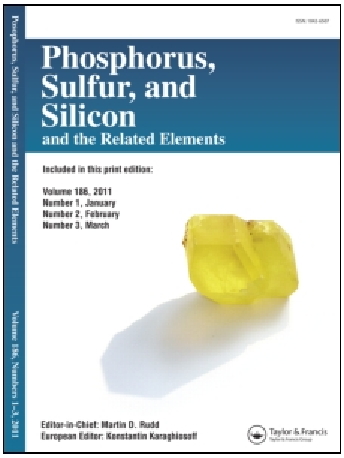

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INVESTIGATIONS ON THE SULFITE DEGRADATION OF POLYTHIONATES

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INVESTIGATIONS ON THE SULFITE DEGRADATION OF POLYTHIONATES

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Sulfite attacks pentathionate at the γ-S-atom of the sulfur chain leading to thiosulfate and tetrathionate as reaction products. Excess of sulfite leads to degradation of the intermediate tetrathionate to thiosulfate and trithionate as final products. In this paper we report on the reaction of ^{35}S-labelled tetrathionate and pentathionate with sulfite.

INTRODUCTION

The reaction[1,2] of polythionates and an excess of sulfite follows quantitatively Eq. (1). In the literature several different reaction mechanisms of the sulfite degradation are discussed.

$$S_xO_6^{2-} + (x-3)SO_3^{2-} \rightarrow S_3O_6^{2-} + (x-3)S_2O_3^{2-} \qquad (1)$$

In the case of the $S_4O_6^{2-}$ the course of the reaction is unequivocal. Nucleophilic attack of the SO_3^{2-} occurs at the β- or β'-S-atom of the chain and equimolar amounts of $S_3O_6^{2-}$ and $S_2O_3^{2-}$ are formed. The earlier assumption that sulfur splits from $S_4O_6^{2-}$ and reacts with SO_3^{2-} to form $S_2O_3^{2-}$ is further not maintainable after $^{35}SO_3^{2-}$ was used in the reaction.[3]

Due to the different chemical properties of the sulfur atoms in the chain of pentathionate several courses of the reaction are thinkable. Earlier formulations[4,5] interpret the stepwise reaction as attack of SO_3^{2-} at the sulfur atom in the chain leading to abstraction of sulfur out of the chain. Other authors[6,7] assume an exchange of the $S_2O_3^{2-}$-groups for the SO_3^{2-}-group. Nucleophilic attack of the SO_3^{2-} at the β- or β'-S-atom of the chain constitutes another possible mechanism[8–10]. The resulting instable intermediate disulfanemonosulfonate will be degradated beginning at the end of the chain.

$$^{-}O_3SS\overset{\gamma}{S}SSO_3^{-} + SO_3^{2-} \rightarrow {}^{-}O_3SS\overset{\gamma}{S}SO_3^{-} + SSO_3^{2-} \qquad (2)$$

$$^{-}O_3S\overset{\beta}{S}S\overset{\beta'}{S}SO_3^{-} + SO_3^{2-} \rightarrow {}^{-}O_3S\overset{\beta}{S}S^{-} + {}^{-}O_3S\overset{\beta'}{S}SO_3^{-} \qquad (3)$$

$$^{-}O_3S\overset{\beta}{S}S^{-} + SO_3^{2-} \rightarrow 2SSO_3^{2-} \qquad (4)$$

EXPERIMENTAL

For our investigations the high voltage ionophoresis with labelled compounds[11] is used. This method permits the determination of the reaction mixture composed of polythionates, thiosulfate and sulfite.

^{35}S-labelled polythionates (Table I) were synthesized from purchasable starting material like $Na_2{}^{35}SSO_3$, $Na_2S^{35}SO_3$ or $^{35}S_8$. The amount of the incorrect labelling in the $^{35}S_2O_3^{2-}$-molecules was determined and has been taken into account for calculations.

TABLE I

^{35}S-labelled polythionates[12]

$^{-}O_3S^{35}S^{35}SSO_3^{-}$
$^{-}O_3{}^{35}SSS^{35}SO_3^{-}$
$^{-}O_3SS^{35}SSSO_3^{-}$
$^{-}O_3S^{35}SS^{35}SSO_3^{-}$
$^{-}O_3{}^{35}SSSS^{35}SO_3^{-}$

The radioactive and inactive compounds are weighed using an ultramicrobalance and put into the cylindrical reaction vessel. Immediately after addition of 1 ml of water the vessel is thermostatic controlled. This is the starting point of the reaction.

The high voltage ionophoretic separation is performed by using paper strips as carrier material which are impregnated with the basis electrolyte (pH = 8 and HCHO). The fast moving ^{36}Cl-ion is used as reference ion. The locations of the active zones on the pherogram are determined using the paper-chromatogram-scanner. The R_B-values, determined by the curve for the distribution of the activity, serve for identification. The quantitative evaluation is made directly at the pherogram using the liquid scintillation method. The random measurement error is influenced mainly by the statistics of the radioactive decay.

RESULTS AND DISCUSSION

Sulfite Degradation of the Tetrathionate

The attack occurs at one of the chemical equivalent sulfur atoms in the chain, leading to the cleavage of the bond connecting them. Therefore equimolar amounts of $S_2O_3^{2-}$ and $S_3O_6^{2-}$ are formed and the activity ratio is 1 : 1 both with outer or inner-S labelling of the $S_4O_6^{2-}$. Table II shows a comparison of theoretical and experimentally determined activity ratios.

TABLE II
Activity ratio $S_2O_3^{2-}$:$S_3O_6^{2-}$ for the SO_3^{2-} degradation of the $S_4O_6^{2-}$

	$^{35}SS_2O_6^{2-}$	$S_2{}^{35}S_2O_6^{2-}$
Theoretical activity ratio	1 : 1	1 : 1
Determined activity ratio	1 : 1	0.99 : 1

Sulfite Degradation of the Pentathionate

Using an excess of SO_3^{2-} the degradation of $S_5O_6^{2-}$ proceeds in several steps to form quantitatively $S_2O_3^{2-}$ and $S_3O_6^{2-}$ as end products (Eq. 1). Thereby the attack occurs at the γ-S atom of the molecule, leading to cleavage between the β- and the γ-S atom. Calculation of the activity ratio is carried out with three kinds of specifically labelled $S_5O_6^{2-}$ (Eqs. 5–13). The starting activity is considered to be 1.

Reaction Mechanism A

$${}_3^{-}OSS\overset{1}{S}SSO_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}OSS\overset{1}{S}SO_3^{-} + SSO_3^{2-} \qquad (5)$$

$${}_3^{-}OSS\overset{1}{S}SO_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}OS\overset{\frac{1}{2}}{S}SO_3^{-} + \overset{\frac{1}{2}}{S}SO_3^{2-} \qquad (6)$$

$${}_3^{-}OSS\overset{1}{S}SSO_3^{-} + 2SO_3^{2-} \rightarrow {}_3^{-}OS\overset{\frac{1}{2}}{S}SO_3^{-} + 2\overset{\frac{1}{2}}{S}SO_3^{2-} \qquad (7)$$

$${}_3^{-}O\overset{\frac{1}{2}}{S}SS\overset{\frac{1}{2}}{S}SO_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}OS\overset{\frac{1}{2}}{S}SSO_3^{-} + \overset{\frac{1}{2}}{S}SO_3^{2-} \qquad (8)$$

$${}_3^{-}OS\overset{\frac{1}{2}}{S}SSO_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}O\overset{\frac{1}{4}}{S}SSO_3^{-} + \overset{\frac{1}{4}}{S}SO_3^{2-} \qquad (9)$$

$${}_3^{-}O\overset{\frac{1}{2}}{S}SSS\overset{\frac{1}{2}}{S}O_3^{-} + 2SO_3^{2-} \rightarrow {}_3^{-}OS\overset{\frac{1}{4}}{S}SO_3^{-} + 2\overset{\frac{3}{4}}{S}SO_3^{2-} \qquad (10)$$

$${}_3^{-}O\overset{\frac{1}{2}}{S}SSS\overset{\frac{1}{2}}{S}O_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}O\overset{\frac{1}{2}}{S}SSSO_3^{-} + S\overset{\frac{1}{2}}{S}O_3^{2-} \qquad (11)$$

$${}_3^{-}O\overset{\frac{1}{2}}{S}SSSO_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}O\overset{\frac{1}{4}}{S}SSO_3^{-} + S\overset{\frac{1}{4}}{S}O_3^{2-} \qquad (12)$$

$${}_3^{-}O\overset{\frac{1}{2}}{S}SSS\overset{\frac{1}{2}}{S}O_3^{-} + 2SO_3^{2-} \rightarrow {}_3^{-}O\overset{\frac{1}{4}}{S}SSO_3^{-} + 2S\overset{\frac{3}{4}}{S}O_3^{2-} \qquad (13)$$

If the attack of SO_3^{2-} would occur at the β- or β′-S atom of the chain, this is followed by cleavage between the γ- and β-S atom. As an intermediate, disulfanemonosulfonate is formed which is degradated by excess SO_3^{2-} beginning at the chain end and leading to $S_2O_3^{2-}$. The calculation of the activity ratio is shown for inner-S labelled $S_5O_6^{2-}$ only (Eqs. 14–16). The total activity is found in the $S_2O_3^{2-}$ ion.

Reaction Mechanism B

$${}_3^{-}OSS\overset{1}{S}SSO_3^{-} + SO_3^{2-} \rightarrow {}_3^{-}OSSSO_3^{-} + \overset{1}{S}SSO_3^{2-} \qquad (14)$$

$$\overset{1}{S}SSO_3^{2-} + SO_3^{2-} \rightarrow \overset{1}{S}SO_3^{2-} + SSO_3^{2-} \qquad (15)$$

$${}_3^{-}OSS\overset{1}{S}SSO_3^{-} + 2SO_3^{2-} \rightarrow {}_3^{-}OSSSO_3^{-} + 2\overset{1}{S}SO_3^{2-} \qquad (16)$$

The reactions were performed at 0°C using a tenfold excess of SO_3^{2-} to exclude isotopic exchange[13] between $S_2O_3^{2-}$, $S_4O_6^{2-}$ and $S_5O_6^{2-}$. The experimental results (Table III) confirm reaction mechanism A.

At the chosen reaction conditions isotopic exchange between $S_3O_6^{2-}$ and $S_2O_3^{2-}$ is negligible.

TABLE III
Activity ratio $S_2O_3^{2-}$: $S_3O_6^{2-}$ for the SO_3^{2-} degradation of $S_5O_6^{2-}$

	Theoretical activity ratio		Determined activity ratio
	A	B	
$S^{35}S_2S_2O_6^{2-}$	3 : 1	1 : 1	2.96 : 1
$^{35}SS_2S_2O_6^{2-}$	1 : 1	1 : 0	1.02 : 1
$SS_2{}^{35}S_2O_6^{2-}$	3 : 1	1 : 1	3.00 : 1

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