

Studies on Polythionates. IV. The Action of the Cyanide Ion on the Selenotrithionate Ion and the Diselenotetrathionate Ion in Acetonitrile

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The reactions of the selenotrithionate ion and the diselenotetrathionate ion with ionic cyanide have been studied in acetonitrile. Kinetic studies showed both of the reactions to be of second order, first order in each of the reactants. Reaction mechanisms have been worked out that conform favourably with each other.

The electrophilic nature of divalent selenium and sulfur toward ionic cyanide is discussed by comparing the activation parameters.

As part of our work concerning polythionates in dipolar aprotic solvents, this paper reports a kinetic study on the selenotrithionate-cyanide reaction and the diselenotetrathionate-cyanide reaction in acetonitrile. Previous work has shown that ionic cyanide reacts with the tetrathionate ion, but it does not react with the trithionate ion even in boiling acetonitrile.¹

With regard to the cyanide ion as the nucleophilic agent, it is further known that the activation energy for nucleophilic attack at divalent selenium is lower than the activation energy for nucleophilic substitution at the corresponding sulfur compound.² The purpose of this work was therefore to get some more knowledge about nucleophilic substitution at divalent selenium and to determine the reaction mechanisms of the two reactions mentioned above.

The reactions are studied in acetonitrile to prevent hydrolysis of the reaction intermediates. In this way the study of the mechanisms became easier, and one was able to detect some of the reaction intermediates. Tetraphenylarsonium salts of the polythionates were used as the substrates, and tetraphenylphosphonium cyanide was used as the nucleophilic agent.

To understand the reaction mechanisms, it appears necessary to present some notes dealing with the sulfite ion and the selenosulfate ion in dipolar aprotic solvents.

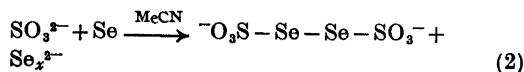
Notes on the sulfite ion and the selenosulfate ion. In aqueous solution, ionic sulfite is slowly oxidized to ionic sulfate, which makes quantitative determinations by means of iodometric titrations difficult. In acetonitrile, however, tetraphenylarsonium sulfite is nearly immediately oxidized to the corresponding sulfate salt, probably due to traces of oxygen in the solvent. Therefore, when working with ionic sulfite in acetonitrile, the solvent has to be carefully flushed with nitrogen prior to use.

In protic solvents ionic sulfite reacts with elemental selenium, and the equilibrium (1) is set up.

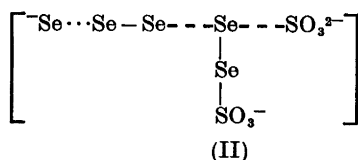
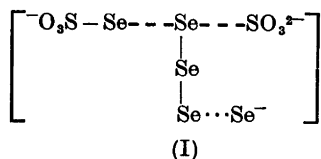


The reaction between the sulfite ion and sulfur S_8 has been formulated as an initial attack on the sulfur ring with ring opening followed by a series of displacements of ionic thiosulfate by the sulfite ion.³ In view of the similarity of the sulfite-selenium reaction and the sulfite-sulfur reaction, it seems reasonable to assume that the mechanism is the same in both cases.

In acetonitrile free from oxygen, the sulfite ion reacts with elemental selenium in a way different from the one depicted by eqn. (1). The products were found to be ionic diselenotetrathionate and probably some unidentified polyselenide ions, Se_x^{2-} , eqn. (2).

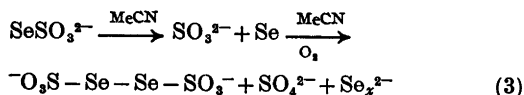


The second step of the sulfite-selenium reaction in acetonitrile probably is different from what happens in aqueous solution, where the selenosulfate ion appears to be the leaving group.



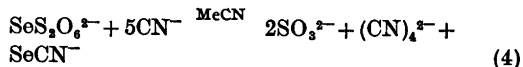
With regard to the two transition states visualized by (I) and (II), the transition state (I) thus appears to be favoured in the protic solvents, while the transition state (II) probably is more favourable in acetonitrile. The poor solvation of the sulfonate group by acetonitrile may explain this change in the leaving group when going from a protic to a dipolar aprotic solvent.

No liberation of red selenium is observed when tetraphenylarsonium selenosulfate is dissolved in acetonitrile. However, the solution turned yellowish-green, and ionic diselenotetrathionate, sulfate and probably some polyselenide ions were formed.⁴ The reaction may take place as depicted schematically in eqn. (3).



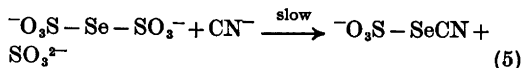
The selenotrithionate-cyanide reaction. The selenotrithionate ion was found to react very slowly with ionic cyanide in acetonitrile. The rate of this reaction was followed by measuring the formation of ionic selenocyanate by means of IR. The reaction was observed to be of second order, first order in each of the reactants. Furthermore, the kinetic plots indicate that 1 mol of ionic selenotrithionate consumes 5 mol of cyanide ions to give 1 mol of ionic selenocyanate.

On these observations the following stoichiometry is postulated, eqn. 4.

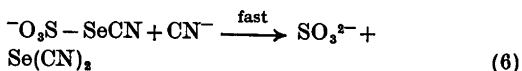


Due to traces of oxygen in the acetonitrile solution, the sulfite ion is, however, immediately oxidized to ionic sulfate.

With regard to the mechanism of the reaction, it appears likely that the first step involves a nucleophilic attack by the cyanide ion at the selenium atom, displacing the sulfite ion, eqn. 5.



The selenocyanato sulfonate ion, $\text{O}_3\text{S}-\text{SeCN}$, is then susceptible to nucleophilic attack by a second cyanide ion. The electrophilic centre appears to be the selenium atom, and ionic sulfite is displaced, eqn. 6.



It is further known that selenium dicyanide reacts rapidly with 3 mol of cyanide ions in acetonitrile, probably according to eqn. 7.⁵



This reaction mechanism is consistent with the mole ratio of the reactants observed in the kinetic runs. The second order rate constants and the activation parameters are presented in Table 1.

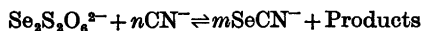
The reaction mechanism outlined above gains support from a study of the diselenotetrathionate-cyanide reaction.

The diselenotetrathionate-cyanide reaction. Potassium diselenotetrathionate was synthesized

Table 1. Second order rate constants and activation parameters for the selenotrithionate-cyanide reaction in acetonitrile ($\mu = 6.0 \times 10^{-2}$).

$k_2 \times 10^5 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$		
20 °C	3.42	3.33
30 °C	7.15	6.85
45 °C	10.1	9.70
ΔH^* (kcal/mol)	9.2	
ΔS^* (cal/mol deg.)	-47	
ΔF^* (kcal/mol)	23.3	

Table 2. Verification of the stoichiometry of the diselenotetrathionate-cyanide reaction in acetonitrile.

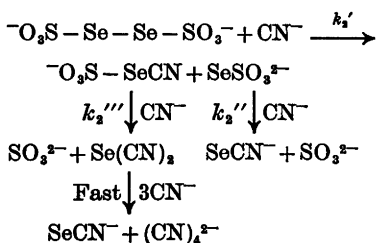


<i>n</i>	<i>m</i>	Rate
1	$\frac{1}{2}$	fast
2	1	fast
6	2	1st mol fast, 2nd mol slow

for the first time by Janickis and co-workers in 1954.⁶ The compound was made by oxidation of selenosulfate (K_2SeSO_5) with iodine or hydrogen peroxide. In this work, tetraphenylarsonium diselenotetrathionate has been synthesized by the action of the sulfite ion on elemental selenium in acetonitrile, which was carefully flushed with nitrogen prior to use.

The reaction between ionic diselenotetrathionate and the cyanide ion was very fast in acetonitrile. The stoichiometry of the reaction was examined by varying the cyanide concentration, and measuring the formation of ionic selenocyanate by means of IR. The results are listed in Table 2.

According to Table 2, the diselenotetrathionate ion consumes 2 mol of cyanide ions to give 1 mol of ionic selenocyanate in a very fast reaction. On the addition of more ionic cyanide, a second mol of ionic selenocyanate started to form. However, this second mol of selenocyanate ion was formed at a much slower rate than the first mol, and furthermore, the concentration of the cyanide ions had to be six times the concentration of ionic diselenotetrathionate to give 2 mol of ionic selenocyanate quantitatively. According to these observations, the reaction in Scheme 1 may be written.



Scheme 1.

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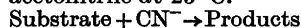
The first step probably involves a nucleophilic substitution at one of the selenium atoms of the polythionate ion, and ionic selenosulfate is displaced. Due to the instability of the selenosulfate ion in acetonitrile, it reacts immediately with a second cyanide ion to give ionic sulfite and selenocyanate. An approximate value of the second order rate constant of the first step, k_2' , has been obtained using the stopped-flow technique. The rate was followed at $\lambda = 300$ nm, and the results are presented in Table 3. The fact that 1 mol of each of the reactants gave $\frac{1}{2}$ mol of ionic selenocyanate, Table 2, appears to justify that $k_2' \ll k_2''$.

The selenocyanatosulfonate ion, $^{-}\text{O}_3\text{SSeCN}$, formed in the first step, consumes 4 mol of cyanide ions at a rate that is much slower than the rate of the first step. The rate of the selenocyanatosulfonate-cyanide reaction was followed by measuring the formation of the second mol of ionic selenocyanate by means of IR. When analysing the rate according to the assumption that 1 mol of ionic selenocyanatosulfonate reacts with 4 mol of cyanide ions, the kinetic plots showed excellent second order kinetics, up to three half lives, Table 3.

DISCUSSION

The reaction mechanism postulated for the selenotrithionate-cyanide reaction appears to be supported by the rate experiments of the diselenotetrathionate-cyanide reaction. From the rate constants presented in Tables 1 and 3 it is seen that $k_2(\text{SeS}_2\text{O}_6^{2-} + \text{CN}^-) \ll k_2(^{-}\text{O}_3\text{SSeCN} + \text{CN}^-) \ll k_2(\text{Se}_2\text{S}_2\text{O}_6^{2-} + \text{CN}^-)$ which is in ac-

Table 3. Second order rate constants between different substrates and the cyanide ion in acetonitrile at 25 °C.



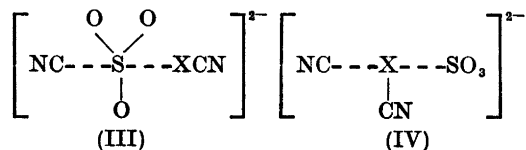
Substrate	k_2 , $\text{M}^{-1} \text{s}^{-1}$	μ
$^{-}\text{O}_3\text{S}-\text{Se}-\text{Se}-\text{SO}_3^{-}$	2500	6.28×10^{-3}
$^{-}\text{O}_3\text{S}-\text{S}-\text{S}-\text{SO}_3^{-}$	2.90×10^{-2a}	2.55×10^{-2a}
$^{-}\text{O}_3\text{S}-\text{SeCN}$	1.92×10^{-1}	9.0×10^{-3}
	2.01×10^{-1}	9.0×10^{-3}
$^{-}\text{O}_3\text{S}-\text{SCN}$	2.95×10^{-2b}	1.7×10^{-2b}

^a Ref. 1. ^b Ref. 2; 30 °C.

cordance with the reaction mechanisms outlined above.

A first step involving nucleophilic attack at one of the sulfonyl sulfur atoms of the selenotrichionate ion, displacing ionic selenosulfate, can hardly be made to fit the stoichiometry of the reactants that was experimentally observed.

In acetonitrile the thiocyanatosulfonate ion, $^-O_3SSCN$, which is believed to be an intermediate in other polythionate-cyanide reactions, probably is attacked by ionic cyanide at the sulfonyl sulfur in an S_N2 reaction to displace ionic thiocyanate,³ Table 3. With regard to the corresponding step of the selenocyanatosulfonate-cyanide reaction, the nucleophilic attack has to take place at the divalent selenium atom, otherwise the mol ratio of the reactants will not be in accordance with the experiments.



The transition state (III) for the intermediate step is thus believed to be the most favourable one for $X=S$, and the transition state (IV) for $X=Se$. The energy of activation for nucleophilic substitution at divalent selenium by the cyanide ion is found to be much lower than the energy of activation for the analogous reaction at divalent sulfur.³ The change of the electrophilic positions in the thiocyanatosulfonate ion and the selenocyanatosulfonate ion thus appears reasonable. Furthermore, the more negative charge probably found on the sulfonate group of the selenocyanatosulfonate ion relative to that of the thiocyanatosulfonate ion, may lower the electrophilic nature of the sulfonyl sulfur of the former.

The activation parameters of the selenotrichionate-cyanide reaction are presented in Table 1. From the activation parameters of the selenopentathionate-cyanide reaction previously obtained ($\Delta H^* = 1.7$ kcal/mol, $\Delta S^* = -48$ cal/mol deg.),³ it is seen that the difference in the enthalpy of activation is responsible for the large difference in the rate constants, by a factor of 10^4 .

The accumulation of three negative charges in a small volume near the reactive position may

be responsible for the relatively large value of ΔH^* in the selenotrichionate-cyanide reaction. The electrostatic repulsion between the two negatively charged sulfonate groups may work against the formation of the T-shaped transition state. The relatively smaller ability of the sulfonyl sulfur to participate in a three-centre four-electron bonding system appears to explain why the trithionate ion does not react with the cyanide ion in acetonitrile, while selenotrichionate reacts, albeit slowly. (The value of the enthalpy of activation probably is too high).

With regard to the diselenotetrathionate-cyanide reaction, it is seen from Table 3 that this reaction is about 10^6 times faster than the analogous tetrathionate-cyanide reaction in acetonitrile. Due to the low accuracy of the rate constant of the diselenotetrathionate-cyanide reaction, activation parameters of this reaction have not been calculated. However, previous work³ indicates that the great difference in the rate constants is caused by a relatively lower energy of activation of the diseleno-tetrathionate-cyanide reaction.

EXPERIMENTAL

Acetonitrile and tetraphenylphosphonium cyanide were purified as reported.¹

Tetraphenylarsonium selenotrichionate was precipitated from an aqueous solution of potassium selenotrichionate⁷ by means of tetraphenylarsonium chloride in nearly quantitative yield. The product was recrystallized from acetonitrile by adding acetone. Dec. 245 °C. (Found: C 56.54; H 3.86; S 6.63. Calc. for $C_{24}H_{20}O_5S_2SeAs_2$: C 57.34; H 3.98; S 6.38.)

Tetraphenylarsonium sulfite 10.5 g (2.06×10^{-2} mol) of tetraphenylarsonium iodide was dissolved in 150 ml absolute methanol. 7.0 g freshly prepared dry silver sulfite was added, and the reaction mixture was left stirring at room temperature for 2 h. After filtration, the solvent was removed *in vacuo*. The residue was dissolved in 30 ml methanol and once more filtered to remove traces of elemental silver. On the addition of about 250 ml diethyl ether, an oily precipitate appeared. On standing in a refrigerator over night the product crystallized. Yield, 7.0 g or 82 %, based on the amount of tetraphenylarsonium iodide used.

Iodometric analysis of tetraphenylarsonium sulfite showed 3.9 % smaller value than the theoretical one.² If, however, the composition of the salt is $(Ph_4As)_2SO_3 \cdot 2H_2O$, the iodometric results agree with the theoretical value.

Oxidation of ionic sulfite in acetonitrile. 0.0480 g tetraphenylarsonium sulfite was dissolved in

6 ml of acetonitrile. After standing for 5 min in an open beaker, iodometric analysis showed that the solution did not contain any ionic sulfite. The only product isolated was tetraphenylarsonium sulfate.

Tetraphenylarsonium diselenotetrathionate. To a mixture containing 2.0 g grey selenium and 20 ml acetonitrile, which was carefully flushed with dry nitrogen, was added 2.0 g of tetraphenylarsonium sulfite. The temperature was raised to 50°C and the reaction mixture acquired a deep green colour. After stirring for about 1 h, excess selenium was filtered off. The solvent was removed *in vacuo* and the residue was washed with 20 ml acetone. Most of the colour then transferred to the mother liquor. Afterwards the product was dissolved in 10–15 ml of acetonitrile and 100 ml of acetone was added to this yellowish–green solution, whereupon the salt crystallized. The yield was 0.70 g, or 59 % based on the amount of tetraphenylarsonium sulfite used.

Pure material was finally obtained by recrystallization from 10 ml warm acetonitrile. Yield, 0.35 g. Dec. 230 °C. (Found: C 52.41; H 3.54; S 6.48. Calc. for $C_{48}H_{40}O_6S_2Se_2As_2$: C 52.70; H 3.66; S 5.88.)

Kinetic experiments

The rate of the selenotrithionate-cyanide reaction was followed by measuring the formation of ionic selenocyanate applying IR. The kinetic plots were calculated by means of the rate equation:

$$dx/dt = k_1(a-x)(b-5x)$$

where x is the concentration of ionic selenocyanate, and a and b are the concentrations of ionic selenotrithionate and cyanide, 8.0×10^{-3} and 4.0×10^{-3} M, respectively.

The rate of the first step of the diselenotetrathionate-cyanide reaction was determined by stopped-flow measurements. Due to absorption of the onium ion, the rate constant could only be approximately determined by measuring the disappearance of the absorption of the diselenotetrathionate ion at $\lambda = 300$ nm. Solutions containing 1.0×10^{-3} M of substrate and 9.56×10^{-3} M of the nucleophile were used.

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

$$x/[a(a-x)] = 4 k_1'''t$$

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where x is the concentration of the second mol of ionic selenocyanate and a is the initial concentration of the selenocyanato sulfonate ions, 2.0×10^{-3} M.

The rate constants of the selenotrithionate-cyanide reaction and the selenocyanatosulfonate-cyanide reaction were reproduced with an accuracy better than ± 5 %.

The IR measurements were performed on a SP 200 G Infrared Spectrophotometer applying 0.1 cm liquid cells, and the stopped-flow measurements were performed with a Durrum Stopped-Flow Model D-110.

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