O$	8.26	11.07	15.73
	1	8.49	12.35	16.86	2:6.7	10				
30	2	–	8.37	–	–	8	$\approx P_2SeS_5O_6 \cdot 6H_2O$	8.81	5.90	11.98
	3	9.48	5.47	11.98	1:5.4	5				
	„	–	6.50	12.23	1:4.6	5				
40	1	8.74	11.35	17.66	2:7.7	10	$P_2Se_2S_8O_6 \cdot 3H_2O$	8.08	10.82	17.58
	„	–	11.62	16.26	2:6.9	10	$P_2Se_2S_7O_6 \cdot 3H_2O$			
	2	8.94	10.00	15.21	2:7.5	11	– „ – „ –			
60	1	8.74	7.61	17.04	1.5:8.3	7	Mixtures of mono- and diselenopolythionates			
	2	–	7.70	15.84	1.5:7.6	12				
80	1	8.78	6.10	17.00	1:6.9	5	$P_2SeS_7O_6 \cdot 3H_2O$	8.74	5.86	16.65
	2	8.85	5.19	16.62	1:7.9	5	\approx – „ – „ –			
	„	–	6.26	16.25	1:6.4	6	\approx – „ – „ –			
100	1	8.86	5.43	17.89	1:8.1	4	$\approx P_2SeS_8O_6 \cdot 3H_2O$	8.54	5.72	18.59
	2	9.18	5.31	17.12	1:7.9	5	$\approx P_2SeS_7O_6 \cdot 3H_2O$			

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

H ₂ S, %	No. of fraction	Found, %				Yield, %	Compound	Calculated, %		
		Co	Se	S	Se:S			Co	Se	S
20	1	–	13.01	14.29	2:5.4	9	$P_2Se_2S_6O_6 \cdot 3H_2O$	8.45	11.32	13.79
	„	8.67	11.72	13.86	2:5.8	11				
	2	–	7.40	–	–	9				
40	1	8.59	11.35	15.05	2:6.5	11	$\approx P_2Se_2S_7O_6 \cdot 3H_2O$	8.26	11.07	15.73
	2	–	7.58	–	–	9				
50	1	8.47	9.26	15.36	1.5:6.1	7	$P_2SeS_5O_6 \cdot 6H_2O$	8.81	5.90	11.98
	2	8.97	5.82	11.70	1:5	6				
	3	8.77	8.12	13.99	1.5:6.4	12				
60	1	–	9.71	15.79	2:8.0	10	Mixture of mono- and diselenopolythionates			
80	1	–	7.89	16.28	1.5:7.6	7	– „ – „ –	8.96	6.00	14.62
	2	8.96	6.16	15.25	1:6.1	7	$P_2SeS_6O_6 \cdot 3H_2O$			
100	1	8.94	7.02	16.51	1:5.8	5	$\approx P_2SeS_7O_6 \cdot 3H_2O$	8.74	5.86	16.65
	2	9.03	6.38	16.47	1:6.4	7				
	3	9.50	5.43	14.68	1:6.7	–				

po-lythionates (% 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 $[Co(DH)_2Py_2]HSO_4$ used for the isolation are 63–76%, indicating a low solubility of the higher mono- and diselenopolythionates of this complex cation isolated. The content of selenium found in a number of products exceeds its content in diselenopolythionates (for example, Table 2, experiment 2; Table 3, experiment 1) implying the presen-

ce of anions $SeS_xO_6^{2-}$ 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(dimethylglyoximate)cobalt(III) cation we succeeded in isolation of a series of mono- and diselenopolythionates containing 5 to 7 sulfur atoms in the molecule. The reproduction of isolation of mono- and diselenopolythionates containing 8 sulfur atoms in the molecule is complicated.

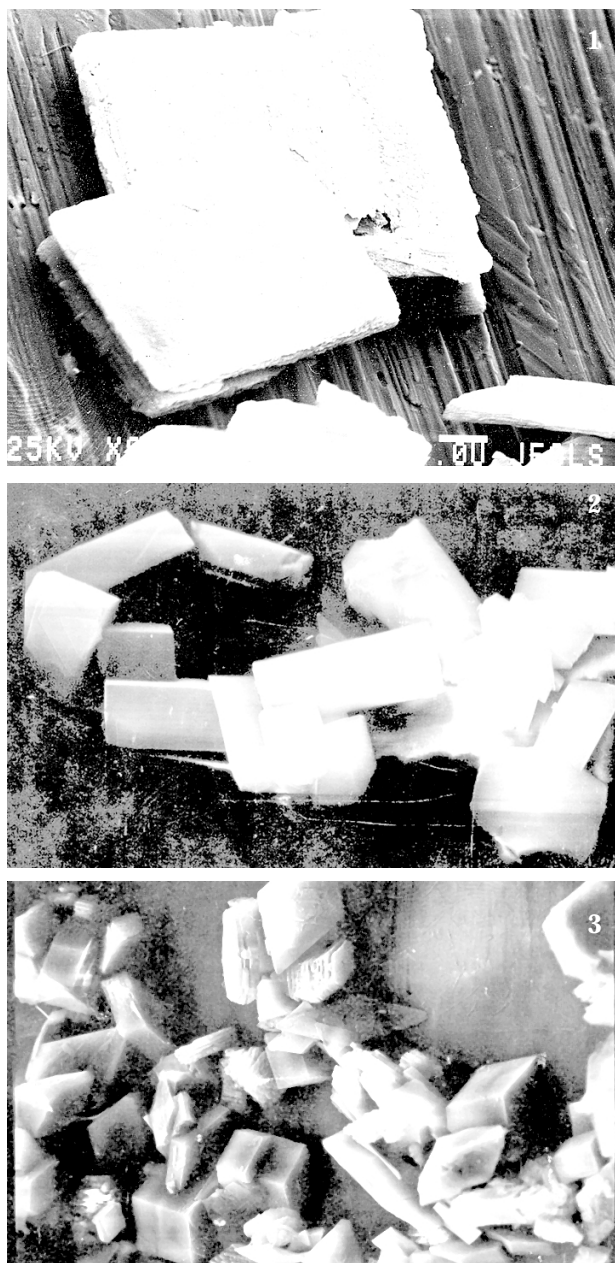


Fig. 7. Microphotographs of crystals of higher monoselenopolythionates (magnification):

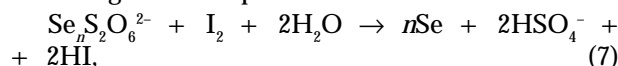
1 - $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_5\text{O}_6 \cdot 6\text{H}_2\text{O}$ ($\times 860$), 2 - $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_6\text{O}_6 \cdot 3\text{H}_2\text{O}$ ($\times 2400$), 3 - $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_7\text{O}_6 \cdot 3\text{H}_2\text{O}$ ($\times 780$)

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 = 6.01%, S = 11.87%; in freshly isolated $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_7\text{O}_6 \cdot 3\text{H}_2\text{O}$ found Se = 5.30%, S = 17.00% and in the recrystallized one Se = 5.99%, S = 16.76%.

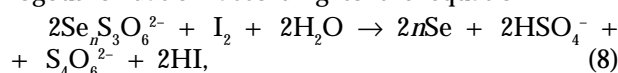
The reactions characteristic of selenopolythionates for the new compounds were performed loo-

king for the data concerning the structure of mono- 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 $-\text{O}_3\text{S}-\text{Se}_n-\text{SO}_3^-$ [11-13, 20], *i.e.* containing two sulfite groups, undergo oxidation in these conditions according to the equation



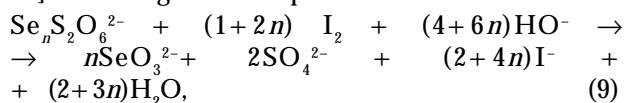
consuming 2 equiv. I_2 per 1 mol of the selenopolythionate; the selenopolythionates of $\text{Se}_n\text{S}_3\text{O}_6^{2-}$ type, the structure of which is $-\text{O}_3\text{S}-\text{Se}_n-\text{S}_2\text{O}_3^-$ [11, 14, 20], *i.e.* containing 1 sulfite group, undergo an analogous oxidation according to the equation



consuming 1 equiv. I_2 per 1 mol of the selenopolythionate. Monoselenopentathionate, $\text{O}_3\text{S}_2-\text{Se}-\text{S}_2\text{O}_3^-$, [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. I_2 per 1 mol 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 hydrogencarbonate 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



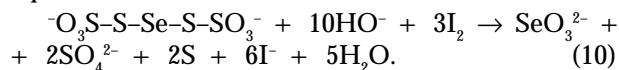
i.e. all selenium of the selenopolythionate oxidizes into a selenite and the sulfite groups into a sulfate. No data concerning oxidation in these conditions of selenopolythionates of other types are available. But on the basis of the study [21] we could expect that the purely sulfur polythionates may undergo partial oxidation by iodine in a weakly alkaline solution. We firstly studied this reaction on potassium selenopentathionate, $\text{K}_2\text{SeS}_4\text{O}_6 \cdot 3/2\text{H}_2\text{O}$, 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

Table 4. Reactions of the selenopolythionates $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{Se}_x\text{S}_y\text{O}_6$ ($x = 1, 2; y = 4-7$)

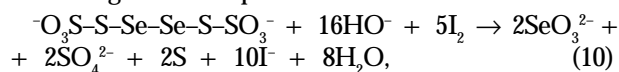
		No. of experiment	1	2	3	4	5	6	7	8	9
Oxidation with I_2 in acidic medium	$\text{Se}_x\text{S}_y\text{O}_6^{2-}$ taken, $\text{mmol} \times 10^2$		4.03	3.77	3.76	3.63					
	x/y		1/4	1/5	1/5	2/6					
	Consumed 0.02 N		7.25	7.25	7.5	7.4					
	I_2 , ml Equiv. I_2/mol		3.59	4.84	3.99	4.08					
Oxidation with I_2 in HCO_3^- medium	$\text{Se}_x\text{S}_y\text{O}_6^{2-}$ taken, $\text{mmol} \times 10^2$		4.05	3.74	3.70	3.53	2.85	3.77	3.72	3.58	3.49
	x/y		1/4	1/5	1/7	2/6	2/7	1/5	1/7	2/6	2/7
	Consumed 0.05 N		8.3	8.2	8.1	10.9	8.6	9.2	10.4	12.6	12.5
	I_2 , ml Equiv. I_2/mol		10.2	11.0	10.9	15.4	15.1	12.2*	14.0*	17.6*	17.9*
Cyanide decomposition	$\text{Se}_x\text{S}_y\text{O}_6^{2-}$ taken, $\text{mmol} \times 10^2$		3.96	4.0	3.76	3.76	3.86	3.73	3.76	3.63	3.53
	x/y		1/4	1/4	1/5	1/5	1/6	1/7	1/7	2/6	2/7
	Consumed 0.02 N		9.5	9.5	9.5	9.5	9.75	9.0	9.75	9.25	9.0
	I_2 , ml Equiv. I_2/mol		4.79	4.74	5.05	5.05	5.05	4.82	5.19	5.10	5.10

* Consumption of iodine during the oxidation of warm solution of selenopolythionate.

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 SO_4^{2-} ions (found S 15.39, 15.63%, calculated for the four sulfur atoms of $\text{K}_2\text{SeS}_4\text{O}_6$ 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:



Consumption of iodine in the iodine oxidation reaction of selenopolythionates richer in sulfur in the hydrogencarbonate medium was found higher, exceeding 10 equiv. of I_2 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, low oxidation sulfur atoms of a higher selenopolythionate for oxidation in these conditions. In the case of the simplest selenopolythionate of $\text{Se}_2\text{S}_y\text{O}_6^{2-}$ ($y \geq 4$) type (hypothetic diselenohexathionate, $\text{Se}_2\text{S}_4\text{O}_6^{2-}$) of the cation which does not consume iodine for the oxidation, on analogy with $\text{K}_2\text{SeS}_4\text{O}_6$ one could expect the reaction to proceed according to the equation

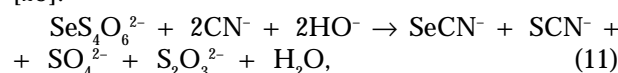


i.e. with the consumption of 10 equiv. of I_2 per 1 mol of the compound and in the case of $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{Se}_2\text{S}_4\text{O}_6$ 14 equiv. of I_2 per mol, *i.e.* additional four equiv. of I_2 should be consumed by the second selenium atom.

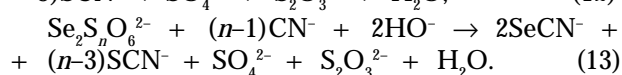
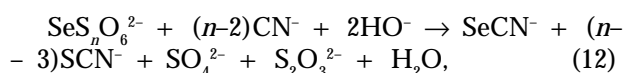
The diselenopolythionates $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{Se}_{1-2}\text{S}_{5-7}\text{O}_6$ isolated in the present study consume a little more of iodine (~15 equiv./mol) for the oxidation. These compounds are less soluble compared to the selenopentathionate of the same cation, therefore 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 I_2 per mol of $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_5\text{O}_6$ and $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_7\text{O}_6$, respectively. The difference between the consumptions during the oxidation of warm solutions of $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{SeS}_7\text{O}_6$ and $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{Se}_2\text{S}_7\text{O}_6$ was (as expected) ~4 equiv. of I_2 per mol, since the additional selenium atom consumes four equiv. of I_2 for the oxidation into a selenite.

Decomposition under the action of cyanide ions.

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

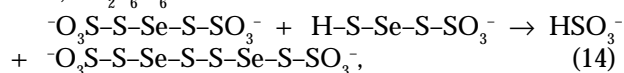


i.e. the consumption of iodine after cyanide decomposition is 1 equiv. per mol of a compound. The consumption of iodine during a study of cyanide decomposition reaction of the mono- and diselenopolythionates isolated in the present work was equal to 1 equiv. of I_2 per anion, too (Table 4), *i.e.* the reaction proceeds according to the overall equations:

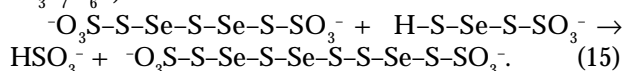


Thus, the described above reactions of the newly isolated mono- and diselenopolythionates indicate that the structure of these compounds should be analogous to the structure of selenopentathionate and pure sulfur polythionates [3, 10], *i.e.* a chain of sulfur-selenium atoms with the thiosulfate groups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

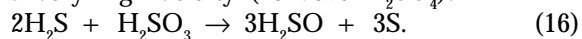
On the mechanism of $\text{Se}_x\text{S}_y\text{O}_6^{2-}$ ($y > 4$) type selenopolythionate formation from selenopentathionate. The first stage of acidic selenopentathionate decomposition undoubtedly must be hydrolysis. The liberation of hydrogen sulfide and the known condensation of sulfanemonosulfonates into the polythionates [11, 17] (equation 2)) show that the cleavage of a bond between the terminal sulfur atoms and formation of sulfanemonoselenanemonosulfonate, $\text{H-S-Se-S-SO}_3\text{H}$, according to equation (3) occurs at first as proposed by Zelionkaitė ir Đukytė [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 diselenooctathionate, $\text{Se}_2\text{S}_6\text{O}_6^{2-}$:



or later - with the diselenoheptathionate formed according to equation (5), furnishing even higher polyselenopolythionates (*e.g.*, triselenodecathionate, $\text{Se}_3\text{S}_7\text{O}_6^{2-}$):



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_2S interaction with H_2SO_3 in the conditions of a very high acidity (45–75% H_2SO_4):



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 mono- 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 decomposition are liberated when a 50–60% H_2SO_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(dimethylglyoximate)cobalt(III) as intermediate products of selenopentathionate decomposition. The new type $\text{SeS}_n\text{O}_6^{2-}$ and $\text{Se}_2\text{S}_n\text{O}_6^{2-}$ 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 thiosulfate 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, $\text{H-S-Se-S-SO}_3\text{H}$, 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

1. B. Rathke, *J. Pr. Chem.*, **95**, 1 (1865).
2. O. Foss, *Acta Chem. Scand.*, **3**, 435 (1949).
3. O. Foss, in *Advances in Inorganic Chemistry and Radiochemistry*, **2** (eds. H. J. Emeleus, A. G. Sharpe) Academic Press, New York, 237 (1960).
4. V. I. Zelionkaitė, *Studies in Area of Selenium Oxygen Compounds*, Doctoral Dissertation, Kaunas, 1964 (in Russian).
5. E. Blasius and G. Schonhard, *J. Chromatogr.*, **28**, 385 (1967).
6. J. Janickis, *Accounts of Chemical Research*, **2**, 316 (1969).
7. V. Zelionkaitė and V. Đukytė, *Zh. Neorg. Khim.*, **18**, 2346 (1973).
8. E. Blasius and A. Knochel, *J. Radioanalyt. Chem.*, **13**, 363 (1973).
9. E. Blasius and A. Knochel, *J. Radioanalyt. Chem.*, **13**, 373 (1973).
10. K. Maroy, *Crystal Structures of Penta-, Selenopenta-, Telluropenta- and Hexathionates*, Ph. D. Thesis, Bergen (Norway), 1975.
11. V. J. Janickis, *Formation, Structure and Physical-chemical Properties of Sulfane and Selenane Derivatives*, Doctoral Dissertation, Kaunas, 1983 (in Russian).
12. A. Foust, V. Janickis and K. Maroy, *Inorg. Chem.*, **19**, 1063 (1980).

13. A. Foust, V. Janickis and K. Maroy, *Inorg. Chem.*, **19**, 1044 (1980).
14. A. Foust, V. Janickis and K. Maroy, *Inorg. Chem.*, **19**, 1040 (1980).
15. E. Blasius and A. Knochel, *J. Radioanalyt. Chem.*, **13**, 381 (1973).
16. V. Zelionkaitė, J. Ėukytė, *Chemistry and Chemical Technology, Proc. Republic. Conf.*, Kaunas, Febr. 12–17, p. 107 (1973).
17. V. Janickis and V. Zelionkaitė, *Chemistry and Chemical Technology, Proc. XXII Republic. Conf.*, Kaunas, January 12 – February 17, p. 37 (1972).
18. I. Soos, C. Varhelyi and M. Somaly, *Studia Univ. Babeş-bolyai. Ser. Chem.*, **8**, 51 (1963).
19. J. V. Janickis, V. J. Zelionkaitė and E. J. Pacauskas, *Zh. Neorg. Khim.*, **2**, 1341 (1957).
20. V. Janickis and J. Janickis, *Trans. Lithuanian Acad. Sci. B*, **2(159)**, 40 (1987).
21. V. J. Zelionkaitė, V. J. Janickis and S. A. Grevys, *Abstracts of II Scient. Conf. Analyt. Chem. Baltic Rep. Beloruss. SSR and Kaliningrad Region*, Ryga, Vol. 2, p. 88 (1976).
22. V. J. Zelionkaitė, G. L. Monkeviėiūtė and L. J. Bernatonienė, *Trans. Lithuanian Higher Schools, Chemistry and Chemical Technology*, **11**, 287 (1969).
23. O. Foss, *Acta Chem. Scand.*, **4**, 1241 (1950).

Vitalijus Janickis, Virginė Albina Amankaviėienė

**SELENOPENTATIONATO RŪGŪTINIO SKILIMO
TARPINIŲ PRODUKTŲ IŠSKYRIMAS:
SELENOPOLITIONATAI, TURINTYS DAUGIAU NEI 4
SIEROS ATOMUS MOLEKULĖJE**

Santrauka

Tirtas kalio monoselenopentationato skilimas aukštos koncentracijos sieros rūgšties (45–75%) terpėje, išsiskiriant vandenilio sulfidui ir susidarant mono- ir poliselenopolitionatams, turintiems daugiau nei 4 sieros atomus molekulėje. Nustatytomis optimaliomis sąlygomis kristaliniuose *trans*-dipiridino-bis(dimetilglioksimato)kobalto(III) kationo druskose pavaldai išskirti šio skilimo tarpiniai produktai – mono- ir diselenopolitionatai, turintys nuo 5 iki 7 sieros atomų molekulėje. Ėitaip atrastos naujos $\text{Se}_n\text{O}_6^{2-}$ ir $\text{Se}_2\text{S}_n\text{O}_6^{2-}$ tipo selenopolitionatų homologų eilės. Įtirtos naujų selenopolitionatų cheminės reakcijos: oksidacija jodu rūgštyje ir hidrokarbonatinėje terpėje, skilimas dėl cianido jonų poveikio. Jos patvirtino siūlomą šio junginio struktūrą, kaip analogišką ėinomai monoselenopentationato struktūrai – sieros-seleno atomų grandinė su tiosulfatinėmis grupėmis galuose. Pasiūlytas sieringiesnių mono- ir diselenopolitionatų susidarymo selenopentationato rūgštinio skilimo metu mechanizmas, kuriame svarbiausias vaidmuo susidarant sieringiems selenopolitionatams priskirtas tarpiniam junginiui – monoselenandisulfanmonosulfonatui, $\text{H-S-Se-S-SO}_3\text{H}$, susidarantiam pirminės selenopentationato hidrolizės metu, suyrant jungėiai tarp galinių sieros atomų pastarojo anijone.

Raktaþodþiai: kalio selenopentationatas, rūgštinis skilimas, aukštesnieji mono- ir diselenopolitionatai