The Reaction between $X(CN)_2$ (X = S, Se, and Te) and the Cyanide Ion in Acetonitrile. A Study of the Mechanism using Ionic ¹³C Cyanide

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Sulfur dieyanide and selenium dieyanide react quantitatively with ionic cyanide in acetonitrile in the mol ratio of 1:3 respectively, forming one mol of the corresponding pseudohalide ion and an unidentified product, probably having the composition $(C_4N_4)^2$. Tellurium dieyanide reacts with excess ionic cyanide to give ionic tellurocyanate and presumably the same unidentified product through an intermediate step where elemental tellurium was separated.

Product analysis using ionic ¹⁸C cyanide suggests the mechanism of the sulfur dicyanide-cyanide reaction to be a nucleophilic attack at the sulfur atom, followed by a fast pseudorotation prior to the decomposition of the intermediate. In the selenium dicyanide-cyanide reaction a fast exchange of the cyanide groups takes place prior to the decomposition of the intermediate.

The chalcogen dicyanides can be regarded as mixed pseudohalogens, (NC)(XCN) (X=S, Se, and Te), and they can be looked upon as ambident electrophiles. According to the HSAB terminology, the carbon atoms appear to be the harder electrophilic centres, while the chalcogen atoms are the soft ones. The softness of the chalcogen atoms increases in the order S < Se < Te.

The purpose of this paper is to discuss the reaction mechanism of the chalcogen dicyanide-cyanide reaction. Acetonitrile was chosen as the solvent because in this solvent tellurium dicyanide was found to be quite stable. Tetraphenylarsonium cyanide was used as the nucleophilic reagent.

Sulfur dicyanide and selenium dicyanide were found to react quantitatively with the cyanide ion in acetonitrile at room temperature in the mol ratio of 1:3. One mol of the corresponding pseudohalide ion was formed, and the second product (provided only one other product is formed) has to have the composition (CN)₄²-as shown by eqn. 1.

$$X(CN)_2 + 3CN^- \xrightarrow{MeCN} XCN^- + (CN)_4^{2-}$$
 (1)
 $X = S$ and Se.

Isolation and characterisation of products other than tetraphenylarsonium thiocyanate (selenocyanate) proved to be most difficult. If, however, only two products are formed, as indicated by reaction (1), the anion (CN)₄²-might be the diiminosuccinonitrile dianion, (DISN)²-. Diiminosuccinonitrile, DISN, has recently been isolated by Webster and coworkers ¹ by base-catalyzed addition of hydrogen cyanide to cyanogen. It appears not unreasonable to assume that a dianion having the structure of the DISN molecule can exist in the aprotic solvent acetonitrile.

When one mol of $X(CN)_2$ (X=S and Se) was reacted with one mol of ionic cyanide, 1/3 mol of the pseudohalide ion was obtained. Supposing the first step of this reaction to be bimolecular, to give the pseudohalide ion and cyanogen, the second step, which might be the addition of 2 mol of cyanide ions to the cyanogen, is believed to be much faster. This is shown by eqns. (2) and (3).

$$X(CN)_2 + CN^- \xrightarrow{MeCN} XCN^- + (CN)_2$$
 (2)

$$(CN)_2 + 2CN^- \xrightarrow{\text{MeCN}} (CN)_4^{2-}$$
 (3)

X = S and Se.

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Tellurium dicyanide reacted with ionic cyanide in a different way. A yellowish colour of the reaction mixture was first observed. After about 10 s elemental tellurium separated. When excess of ionic cyanide was used the tellurium went into solution again due to the formation of ionic tellurocyanate.²

The following two mechanisms may be possible (Schemes 1 and 2).

$$\begin{array}{c} X \\ CN \\ -CN \end{array} + CN^{-} \longrightarrow \begin{bmatrix} NCX \cdots C \cdots CN \\ \parallel \\ N \end{bmatrix}^{-} \\ \longrightarrow XCN^{-} + (CN)_{2} \end{array}$$

Scheme 1.

$$\begin{array}{c} X \stackrel{\text{CN}}{\longleftarrow} + \text{CN} \stackrel{\text{--}}{\longrightarrow} \begin{bmatrix} \text{NC} - X - \text{CN} \\ \text{I} \\ \text{CN} \end{bmatrix}^{-} \\ \longrightarrow X \text{CN}^{-} + (\text{CN})_{\bullet} \end{array}$$

Scheme 2. X = S and Se.

Scheme 1 involves a nucleophilic attack at one of the carbon atoms displacing the pseudohalide ion. Scheme 2 involves a nucleophilic attack at the chalcogen atom forming an activated intermediate [X(CN)_s], which then decomposes to the pseudohalide ion and cyanogen. In both cases the cyanogen formed will add 2 mol of cyanide ions according to eqn. 3.

In order to verify which of these two possible mechanisms really takes place in the different chalcogen dicyanide-cyanide reactions, ionic ¹³C cyanide was used as the nucleophile. The amounts of XCN⁻ and X¹³CN⁻ were measured using IR in the 2000 cm⁻¹ region. ² In acetonitrile the ¹³C-pseudohalides were found to absorb about 50 cm⁻¹ lower than did the corresponding

Table 1. Some data for the reaction $XCN^-+{}^{13}CN^- \rightleftharpoons X^{13}CN^-+CN^-$ where X=S, Se, or Te in acetonitrile.

X	Rate, R $M h^{-1}$	ν(XCN) cm ⁻¹ a	$ u(\mathrm{X^{13}CN^-}) $ $ \mathrm{cm^{-1}} $
S	0	2059	2010
Se	1.6×10^{-4b}	2068	2022
Te	very fast	2081	2035

^a Ref. 2. ^b Total rate of exchange at 40 °C.

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¹²C-pseudohalides (Table 1). The sharp peaks were thus sufficiently apart for quantitative measurements. The extinction coefficients of X¹³CN⁻ and XCN⁻ were assumed to be equal.

No isotopic exchange occurs between the thiocyanate ion and the cyanide ion in aqueous solution, ¹² and the same was found to apply in acetonitrile. Isotropic exchange between the selenocyanate ion and the cyanide ion does occur in water ¹³ and methanol. ¹⁴ The isotopic exchange in acetonitrile at 40 °C when applying [SeCN]₀=[¹³CN]₀=8.00 × 10⁻³ M was found to be very slow, having a half-life of 17 h. The yields of XCN and X¹³CN (X=S and Se) in the chalcogen dicyanide-cyanide reactions are thus not affected by isotopic exchange between the pseudohalide ion and the cyanide ion.

The exchange of cyanide between the tellurocyanate ion and ionic ¹³C cyanide in acetonitrile was found to be very fast, and the rate could not be measured by the IR technique. Because of the separation of elemental tellurium in the tellurium dicyanide-cyanide reaction, isotopic experiments were not carried out on this reaction. The result in the other two reactions are shown in Table 2.

According to Table 2, a mechanism described by Scheme 1 may be rejected as a possible first step for the sulfur dicyanide-cyanide reaction. Such a mechanism will not give any ¹³C thiocyanate at all. A reaction route proposed by Scheme 2 appears to be more consistent with the experimental data. Steric effects on divalent sulfur have been studied with nucleophiles bearing a negative charge, and a linear transition state might be favoured in this case.³

Table 2. Isotopic experiments on the reaction $X(CN)_2 + 3^{13}CN^- \rightarrow Products$

where X=S or Se in acetonitrile at room temperature.

X	Relative amounts X ¹⁸ CN XCN		
S	1/3	2/3	
Se	3/5	2/5	

The bonding in the intermediate I might, according to Foss,⁴ be looked upon as a linear three-center four-electron type. The structure of the trithiocyanate ion is presumably analogous to that of the triselenocyanate ion, which has a linear three-center four-electron bonding system.⁴

The ratio of SCN⁻/S¹³CN⁻ = 2/1 indicates that no exchange of the cyano groups takes place during the lifetime of the intermediate I. Furthermore, the product analysis indicates that the three cyano groups of the transition state are equivalent. The intermediate complex I then has to undergo a fast pseudorotation of the cyano groups before its decomposition to ionic thiocyanate and cyanogen. Presumably I is very unstable, due to the large trans effect commonly exerted by the cyano groups. The energy barrier of pseudorotation might then be low. The following reaction sequence can then be suggested for the sulfur dicyanide-cyanide reaction in acetonitrile.

$$S(CN)_2 + CN^{-} \xrightarrow{slow} \begin{bmatrix} NC - S - CN \\ CN \end{bmatrix}^{-}$$

$$\xrightarrow{fast} [S(CN)_3]^{-} \longrightarrow SCN^{-} + (CN)_2$$

$$\xrightarrow{pseudorota-tion}$$
all the cyano groups equivalent

According to the literature, nucleophilic substitution at sulfur dicyanide in most cases takes place at one of the carbon atoms.⁵⁻⁷ Wilson and co-workers,⁷ however, have shown that a nucleophilic attack by the thiocyanate ion takes place at the divalent sulfur atom of sulfur dicyanide in an acid aqueous solution.

Nor can the selenium dicyanide-cyanide reaction follow the mechanism depicted by Scheme 1. The results listed in Table 2 indicate that a fast exchange of the cyano groups of selenium dicyanide occurs. A statistical distribution of ¹²C and ¹³C cyanide will then apply in the intermediate selenium tricyanide anion, [Se(CN)₃]. Visually, the selenium dicyanide-cyanide reaction was observed not to take place in the same spontaneous way as the analogous sulfur dicyanide-cyanide reaction. No kinetic data

concerning nucleophilic attack at divalent selenium are available in the literature. According to Foss, 4 structural evidence points to a linear transition state, with bonds of the three-center four-electron type. Due to the very fast exchange of the cyano groups, we cannot say whether pseudorotation in the intermediate, [Se(CN)₃], takes place or not.

The following reaction scheme might then be suggested.

$$\begin{array}{c} \operatorname{Se(CN)_2} + 3 * \operatorname{CN}^- \xrightarrow{\begin{subarray}{c} \textbf{Fast} \\ \textbf{exchange} \end{subarray}} [\operatorname{Se(CN)_3}]^- \\ & * \operatorname{CN/CN} = 3/2 \\ & \\ \hline & \\ \operatorname{slow} \\ \hline & \\ \operatorname{decomposition} \end{array} \\ \begin{array}{c} 2/5 \operatorname{SeCN}^- + 3/5 \operatorname{Se*CN}^- + (\operatorname{CN})_2 \\ \end{array}$$

Hauge ⁸ has proposed that in the reaction of selenium dicyanide with selenocyanate ion to form the triselenocyanate ion, the first step is an attack by the selenocyanate ion at the selenium atom of selenium dicyanide to displace ionic cyanide. There are, as far as the authors know, no examples in the literature suggesting nucleophilic attack at the carbon atoms of selenium dicyanide.

With regard to the tellurium dicyanide-cyanide reaction, a nucleophilic attack by the cyanide ion at one of the carbon atoms would probably not lead to the precipitation of elemental tellurium. It appears more reasonable that the yellowish colour firstly observed is due to the tellurium tricyanide ion, [Te(CN)₃], formed through a nucleophilic attack at the divalent tellurium atom. The large decrease in the strength of the chalcogen-carbon bond of the pseudohalides from sulfur to tellurium ^{2,9} may explain the separation of tellurium during the decomposition of [Te(CN)₃]. It appears reasonable to propose the following mechanism.

$$Te(CN)_{2} + CN^{-} \longrightarrow \begin{bmatrix} NC - Te - CN \\ CN \\ yellow \end{bmatrix}^{-}$$

$$\longrightarrow Te + CN^{-} + (CN)_{2} \longrightarrow \underbrace{excess}_{CN^{-}}$$

$$TeCN^{-} + (CN)_{4}^{2-}$$

Stable salts of tellurium anions with bonds of the three-center four-electron type have recently been prepared.^{10,11}

In the three reactions studied, the electrophilic centre of the chalcogen dicyanides towards the cyanide ion in acetonitrile thus appears to be the chalcogen atom. The experimental results further indicate that the relative stability of the chalcogen tricyanide intermediates is $[S-(CN)_3]^- < [S-(CN)_3]^- < [T-(CN)_3]^-$. An intermediate complex of the type $[X-(CN)_3]^-$ should be more stable in a dipolar aprotic solvent containing large onium cations than in a protic solvent.

The reaction mechanisms outlined above are based on the assumption that cyanogen is formed as a result of decomposition of chalcogen tricyanide ions, [X(CN)₃]. The problem may be more complex, but attempts to explain the isotopic data when supposing the reaction to be second order in the cyanide ions were not successful.

EXPERIMENTAL

Acetonitrile and tetraphenylarsonium cyanide, Ph₄AsCN, were purified as reported.² Ph₄As¹³CN was prepared from K¹³CN, British Company Oxygen Limited, and contained more than 90 % ¹³C.

Sulfur dicyanide was prepared from sulfur dichloride and silver cyanide in carbon disulfide as reported by Long and Stelle. ¹⁵ Selenium dicyanide was prepared by the method of Hauge ⁸ from cyanogen bromide and potassium selenocyanate in diethyl ether. The product was finally sublimed in vacuum to remove traces of selenium diselenocyanate, Se(SeCN)₂. Tellurium dicyanide was prepared in 50 % yield from tellurium tetrabromide and freshly prepared silver cyanide in dry benzene according to the method of Cocksedge. ¹⁶ Sulfur dicyanide, selenium dicyanide and tellurium dicyanide were all stored in a refrigerator.

The chalcogen dicyanide-cyanide reactions. A solution containing 5.0×10^{-3} mol (0.420 g) of $S(CN)_3$ in 10 ml acetonitrile was added to a solution of Ph_4AsCN , made by dissolving 1.64×10^{-2} mol (7.0 g) of Ph_4AsCN in 50 ml acetonitrile. The reaction was slightly exothermic and the reaction mixture turned reddish, probably due to some polymerization products. After most of the solvent was removed in vacuum, the salts were precipitated by adding diethyl ether and were filtered off. The product was washed with 150 ml lukewarm acetone $(40 \,^{\circ}C)$. The salt of the thiocyanate ion and most of the red polycyanic compound dissolved in acetone. On standing in a refrigerator, some tetraphenylarsonium salt crystallized (about $0.4 \, g$), which was added to the acetone-insoluble part. The acetone solution was evaporated to dryness, and

the residue was washed with some ice-cold acetone to remove the red colour. Yield of Ph₄AsSCN, 2.0 g, or 91 % based on the amount of S(CN)₂ used. The tetraphenylarsonium thiocyanate was finally crystallized from warm acetonitrile.

The other product could not be isolated, due to its instability. This unidentified salt probably reacts with acetone to form a salt nearly insoluble in this solvent which facilitated the separation. The acetone-insoluble salt was not further studied.

The selenium dicyanide-cyanide reaction was performed in the same way as described for the sulfur dicyanide-cyanide reaction, and Ph₄-AsSeCN was isolated in 88 % yield based on the amount of Se(CN)₂ used. Tetraphenylarsonium selenocyanate was finally crystallized from warm acetonitrile.

The tellurium dicyanide-cyanide reaction was not studied in detail. When the reactants were mixed in the mol ratio of 1:1, a yellowish colour was first observed which lasted for about 10 s, then elemental tellurium separated. With excess cyanide ions (about 1:10), the precipitated tellurium reacted to give ionic tellurocyanate.²

The stoichiometry of the chalcogen dicyanide-cyanide reactions was determined by applying IR liquid cells measuring the amount of XCN-formed. The concentration of ionic cyanide was varied from one up to three times the concentrations of the chalcogen dicyanides. In all the reactions studied the concentration of XCN-formed was exactly 1/3 of the cyanide concentration used.

Isotopic experiments. 1 ml of a 1.00×10^{-2} M solution of S(CN)₂ was added to a solution of 0.0137 g Ph₄As¹³CN dissolved in 1 ml acetonitrile $(3.20\times10^{-2}$ M). The solution turned instantaneously orange. The results from the product analysis are listed in Table 2.

The selenium dicyanide-¹³C cyanide reaction was carried out by adding 1 ml of a 1.60 × 10⁻² M solution of Se(CN)₂ to a solution of 0.0214 g Ph₄As¹³CN dissolved in 1 ml acetonitrile (5.00 × 10⁻² M). The orange colour did not arise in the same instantaneous way as in the sulfur dicyanide-cyanide reaction. The yields of SeCN and Se¹³CN are shown in Table 2.

The rate of isotopic exchange between SeCN⁻ and ¹³CN⁻ in acetonitrile was determined at 40 °C using [SeCN⁻]₀ = [¹³CN⁻] = 8.00×10^{-3} M. The total rate of exchange, R, was evaluated by means of the equation ¹⁷

$$\ln (1-F) = -Rt(a+b)/ab$$

where a and b are the concentrations of SeCN-and 18 CN-, respectively, t the reaction time and F the fractional exchange. The total rate constant was found to be $R=1.6\times 10^{-4}$ M h⁻¹ (half-lifes about 17 h).

The IR measurements were performed on a Unicam SP 200 G Infrared Spectrophotometer applying 0.1 cm liquid cells.

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