

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

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Sulfur dicyanide and selenium dicyanide 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 dicyanide reacts with excess ionic cyanide to give ionic tellurocyanate and presumably the same unidentified product through an intermediate step where elemental tellurium was separated.

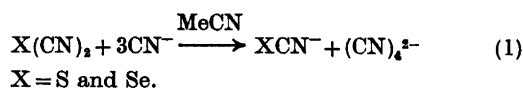
Product analysis using ionic ^{13}C cyanide suggests the mechanism of the sulfur dicyanide-cyanide reaction to be a nucleophilic attack at the sulfur atom, followed by a fast pseudorotation prior to the decomposition of the intermediate. In the selenium dicyanide-cyanide reaction a fast exchange of the cyanide groups takes place prior to the decomposition of the intermediate.

The chalcogen dicyanides can be regarded as mixed pseudohalogens, $(NC)(XCN)$ ($X = S, Se, \text{ and } Te$), 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.

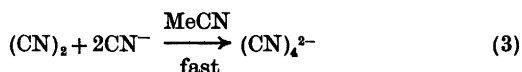
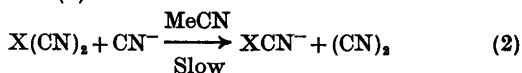
Sulfur dicyanide and selenium dicyanide were found to react quantitatively with the cyanide ion in acetonitrile at room temperature in the mol ratio of 1:3. One mol of the corresponding

pseudohalide ion was formed, and the second product (provided only one other product is formed) has to have the composition $(CN)_4^{2-}$ as shown by eqn. 1.



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 $(CN)_4^{2-}$ might be the diiminosuccinonitrile dianion, $(DISN)^{2-}$. Diiminosuccinonitrile, DISN, has recently been isolated by Webster and co-workers¹ 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.

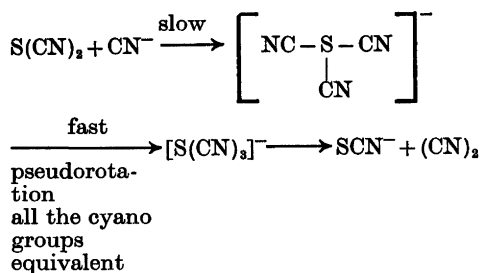
When one mol of $X(CN)_2$ ($X = S \text{ and } Se$) was reacted with one mol of ionic cyanide, 1/3 mol of the pseudohalide ion was obtained. Supposing the first step of this reaction to be bimolecular, to give the pseudohalide ion and cyanogen, the second step, which might be the addition of 2 mol of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



$X = S \text{ and } Se.$

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 $\text{SCN}^-/\text{S}^{13}\text{CN}^- = 2/1$ 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.

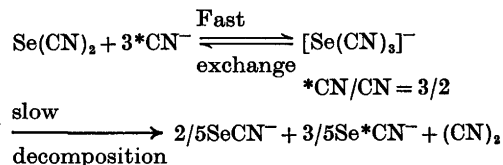


According to the literature, nucleophilic substitution at sulfur dicyanide in most cases takes place at one of the carbon atoms.⁵⁻⁷ Wilson and co-workers,⁷ however, have shown that a nucleophilic attack by the thiocyanate ion takes place at the divalent sulfur atom of sulfur dicyanide in an acid aqueous 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, $[\text{Se}(\text{CN})_3]^-$. 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

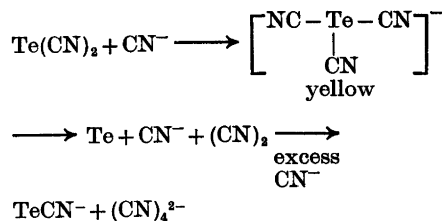
concerning nucleophilic attack at divalent selenium are available in the literature. According to Foss,⁴ structural evidence points to a linear transition state, with bonds of the three-center four-electron type. Due to the very fast exchange of the cyano groups, we cannot say whether pseudorotation in the intermediate, $[\text{Se}(\text{CN})_3]^-$, takes place or not.

The following reaction scheme might then be suggested.



Hauge⁸ 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, $[\text{Te}(\text{CN})_3]^-$, 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 tellurium⁹ may explain the separation of tellurium during the decomposition of $[\text{Te}(\text{CN})_3]^-$. It appears reasonable to propose the following mechanism.



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 $[\text{S}(\text{CN})_3]^- < [\text{Se}(\text{CN})_3]^- < [\text{Te}(\text{CN})_3]^-$. An intermediate complex of the type $[\text{X}(\text{CN})_3]^-$ should be more stable in a dipolar aprotic solvent containing large onium cations than in a protic solvent.⁹

The reaction mechanisms outlined above are based on the assumption that cyanogen is formed as a result of decomposition of chalcogen tricyanide ions, $[\text{X}(\text{CN})_3]^-$. 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, Ph_4AsCN , were purified as reported.² $\text{Ph}_4\text{As}^{13}\text{CN}$ was prepared from K^{13}CN , British Company Oxygen Limited, and contained more than 90% ^{13}C .

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 Hauge⁸ from cyanogen bromide and potassium selenocyanate in diethyl ether. The product was finally sublimed in vacuum to remove traces of selenium diselenocyanate, $\text{Se}(\text{SeCN})_2$. 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 $\text{S}(\text{CN})_2$ 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 °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 Ph_4AsSCN , 2.0 g, or 91% based on the amount of $\text{S}(\text{CN})_2$ 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 Ph_4AsSeCN was isolated in 88% yield based on the amount of $\text{Se}(\text{CN})_2$ 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.² 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 $\text{S}(\text{CN})_2$ was added to a solution of 0.0137 g $\text{Ph}_4\text{As}^{13}\text{CN}$ dissolved in 1 ml acetonitrile (3.20×10^{-2} M). The solution turned instantaneously orange. The results from the product analysis are listed in Table 2.

The selenium dicyanide- ^{13}C cyanide reaction was carried out by adding 1 ml of a 1.60×10^{-2} M solution of $\text{Se}(\text{CN})_2$ to a solution of 0.0214 g $\text{Ph}_4\text{As}^{13}\text{CN}$ 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 $\text{Se}^{13}\text{CN}^-$ are shown in Table 2.

The rate of isotopic exchange between SeCN^- and $^{13}\text{CN}^-$ in acetonitrile was determined at 40 °C using $[\text{SeCN}^-]_0 = [^{13}\text{CN}^-] = 8.00 \times 10^{-3}$ M. The total rate of exchange, R , was evaluated by means of the equation¹⁷

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

where a and b are the concentrations of SeCN^- and $^{13}\text{CN}^-$, 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-lives 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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