

Short Communications

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

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As part of a study of polythionic compounds in dipolar aprotic solvents, it was found necessary to study the action of ionic cyanide on thiocyanogen and selenocyanogen in acetonitrile.¹ In a previous paper we have studied the reaction between chalcogen dicyanides, $\text{X}(\text{CN})_2$ ($\text{X} = \text{S}$, Se and Te), and the cyanide ion in acetonitrile.² In all cases the chalcogen atom was found to be the electrophilic centre.

Selenocyanogen has been found to react with ionic selenocyanate to form the triselenocyanate ion, $(\text{SeCN})_3^-$.³ Likewise, the trithiocyanate ion, $(\text{SCN})_3^-$, is formed when thiocyanogen and ionic thiocyanate are mixed.⁴ The trithiocyanate ion is far more unstable than the triselenocyanate ion and it has not yet been isolated as stable salts. In the dipolar aprotic solvent, acetonitrile, the cyanide ion is believed to be a more powerful nucleophile towards divalent sulfur and selenium than is the thiocyanate ion and the selenocyanate ion. Consequently, a displacement reaction is to be expected upon mixing ionic cyanide with the two pseudohalogens, $(\text{SCN})_2$ and $(\text{SeCN})_2$, in acetonitrile.

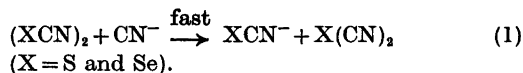
The stoichiometry of the thiocyanogen-cyanide reaction and the selenocyanogen-cyanide reaction was found by varying the amount of the nucleophilic reagent, tetraphenylarsonium cyanide, and measuring the yield of the corresponding pseudohalide ion applying IR ($\nu_{\text{SCN}^-} = 2059 \text{ cm}^{-1}$ and $\nu_{\text{SeCN}^-} = 2068 \text{ cm}^{-1}$).⁵ The nucleophilic reagent was always added to the substrate. The results are collected in Table 1.

Four mol of cyanide ions are consumed per mol of the substrate in order to give 2 mol of the corresponding pseudohalide ion. Table 1 further indicates that one mol of each of the reactants forms one mol of the pseudohalide ion, and in addition 3 mol of cyanide ions have to be used to form the second mol of the pseudohalide ion.

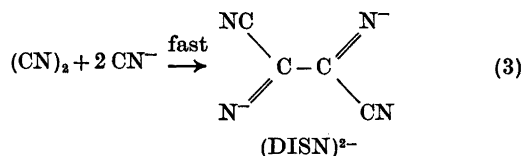
Table 1. Determination of the stoichiometry of the reaction $(\text{XCN})_2 + n\text{CN}^- \rightarrow \text{Products}$ where $\text{X} = \text{S}$ or Se in acetonitrile at room temperature.

n	Amount of XCN^- formed (mol)
2	1 1/3
3	1 2/3
4	2

A mechanism satisfying these observations involves a fast substitution by the cyanide ion at one of the chalcogen atoms displacing ionic thiocyanate (selenocyanate) in the first step, eqn. (1).



The chalcogen dicyanide that is being formed, is believed to react with ionic cyanide in acetonitrile according to eqns. (2) and (3).³



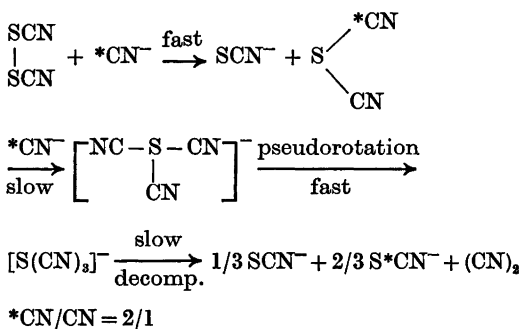
IR of the reaction mixture showed a sharp peak at 2140 cm^{-1} which has been attributed to the postulated diiminosuccinonitrile dianion, (DISN)²⁻.²

To verify this mechanism, ionic ^{13}C cyanide has been used as the nucleophilic reagent. The reactions were performed by adding 4 mol of ^{13}C cyanide ions to the substrates. The sharp peaks in IR of the ^{13}C -pseudohalides and the ^{13}C -pseudohalides were sufficiently apart for quantitative measurements ($\nu_{\text{S}^{13}\text{CN}^-} = 2010 \text{ cm}^{-1}$ and $\nu_{\text{Se}^{13}\text{CN}^-} = 2022 \text{ cm}^{-1}$).² The data are listed in Table 2. The data of the isotopic

Table 2. Isotopic experiments on the reaction $(\text{XCN})_2 + 4^{13}\text{CN}^- \rightarrow \text{Products}$ where $\text{X} = \text{S}$ or Se in acetonitrile at room temperature.

X	Amounts formed (mol)	
	XCN^-	X^{13}CN^-
S	1 1/3	2/3
Se	1 1/5	4/5

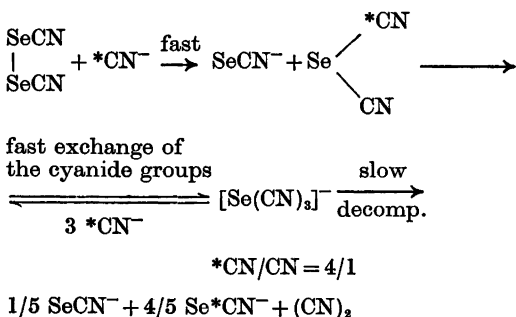
experiments are in complete accordance with the mechanism previously reported for the sulfur dicyanide-cyanide reaction and the selenium dicyanide-cyanide reaction.² The overall reaction between thiocyanogen and ionic ^{13}C cyanide may then be pictured by Scheme 1.



Scheme 1.

The cyanogen formed in the last step adds 2 mol of cyanide ions in a fast reaction, eqn. (3).

The mechanism of the selenocyanogen-cyanide reaction is schematically shown by Scheme 2.



Scheme 2.

Finally some comment concerning the first step of the Schemes 1 and 2 will be given. The first steps in both reactions are irreversible, and

the data of Table 2 are in agreement with such reactions. In aqueous solution Hauge³ has, however, found the cyanide ion and the selenocyanate ion to be of comparable nucleophilicity toward divalent selenium. The data in this paper may be explained by the fact that the nucleophilicity of the cyanide ion toward methyl iodide is 4.1×10^4 times greater in acetonitrile than in methanol.⁴ The increase in the nucleophilicity of the thiocyanate ion and the selenocyanate ion toward the same substrate when going from methanol to acetonitrile is, however, 36 and 19, respectively.⁵ Thus in a dipolar aprotic solvent the nucleophilicity of the cyanide ion toward divalent sulfur and selenium appears to be much greater than the nucleophilicity of the thiocyanate ion and the selenocyanate ion toward the same substrates.

Experimental. Acetonitrile and tetraphenylarsonium cyanide, Ph_4AsCN , were purified as reported previously.⁵ $\text{Ph}_4\text{As}^{13}\text{CN}$ was prepared from K^{13}CN , British Oxygen Limited, and contained more than 90% ^{13}C .

A standard solution of thiocyanogen in acetonitrile was made by the method of Jenkins and Kochi⁶ applying bromine and excess of lead thiocyanate, $\text{Pb}(\text{NCS})_2$. The solution was stored in a refrigerator.

Selenocyanogen was made from silver selenocyanate and iodine in dry ether.⁷

The thiocyanogen-cyanide reaction was quantitatively studied by measuring the amount of ionic thiocyanate formed applying IR.⁵ The reaction was studied using 1.54×10^{-3} M of the substrate and varying the concentration of the nucleophile up to four times the concentration of the substrate. During all the experiments the nucleophilic reagent was always added to the thiocyanogen solution. The IR of the solution further showed a sharp peak at 2140 cm^{-1} which is supposed to be due to the diimino-succinonitrile dianion, $(\text{DISN})^{2-}$.

The selenocyanogen-cyanide reaction was studied in the same way as described for the thiocyanogen-cyanide reaction. 3.0×10^{-3} M of selenocyanogen was applied.

Both of the reactions were found to be very fast, and the amounts of XCN^- ($\text{X} = \text{S}$ and Se) were measured shortly after mixing the reactants.

The amounts of XCN^- and X^{13}CN^- were reproduced within $\pm 3\%$ of the exact figures which are presented in Tables 1 and 2.

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

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The Crystal Conformation of 1,1,9,9-Tetramethylcyclohexadecane

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By semiempirical calculations of cyclohexadecane Dale¹ has found the square, diamond

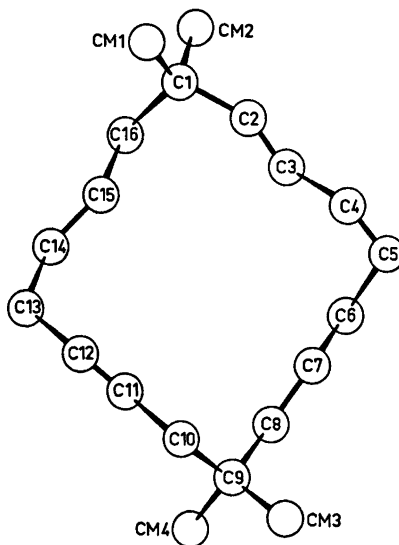


Fig. 1. Schematic drawing showing the molecular conformation.

Table 1. Final fractional coordinates and anisotropic thermal vibration parameters with estimated standard deviations (multiplied by 10^4) for carbon atoms. The symbol CM is used for the methyl carbons.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
C1A	506(11)	3460(4)	2755(4)	263(23)	26(3)	27(3)	41(15)	34(14)	-1(5)
C2A	1383(11)	3320(4)	3366(4)	321(24)	20(3)	23(3)	10(14)	15(14)	-9(4)
C3A	3197(11)	3114(4)	3374(4)	238(23)	20(3)	23(3)	-16(14)	-3(13)	-4(5)
C4A	3957(12)	2958(4)	3983(4)	334(27)	27(3)	26(3)	17(16)	-36(15)	-7(5)
C5A	5730(13)	2741(5)	4029(4)	368(28)	46(5)	29(3)	-24(19)	-75(16)	-0(6)
C6A	6083(10)	2154(5)	3687(4)	181(21)	38(4)	31(3)	-23(15)	-46(13)	-4(6)
C7A	5139(10)	1559(4)	3835(4)	237(23)	36(4)	24(3)	-1(15)	2(13)	-2(5)
C8A	5561(9)	976(4)	3511(3)	167(19)	29(3)	22(2)	21(13)	-9(11)	4(5)
C9A	4622(11)	348(4)	3616(4)	243(23)	27(4)	21(3)	58(15)	-4(14)	9(5)
C10A	2739(11)	433(4)	3525(4)	282(25)	22(3)	24(3)	4(14)	7(14)	3(5)
C11A	2023(10)	679(4)	2948(4)	208(21)	34(3)	24(3)	23(14)	5(13)	-5(5)
C12A	145(10)	816(4)	2912(4)	147(20)	28(3)	42(3)	-0(13)	12(13)	-0(5)
C13A	-640(10)	1080(4)	2347(4)	195(21)	31(4)	41(3)	5(15)	-42(14)	-22(6)
C14A	58(10)	1719(4)	2166(4)	230(22)	21(3)	35(3)	-12(14)	-72(13)	-12(5)
C15A	-129(10)	2254(4)	2575(3)	194(20)	28(3)	23(3)	-13(14)	-2(12)	-9(5)
C16A	548(9)	2472(4)	2374(3)	199(19)	24(3)	23(3)	23(13)	5(12)	6(5)
CM1A	1329(13)	4028(4)	2489(4)	508(33)	29(4)	29(3)	2(18)	6(17)	22(5)
CM2A	-1288(12)	3628(5)	2446(4)	339(27)	47(4)	39(3)	79(19)	-10(17)	-21(6)
CM3A	5069(12)	131(4)	4238(4)	395(29)	39(4)	31(3)	63(18)	-3(15)	24(5)
CM4A	5243(11)	-164(5)	3220(4)	332(27)	53(5)	34(3)	167(18)	39(15)	-18(6)
C1B	-461(11)	6475(4)	9728(3)	289(21)	24(4)	21(3)	4(14)	8(13)	7(5)
C2B	-2273(10)	6589(4)	9652(4)	156(18)	27(3)	25(3)	-31(13)	21(12)	-1(5)
C3B	-3029(10)	6440(4)	9989(4)	169(19)	31(3)	24(3)	-2(13)	14(12)	-3(5)
C4B	-4845(10)	6954(4)	9775(4)	177(22)	24(3)	37(3)	-37(14)	3(14)	2(5)
C5B	-5696(11)	7188(4)	8504(5)	195(22)	34(4)	49(4)	-15(16)	-7(15)	-14(6)
C6B	-5033(10)	7434(4)	8286(4)	183(21)	30(4)	31(3)	37(14)	-69(13)	-12(5)
C7B	-5187(10)	8395(4)	8699(4)	175(20)	29(4)	23(2)	-5(14)	13(12)	-8(5)
C8B	-4531(9)	9317(4)	8451(3)	178(19)	29(3)	17(2)	-14(13)	-3(11)	-3(4)
C9B	-4526(10)	9491(4)	8863(3)	208(21)	28(3)	13(2)	17(14)	11(12)	4(4)
C10B	-3601(10)	9178(4)	9439(3)	234(21)	24(3)	15(2)	8(13)	30(12)	-4(4)
C11B	-1811(10)	9253(4)	9440(3)	210(21)	31(3)	21(2)	-11(14)	-2(12)	3(4)
C12B	-1044(10)	9110(4)	10039(4)	186(21)	27(3)	23(3)	-28(14)	1(12)	-1(4)
C13B	798(11)	8599(4)	10007(4)	262(23)	30(4)	29(3)	-37(15)	-11(14)	4(5)
C14B	1056(9)	8284(4)	9705(3)	153(18)	35(3)	19(2)	-5(13)	-5(11)	16(5)
C15B	142(10)	7693(4)	9932(4)	193(20)	23(3)	27(3)	-31(13)	49(12)	-0(5)
C16B	553(9)	7983(4)	9609(3)	201(19)	32(3)	22(2)	-2(14)	32(11)	-7(5)
CM1B	114(11)	6264(4)	10343(4)	300(25)	31(4)	29(3)	-17(16)	-4(15)	14(5)
CM2B	96(11)	5953(4)	9336(4)	254(22)	35(4)	49(3)	50(15)	1(14)	-9(6)
CM3B	-6333(11)	9791(4)	8929(4)	253(24)	39(4)	26(3)	76(15)	-11(14)	-2(5)
CM4B	-3686(11)	10160(4)	8557(3)	346(27)	26(3)	24(3)	-19(15)	5(14)	-1(5)