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# Reduction of tellurite with hydrogen sulphite. Isolation and properties of tellurotrithionate

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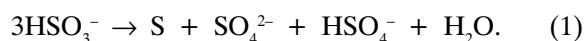
The kinetics of tellurite reduction with the excess of hydrogen sulphite in water has been studied. Liberated at the beginning of this heterogeneous reaction, hydrated tellurium dioxide  $\text{TeO}_3^{2-} + 2\text{HSO}_3^- \rightarrow \text{TeO}_2\downarrow + 2\text{SO}_3^{2-} + \text{H}_2\text{O}$  dissolves under stirring, and the gradual formation of an intermediate product, tellurotrithionate,  $\text{TeS}_2\text{O}_6^{2-}$ , which imparts the yellow colour to the solution takes place:  $\text{TeO}_2 + 3\text{HSO}_3^- \rightarrow \text{Te}(\text{SO}_3)_2^{2-} + \text{HSO}_4^- + \text{H}_2\text{O}$ . The change in the amount of this intermediate product in the course of the reaction passes the maximum and then liberation of elemental tellurium begins:  $\text{Te}(\text{SO}_3)_2^{2-} + \text{H}_2\text{O} \rightarrow \text{Te}\downarrow + \text{H}_2\text{SO}_3 + \text{SO}_4^{2-}$ . The amount of tellurotrithionate increases with an increase in the concentration of hydrogen sulphite and the acidity of its solution. The tellurotrithionate anion is isolated in the form of crystalline salts of potassium and *trans*-dipyridinebis(dimethylglyoxime)cobalt(III),  $\text{K}_2\text{TeS}_2\text{O}_6$  and  $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{TeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ , respectively. When dry, these compounds are stable for a long period of time, but under the action of water, acids and alkali their decomposition with the liberation of tellurium occurs. The characteristic of polythionate reactions confirmed the chemical nature of the tellurotrithionic acid salts isolated, *i.e.* an analogy of the tellurotrithionate anion with the previously known anions of selenotrithionate,  $\text{SeS}_2\text{O}_6^{2-}$ , and pure sulphur trithionate,  $\text{S}_3\text{O}_6^{2-}$ .

**Key words:** reduction, tellurite, hydrogen sulphite, tellurotrithionate

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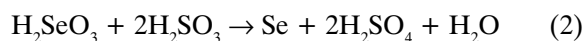
## INTRODUCTION

Reduction of sulphurous acid,  $\text{H}_2\text{SO}_3$ , or of  $\text{SO}_2$  solution in water (compounds of S(IV)) with hydrogen sulphide,  $\text{H}_2\text{S}$  (the classical reaction of sulphur chemistry – Wackenroder reaction [1]) finally leads to the liberation of elemental sulphur (S(0)). This extensively studied [2] reaction proceeds via intermediate formation of polythionates – sulphane-disulphonates,  $\text{S}_n(\text{SO}_3)_2^{2-}$ , *i.e.* compounds containing chains of divalent sulphur atoms and terminated by  $\text{SO}_3$  groups [3]. Polythionates are intermediate compounds of spontaneous decomposition of  $\text{SO}_2$  water solutions and hydrogen sulphites [4] proceeding according to the following general equation:



Hence the spontaneous decomposition or reduction of S(IV) compounds in water solution, finally leading to the liberation of the element proceeds via an intermediate formation of S(II) compounds.

Reduction of selenious acid,  $\text{H}_2\text{SeO}_3$  (compound of Se(IV)) with sulphurous acid,  $\text{H}_2\text{SO}_3$  (or with water solution of  $\text{SO}_2$ ) leading to the liberation of elemental selenium, (Se(0)),



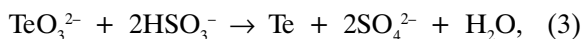
also proceeds via intermediate formation of Se(II) compounds – selenopolythionates = selenanedisulphonates,  $\text{Se}_n(\text{SO}_3)_2^{2-}$ , *i.e.* compounds containing chains of divalent selenium atoms and terminated by  $\text{SO}_3$  groups [3, 5–9]. Reactions of selenopolythionate formation and decomposition, their chemical and physical chemical properties have been extensively studied [3, 10–12]. Reduction of tellurite

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with hydrogen sulphite according to the general equation



leads to liberation of elemental tellurium, too [13]. Therefore one could expect that this reaction also proceeds via intermediate formation of Te(II) compounds which are similar to selenopolythionates. When solutions of the alkali metal tellurite and hydrogen sulphite are mixed, a white precipitate of hydrated tellurium dioxide ( $\text{TeO}_2 \cdot n\text{H}_2\text{O}$ ) liberates. But if excess hydrogen sulphite has been used and heterogeneous reactions proceed on stirring, the solution acquiring first yellow and then orange colour, gradual liberation of elemental tellurium starts. The kinetics of this reaction and its dependence on conditions (the ratio of reagents and their concentrations, acidity and temperature of the solution), as well as its intermediate products has not been systematically studied. We attempted to study this reaction applying our experience in the chemistry of selenopolythionates [8–12] and improved chemical analytical methods for determination of tellurium compounds in their mixtures with sulphur compounds. To isolate the intermediate product of tellurite reduction with hydrogen sulphite – tellurotrithionate,  $\text{Te}(\text{SO}_3)_2^{2-}$ , – complex cation *trans*-dipyridinebis(dimethylglyoxime)cobalt(III) was used, which forms hardly soluble, stable salts [9] with anions of selenopolythionates. After the optimal conditions of intermediate reaction product formation had been determined, the tellurotrithionate anion was isolated as a potassium salt and some of its chemical properties characteristic of polythionates were studied.

## EXPERIMENTAL

**Reaction kinetics.** For preparation of tellurite reduction with hydrogen sulphite, reaction mixtures  $\text{KHSO}_3$ ,  $\text{Na}_2\text{TeO}_3$  and  $\text{K}_2\text{TeO}_3$  solutions were used. An individual mixture was prepared for every experiment. Often 10 ml of  $\text{KHSO}_3$  solution of desired concentration was taken and some solution of  $\text{K}_2\text{TeO}_3$  was added under stirring. If the decrease in the solution acidity was needed the calculated amount of  $\text{K}_2\text{SO}_3$  was added, and to increase the solution acidity some water solution of  $\text{SO}_2$  was used. The mixtures were kept in small closed flasks under stirring at 20 °C.

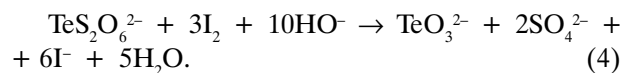
As mentioned above, after mixing the reagent forms white heterogeneous mixtures, i.e. white precipitates are liberated. The solution above the precipitates gradually acquires a yellow and then an

orange colour, and after some period of time liberation of black powder-like elemental tellurium begins. The reaction may be slowed down by rapid cooling of the reaction mixture or by its dilution in ice water. After a selected period of time the reaction mixture was fast filtered into cold water and diluted up to 100 ml, and both the liquid and the solid phases were analysed. For the analysis, the chemical analytical methods of tellurium and sulphur compound mixtures worked out in our laboratory by modifying the analogous analytical methods of mixtures of selenium and sulphur compounds [14] were used.

**Analysis of the liquid phase – filtrate.** The qualitative reactions showed that the filtrate together with non-reacted hydrogen sulphite and tellurite contains the final product of the reaction, sulphate, and an intermediate product, the latter imparting a yellow colour to the solution. In hydrogen carbonate solution this intermediate product like the selenopolythionates of the  $\text{Se}_n(\text{SO}_3)_2^{2-}$  type [10, 15] decomposes fast with liberation of elemental tellurium. The assumption that liberation of elemental tellurium occurs during the decomposition of the intermediate compound was confirmed when this intermediate compound – tellurotrithionate was isolated in the form of crystalline salts (see further). But this reaction is only a qualitative one, because the amount of the liberated tellurium depends on the excess of hydrogen sulphite used in the experiment.

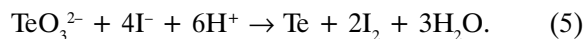
While analysing, the liquid phase has been determined in the following way:

1. Consumption of iodine during oxidation in a solution containing hydrogen carbonate. A sample of the reaction mixture was added into a mixture made of 10 ml 10%  $\text{KHCO}_3$  and excess of 0.1 n  $\text{I}_2$  and starch. After 5 min 20 ml 10% acetic acid was added, and non-reacted iodine was retitrated with 0.1 n  $\text{Na}_2\text{S}_2\text{O}_3$ . Under these conditions iodine oxidizes hydrogen sulphite present in the reaction mixture (non-reacted) into sulphate and tellurotrithionate (analogously to selenotrithionate) into tellurite and sulphate:



The iodine consumption is 6 equiv/mol  $\text{TeS}_2\text{O}_6^{2-}$ .

2. The mixture of the sample after oxidation in hydrogen carbonate (i.e. after determination 1) is acidified by 10 ml 23% HCl and tellurite is determined iodometrically:



The iodine liberated is titrated with 0.1 n  $\text{Na}_2\text{S}_2\text{O}_3$ . The consumption of iodine in this case is – 4 equivalents of  $\text{I}_2$  for  $\text{TeO}_3^{2-}$  present in the reaction mixture (non-reacted) and 4 equivalents of  $\text{I}_2$  for the intermediate product previously oxidized in hydrogen carbonate. By combining the determinations 1 and 2, the amounts of hydrogen sulphite (not reacted but present in the reaction mixture) and of the intermediate product were calculated. For verification, the overall amount of tellurium present in all experiments was determined by dissolving the sample (0.5–2.0 mmol Te) in 5 ml 1:2  $\text{HNO}_3$ , heating on water bath and then adding a little of a solution of acetanilide in ethanol to remove nitrogen oxides. The tellurite formed then was determined as described above.

*Analysis of the solid phase.* Qualitative experiments showed that beside tellurium dioxide, elemental tellurium and cations, also sulphate and sulphite ions are present in the solid phase. Such mixtures were analysed by dissolving samples (washed with ethanol and dried) of the precipitate in the solutions of corresponding reagents and determining them by well known methods: sulphite and tellurite – iodometrically, sulphate – gravimetrically as  $\text{BaSO}_4$ . The overall amount of tellurium was determined as described above. The analytical data of the mixtures of the three different experiments are presented in Table 1. A satisfactory matching of the taken and the determined amounts of tellurium and its compounds and of the sum of sulphur compounds indicates a sufficient reliability of the chemical analytical methods used. As is seen from the presented data, the amounts of the intermediate product formed under conditions of these experiments is not large and equal to 5–18% of the tellurite used. The methods described above were used to study the kinetics of the interaction of tellurite with hydrogen sulphite and as well as to determine the dependencies between the amount of the intermediate product formed and the concentrations of reagents, their

molar ratio and the acidity of the initial reaction mixture. The acidity was expressed by the ratio of the initial concentration of hydrogen sulphite ions ( $\text{H}^+$ ) and iodometrically determined sulphite concentration (S). For example, the ratio  $\text{H}^+/\text{S} = 1.0$  for pure hydrogen sulphite and the ratio  $\text{H}^+/\text{S} = 0.5$  for mixture  $\text{HSO}_3^-/\text{SO}_3^{2-} = 1:1$ .

*Trans*-dipyridinebis(dimethylglyoxime)cobalt(III) hydrogen sulphate dihydrate,  $[\text{Co}(\text{DH})_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ , was prepared [12] from acetate [16].

Tellurium in the tellurotrithionates  $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{TeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{TeS}_2\text{O}_6$  was determined by dissolving the samples in  $\text{HNO}_3$ , and the tellurite formed was determined as described above. Sulphur was determined as  $\text{BaSO}_4$ , potassium – as  $\text{K}_2\text{SO}_4$  and cobalt – as  $\text{Co}_3\text{O}_4$ .

Light absorption spectra were recorded on a SPECORD UV-VIS spectrometer and IR absorption spectra on a UR-20 spectrometer.

## RESULTS AND DISCUSSION

Changes of tellurium compound concentrations during the tellurite interaction with hydrogen sulphite in one of the experiments are shown in Fig. 1. It is seen that the rate of interaction slows down rather fast with time. Therefore the duration of the reaction is presented by logarithmic coordinates. A significant part of the tellurite taken at the beginning of the reaction liberates from the solution as  $\text{TeO}_2$ . But a part of it gets into the solution again in the course of the reaction and the overall concentration of tellurium in the solution increases (Fig. 1, curve *b*). The concentration of the intermediate product of the reaction ( $\text{Te}_p$  – polythionic tellurium) also increases (Fig. 1, curve *c*). The both curves pass the maximum and exactly from the moment of these maximums the liberation of elemental tellurium begins (Fig. 1, curve *d*). Its amount constantly increases, and at the end of reaction all tellurium is found in the elemental form.

Table 1. Analytical data of mixtures of tellurite reduction with hydrogen sulphite

	Taken, mmol $\text{TeO}_3^{2-}$	Found, mmol				Total amount	$\text{TeS}_2\text{O}_6^{2-}$ , % of $\text{TeO}_3^{2-}$ used
		in precipitate		in solution			
		element. Te	$\text{TeO}_2$	$\text{TeS}_2\text{O}_6^{2-}$	$\text{TeO}_3^{2-}$		
1.	2.55	1.68	0.75	0.14	0.04	2.61	5.0
2.	5.06	–	3.06	0.90	1.13	5.09	18.0
3.	14.10	0.85	11.10	1.13	0.94	14.02	8.0
	$\text{HSO}_3^-$	$\text{HSO}_3^-$		$\text{HSO}_3^-$	$\text{SO}_4^{2-}$		
1.	22.24	1.51		17.28	3.61	22.40	
2.	47.50	2.86		44.92	–	47.78	
3.	54.20	6.95		45.44	1.70	54.09	

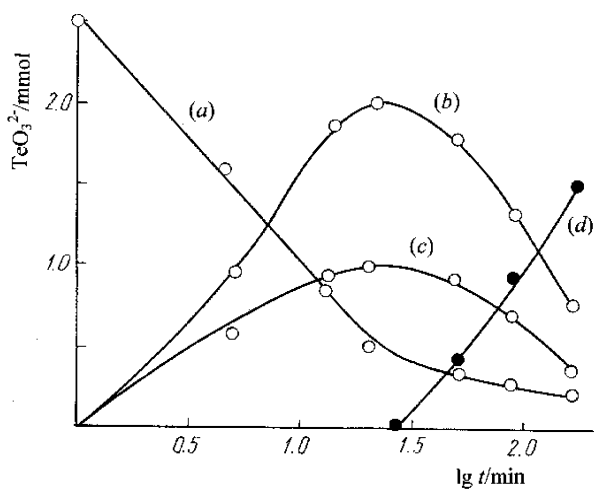


Fig. 1. Change in the concentrations of tellurium and its compounds during the interaction of tellurite with hydrogen sulphite. Reagents:  $\text{TeO}_3^{2-} - 2.55 \text{ mol}\cdot\text{l}^{-1}$ ,  $\text{HSO}_3^- - 4.75 \text{ mol}\cdot\text{l}^{-1}$ ,  $\text{H}^+/\text{S} = 0.61$ . *a* –  $\text{TeO}_2$  in precipitate, *b* – total Te in solution, *c* – polythionic tellurium ( $\text{Te}_p$ ) in solution, *d* – elemental tellurium

An analogous character of kinetic curves is observed when the reagents of the same concentrations are used, but the acidity of hydrogen sulphite initial solutions is different. However, the ratio between the rates of intermediate product formation and decomposition as determined by our experiments strongly depend on the acidity of the initial solution of hydrogen sulphite, *i.e.* on the value of  $\text{H}^+/\text{S}$ . The rate of the  $\text{Te}_p$  maximum formation increases when the  $\text{H}^+/\text{S}$  is increased. At the same acidity of the hydrogen sulphite solutions the reaction of  $\text{Te}_p$  formation is faster when the concentration of  $\text{HSO}_3^-$  is higher (Fig. 2); the reached concentrations of  $\text{Te}_p$  are higher and the duration of  $\text{Te}_p$  maximum concentration formation ( $t \text{ Te}_p \text{ max}$ ) is shorter (Fig. 3). Analogous results are obtained using the solutions of hydrogen sulphite of different acidity (Fig. 4). But the percentage of  $\text{Te}_p$  in the solution increases when the concentration of the initial hydrogen sulphite solution is decreased. For example, when the concentration of initial  $\text{HSO}_3^-$  is  $4.75 \text{ mol}\cdot\text{l}^{-1}$ ,  $\text{Te}_p \text{ max.} = 21\%$ ; when the concentration of initial  $\text{HSO}_3^-$  is  $2.85 \text{ mol}\cdot\text{l}^{-1}$ ,  $\text{Te}_p \text{ max.} = 28\%$ ; when the concentration of initial  $\text{HSO}_3^-$  is  $1.85 \text{ mol}\cdot\text{l}^{-1}$ ,  $\text{Te}_p \text{ max.} = 32.4\%$ . At the same concentration of the initial hydrogen sulphite solution the period of time from the start of the reaction till the beginning of elemental tellurium liberation increases when the value of  $\text{H}^+/\text{S}$  is lowered (compare curves *d* and *e* in Fig. 4); simultaneously the rate of the reaction slows down. At the same acidity of the hydrogen sulphite solution, when the concentration of the solution increases, the period of time till the beginning of the elemental tellurium liberation shortens. The ki-

netic curves obtained are very similar (Fig. 4) and seem moved in respect to one another.

Comparing the data given in Fig. 2–4, one can state that the liberation of elemental tellurium occurs as a result of the decomposition of the intermediate product of the reaction; its concentration characterizes the value of  $\text{Te}_p$ .

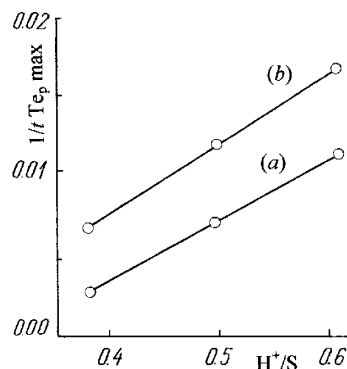


Fig. 2. Influence of hydrogen sulphite solution acidity on the duration of the formation of polythionic tellurium maximum concentration,  $t \text{ Te}_p \text{ max}$ , during the interaction of tellurite with hydrogen sulphite. The initial concentration of  $\text{K}_2\text{TeO}_3 - 0.23 \text{ mol}\cdot\text{l}^{-1}$ . The initial concentration of hydrogen sulphite: *a* –  $1.85$ , *b* –  $2.85 \text{ mol}\cdot\text{l}^{-1}$

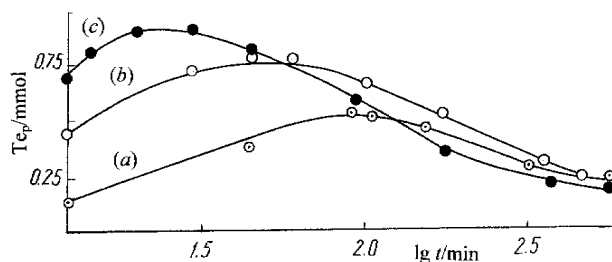


Fig. 3. Influence of hydrogen sulphite solution concentration on the formation of polythionic tellurium during the interaction of tellurite with hydrogen sulphite.  $\text{H}^+/\text{S} = 0.61$ . The initial concentration of  $\text{K}_2\text{TeO}_3 - 0.23 \text{ mol}\cdot\text{l}^{-1}$ . The initial concentration of hydrogen sulphite: *a* –  $1.85$ , *b* –  $2.85$ , *c* –  $4.75 \text{ mol}\cdot\text{l}^{-1}$

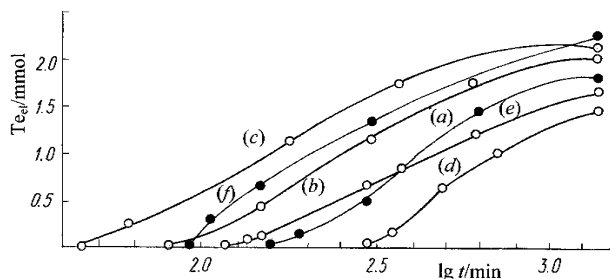


Fig. 4. Dependence of the amount of tellurium liberated on the acidity and concentration of the initial solution of hydrogen sulphite. The initial concentration of  $\text{K}_2\text{TeO}_3 - 0.23 \text{ mol}\cdot\text{l}^{-1}$ .  $\text{H}^+/\text{S}$ : *a, d* –  $0.38$ ; *b, e* –  $0.50$ ; *c, f* –  $0.61$ . The initial concentration of  $\text{HSO}_3^-$ ,  $\text{mol}\cdot\text{l}^{-1}$ : *a, b, c* –  $2.85$ ; *d, e, f* –  $1.85$

In this work only the solutions of rather high concentrations were studied and large excess of  $\text{HSO}_3^-$  ions was used to obtain the higher concentrations of  $\text{Te}_p$  in the reaction mixture. However, an increase in the reagent concentration leads to a significant increase of the reaction rate, too. Then, to follow the rate of the reaction, it was necessary to reduce the acidity of the reaction mixture. That could be achieved by adding a concentrated  $\text{K}_2\text{SO}_3$  solution. The acidity of the reaction mixture reduces and the reaction slows down when the amount of tellurite as well as that of the reagent is increased. Therefore a number of experiments were performed studying the dependencies of the duration of  $\text{Te}_p$  formation and of elemental Te liberation on the initial amount of tellurite used when the same amount of another reagent,  $\text{KHSO}_3$  (47.5 mmol/in 10 ml solution), was taken (Fig. 5). The kinetic data presented in Fig. 5 show that the amount of  $\text{Te}_p$  increases when the amount of tellurite in the initial reaction mixture is increased. But the reaction slows down because of a decrease in the acidity of the reaction mixture (compare curves *a*, *b*, *c* in Fig. 5). The liberation of elemental tellurium increases in proportion to the amount of the initial  $\text{TeO}_3^{2-}$  used.

Using the data presented in Fig. 5, *i.e.* the optimal quantities of  $\text{HSO}_3^-$  and  $\text{TeO}_3^{2-}$  for the formation of the maximum amount of  $\text{Te}_p$ , in a number of experiments the acidity of the initial reaction mixture was increased by addition of  $\text{SO}_2$  solution into the solution of  $\text{KHSO}_3$ . From the data presented in Fig. 6 it follows that when the acidity of the initial reaction mixture is increased, the maximum amount of  $\text{Te}_p$  formed decreases and the liberation of elemental tellurium becomes faster. How-

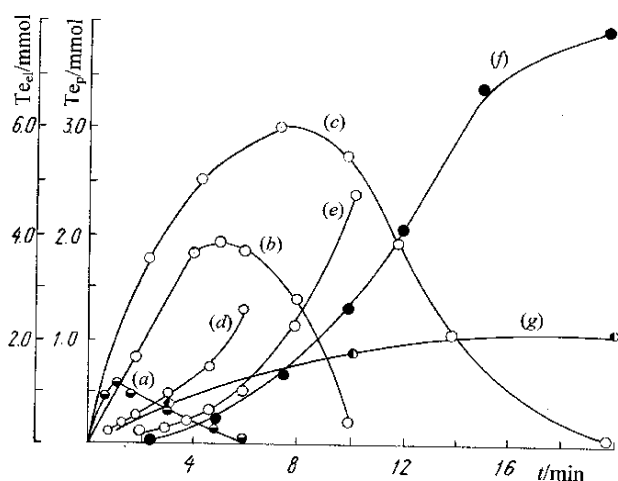


Fig. 5. The dependencies of the amounts of the formed polythionic tellurium and of the liberated elemental tellurium on the initial amount of the tellurite taken.  $\text{K}_2\text{TeO}_3$ , mmol: *a*, *d* - 2.55; *b*, *e* - 5.1; *c*, *f* - 7.65;  $\text{HSO}_3^- = 47.5$  mmol;  $\text{H}^+/\text{S}$ : *a* - *f* = 1.1, *g* - 0.61

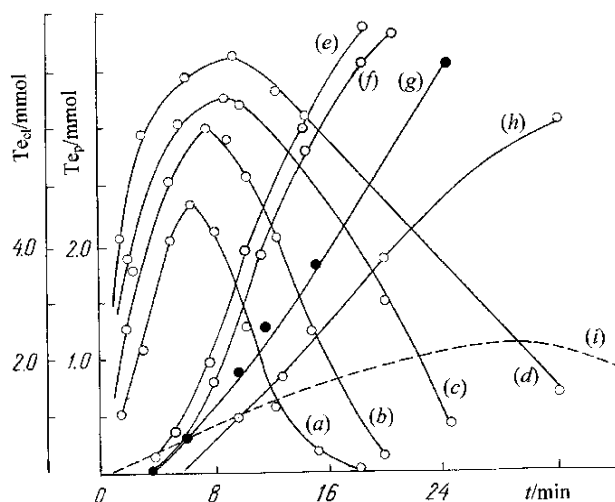


Fig. 6. The dependencies of the amounts of the formed polythionic tellurium and of the liberated elemental tellurium on the acidity of the initial hydrogen sulphite solution. ( $\text{HSO}_3^- = 47.5$  mmol.  $\text{TeO}_3^{2-} = 7.65$  mmol).  $\text{H}^+/\text{S}$ : *a*, *e* - 1.2; *b*, *f* - 1.1; *c*, *g* - 1.05; *d*, *h* - 1.0; *i* - 0.61

ever, it is interesting to point out that in all cases the maximum values of  $\text{Te}_p$  are reached after the same duration of the reaction - 7-10 min. The maximum amount of  $\text{Te}_p$  (about 45% of the  $\text{TeO}_3^{2-}$  used) is obtained when a non-acidified solution of hydrogen sulphite ( $\text{H}^+/\text{S} = 1$ ) is used. But the maximum values of  $\text{Te}_p$  are reached in a narrow interval of the reaction time, therefore the isolation of the intermediate product is most purposeful between 10 and 15 min from the start of the reaction.

As mentioned above, during the interaction of hydrogen sulphite with tellurite the reaction mixture acquires a yellow colour, which may be explained by the formation of polythionic tellurium,  $\text{Te}_p$ , actually by the formation of  $\text{TeS}_2\text{O}_6^{2-}$ . Since the maximum values of  $\text{Te}_p$  are reached in a short interval of time and the study of the reaction is limited by the duration of some analytical procedures, we tried to apply a spectrophotometric method to study the intermediate product formation. The reaction mixture was prepared as in the previous experiments, *i.e.* by adding various quantities of  $2.55 \text{ mol}\cdot\text{l}^{-1}$   $\text{K}_2\text{TeO}_3$  to 10 ml of  $4.75 \text{ mol}\cdot\text{l}^{-1}$   $\text{KHSO}_3$  solution. The heterogeneous mixture was kept at  $20^\circ\text{C}$  under stirring. After some period of time the reaction mixture was filtered, 1 ml of the filtrate was diluted with cold water to 50 ml and the absorption spectra were recorded. The spectral curves recorded at different periods of time from the start of the reaction were similar. The absorption maximums are at  $\nu = 23\cdot 10^3$  and  $\nu = 29\cdot 10^3 \text{ cm}^{-1}$ . Using the curves of the light absorption spectra, the kinetic curves of the reaction were obtained (Fig. 7). It is seen that the sensitivity to light reaction products increases

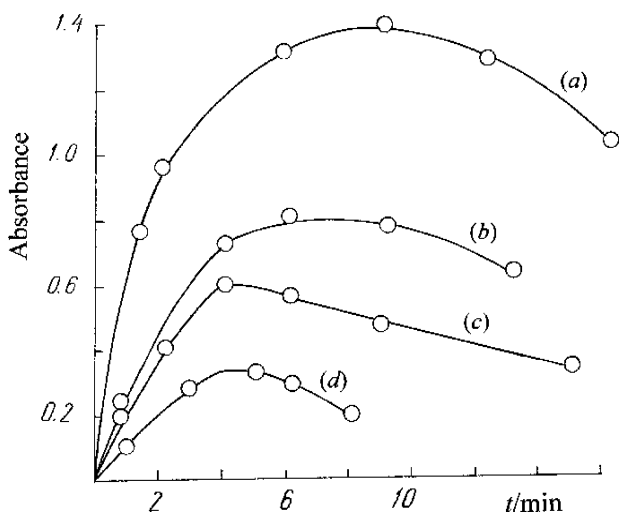


Fig. 7. Change in the optical density at  $\nu = 23 \cdot 10^3 \text{ cm}^{-1}$  with time ( $\text{HSO}_3^- = 47.5 \text{ mmol}$ ).  $\text{TeO}_3^{2-}$ , mmol: a – 7.65; b – 5.1; c – 2.55; d – 1.275

when the ratio  $\text{TeO}_3^{2-}/\text{HSO}_3^-$  is increased. A comparison of the data obtained by the spectrophotometric method with the data obtained by chemical methods of analysis shows that the absorption maximum at  $\nu = 23 \cdot 10^3 \text{ cm}^{-1}$  is characteristic of polythionic tellurium, actually of  $\text{TeS}_2\text{O}_6^{2-}$  ions. The absorption maximum at  $\nu = 29 \cdot 10^3 \text{ cm}^{-1}$  most probably corresponds to another, even less stable intermediate compound which could be (in analogy with the chemistry of selenopolythionates) ditellurium-tetrathionate,  $\text{Te}_2\text{S}_2\text{O}_6^{2-}$ . A comparison of the data from Figures 7, 6 and 5 reveals a good reproduction of the maximum value of  $\text{Te}_p$  formation: the highest concentration of polythionic tellurium is reached in 8–10 min, using the reagents in a proportion  $\text{HSO}_3^-/\text{TeO}_3^{2-} = 47.5 \text{ mmol}/7.65 \text{ mmol}$ . Thus, after these optimal conditions for the formation of polythionic tellurium had been determined, the hopes to isolate the intermediate product in the form of crystalline salts became realistic.

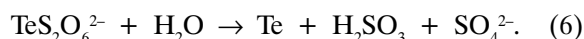
*Isolation of trans-dipyridinebis(dimethylglyoxime)cobalt(III) tellurotrithionate hexahydrate,  $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{TeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ .* To isolate the intermediate product of tellurite interaction with hydrogen sulphite we applied the cation *trans*-dipyridinebis(dimethylglyoxime)cobalt(III) which (as above) forms hardly soluble in water salts [9] with anions of polythionates and selenopolythionates. It was determined that by use of this complex cation isolation of intermediate product from the reaction mixtures of different compositions is possible. For example, 2 ml  $3.6 \text{ mol} \cdot \text{l}^{-1}$   $\text{K}_2\text{TeO}_3$  is added to 20 ml  $4.7 \text{ mol} \cdot \text{l}^{-1}$   $\text{KHSO}_3$  and the reaction mixture is left under stirring for 5 min. Then a white precipitate of  $\text{TeO}_2 \cdot x\text{H}_2\text{O}$  is filtered off and the filtrate diluted

with cold water to 50 ml. A solution of 2 g of  $[\text{Co}(\text{DH})_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$  in 50 ml of water is added to this diluted filtrate. The precipitated small yellow-brown crystals are filtered off, washed with a small amount of cold water, then with some ethanol and ether, and dried in vacuum, preferably in a refrigerator (2.32 g, 89%). Found: Co, 9.80; Te, 10.21; S, 5.24;  $\text{H}_2\text{O}$ , 8.10.  $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{TeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$  requires Co, 9.13; Te, 9.89; S, 4.97;  $\text{H}_2\text{O}$ , 8.38;  $\nu_{\text{max}}/\text{cm}^{-1}$  [ $\nu(\text{H}_2\text{O})$ ] 3500 m, 3435 s; [ $\delta(\text{H}_2\text{O})$ ] 1662 m; [ $\nu_{\text{as}}(\text{SO})$ ] 1220 s, 1200 s; [ $\nu_s(\text{SO})$ ] 1020 m, 996 vs; [ $\delta(\text{OSO})$ ] 625 s and 578 vs (Nujol). Thus the composition of the isolated products corresponds to a formerly unknown tellurotrithionate. Some products of analogous composition were also isolated from the reaction mixtures of other compositions, for example, by adding 2 ml  $1.4 \text{ mol} \cdot \text{l}^{-1}$  solution of  $\text{K}_2\text{TeO}_3$  to 20 ml  $2.0 \text{ mol} \cdot \text{l}^{-1}$  solution of  $\text{KHSO}_3$ .

When dried, salt *trans*-dipyridinebis(dimethylglyoxime)cobalt(III) tellurotrithionate dihydrate is stable at room temperature for a long time. Under the action of water, acids or alkali it decomposes with liberation of tellurium, but remains unchanged if affected by the solution of  $\text{KHSO}_3$ . It slightly dissolves in methanol, ethanol and acetone but soon decomposes in these solvents.

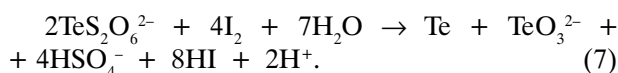
For the confirmation of the nature of the products isolated, decomposition under the action of water and some reactions characteristic of polythionates and selenopolythionates were studied and confirmed the similarity to these compounds. Since the compound isolated is little soluble, its samples have been affected with the excess of a reagent. The suspension obtained was stirred till the reaction was completed and then the obtained mixture was analysed. Simultaneously experiments with the preparations of  $[\text{Co}(\text{DH})_2\text{Py}_2]\text{HSO}_4 \cdot 2\text{H}_2\text{O}$  have been performed, since the cation *trans*-dipyridinebis(dimethylglyoxime)cobalt(III) slowly reacts with iodine [12] and thus presents difficulties in obtaining accurate results. Data presented in Table 2 show that under the action of water all tellurium from tellurotrithionate anions liberates in an elemental state. Decomposed under the action of water, the tellurotrithionate solution is titrated with iodine, whose amount per mol of tellurotrithionate taken before the decomposition equals to about 2 equivalents. Since neither tellurium nor  $\text{TeO}_3^{2-}$  in neutral or weakly acidic solution oxidise with iodine, one may assume that all iodine consumed during the titration of decomposed  $\text{TeS}_2\text{O}_6^{2-}$  has been used for  $\text{SO}_3^{2-}$  oxidation into  $\text{SO}_4^{2-}$ . The remaining sulphur before the titration with iodine was found in the form of  $\text{SO}_4^{2-}$ . These results indicate that under the action of water the tellurotrithionate anion decomposes according to the following equation:

Sample	Reaction	Molar ratios of the products			Amount of $\text{I}_2$ , equiv/mol
		Elem. Te	$\text{SO}_4^{2-}$	$\text{SO}_3^{2-}$	
1.	Decomposition	0.92	1.16	0.71	1.42
2.	in water	0.89	1.33	0.87	1.74
3.		0.87	1.11	0.65	1.30
Calculated	for reaction (6)	1.00	1.00	1.00	2.00
4.	Oxidation with	0.47	–	2.07	4.14
5.	$\text{I}_2$ in acid	0.44	–	2.05	4.10
6.	solution	0.49	–	1.95	3.90
7.	Oxidation with	0.55	–	2.05	4.10
8.	$\text{I}_2$ in neutral	0.50	–	1.87	3.74
9.	solution	0.49	–	2.10	4.20
Calculated	for reaction (7)	0.50	–	2.00	4.00
10.	Cyanic	0.52	–	1.83	3.66
11.	decomposition	0.46	–	1.85	3.70
12.		0.51	–	1.75	3.50
Calculated	for reaction (8)	0.50	–	2.00	4.00



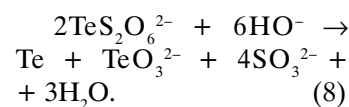
But the amount of  $\text{H}_2\text{SO}_3$  determined is smaller than the expected one by the equation (6), probably because of the volatility of  $\text{SO}_2$  and partially of the oxidation of  $\text{H}_2\text{SO}_3$  by the oxygen of the air. The reaction (6) is analogous to the reaction of selenotrithionate,  $\text{SeS}_2\text{O}_6^{2-}$ , decomposition in acidic media [17, 18], but the tellurium homologue is a significantly less stable compound.

The tellurotrithionate decomposition reaction proceeds differently when this compound is affected with the solution of iodine (Table 2, experiments 7–9) and the excess of  $\text{I}_2$  is retitrated with thiosulphate. Then the consumption of iodine equals 4 equivalents per mol of tellurotrithionate and the reaction proceeds according to the equation:



Analogous results are obtained when the samples of tellurotrithionate are affected by acidified solution of iodine (Table 2, samples 4–6). Since iodine in a neutral and acidic solution does not oxidise tellurium, one may accept that it is used for the oxidation of sulphur atoms present in the anion of tellurotrithionate into sulphate ions.

The decomposition under the action of cyanide ions has been studied applying procedures used to study an analogous reaction of selenotrithionate and other selenopolythionates [11, 15]. Since, unlike sulphur and selenium, elemental tellurium does not react with cyanide ions, this reaction of tellurotrithionate may be regarded as its hydrolysis in an alkaline solution:



Then, for the oxidation of sulphite formed during the decomposition in these conditions of tellurotrithionate 4 equivalents of equivalents of iodine are used per mol of tellurotrithionate taken (Table 2, experiments 10–12). The studied reactions of tellurotrithionate described here which principally are reactions characteristic of the selenopolythionates, confirm that the isolated compound represents tellurotrithionate previously unknown.

*Isolation of potassium tellurotrithionate,  $\text{K}_2\text{TeS}_2\text{O}_6$ .* A kinetic study of tellurite interaction with hydrogen sulphite showed that under optimal conditions for intermediate product formation a rather high concentration of tellurotrithionate ions may be obtained. That stimulated attempts to isolate this anion as a potassium salt. The solubility of potassium tellurotrithionate in water may be reduced by adding ethanol or methanol. The results are better with methanol. 2 ml (2 mol·l<sup>-1</sup>) solution of  $\text{K}_2\text{TeO}_3$  was added to 10 ml of concentrated (4–5 mol·l<sup>-1</sup>) solution of  $\text{KHSO}_3$ . The heterogeneous mixture was stirred for 5–10 min, then 10 ml of methanol was added and white precipitate consisting of  $\text{TeO}_2$  as well as non-reacted  $\text{KHSO}_3$  were filtered. 10 ml of methanol was added to the filtrate, and the bright orange clear solution was placed into a refrigerator (–6 °C) or into a cooling mixture NaCl/ice. Orange or sometimes yellow needle-like crystals were separated after 15–20 min. They were filtered off, washed with a small amount of methanol and dried in a vacuum in a refrigerator (0.146 g, 40%). If kept under these conditions, the product is stable for a prolonged period of time. Under the action of water, acids or alkali it quickly decomposes with liberation of elemental tellurium. But in hydrogen sulphite solutions the compound dissolves without decomposing. Found: Te, 34.10; S, 18.02; K, 22.11.  $\text{K}_2\text{TeS}_2\text{O}_6$  requires Te, 34.87; S, 17.53; K, 21.37.  $\nu_{\text{max}}/\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{SO})$ ] 1211vs, 1178vs, 1123s; [ $\nu_{\text{s}}(\text{SO})$ ] 1056m, 1021s, 998vs, 977s (sh); [ $\delta_{\text{s}}(\text{OSO})$ ] 634vs, 620s, 585vs; [ $\delta_{\text{as}}(\text{OSO})$ ] 539s, 522s and 513s (sh) (Nujol).

Characteristic qualitative reactions performed analogously as with the compound  $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{TeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$

confirmed that the compound isolated represents potassium tellurotrithionate,  $K_2TeS_2O_6$ .

## CONCLUSIONS

1. The kinetics of tellurite reduction with the excess of 1.8–5.0 mol·l<sup>-1</sup> solution of hydrogen sulphite in water has been studied. Hydrated tellurium dioxide liberated at the beginning of this heterogeneous reaction dissolves under stirring and the gradual formation of an intermediate product, tellurotrithionate,  $TeS_2O_6^{2-}$ , which imparts the yellow colour to the solution takes place. The change in the amount of this intermediate product in the course of reaction passes the maximum, and then liberation of elemental tellurium begins.

2. The amount of tellurotrithionate increases with an increase in the concentration of hydrogen sulphite and the acidity of its solution. The tellurotrithionate anion is isolated in the form of crystalline salts of potassium and *trans*-dipyridinebis(dimethylglyoxime)cobalt(III),  $K_2TeS_2O_6$  and  $[Co(DH)_2Py_2]_2TeS_2O_6 \cdot 6H_2O$ , respectively. When dry, these compounds remain stable for a long period of time, but under the action of water, acids and alkali their decomposition with the liberation of tellurium occurs. The stability of tellurotrithionate is increased by the admixture of hydrogen sulphite.

3. The decomposition of tellurotrithionate anion in water proceeds according to the equation  $TeS_2O_6^{2-} + H_2O \rightarrow Te + H_2SO_3 + SO_4^{2-}$ .

Its oxidation by iodine in neutral and acid solutions takes place according to the following equation:  $2TeS_2O_6^{2-} + 4I_2 + 7H_2O \rightarrow 2Te + 2TeO_3^{2-} + 4HSO_4^- + 8HI + 2H^+$ .

Decomposition of tellurotrithionate ion under the action of cyanide ions proceeds according to the equation  $2TeS_2O_6^{2-} + 6HO^- \rightarrow 2Te + 2TeO_3^{2-} + 4SO_3^{2-} + 3H_2O$ , *i.e.* it may be regarded as hydrolysis in alkaline solution. These reactions are characteristic of polythionates and confirm the chemical nature of the tellurotrithionic acid salts isolated, *i.e.* an analogy of tellurotrithionate anion with the anions of the previously known selenotrithionate,  $SeS_2O_6^{2-}$ , and pure sulphur trithionate,  $S_3O_6^{2-}$ .

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## TELURITO REDUKCIJA HIDROSULFITU.

## TELŪOTRITIONATO IŠSKYRIMAS IR SAVYBĖS

### S a n t r a u k a

Ištirta telurito redukcijos hidrosulfito pertekliumi kinetika vandens tirpale. Hidratuotas telūro dioksidas, išsiskyres šios heterogeninės reakcijos pradžioje,  $TeO_3^{2-} + 2HSO_3^- \rightarrow TeO_2 \downarrow + 2SO_3^{2-} + H_2O$ , maišant palaipsniui tirpsta ir susidaro tarpinis reakcijos produktas – telūotritionatas,  $TeO_2 + 3HSO_3^- \rightarrow Te(SO_3)_2^{2-} + HSO_4^- + H_2O$ , kuris suteikia tirpalui geltoną spalvą. Šio tarpinio produkto kiekis reakcijos eigoje pasidaro maksimalus, o po to prasideda elementinio telūro išsiskyrimas:

$Te(SO_3)_2^{2-} + H_2O \rightarrow Te \downarrow + H_2SO_3 + SO_4^{2-}$ . Telūotritionato kiekis didėja, didėjant hidrosulfito tirpalo koncentracijai ir rūgštingumui. Telūotritionato anijonas išskirtas kristalinių kalio,  $K_2TeS_2O_6$  ir *trans*-dipiridinobis(dimetilglioksimo)cobalto(III),  $[Co(DH)_2Py_2]_2TeS_2O_6 \cdot 6H_2O$ , druskų pavidalu. Sausoje aplinkoje šie junginiai yra patvarūs, tačiau dėl vandens, rūgščių ir šarmų poveikio jie suskyla, išsiskiriant elementiniam telūriui. Išskirtų telūotritionatinės rūgšties druskų cheminę prigimtį patvirtino politionatams būdingos reakcijos, t. y. telūotritionato anijono analogiją su anksčiau žinomais,  $SeS_2O_6^{2-}$ , ir grynai sierinio tritronato,  $S_3O_6^{2-}$ , anijonais.



В. Зелёнкайте, В. Яницкис, А. Юодзявичюс

**ВОССТАНОВЛЕНИЕ ТЕЛЛУРИТА  
ГИДРОСУЛЬФИТОМ. ВЫДЕЛЕНИЕ И  
СВОЙСТВА ТЕЛЛУОТРИТИОНАТА**

**Резюме**

Изучена кинетика восстановления теллуриата избытком гидросульфита в водном растворе. Гидратированный диоксид теллура, выделившийся в начале реакции,  $\text{TeO}_3^{2-} + 2\text{HSO}_3^- \rightarrow \text{TeO}_2\downarrow + 2\text{SO}_3^{2-} + \text{H}_2\text{O}$ , при перемешивании постепенно растворяется и образуется промежуточный продукт реакции – теллуотритионат,  $\text{TeO}_2 + 3\text{HSO}_3^- \rightarrow \text{Te}(\text{SO}_3)_2^{2-} + \text{HSO}_4^- + \text{H}_2\text{O}$ , который придает раствору желтую окраску. Количество этого промежуточного соединения в течение реакции проходит максимум, после чего начинается выделение

элементарного теллура:  $\text{Te}(\text{SO}_3)_2^{2-} + \text{H}_2\text{O} \rightarrow \text{Te}\downarrow + \text{H}_2\text{SO}_3 + \text{SO}_4^{2-}$ . Количество образующегося теллуотритионата возрастает при повышении концентрации и кислотности исходного раствора гидросульфита. Теллуотритионат-анион выделен в виде кристаллических солей калия,  $\text{K}_2\text{TeS}_2\text{O}_6$ , и *транс*-дипиридин-бис(диметилглиоксимато)кобальта(III),  $[\text{Co}(\text{DH})_2\text{Py}_2]_2\text{TeS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ . Эти соединения в сухом виде устойчивы, однако под воздействием воды, кислот и щелочей они разлагаются, с выделением элементарного теллура. Химическая природа выделенных солей теллуотритионовой кислоты подтверждена характерными для полиитионатов реакциями, т.е. подтверждена аналогия теллуотритионат-аниона ранее известным анионам селенотритионата,  $\text{SeS}_2\text{O}_6^{2-}$ , и чисто серного тритионата,  $\text{S}_3\text{O}_6^{2-}$ .