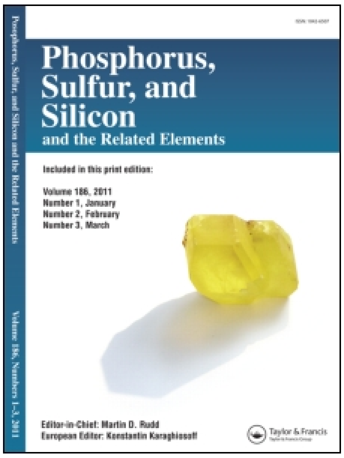

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INVESTIGATIONS ON THE ALKALINE DEGRADATION OF THE PENTATHIONATE

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Specifically ^{35}S-labelled pentathionate is hydrolized under various reaction conditions. From the experimental activity behaviour of the hydrolization products a reaction mechanism can be deduced. Attack of the OH^- occurs at the γ-S-atom of the sulfur chain leading to sulfoxylic acid and thiosulfate as reaction products. Sulfoxylic acid disproportionates to sulfur and sulfite which combine to thiosulfate.

INTRODUCTION

For a long time the reactions of polythionates with nucleophilic and electrophilic reagents are known and may be used in the indirect analysis of mixtures of polythionates.[1–3]

For these reactions several mechanisms are described in the literature[4–10] assuming different intermediates, especially for ^{35}S-labelled trithionate and tetrathionate, results[11] of which exist in our laboratory. The asymmetrical $^-O_3S—SOH$ is formed as intermediate and disproportionates to thiosulfate and sulfite as end products. End product of the alkaline degradation of pentathionate, however, is only thiosulfate:

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \qquad (1)$$

Unlike the hydrolysis of $S_3O_6^{2-}$ and $S_4O_6^{2-}$, sulfur is formed as an intermediate, but is dissolved in course of the reaction.

EXPERIMENTAL

Initial substances for the synthesis of the specifically ^{35}S-labelled pentathionates are innerlabelled $Na_2S^{35}SO_3$, outerlabelled $Na_2{}^{35}SSO_3$ or cristalline ^{35}S-sulfur. The chemical and the radiochemical purities are controlled by means of high voltage ionophoresis. In addition, the percentage of wrong labelling in $Na_2{}^{35}S_2O_3$ is determined. The corresponding values are 0.9% for the inner-S-labelled and 2.8% of the total activity for the outer-S-labelled molecule.

Synthesis of $^{35}SCl_2$[12]

1.5 ml of SCl_2 are pipetted into a test tube which has been washed with chlorine and is fitted with a gas distribution and a gas discharge branch. This solution is saturated with dried chlorine at 5°C. After addition of 40 mg ^{35}S (16 mCi) and some Fe-turnings, chlorine is passed into the solution for another hour.

The reaction mixture is then transferred into a ground joint flask and, after a rest of two hours, distilled in presence of some drops of PCl_3. At 60°C, 1.1 ml $^{35}SCl_2$ are yielded.

Synthesis of $K_2{}^{35}S_5O_6$[13]

Freshly distilled SCl_2 is dissolved in CCl_4 and cooled to −20°C in a big test tube. In addition, a solution of $Na_2S_2O_3$ is cooled to 0°C and a 20% HCl is cooled to −10°C. The reaction proceeds at 0°C while slowly pouring the solutions of $Na_2S_2O_3$ and HCl together into the vigorously stirred CCl_4-phase. The upper aqueous phase is almost clear and shows only a flint turbidity caused by the precipitated sulfur. Excess $Na_2S_2O_3$ is eliminated by addition of 5 ml of a 0.3 M solution of $FeCl_3$. After separation in a separatory funnel the aqueous phase is evaporated at 40°C and 15 Torr to half its volume using a rotation evaporator. The precipitated NaCl is sucked off, the filtrate cooled to 0°C and methanolic KOH is added (2 g of KOH dissolved in 10 ml of CH_3OH). At pH = 3 the addition is stopped, the crystal pulp is sucked off and washed with acetone. Subsequently the product is recrystallized from water which contains a few drops of diluted HCl.

1) 1 g SCl_2 in 4 ml CCl_4, 5 g $Na_2S_2O_3 \cdot 5H_2O$ and 77.3 mg $Na_2{}^{35}SSO_3$ (15.5 mCi) in 5 ml H_2O and 12 ml 20% HCl.

Yield: 780 mg $K_2S^{35}S_2S_2O_6$, 3.4 mCi = 22%.

2) 1 g SCl_2 in 4 ml CCl_4, 5 g $Na_2S_2O_3 \cdot 5H_2O$ and 124 mg $Na_2S^{35}SO_3$ (12.3 mCi) in 5 ml H_2O and 12 ml 20% HCl.

Yield: 808 mg $K_2SS_2{}^{35}S_2O_6$, 2.8 mCi = 23%.

3) 1 g $^{35}SCl_2$ (4 mCi) in 4 ml CCl_4, 5 g $Na_2S_2O_3 \cdot 5H_2O$ in 5 ml H_2O and 12 ml 20% HCl.

Yield: 880 mg $K_2{}^{35}SS_2S_2O_6$, 1 mCi = 25%.

The synthesized compounds are free from side products. Using $^{35}SSO_3^{2-}$ the β- and β'-S-atoms of the chain, using $S^{35}SO_3^{2-}$ the sulfonic acid groups of the pentathionate are labelled. In the case of $^{35}SCl_2$, the γ-S atom is labelled.

High Voltage Paper Ionophoresis[14]

The active polythionates are weighed in the reaction vessel with an ultra micro balance. A solution of KOH is added. The reaction temperature is controlled by a thermostat. The reaction products are separated using the high voltage ionophoresis method. Paper strips which are impregnated with a basis electrolyte serve as carrier material.

The locations of the active zones on the pherogram are obtained by recording of the activity distribution curves by means of a paper chromatogram scanner. The R_B-values, using $^{36}Cl^-$ as reference ion, together with the quenching of the fluorescence are used for the identification. By spraying with a $AgNO_3$-solution, $S_2O_3^{2-}$ and S^{2-} are visible as brown coloured zones besides the polythionates. The quantitative evaluation is carried out directly on the carrier using the liquid scintillation method.[15] In addition, the distribution of the activity in the $S_2O_3^{2-}$ molecule is determined by cleavage with $AgNO_3$-solution.

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4 \qquad (2)$$

The reaction takes place directly on the pherogram, 150 μl of a 0.1 M $AgNO_3$-solution are pipetted onto the $^{35}S_2O_3^{2-}$ zones. Subsequently a second separation is carried out. After drying, the activities of the fixed $Ag_2{}^{35}S$ and of the migrated $^{35}SO_4^{2-}$ are determined.

RESULTS AND DISCUSSION

The alkaline degradation of the $S_5O_6^{2-}$ proceeds very quickly according to Eq. (1). In the beginning, sulfur precipitates, but is dissolved in course of the reaction. Using $^{35}SS_2S_2O_6^{2-}$, the sulfur is radioactive and the cleavage of the formed $S_2O_3^{2-}$ yields an equipartition of the activity in the molecule (Figure 1).

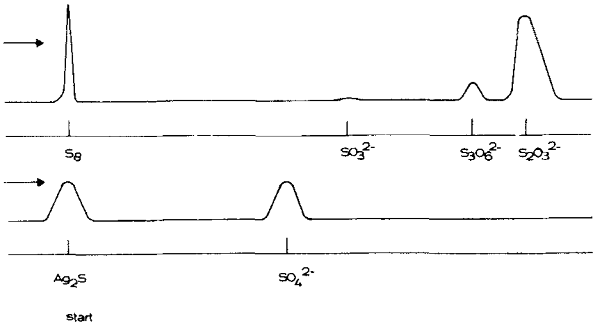

FIGURE 1 Alkaline degradation of $^{35}SS_2S_2O_6^{2-}$.
Above: Curve of the activity distribution after 1 min reaction time.
Below: Curve of the activity distribution after cleavage of $^{35}S_2O_3^{2-}$.
Reaction temperature: 30°C.

If the β, β′-S atoms or the sulfonic acid groups are labelled, the precipitated sulfur is inactive and the formed $S_2O_3^{2-}$ is either outer-S- or inner-S-labelled.

The respective activity behaviour of the intermediate and end products of the total reaction is shown in Figures 2–4. The experimental values of the activity distribution in the $S_2O_3^{2-}$ molecule are listed additionally.

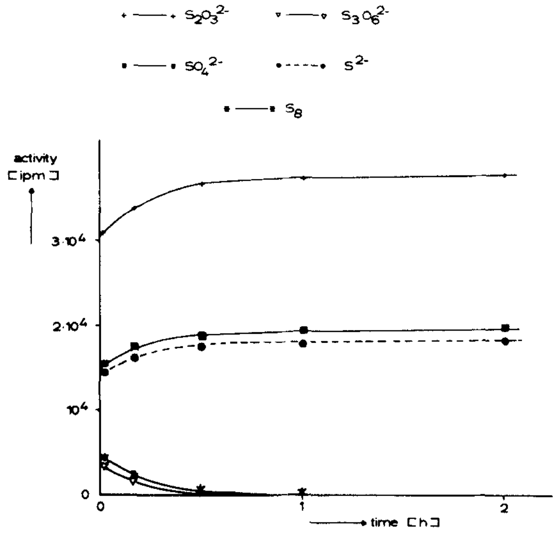

FIGURE 2 Alkaline degradation of $^{35}SS_2S_2O_6^{2-}$. Course of activity in dependence on time.

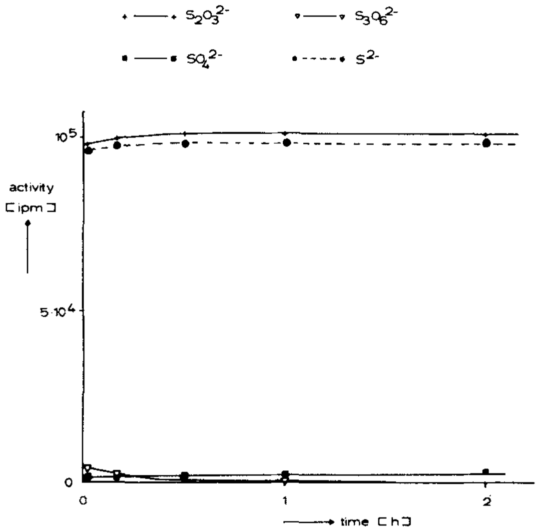

FIGURE 3 Alkaline degradation of $S^{35}S_2S_2O_6^{2-}$. Course of activity in dependence on time.

The attack of the OH^- occurs at the γ-S-atom. The instable intermediate is subsequently degradated

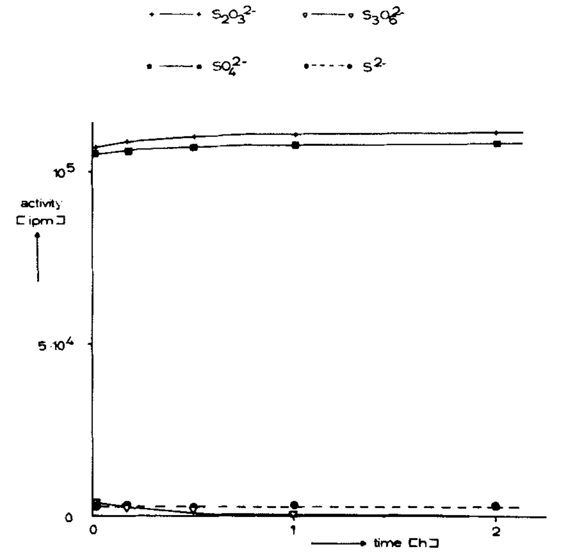

FIGURE 4 Alkaline degradation of $SS_2{}^{35}S_2O_6^{2-}$. Course of activity in dependence on time.

to $S_2O_3^{2-}$ and $S(OH)_2$. $S(OH)_2$ disproportionates to S and SO_3^{2-} leading to $S_2O_3^{2-}$.

$$2\,{}^-O_3SSSSSO_3^- + 2OH^- \rightarrow 2\,{}^-O_3SSSOH + 2SSO_3^{2-} \quad (3)$$

$$2\,{}^-O_3SSSOH + 2OH^- \rightarrow 2SSO_3^{2-} + 2S(OH)_2 \quad (4)$$

$$2S(OH)_2 + 2OH^- \rightarrow HSOH + SO_3^{2-} + 2H_2O \quad (5)$$

$$HSOH + SO_3^{2-} \rightarrow SSO_3^{2-} + H_2O \quad (6)$$

$$2\,{}^-O_3SSSSSO_3^- + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \quad (7)$$

Based on this reaction mechanism one should find the following activity distributions in the three differently labelled $^{35}S_5O_6^{2-}$ molecules (the original activity is set equally to one).

$$2{}_3^-OSS\overset{1}{S}SSO_3^- + 2OH^- \rightarrow 2{}_3^-OSS\overset{1}{S}OH + 2SSO_3^{2-} \quad (8)$$

$$2{}_3^-OSS\overset{1}{S}OH + 2OH^- \rightarrow 2SSO_3^{2-} + 2\overset{1}{S}(OH)_2 \quad (9)$$

$$2\overset{1}{S}(OH)_2 + 2OH^- \rightarrow H\overset{1}{S}OH + \overset{1}{S}O_3^{2-} + 2H_2O \quad (10)$$

$$H\overset{1}{S}OH + \overset{1}{S}O_3^{2-} \rightarrow \overset{1}{S}\overset{1}{S}O_3^{2-} + H_2O \quad (11)$$

$$2{}_3^-OSS\overset{1}{S}SSO_3^- + 6OH^- \rightarrow 4SSO_3^{2-} + \overset{1}{S}\overset{1}{S}O_3^{2-} + 3H_2O \quad (12)$$

$$2{}_3^-O\overset{\frac{1}{2}}{S}SSS\overset{\frac{1}{2}}{S}O_3^- + 2OH^- \rightarrow 2{}_3^-O\overset{\frac{1}{2}}{S}SSOH + 2S\overset{\frac{1}{2}}{S}O_3^{2-} \quad (13)$$

$$2{}_3^-O\overset{\frac{1}{2}}{S}SSOH + 2OH^- \rightarrow 2S\overset{\frac{1}{2}}{S}O_3^{2-} + 2S(OH)_2 \quad (14)$$

$$2S(OH)_2 + 2OH^- \rightarrow HSOH + SO_3^{2-} + 2H_2O \quad (15)$$

$$HSOH + SO_3^{2-} \rightarrow SSO_3^{2-} + H_2O \quad (16)$$

$$2{}_3^-O\overset{\frac{1}{2}}{S}SSS\overset{\frac{1}{2}}{S}O_3^- + 6OH^- \rightarrow 4S\overset{\frac{1}{2}}{S}O_3^{2-} + SSO_3^{2-} + 3H_2O \quad (17)$$

$$2{}_3^-OS\overset{\frac{1}{2}}{S}S\overset{\frac{1}{2}}{S}SO_3^- + 2OH^- \rightarrow 2{}_3^-OS\overset{\frac{1}{2}}{S}SOH + 2\overset{\frac{1}{2}}{S}SO_3^{2-} \quad (18)$$

$$2{}_3^-OS\overset{\frac{1}{2}}{S}SOH + 2OH^- \rightarrow 2\overset{\frac{1}{2}}{S}SO_3^{2-} + 2S(OH)_2 \quad (19)$$

$$2S(OH)_2 + 2OH^- \rightarrow HSOH + SO_3^{2-} + 2H_2O \quad (20)$$

$$HSOH + SO_3^{2-} \rightarrow SSO_3^{2-} + H_2O \quad (21)$$

$$2{}_3^-OS\overset{\frac{1}{2}}{S}S\overset{\frac{1}{2}}{S}SO_3^- + 6OH^- \rightarrow 4\overset{\frac{1}{2}}{S}SO_3^{2-} + SSO_3^{2-} + 3H_2O \quad (22)$$

The occurrence of S and SO_3^{2-} as intermediates can be proved by reaction with HCHO. Hereby the major part of SO_3^{2-} is caught, only about 25% react to form $S_2O_3^{2-}$ (Figure 5). In the case of the further inner labelled $^{35}SS_2S_2O_6^{2-}$, the activity relation comes to $S:SO_3^{2-} = 0.95:1$. This result is in good agreement with the theoretical expectation.

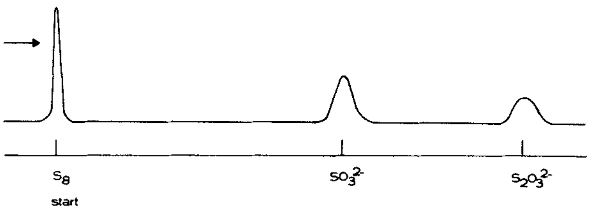

FIGURE5 Alkaline degradation of $^{35}SS_2S_2O_6^{2-}$ in presence of HCHO.
Curve of the activity distribution after 1 min reaction time.
Reaction temperature: 30°C.

The interim occurrence of $S_3O_6^{2-}$ can be explained out of the side reaction of SO_3^{2-} and $S_5O_6^{2-}$; a corresponding amount of sulfur remains as a residue. In course of the reaction this sulfur reacts with the SO_3^{2-}, which was generated during the slow alkaline hydrolysis of the $S_3O_6^{2-}$ ion. Therefore the gross equation is satisfied (Eq. 1). The overall course of the side reaction can be reproduced by the following equations:

$$2S_5O_6^{2-} + 4SO_3^{2-} \rightarrow 2S_3O_6^{2-} + 4S_2O_3^{2-} \quad (23)$$

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (24)$$

$$\frac{4}{X}\,S_X + 4SO_3^{2-} \rightarrow 4S_2O_3^{2-} \quad (25)$$

Equation 25 describes the total reaction of sulfur to $S_2O_3^{2-}$.

The obtained experimental values are in agreement with the calculated expectation values which are based on the suggested reaction mechanism (Table I).

TABLE I

Activity distribution in $^{35}S_2O_3^{2-}$ for the alkaline degradation of $S_5O_6^{2-}$

	Theoretical activity distribution		Determined activity distribution	
	S^{2-}	SO_4^{2-}	S^{2-}	SO_4^{2-}
$^{35}SS_2S_2O_6^{2-}$	0.5	0.5	0.48	0.52
$S^{35}S_2S_2O_6^{2-}$	1	0	0.98	0.02
$SS_2{}^{35}S_2O_6^{2-}$	0	1	0.03	0.97

Looking at the experimental values it has to be taken into consideration that in $S^{35}S_2S_2O_6^{2-}$, respectively $SS_2{}^{35}S_2O_6^{2-}$, a certain amount of wrong labelling is found. This is due to the wrong labelling of the purchasable starting materials $^{35}SSO_3^{2-}$ (0.91%) and $S^{35}SO_3^{2-}$ (2.8%).

4 ACKNOWLEDGEMENT

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