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Short Communication

The preparation of fluoroformyl sulphur chlorofluoroimide by isomerization of chloroformyl sulphur difluoride imide

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We recently reported the preparation of $[SF_2NCO]^+[AsF_6]^-$ [1] and $[OSF_2NCO]^+[AsF_6]^-$ [2] from AsF_5 and $COFNSF_2$ [3] and $COFNSOF_2$ [4], respectively. Spectroscopic investigations indicated these compounds to be isocyanate derivatives of SF_3^+ or OSF_3^+ cations rather than sulphur difluoride imide or oxide imide acylium salts. In these species, although the positive charge should be located mainly on the sulphur atom, reactions with NOCl occur through nucleophilic attack of Cl^- at the carbon atom of the isocyanate group.

$$[SF_2NCO]^+[AsF_6]^- + NOCl \rightarrow \underset{(I)}{ClC(O)NSF_2} + [NO]^+[AsF_6]^-$$

$$[OSF_2NCO]^+[AsF_6]^- + NOCl \rightarrow \underset{(II)}{ClC(O)NSOF_2} + [NO]^+[AsF_6]^-$$

Compound (I) is unstable and isomerizes rapidly, even in the gaseous phase at low pressure, to give COFNSClF (III) (see Fig. 1).

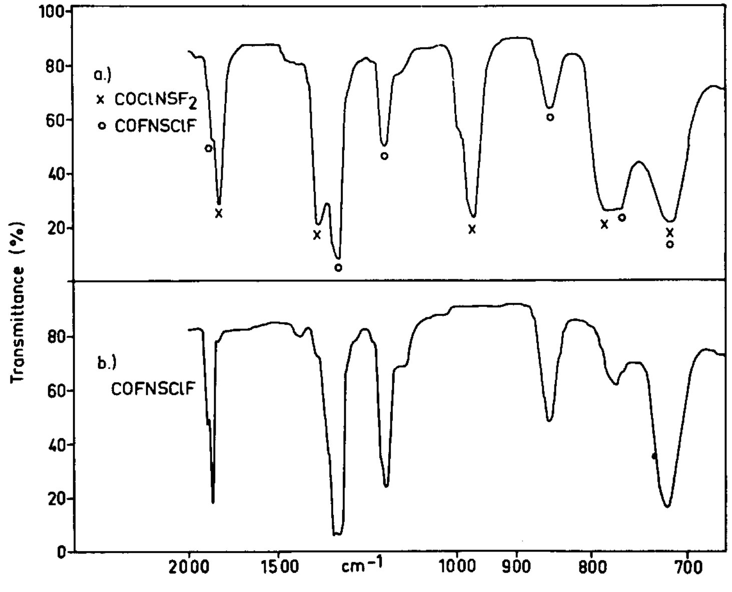

Fig. 1. IR spectra (in the gaseous phase) of (a) a mixture of $COClNSF_2$ and COFNSClF, and (b) COFNSClF [mixture (a) left in the IR cell for 10 min].

(I) (III)

It is not therefore possible to isolate (I) in the pure state and the following spectral data were obtained for its mixture with (III): IR (gas)*: 1790(s) [ν(CO)], ~1350(vs) [ν(SN)], 967(vs) [ν(Cl)], ~770(vs) [$\nu(SF)_{sym}$], ~ 720 cm^{-1} (vs) [$\nu(SF)_{asym}$]; ^{19}F NMR (35 °C with $CFCl_3$ as internal standard): $\delta_{SF} = -47.6$ ppm. It is probable that a similar, but more complicated, rearrangement occurs in the chlorination of CH_3NSF_2, where in addition to CH_2ClNSF_2 and $CHCl_2NSF_2$, CF_3NSCl_2 is also formed [5].

The chlorofluoroimide is a colourless liquid, stable only at low temperatures. At room temperature it rapidly dismutates:

$$\underset{(III)}{2COFNSClF} \rightarrow COFNSCl_2 + COFNSF_2$$

Compound (III) was characterized by its IR and NMR spectra. IR (gas)*: 1860(sh), 1828(vs) [ν(CO)], 1275(vs) [ν(SN)], 1152(s), 1112(sh) [ν(CF)], 850(s) [ν(CN)?], 772(m) [π(OCFN)?], 717(vs) [ν(SF)], 510(m), 505(sh)(δ), 477 cm^{-1}(vs) [ν(S–Cl)]; ^{19}NMR†: (at 35 °C) $\delta_{SF} = -46.1$ (s, br); $\delta_{CF} = -19.7$ (s, br); (at −60 °C) $\delta_{SF} = -37.4$ (d), $\delta_{CF} = -19.5$ ppm (d), $J(FF) = 12.6$ Hz. The mass spectrum exhibited the molecular ion of (III) in addition to those of $COFNSCl_2$ and $COFNSF_2$. A 1:1 adduct is formed with AsF_5 as shown by elemental analysis. Because of the poor quality of the spectra obtained so far it is not possible to decide whether a salt of $[SFClNCO]^+$ or a mixture of a salt of $[SCl_2NCO]^+$ and $[SF_2NCO]^+[AsF_6]^-$ is present.

Probably because of the presence of the more stable S^{VI}–F bond, compound (II) shows no tendency to isomerize. It exhibits the following IR and NMR spectra. ^{19}F NMR: $\delta_{SF} = -44.3$ ppm; IR: 1830(w), 1766(s) [ν(CO)], 1434(vs) [$\nu(NSO)_{asym}$], 1276(w), 1229 (vs) [$\nu(NSO)_{sym}$], 1021 [ν(CCl)], 868(m), 829(vs) [ν(SF)], 782(w), 558(m), 502 cm^{-1}(w). The mass spectrum (highest peak observed 128 [M–Cl] (rel. int. 100)) exhibited the expected pattern.

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* The assignment given is tentative. † s = singlet, br = broad, d = doublet.