138. *The Oxidation of Potassium Selenocyanate by Iodine Pentafluoride.*

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Potassium selenocyanate reacts with iodine pentafluoride to give selenium dicyanide, $Se(CN)_2$, and selenium selenocyanate, $Se(SeCN)_2$. The reaction is an unusual example of a mild oxidation in which the selenocyanate ion is first converted into selenocyanogen, $(SeCN)_2$, which then disproportionates into the two products. The infrared spectra of the compounds $Se(CN)_2$, $(SeCN)_2$, and $Se(SeCN)_2$ are reported and compared with those of related compounds.

VERNEUIL [1] found that both chlorine and bromine (but not iodine) react with sodium, potassium, or ammonium selenocyanate to give selenium selenocyanate, $Se(SeCN)_2$, and Muthmann *et al.* [2] obtained this product by treating a suspension of potassium seleno-cyanate in ice-cold water with dinitrogen tetroxide and a little fuming nitric acid. Selenium selenocyanate has also been prepared by reactions between lead selenocyanate and bromine,[3] between diselenium dibromide and silver cyanide,[4] by heating sulphenyl selenocyanates,[5,6] and by the disproportionation of selenocyanogen, $(SeCN)_2$.[4]

[1] Verneuil, *Ann. Chim. Phys.*, 1886, **9**, 326.
[2] Muthmann and Schröder, *Ber.*, 1900, **33**, 1765.
[3] Challenger, Peters, and Halevy, *J.*, 1926, 1648.
[4] Kaufmann and Kögler, *Ber.*, 1926, **59**, 178.
[5] Rheinboldt and Giesbrecht, *J. Amer. Chem. Soc.*, 1949, **71**, 1740.
[6] Emeléus and Haas, *J.*, 1963, 1272.

It is now found that potassium selenocyanate, when treated with an excess of solid iodine pentafluoride in a sealed evacuated system below room temperature, gives yields of up to 40% of selenium selenocyanate, calculated on the basis of the equations given below, together with a smaller yield of selenium dicyanide. Elemental iodine and potassium fluoride were also formed. The first two compounds are considered to arise by disproportionation of the primary oxidation product, selenocyanogen, $(SeCN)_2$, in accordance with the equations:

$$10KSeCN + 2IF_5 = 10KF + 5(SeCN)_2 + I_2$$
$$2(SeCN)_2 = Se(SeCN)_2 + Se(CN)_2$$
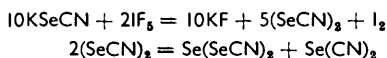
Other products included small amounts (up to 1% each) of carbon tetrafluoride, trifluoromethyl cyanide, carbonyl fluoride, and silicon tetrafluoride. The last two compounds clearly indicate slight attack on the glass vessel. Separate experiments suggest that carbon tetrafluoride and carbonyl fluoride arise from a secondary reaction of selenium cyanide with iodine pentafluoride, but trifluoromethyl cyanide appears to result from the direct reaction of iodine pentafluoride with potassium selenocyanate since it was not detected when either of the main products was treated with iodine pentafluoride.

When iodine pentafluoride and potassium selenocyanate (initially at room temperature) were allowed to react spontaneously, a vigorous exothermic reaction occurred. In this case the yield of selenium selenocyanate was much lower and selenium cyanide could not be isolated.

Both selenium selenocyanate and selenium cyanide have been identified by chemical analysis and infrared spectroscopy. The spectroscopic identification of selenium selenocyanate was confirmed by the independent preparation of the compound by oxidation of potassium selenocyanate with dinitrogen tetroxide. The reaction produced both selenium selenocyanate and selenium cyanide in approximately equivalent amounts. The absence of selenium cyanide in the products of Muthmann's reaction referred to above [2] has been shown to be due to the rapid oxidation of this compound by fuming nitric acid.

Selenium selenocyanate is a yellow powder, m. p. 133—134° (decomp., sealed tube). Selenium cyanide, m. p. 134°, forms orthorhombic crystals, and an X-ray study in this laboratory [7] shows them to have unit-cell dimensions $a = 8.71$, $b = 6.98$, and $c = 13.41$ Å. The V-shaped molecules lie in parallel planes, 3.35 Å apart, perpendicular to the c-axis. This layer structure accounts for the ease of cleavage of the crystals. Bond lengths (standard deviation 0.1 Å) are Se–C 1.86 Å, C–N 1.42 Å and bond angles (standard deviation 6°) Se–C–N 177°, C–Se–C 119°.

Because the crystal structure indicates close approach between neighbouring molecules within a layer it was thought possible that there might be some intermolecular association in solution. However, cryoscopic molecular-weight determinations in benzene show that selenium cyanide (like sulphur cyanide) is monomeric in this solvent (Found: M, 133.9. Calc.: M, 131.0).

The infrared and Raman spectra of selenium cyanide have not previously been

Infrared and Raman Spectra.

Infrared S(CN)₂		Infrared Se(CN)₂		Raman Se(CN)₂		Assignments for Se(CN)₂
ν (cm.⁻¹)	ε_{rel}	ν (cm.⁻¹)	ε_{rel}	ν (cm.⁻¹)	ε_{rel}	
2188	(4sh)	2183	(1sh)	—	—	ν_1, ν_6 sym, antisym C≡N stretch
2179	(7)	2175	(1½)	2178	(35pol.)	
684	(8)	608	(1)	598	(2)	(ν_7? antisym C–Se stretch?)
665	(10)	516	(10)	514	(22)	ν_2 sym C–Se stretch
635	(4)	436	(1½)	449	(4½)	ν_4 sym Se–C₂ bend
499	(½)	345	(½sh)	348	(1)	ν_3, ν_8 sym, antisym Se–C≡N bend
374	(2)	336	(3)	—		
329	(2)	312	(½)	308	(1)	ν_9 out-of-plane deformation
		302	(½)	—		?

* Band occurs at 2171 cm.⁻¹ in KBr or Nujol and is resolved only in acetonitrile solution.

⁷ Hazell, *Acta Cryst.*, 1963, **16**, 843.

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reported; they are tabulated below together with suggested assignments; infrared data for sulphur cyanide are included for comparison. The infrared spectra of selenocyanogen and selenium selenocyanate, which are also here reported for the first time, are listed in the Experimental section.

The selenium cyanide molecule has C_{2v} symmetry with eight infrared active and nine Raman-active normal modes of vibration. The symmetric and antisymmetric C≡N stretching modes are observed at 2183 and 2175 cm.$^{-1}$. These occur as an unresolved band at 2171 cm.$^{-1}$ in a KBr-pressed disc, and when this figure is compared with the values of 2152 cm.$^{-1}$ for selenocyanogen and 2131 cm.$^{-1}$ for selenium selenocyanate it is clear that the C≡N stretching frequency diminishes by about 20 cm.$^{-1}$ for each added selenium atom in the chain. This is somewhat analogous to the decrease in C≡N stretching frequency with n, observed in the Raman spectra of the sulphur cyanides, $S_n(CN)_2$, although here the frequency tends to reach a limiting value; [8] thus, for $n = 1, 2, 3$, and 4 the value for $v_{C≡N}$ was 2186, 2160, 2155, and 2153 cm.$^{-1}$, and for $n = 5, 6, 7$, and 8 it was 2152 cm.$^{-1}$. By contrast, the C≡N frequencies are much less sensitive to increase in molecular weight in the series sulphur cyanide ($v_{C≡N}$ 2188 and 2179 cm.$^{-1}$), selenium cyanide ($v_{C≡N}$ 2183 and 2175 cm.$^{-1}$) and tellurium cyanide [9] ($v_{C≡N}$ 2181 and 2179 cm.$^{-1}$).

The band at 516 cm.$^{-1}$ can be assigned to the C–Se stretching mode since this occurs also in selenocyanogen at 521 cm.$^{-1}$ and selenium selenocyanate at 513 cm.$^{-1}$, and is within the range 505—545 cm.$^{-1}$ found for the C–Se frequency for a series of dialkyl diselenides.[10] It should be possible in selenium cyanide itself to detect the antisymmetric C–Se mode as well; the weak band at 608 cm.$^{-1}$ is very tentatively assigned to this vibration although the separation from the symmetric mode seems unusually large.

The band at 436 cm.$^{-1}$ is assigned to the Se–C_2 scissor mode since this is expected to have the highest frequency of the bending modes and does not occur in the spectra of selenocyanogen or selenium selenocyanate. It follows that the bands near 345—360 cm.$^{-1}$ in the three compounds are the Se–C≡N bending modes, and there appears to be a definite increase in the frequency of this mode as the chain length increases.

The molecule $(SeCN)_2$ has C_2 symmetry if free rotation about the Se–Se bond in solution is assumed; twelve infrared bands are therefore possible although only the four bands mentioned in the above comparative assignment were observed for this unstable compound.

The selenium selenocyanate molecule has C_s symmetry in the crystal lattice [11] and all fifteen modes would be expected to absorb in the infrared region, some of them at very low frequencies; in fact seven bands were observed but further assignments are not possible with the present data.

The infrared data on sulphur cyanide given in the Table do not agree well with recently· published values for this compound.[12] However, the present results are consistent with the partial data previously reported; infrared bands [13] at 684 and 665 cm.$^{-1}$ and Raman lines [8] at 2186, 680, 419, and 140 cm.$^{-1}$ have been recorded, and it would therefore seem that the present data are to be preferred.

EXPERIMENTAL

Iodine pentafluoride (Matheson Co. Inc., N.J.) was purified by successive vacuum distillations between breakseal units in a preflamed all-glass apparatus, the first and last fractions being discarded in each transfer. When purified in this way the iodine pentafluoride was a clear, colourless liquid which did not attack glass during prolonged periods at room temperature; nevertheless it was normally stored at liquid nitrogen temperature until required.

[8] Feher and Weber, *Chem. Ber.*, 1958, **91**, 642.
[9] Fritz and Keller, *Chem. Ber.*, 1961, **94**, 1524.
[10] Bergson, *Arkiv Kemi*, 1958, **13**, 11.
[11] Asknes and Foss, *Acta Chem. Scand.*, 1954, **8**, 702, 1787.
[12] Kuhn and Mecke, *Chem. Ber.*, 1961, **94**, 3010.
[13] Nelson and Pullin, *J.*, 1960, 604.

Potassium selenocyanate (B.D.H.) was purified by precipitation with diethyl ether from a concentrated solution in acetone. After the white powder had been washed with diethyl ether it was freed from solvent by pumping to a high vacuum in a desiccator over phosphorus pentoxide.

Silver selenocyanate was prepared by adding an aqueous solution of potassium seleno-cyanate to an aqueous solution of silver nitrate. The precipitate was washed with water, dried in an oven at 80°, and stored in a desiccator over calcium chloride.

Reaction between Iodine Pentafluoride and Potassium Selenocyanate.—Evacuated breakseal bulbs containing 4 ml. (63 mmole) of iodine pentafluoride (bulb A) and 9·10 g. (63 mmole) of potassium selenocyanate (bulb B) were attached to a third bulb, C, on an all-glass vacuum line which was flamed, evacuated, and sealed. The bulb of potassium selenocyanate, B, was cooled to −78° by means of a solid carbon dioxide–acetone bath, and the two breakseals were opened. As the iodine pentafluoride distilled on to the potassium selenocyanate the latter turned yellow. When all the iodine pentafluoride had been transferred, bulbs A and C were cooled in liquid nitrogen and the cooling bath around the reaction bulb B was lowered slowly so that the iodine pentafluoride could sublime away without melting. When all the iodine pentafluoride had sublimed, bulb B was shaken to expose a fresh surface of potassium selenocyanate and then re-cooled to −78°. The liquid nitrogen was then removed from around bulbs A and C, and the iodine pentafluoride allowed to distil back on to the potassium selenocyanate. In this way the volatile materials were recycled about 30 times during 2 months. During the process the iodine pentafluoride turned brown due to dissolved iodine. Finally the unchanged iodine pentafluoride, iodine (0·68 g., 2·69 mmole), and other volatile materials were condensed into breakseal bulb C which was then sealed. The volatile materials were fractionated and infrared spectra of the fractions recorded. Among the products detected were silicon tetrafluoride (1031 cm.$^{-1}$), carbon tetrafluoride (1283 cm.$^{-1}$), carbonyl fluoride (1941, 1249, and 775 cm.$^{-1}$), and trifluoromethyl cyanide (2271 and 1215 cm.$^{-1}$). The yellow-grey solid left in bulb B was extracted with boiling benzene and filtered. The benzene-insoluble residue was extracted with water and the filtered aqueous solution acidified with dilute hydrochloric acid to produce 0·89 g. of selenium, corresponding to 1·62 g. (11·3 mmole) of unchanged potassium seleno-cyanate.

The brown benzene extract was evaporated to dryness under reduced pressure and pumped to a high vacuum to remove traces of iodine. A yellow solid composed of a mixture of selenium selenocyanate and selenium cyanide, weighing 1·92 g., remained. This mixture was separated into its components by short-path vacuum sublimation from a bath kept at 50°. The sublim-ation apparatus was opened in a dry, nitrogen-filled glove box, and the colourless selenium cyanide, m. p. 134°, weighed (0·28 g., 2·14 mmole, 16% yield) [Found: Se, 60·5; N, 21·8. Calc. for Se(CN)$_2$: Se, 60·3; N, 21·4%]. The involatile residue, on recrystallisation from benzene, gave 1·38 g. (4·78 mmole, 37% yield) of yellow selenium selenocyanate, m. p. (sealed tube) 133—134° decomp. (lit.,[14] 133—134°) [Found: Se, 81·7; N, 9·8. Calc. for Se(SeCN)$_2$: Se, 82·0; N, 9·7%]. In both cases selenium was determined as the element, and nitrogen by the Kjeldahl method. The infrared spectrum of selenium selenocyanate in potassium bromide or Nujol showed bands at (relative intensity in parentheses) 2131(4), 513(8), 364(1), 360(1½), 265(½), 259(½), and 254(½,sh) cm.$^{-1}$.

Reaction between Iodine Pentafluoride and Selenium Cyanide.—The apparatus described in the preceding section was used for this reaction also. Iodine pentafluoride, 3·8 ml. (60 mmole), were distilled on to 0·88 g. (6·7 mmole) of selenium cyanide contained in a trap cooled to −78°. At room temperature the selenium cyanide dissolved readily in the iodine penta-fluoride and the originally colourless solution slowly turned dark brown due to the liberation of iodine. After 4 weeks the unchanged iodine pentafluoride, elemental iodine, and other volatile materials were removed by distillation into a breakseal bulb. The pale yellow residue in the reaction bulb was extracted with hot benzene, filtered, and the filtrate evaporated to dryness under reduced pressure, leaving a white solid which, on vacuum sublimation at 50°, yielded 0·61 g. (70%) of unchanged selenium cyanide. The volatile materials were fractionated and infrared spectra recorded. These showed the presence of silicon tetrafluoride (2057, 1827, 1294, 1191, and 1031 cm.$^{-1}$), carbon tetrafluoride (1283 cm.$^{-1}$), and carbonyl fluoride (1941, 1249, 965, and 775 cm.$^{-1}$).

[14] Rogers and Gross, *J. Amer. Chem. Soc.*, 1952, **74**, 5294.

Reaction of Dinitrogen Tetroxide with Potassium Selenocyanate.—The method used was similar to that described by Muthmann,[2] except that the addition of fuming nitric acid was omitted. The benzene-soluble product consisted of a mixture of selenium selenocyanate (11 mmole) and selenium cyanide (9 mmole); the latter was removed by vacuum sublimation from a bath kept at 50°.

Preparation of Selenocyanogen and Sulphur Cyanide.—The method of Kaufmann and Kögler[4] was used to prepare selenocyanogen; the infrared spectrum of the yellow solution in chloroform (and benzene) showed bands at 2152, 521, 357, and 333 cm.$^{-1}$.

Sulphur cyanide was prepared by Schneider's method[15] employing sulphur dichloride and silver cyanide.

Infrared and Raman Measurements.—Infrared spectra were obtained on potassium bromide pressed discs and Nujol mulls except in the case of selenocyanogen which was examined in chloroform and benzene solutions. A Grubb-Parsons GS 2 double-beam spectrometer was used in the range 4000—670 cm.$^{-1}$, a Perkin-Elmer model 137 in the range 800—400 cm.$^{-1}$, and a Grubb-Parsons DM 4 in the region 450—200 cm.$^{-1}$.

Raman spectra were obtained on concentrated solutions in acetonitrile (7 ml.). A Hilger model 612 Raman instrument was used; this incorporated two glass prisms and a specially designed Toronto arc source (Hg 4358 Å); the output was connected to a Honeywell-Brown recorder.

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[15] Schneider, *J. prakt. Chem.*, 1885, **32**, 187.