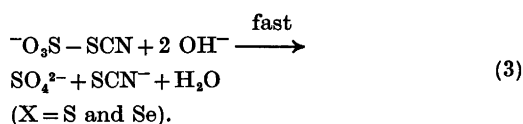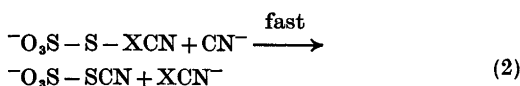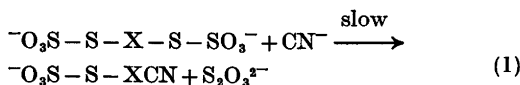# Studies on Polythionates. II. The Action of the Cyanide Ion on the Pentathionate Ion and the Selenopentathionate Ion in Acetonitrile

TOR AUSTAD

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

The pentathionate-cyanide reaction and the selenopentathionate-cyanide reaction have been studied kinetically in acetonitrile. Mechanisms are suggested, which involve substitution at the central sulfur atom of the pentathionate ion, and at the selenium atom of the selenopentathionate ion. The activation parameters of the pentathionate-cyanide reaction, $\Delta H^* = 6.3$ kcal/mol, $\Delta S^* = -40$ cal/mol deg, and of the selenopentathionate-cyanide reaction, $\Delta H^* = 1.7$ kcal/mol, $\Delta S^* = -48$ cal/mol deg, indicate a more tight and stabilized transition state in the case of the selenopentathionate-cyanide reaction.

Foresti[1] in 1934 performed a kinetic study on the pentathionate-cyanide reaction, but so far no kinetic experiments have been made on the reaction between ionic cyanide and the selenopentathionate ion. Because of the similarity of these two reactions in aqueous solution, Foss[2] has proposed the mechanism to be the same in both cases. He proposed an initial ionic displacement of thiosulfate by the cyanide ion, eqn. (1), in the intermediate step ionic displacement of thiocyanate (selenocyanate) by a second cyanide ion, eqn. (2), and in the final step an ionic displacement of thiocyanate by hydroxyl ion, eqn. (3).

$$^-O_3S-S-X-S-SO_3^- + CN^- \xrightarrow{\text{slow}}$$
$$^-O_3S-S-XCN + S_2O_3^{2-} \qquad (1)$$

$$^-O_3S-S-XCN + CN^- \xrightarrow{\text{fast}}$$
$$^-O_3S-SCN + XCN^- \qquad (2)$$

$$^-O_3S-SCN + 2\ OH^- \xrightarrow{\text{fast}}$$
$$SO_4^{2-} + SCN^- + H_2O \qquad (3)$$

$(X = S$ and Se$)$.

To get some further information about the postulated reaction intermediates, the sulfonated sulfur thiocyanate (selenocyanate) ion, $^-O_3SSXCN$, and the thiocyanatosulfonate ion, $^-O_3SSCN$, this paper reports a kinetic study on these reactions in the dipolar aprotic solvent acetonitrile. In such a medium no hydrolysis can take place, and one might be able to detect some of the reaction intermediates. Tetraphenylarsonium pentathionate and tetraphenylarsonium selenopentathionate were used as the substrates, and tetraphenylphosphonium cyanide was used as the nucleophilic reagent. These salts were found to be completely dissociated in acetonitrile in the concentration range used in the kinetic runs.

The pentathionate-cyanide reaction. Product analysis of the pentathionate-cyanide reaction in acetonitrile showed that when reacting 1 mol of ionic pentathionate with 2 mol of cyanide ions, 1 mol of ionic thiocyanate and 1 mol of ionic thiosulfate were formed. The reaction, followed by measuring the formation of ionic thiocyanate, showed good second-order kinetics up to three half-lifes (Table 1). A mechanism similar to the one postulated by Foss[3] in aqueous solution with a first rate determining step according to eqn. (1), followed by a fast step, eqn. (2), appears to be in accordance with these observations. The thiocyanatosulfonate

Table 1. Rate data and activation parameters in the reaction between ionic pentathionate and selenopentathionate with the cyanide ion in acetonitrile.

Reaction	15 °C	25 °C	35 °C	45 °C	ΔH^* kcal/mol	ΔS^* cal/mol	ΔG^* kcal/deg mol
$S_5O_6{}^{2-} + CN^{-a}$	0.150	0.250	0.335		6.3	-40	18.2
$SeS_4O_6{}^{2-} + CN^{-b}$		20.6	22.8	25.9	1.7	-48	16.0

[a] Ionic strength $\mu = 1.25 \times 10^{-2}$. [b] Ionic strength $\mu = 9.88 \times 10^{-3}$.

ion, $^-O_3SSCN$, thus appears to be stable during the kinetic runs.

With excess ionic cyanide (about six times the concentration of ionic pentathionate) a second mol of ionic thiocyanate was formed, but this second mol of ionic thiocyanate was formed at a much slower rate than the first mol. Excess cyanide ions may react with the thiocyanatosulfonate ion to give ionic cyanosulfonate and thiocyanate, eqn. (4).

$$^-O_3S - SCN + CN^- \xrightarrow{k_2'} {}^-O_3SCN + SCN^- \quad (4)$$
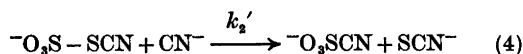
Eqn. (4) is proposed to be the second step in the tetrathionate-cyanide reaction in acetonitrile.[4] The rate of this reaction, eqn. (4), has been followed at 30 °C, and the reaction showed good second order kinetic up to two half-lifes. The second order rate constant was observed to be $k_2' = 2.95 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ at the ionic strength $\mu = 1.7 \times 10^{-2}$. The thiocyanatosulfonate-cyanide reaction thus appears to be 10 times faster than the tetrathionate-cyanide reaction[4] and about 10 times slower than the pentathionate-cyanide reaction, in acetonitrile.

The selenopentathionate-cyanide reaction. The reaction between the selenopentathionate ion and the cyanide ion in acetonitrile was much faster than the corresponding pentathionate-cyanide reaction. The rate could not be followed by applying IR, and the stopped-flow technique had to be used. The second order rate constants are listed in Table 1.

IR and iodometric analysis of the products showed that 1 mol of ionic selenopentathionate reacted with 2 mol of cyanide ions to give 1 mol of ionic selenocyanate and 1 mol of ionic thiosulfate. Only small amounts of ionic thiocyanate could be detected immediately after the

reaction had taken place. These observations are in accordance with the data obtained for the pentathionate-cyanide reaction. Hence, the first two steps of the mechanism suggested by Foss[3] appear to be verified for the selenopentathionate-cyanide reaction.
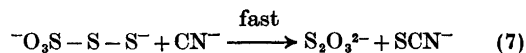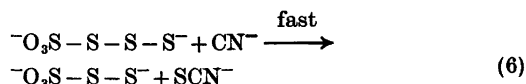
When using excess ionic cyanide 1 mol of ionic thiocyanate was formed according to eqn. (4). The rate of this step is about 10^{-3} times lower than the rate constant of the first step.

DISCUSSION

With regard to the pentathionate-cyanide reaction, Schmidt[5] once proposed a nucleophilic attack by the cyanide ion at one of the sulfonyl sulfur atoms, displacing a sulfanemonosulfonate ion in the rate determining step,

$$^-O_3S - S - S - S - SO_3^- + CN^- \xrightarrow{\text{slow}}$$
$$^-O_3S - S - S - S^- + {}^-O_3SCN \quad (5)$$
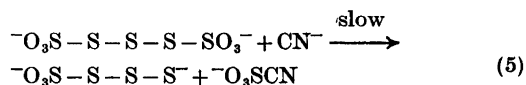
followed by a successive reaction by two other cyanide ions, eqns. (6) and (7).

$$^-O_3S - S - S - S^- + CN^- \xrightarrow{\text{fast}}$$
$$^-O_3S - S - S^- + SCN^- \quad (6)$$

$$^-O_3S - S - S^- + CN^- \xrightarrow{\text{fast}} S_2O_3{}^{2-} + SCN^- \quad (7)$$

According to this mechanism, 3 mol of cyanide ions have to react with 1 mol of ionic pentathionate to give 2 mol of ionic thiocyanate. Such a mechanism is not in accordance with the kinetic results in this work.

A third mechanism, that may be in accordance with the rate data, involves a nucleophilic substitution at the sulfur atom number 2, displacing the sulfanemonosulfonate ion, $^-O_3SSS^-$.

$$^-O_3S-S-S-S-SO_3^- + CN^- \xrightarrow{\text{slow}}$$

$$^-O_3S-S-S-S^- + {}^-O_3S-SCN \quad (8)$$
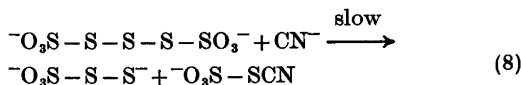
In the intermediate step a second cyanide ion might rapidly react with the sulfanemonosulfonate ion, eqn. (9).

$$^-O_3S-S-S^- + CN^- \xrightarrow{\text{fast}} S_2O_3^{2-} + SCN^- \quad (9)$$
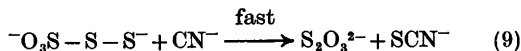
Recently, Schmidt [6] has postulated the sulfur atom number 2 to be the most electrophilic centre of the higher polythionates. His hypothesis was based on polarization of the divalent sulfur — sulfur bonds due to the free p electrons. Harpp,[7] however, has recently shown the polarization effects to be secondary to the basicity of the leaving group. It is generally accepted that the basicity of $^-O_3SS_x^-$ increases with increasing values of x.[8] In this way the thiosulfate ion should be the most easily displaced ion in the first step.
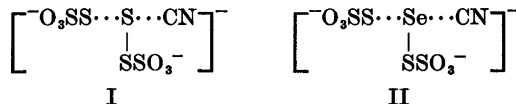
The facts that ionic pentathionate reacts with piperidine to form monosulfur dipiperidide [9] and 2 mol of ionic thiosulfate, and selenopentathionate reacts with ionic dimethyldithiocarbamate [10] to give selenium bis(dimethyldithiocarbamate) and 2 mol of ionic thiosulfate, seem to justify that the electrophilic centre of the pentathionate ion is the sulfur atom number 3, and that the selenium atom is the electrophilic centre of the selenopentathionate ion.

Supposing the mechanism of the two reactions to be the same, a first step according to eqn. (8) would probably give much the same values of the enthalpy and the entropy of activation in the two cases. From Table 1 this is not in accordance with the experimental data.

When considering the significance of the activation parameters, which are presented in Table 1, it is seen that the selenopentathionate-cyanide reaction is characterized by a much smaller ΔH^* value, 4.6 kcal/mol, than the pentathionate-cyanide reaction. However, the entropy of activation of the selenopentathionate-cyanide reaction is 8 cal/mol deg. more negative than the entropy of activation of the pentathionate-cyanide reaction. The free energy of activation ΔG^* is seen to be 2.2 kcal/mol lower in the case of the selenopentathionate-cyanide reaction.

It is reasonable to suppose the geometry of

the transition state of the pentathionate- and the selenopentathionate-cyanide reaction to be as depicted in I and II, respectively.

$$\left[\begin{array}{c} ^-O_3SS\cdots S\cdots CN \\ | \\ SSO_3^- \end{array} \right]^- \qquad \left[\begin{array}{c} ^-O_3SS\cdots Se\cdots CN \\ | \\ SSO_3^- \end{array} \right]^-$$

$$\text{I} \qquad\qquad\qquad \text{II}$$

The entropies of activation indicate that transition state II is more tight than transition state I. Furthermore, the enthalpies of activation point to a more stabilized transition in the case of II than I.

The timing of covalency changes for substitution at sulfenyl sulfur has been found to resemble that for an S_N2 substitution at sp^3 carbon.[11] The participation of the d orbitals of the sulfur atom in substitution at divalent sulfur is thus small.[11] Systematic work on nucleophilic attack at divalent selenium is not available in the literature.

Foss [12] has proposed the bonding of the transition state in nucleophilic attack at divalent sulfur and selenium to be a three-centre four-electron type. The instability of the trithiocyanate ion [13] relative to the triselenocyanate ion,[14] seems to support the explanation of the activation parameters outlined above.

EXPERIMENTAL

Acetonitrile, tetraphenylphosphonium cyanide, and tetraphenylarsonium cyanide were purified as reported previously.[4] Potassium pentathionate was prepared by the method of Goehring and Feldmann.[15] Sodium selenopentathionate was prepared by the method described by Foss.[16]

Tetraphenylarsonium pentathionate was precipitated from an aqueous solution of potassium pentathionate with tetraphenylarsonium chloride in nearly quantitative yield, and purified in the same way as reported for tetraphenylarsonium tetrathionate.[4] Dec. 250 °C. (Found: C 56.70; H 4.03; S 15.85. Calc. for $C_{48}H_{40}O_6S_5As_2$: C 56.30; H 3.90; S 15.85.)

Tetraphenylarsonium selenopentathionate was made in the same way and purified in the same manner. Dec. 245 °C. (Found: C 53.87; H 3.91; S 12.50. Calc. for $C_{48}H_{40}O_6S_4SeAs_2$: C 53.80; H 3.74; S 11.98.)

Iodometric analysis. The amount of ionic thiosulfate formed in the pentathionate-cyanide reaction in acetonitrile was determined as follows. Approx. 0.05 g tetraphenylarsonium pentathionate was dissolved in 3 ml acetonitrile. 5 ml of 0.1 M solution of tetraphenylarsonium

cyanide in acetonitrile was added and the solution was set aside for 15 min. A solution containing 1 ml of 40 % formaldehyde, 3 ml of 1 M sodium perchlorate and 10 ml of water was then added, whereupon tetraphenylarsonium perchlorate precipitated. The precipitated salt was removed by filtration and carefully washed with about 20 ml of water. Prior to the titration with 10^{-2} N iodine solution, 10 ml of 10 % acetic acid, 0.2 g potassium iodide and 2 ml of starch solution were added. The yield of ionic thiosulfate was found to be $92-93$ %, based on the amount of ionic pentathionate used.

With regard to the iodometric analysis of the selenopentathionate-cyanide reaction in acetonitrile 20 ml of 10 % acetic acid and 1 g of potassium iodide were added prior to the titration. The amount of ionic thiosulfate was found to be $89-90$ % based on the amount of ionic selenopentathionate used.

Procedure for the kinetic runs. The rate of the reaction between ionic pentathionate and the cyanide ion was determined by measuring the amount of ionic thiocyanate, using IR liquid cells with a path length of 1 mm. The second order kinetic plots were analysed according to the rate equation

$$dx/dt = k_2 (a-x)(b-2x)$$

where x is the concentration of ionic thiocyanate and a and b are the initial concentrations of ionic pentathionate and cyanide, 2.5×10^{-3} M and 5.0×10^{-3} M, respectively.

The rate of the thiocyanatosulfonate-cyanide reaction was determined by measuring the rate of formation of the second mol of ionic thiocyanate formed in the pentathionate-cyanide reaction, applying the initial concentrations of ionic pentathionate and cyanide, 2.0×10^{-3} M and 1.2×10^{-2} M, respectively. The kinetic plots were analysed according to the equation

$$dx/dt = k_2' (a-x)(b-x)$$

where x is the concentration of the second mol of ionic thiocyanate formed and a and b are the initial concentrations of ionic thiocyanatosulfonate and cyanide, 2.0×10^{-3} and 8.0×10^{-3} M, respectively.

The pseudo first-order rate constants of the selenopentathionate-cyanide reaction were calculated from stoppered-flow experiments at 320 nm, using 1.515×10^{-3} M tetraphenylarsonium selenopentathionate solution and 1.52×10^{-2} M tetraphenylphosphonium cyanide solution.

The second-order rate constants were all reproduced with an accuracy better than ± 3 %.

Conductivity measurements. Applying $\lambda^0{}_{Ph_4As^+} = 55.8$ ohm^{-1} cm^{-2} mol^{-1} [17] the equivalent conductivities at infinite dilution in acetonitrile at 25 °C were found to be

$\lambda^0{}_{(Ph_4As)_2S_5O_6} = 173$ ohm^{-1} cm^{-2} mol^{-1},

$\lambda^0{}_{S_5O_6{}^{2-}} = 61.4$ ohm^{-1} cm^{-2} mol^{-1}

From the plot, λ *versus* $\sqrt{c}$, tetraphenylarsonium pentathionate appeared to be completely dissociated in acetonitrile.

The IR measurements were performed with a Unicam SP 200 G Infrared Spectrophotometer, and the stopped-flow measurements were performed with a Durrum Stopped-Flow Model D-110.

The conductivity measurements were performed on a conductivity cell, type CDC 304 (immersion type) with a cell constant 1.00 cm $\pm$ 10 %.

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