On the Reactions of CF₃SF₄Cl, (CF₃)₂SF₂, SF₄, and OsCl₂ with Trimethylsilyl Cyanide

Ramesh C. Kumar and Jeanne M. Shreve

Department of Chemistry, University of Idaho, Moscow, Idaho 83843 U.S.A.

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(Trifluoromethyl)chlorodicyanodifluorosulfur(VI), Dicyanodifluorosulfur(IV), Dicyanobis(trifluoromethyl)sulfur(IV), Thionyl Cyanide

A moderately stable hexacoordinated sulfur(VI) compound with four different kinds of ligands, CF₃SF₄Cl(CN)₂Cl, results when CF₃SF₄Cl is reacted with (CH₃)₃SiCN. The latter compound also gives F₃S(CN)₂ and (CF₃)₂S(CN)₂ with SF₄ and (CF₃)₂SF₂, respectively. These tetra coordinated sulfur(IV) compounds decompose rapidly at 25 °C but are stable at lower temperatures. With OsCl₂ and SCl₂, the white solids OS(CN)₂ and S(CN)₂ result. This provides a new, convenient route to S(CN)₂.

Although CF₃SF₄Cl has been demonstrated to be a useful precursor of a large number of substituted sulfur(VI) compounds, it is one of few compounds which contains three different groups bonded to hexacoordinated sulfur(VI) [1]. There are only a few such compounds, SF₂X₂ (X = F-alkyl), and none where there are fewer than four fluorine atoms bonded to sulfur, e.g., SF₂X₃ is unknown. Analogously, with the exception of F-alkyl groups as ligands, the simple tetracoordinated derivatives of sulfur tetrafluoride are limited, e.g., R₃SF, R₂SF₂ (R = F-alkyl, phenyl, F-phenyl, arylxy, dialkylamine, C₆F₃). Trisubstituted salts, (R₂N)₃S=F- and exist but the latter does not have a sulfur-fluorine bond.

Fluorinated compounds which contain the cyano group attached to S(II) and three-coordinated S(IV) are often prepared by reacting AgCN with labile bromo or chloro-containing compounds, e.g.,

CF₃SCl (CF₃S(O)Cl) + AgCN → CF₃SCN + (CF₃S(O)CN)₂ + AgCl

or Hg(CN)₂ with thiocyanogen

Hg(CN)₂ + (SCN)₂ → Hg(SCN)₂ + 2 CNSCN.

We have now investigated (CH₃)₃SiCN as a precursor of cyano-containing compounds. The results reported here include the first example of a hexacoordinated sulfur(VI) compound with four different kinds of ligands and only two fluorine atoms, CF₃SF₄Cl(CN)₂Cl, as well as the first example of a tetra coordinated sulfur(IV) compound with two F-methyl and two cyano ligands, (CF₃)₂S(CN)₂ and the first example of a disubstituted sulfur tetrafluoride derivative which contains two simple pseudohalogen ligands, F₃S(CN)₂. Additionally the synthesis of thionyl cyanide, OS(CN)₂ is reported as well as a much more convenient synthesis of sulfur di cyanide, S(CN)₂.

Experimental

All gases and volatile liquids were handled in a conventional Pyrex glass vacuum system by using PVT techniques. Purification of products was conducted by low-temperature vacuum-distillation methods and by sublimation under vacuum. Infrared spectra were recorded with a Perkin-Elmer Model 599 B infrared spectrometer. A Fourier transform Jeol FX-90 Q nuclear magnetic resonance spectrometer was used for ³¹P NMR spectra with CCl₄F as an internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6 E mass spectrometer. Elemental analyses were performed at the University of Idaho.

Literature methods were used to prepare CF₃SF₄Cl [6], SF₃Cl [7], and (CF₃)₂SF₂ [8]. The reactants, (CH₃)₃SiCN (Aldrich), (CH₃)₂SiCl (Aldrich), SCl₂ (ROCl/RIC) and SC₆H₅ (Aldrich), were used as obtained without further purification.

(Trifluoromethyl)chlorodicyanodifluorosulfur(VI)

Into a 150 ml Pyrex reaction vessel, CF₃SF₄Cl (1 mmol) and (CH₃)₃SiCN (2 mmol) were condensed
and the mixture was warmed from −20 to −10 °C over 2 h. The reaction was stopped whenever a yellow color began to appear. Purification was carried out by trap-to-trap distillation. In a trap at −78 °C, CF\(_3\)Cl was found in 40% yield.

The compound is a volatile, colorless liquid with a vapor pressure of about 150 Torr at 25 °C and is stable only very briefly at that temperature. Decomposition gives rise to CF\(_3\)SCN and a brown residue which may be polymeric parathio cyanogen.

IR: 2210 m, 1275 s, 1250 s, 1200 m, 1190 s, 840 m, 760 m, 670 vs (m = medium, s = strong, vs = very strong, sh = shoulder).

MS: 181 (CF\(_3\)SFClCN+, 2%), 165 (CF\(_3\)SFClCN+, 9%), 146 (CF\(_3\)SFCN+, 2%), 136 (CF\(_3\)SCl+, 22%), 127 (CF\(_3\)SCN+, 12%), 120 (CF\(_3\)SF+, 17%), 69 (CF\(_3\)F+, 100%).

\(^{19}\)F NMR: \(\delta_{CF_3} = -57 \) (t); \(\delta_{F} = 14 \) (q); \(J_{CF_3-F} = 19 \) Hz; Peak ratio CF\(_3\):SF = 3:2.

Molecular weight: Cald, 226.5; Found, 234 ±7.

**Dicyanodifluorosulfur(IV)***

Into a Pyrex reaction vessel at −196 °C were condensed SF\(_4\) (3 mmol) and (CH\(_3\))\(_3\)SiCN (6 mmol). The reaction mixture was warmed from −10 to 0 °C in 2 h. Purification via trap-to-trap distillation isolated F\(_2\)S(CN)\(_2\) in about 70% yield at −78 °C. The colorless compound has a vapor pressure of about 50–60 Torr at 25 °C. Pure CF\(_3\)SF(CN)\(_2\)Cl is stable in Pyrex glass at 25 °C for about 42 h when it begins to decompose to CF\(_3\)SCN and other products.

IR: 2205 sh, 2190 m, 890 m, 765 s, 740 m, 520 m, 1750 s, 1680 m, 1300 s, 1120 w, 1090 s, 1040 m, 860 s, 740 m, 670(vs), 534 s, 470 s.

IR: 2210 m, 1275 s, 1250 s, 1200 m, 1190 s, 840 m, 760 m, 670 vs (m = medium, s = strong, vs = very strong, sh = shoulder).

MS: 181 (CF\(_3\)SFClCN+, 2%), 165 (CF\(_3\)SFClCN+, 9%), 146 (CF\(_3\)SFCN+, 2%), 136 (CF\(_3\)SCl+, 22%), 127 (CF\(_3\)SCN+, 12%), 120 (CF\(_3\)SF+, 17%), 69 (CF\(_3\)F+, 100%).

\(^{19}\)F NMR: \(\delta_{CF_3} = -57 \) (t); \(\delta_{F} = 14 \) (q); \(J_{CF_3-F} = 19 \) Hz; Peak ratio CF\(_3\):SF = 3:2.

Molecular weight: Cald, 226.5; Found, 234 ±7.

**Dicyano dibis(trifluoromethyl) sulfur (IV)**

Into a Pyrex reaction vessel at −196 °C were condensed SF\(_4\) (3 mmol) and (CH\(_3\))\(_3\)SiCN (6 mmol). The reaction mixture was warmed from −10 to 0 °C in 2 h. Purification via trap-to-trap distillation isolated F\(_2\)S(CN)\(_2\) in about 70% yield at −78 °C. The colorless compound has a vapor pressure of about 50–60 Torr at 25 °C. Pure CF\(_3\)SF(CN)\(_2\)Cl is stable in Pyrex glass at 25 °C for about 42 h when it begins to decompose to CF\(_3\)SCN and other products.

IR: 2205 sh, 2190 m, 890 m, 765 s, 740 m, 520 m, 1750 s, 1680 m, 1300 s, 1120 w, 1090 s, 1040 m, 860 s, 740 m, 670(vs), 534 s, 470 s.

IR: 2210 m, 1275 s, 1250 s, 1200 m, 1190 s, 840 m, 760 m, 670 vs (m = medium, s = strong, vs = very strong, sh = shoulder).

MS: 181 (CF\(_3\)SFClCN+, 2%), 165 (CF\(_3\)SFClCN+, 9%), 146 (CF\(_3\)SFCN+, 2%), 136 (CF\(_3\)SCl+, 22%), 127 (CF\(_3\)SCN+, 12%), 120 (CF\(_3\)SF+, 17%), 69 (CF\(_3\)F+, 100%).

\(^{19}\)F NMR: \(\delta_{CF_3} = -57 \) (t); \(\delta_{F} = 14 \) (q); \(J_{CF_3-F} = 19 \) Hz; Peak ratio CF\(_3\):SF = 3:2.

Molecular weight: Cald, 226.5; Found, 234 ±7.

**Sulfur dicyanide**

(A) Sulfur dichloride (2.19 mmol) and (CH\(_3\))\(_3\)SiCN (4.38 mmol) were stirred at 0 °C for 2 h. A white crystalline solid, S(CN)\(_2\), was obtained in 80% yield. It can be removed by sublimation under vacuum.

(B) Sulfur tetrafluoride (3 mmol) and (CH\(_3\))\(_3\)SiCN (4 mmol) were stirred for 1 h at 0 to 10 °C. The yield of S(CN)\(_2\) was 40%.

(C) Chlorotetrafluoro(trifluoromethyl)sulfur(VI) (2 mmol) and (CH\(_3\))\(_3\)SiCN (4 mmol) were condensed into a 25 ml Pyrex vessel. After stirring at −10 °C for 3 h and then removing all volatiles, a 30% yield of S(CN)\(_2\) remained.

Sulfur dicyanide was identified from its infrared spectrum (2190 m (C=N) and 1090 w (S-C)), mass spectrum, [84 (M\(^+\), 100%) and correct elemental analysis.

**Reaction of chloropentafluorosulfur(VI) and trimethylsilylethyl cyanide**

The reaction mixture of SF\(_3\)Cl (1 mmol) and (CH\(_3\))\(_3\)SiCl (2 mmol) was held at −10 °C for about 2 h. After trap-to-trap distillation, a white crystalline solid, S(CN)\(_2\), and volatile compounds, CNCl and (CH\(_3\))\(_3\)SiF were found. Infrared spectra were used for identification.

**Reaction of chloropentafluorosulfur(VI) and trimethylsilyl chloride**

The reaction mixture of SF\(_3\)Cl (1 mmol) and (CH\(_3\))\(_3\)SiCl (2 mmol) was held at 0 °C for about 2 h. After trap-to-trap distillation, a dark red liquid, SCl\(_2\) plus (CH\(_3\))\(_3\)SiF and Cl\(_2\) were found.
Results and Discussion

There are many examples of reactions of CF₃SF₄Cl with nucleophiles. Some of these result in the reduction of S(VI) to S(IV).

\[
\text{CF}_3\text{SF}_4\text{Cl} + \text{NOCl} \rightarrow \text{CF}_3\text{NO} + \text{SF}_4 + \text{Cl}_2 [9]
\]

\[
\text{CF}_3\text{SF}_4\text{Cl} + 3 \text{R}_2\text{NSiR}_3 \rightarrow \text{CF}_3\text{S}((\text{NR}_2)_2\text{Cl} + 3 \text{R}_3\text{SiF} [10].
\]

In the latter case, it was proposed that three sulfur-fluorine bonds were replaced stepwise by the formation of sulfur-nitrogen bonds with the final product resulting from loss of R₂NF.

With (CH₃)₃SiCN at -10 °C and 0.5 atmosphere pressure, no appreciable reduction of S(VI) to S(IV) was observed, but rather (trifluoromethyl)chlorodicyanodifluorosulfur(VI), CF₃SF₂(CN)₂Cl, was isolated in 40% yield.

\[
\text{CF}_3\text{SF}_4\text{Cl} + 2 (\text{CH}_3)_3\text{SiCN} \rightarrow 20\text{ to } -10 \text{ °C}
\]

\[
\text{CF}_3\text{SF}_4\text{(CN)}_2\text{Cl} + 2 (\text{CH}_3)_3\text{SiF}.
\]

However, when the reaction pressure is increased twelve fold, reduction of S(VI) to S(II) occurred to form solid S(CN)₂ as well as the volatile compounds, CF₃SCN and (CH₃)₃SiF. Pure CF₃SF₂(CN)₂Cl has a vapor pressure of 50–60 Torr and is stable for 42 h at 25 °C. Thereafter, it slowly decomposes to CF₃SCN, CNCI and a yellow polymeric material which was not identified. The ¹⁹F NMR spectrum of CF₃SF₂(CN)₂Cl is comprised of a triplet assigned to CF₃ at \( \varphi = -57 \) and a quartet for SF₂ at \( \varphi = +14 \) which confirms that the two sulfur-fluorine atoms are equivalent and that they are likely axial (trans). While it is not possible to state with absolute certainty that the cyanide groups are trans, based on the acknowledged trans-influencing effect of CN, it is likely that the first CN in the coordination sphere would tend to weaken the S–F bond in the trans position causing the second CN to enter trans with the second CN to enter trans.

Our investigation is continuing.

While the reaction of SF₃Cl with R₂NSiR₃ results in the introduction of -NR₂ trans to the chlorine, reduction of sulfur(VI) to sulfur(II) occurs with

\[
\text{SF}_3\text{Cl} + R_2\text{NSiR}_3 \rightarrow \text{R}_2\text{NSF}_4\text{Cl} [10]
\]

(CH₃)₃SiCN. Analogous behavior is observed when SF₃Cl is reacted with

\[
\text{SF}_3\text{Cl} + (\text{CH}_3)_3\text{SiCN} \rightarrow -10 \text{ °C}
\]

\[
\text{S(CN)}_2 + \text{CNCI} + (\text{CH}_3)_3\text{SiF}
\]

(\text{CH}_3)_3\text{SiCl}.

\[
\text{SF}_3\text{Cl} + (\text{CH}_3)_3\text{SiCl} \rightarrow \text{SCl}_2 + \text{Cl}_2 + (\text{CH}_3)_3\text{SiF}
\]

Having been successful in obtaining a new compound which contained hexacoordinated sulfur(VI), the next step was to examine the reactions of (CH₃)₃SiCN with tetracoordinated sulfur(IV) compounds. In the case of SF₄, the product(s) formed are very temperature dependent, i.e.,

\[
-10 \text{ to } 0 \text{ °C} \rightarrow \text{P}_2\text{Si(CN)}_2 \text{20%} + 2 (\text{CH}_3)_3\text{SiF}
\]

\[
0 \text{ to } 10 \text{ °C} \rightarrow \text{S(CN)}_2 \text{40%} + 2 (\text{CH}_3)_3\text{SiF}
\]

Dicyanodifluorosulfur(IV), P₂S(CN)₂, has a vapor pressure of about 50–60 Torr at 25 °C but is only stable at lower temperatures. It decomposes rapidly at ambient temperature in glass to S(CN)₂, OSF₂ and other products. The ¹⁹F NMR spectrum at -20 °C is a singlet at \( \varphi + 76.0 \) which confirms the equivalence of the two fluorine atoms and, based on compounds (ArO)SF₃, strongly points to an axial arrangement [11].

A disubstituted derivative of SF₄, i.e., (CF₃)₂SF₂, also reacts rather quickly with (CH₃)₃SiCN at -10 °C to form an interesting new compound, (CF₃)₂S(CN)₂ in about 60% yield. While it is unstable at 25 °C, it can be stored for long periods at -196 °C in glass. At -44 °C, it decomposes to CF₃SCN and a brown involatile material. (CF₃)₂S(CN)₂, which has a vapor pressure of about 150 Torr at 25 °C, is surprisingly volatile passing through a trap at -136 °C into one at -196 °C under dynamic vacuum. The ¹⁹F NMR spectrum at -20 °C contains a single peak at \( \varphi = -53.0 \) which is in a region typical for CF₃ groups bonded to sulfur(IV). A characteristic stretching frequency for ν≡N is observed at 2130 cm⁻¹. Although the mass spectral
data are not convincing, elemental analyses coupled with the NMR and IR support its existence. Thionyl cyanide, OS(CN)₂, resulted when thionyl chloride was reacted with (CH₃)₃SiCN. Thionyl cyanide is a white crystalline solid which melts with decomposition at 120–121 °C and is slightly hygroscopic. It is stable in vacuum for several days and stable indefinitely at lower temperatures. A molecular ion is observed in the mass spectrum. Trimethylsilyl cyanide failed to react with SO₂Cl₂ under any conditions tried.

Sulfur dicyanide was first prepared in 1919 [5] and has been vigorously studied in the meantime. However, we have observed that the reaction of sulfur dichloride with trimethylsilyl cyanide provides a convenient and rather inexpensive route to this material. Sulfur dicyanide is a white crystalline solid which sublimes in vacuum, which is hygroscopic and which is stable at reduced temperatures for long periods. As reported above it often appears as a side product when sulfur(VI) compounds are reacted with (CH₃)₃SiCN.

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