Fluoro–Sulfur Compounds

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Synthesis of the Long Sought After Compound Pentafluoronitrosulfane, SF_5NO_2**

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The chemistry of SF_5-containing molecules[1–3] is no longer just of interest to sulfur and fluorine chemists. Recently, this class of compounds has become a very important issue in the area of atmospheric chemistry. According to a recent report, more than 4000 tons of the super greenhouse gas SF_5CF_3 are present in the stratosphere.[4–6] In addition, scientists have also proposed the use of molecules such as SF_5CF_3, SF_6, fluoroalkanes, and so on to terraform Mars.[7]

As a number of simple SF_5-containing compounds are still unknown although the corresponding CF_3 analogues have been well documented, we undertook the preparation of the long sought after molecule SF_5NO_2.[8] Both the thermal and photochemical reactions of SF_5 radical sources such as SF_5Cl, SF_5Br, and S_2F_{10} have been reviewed recently by Lentz and Seppelt;[9] however, we had to make use of either a new SF_5 radical source in $(SF_5)_3N$ or a different light source to the more commonly used mercury immersion lamp, namely, diazo or superblue lamps ($\lambda_{max} = 420$ nm). Thus, SF_5NO_2 was successfully prepared by two independent methods: A) the thermal reaction of $(SF_5)_3N$ with nitrogen dioxide, NO_2 [Eq. (1)], and B) the photochemical reaction between SF_5Br and NO_2 [Eq. (2)]. Herein, we provide an overview of the spectroscopic and physical properties and structure of SF_5NO_2, as this molecule has the longest S^{VI}–N bond reported to date.

$$(SF_5)_3N + NO_2\,(\text{excess}) \rightarrow SF_5NO_2 + \text{side products} \quad (1)$$

$$SF_5Br + NO_2\,(\text{excess}) \xrightarrow{\lambda_{max}=420\,\text{nm}} SF_5NO_2 + \text{side products} \quad (2)$$

Two methods were used to prepare SF_5NO_2, starting either from the novel amine, $(SF_5)_3N$ (method A), or from SF_5Br (method B).[10] Owing to its elongated and weak N–S bonds, $(SF_5)_3N$ readily forms $(SF_5)_2N$[11,12] and SF_5 radicals, which in turn react with NO_2 (or with NO_2Cl) at room temperature to generate SF_5NO_2. By method A, SF_5NO_2 was prepared for the first time by taking advantage of the weak N–S bonds in $(SF_5)_3N$ in its reaction with NO_2.[13] The ^{19}F NMR spectrum of the SF_5NO_2 thus obtained displayed a typical AB_4 pattern, which is characteristic of the SF_5 group. Furthermore, the IR spectrum of SF_5NO_2 showed the diagnostic stretches and bends for both the SF_5 and NO_2 moieties. The SF_5 group usually displays three strong vibrational peaks below 1000 cm^{-1}; in SF_5NO_2, these appeared at 908, 801, and 594 cm^{-1}. The two NO_2 stretching bands in SF_5NO_2 were unambiguously assigned as $\tilde{\nu}_{as}NO_2 = 1654\ cm^{-1}$ and $\tilde{\nu}_{s}NO_2 = 1303\ cm^{-1}$, respectively.

As a result of the limited availability of $(SF_5)_3N$, SF_5Br was tested as an alternative source of the SF_5 radical in method B. The photochemical reaction between SF_5Br and NO_2 successfully yielded SF_5NO_2 as shown in Equation (2). It is thought that during the photolysis, first, SF_5 and Br radicals are formed during the irradiation, which then react with NO_2 individually. Both $BrNO_2$ and BrONO can be formed from the Br radical.[14] The N-bonded product, $BrNO_2$, is the thermodynamically more stable product, while the O-bonded product, BrONO, is favored kinetically. The N-bonded product can also be formed by attack at the rear side on BrONO by the nitrogen atom of another NO_2 molecule, with elimination of NO_2 as described by Broske and Zabel.[15] The SF_5 radical behaves similarly. Both SF_5NO_2 and SF_5ONO are presumed to be formed during the photochemical reaction. (SF_5ONO is a short-lived species that is thought to have been observed by FTIR spectroscopy during the reaction of $(SF_5)_3N$ with NO_2 at room temperature.) However, in this case attack by NO_2 on SF_5ONO from the rear side is impossible owing to the bulkiness of the SF_5 group. SF_5NO_2

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was isolated in only 3% yield based on SF_5Br used in this reaction. Presumably, a large proportion of SF_5 radicals that were generated during the reaction decomposed before having the opportunity to react. CsF was used to ease the purification of SF_5NO_2 through the concept of fluoride ion affinity. As shown in Equations (3) and (4), CsF is used to

$$CsF + SOF_4 \rightarrow Cs^+SOF_5^- \tag{3}$$

$$CsF + SF_4 \rightarrow Cs^+SF_5^- \tag{4}$$

remove SF_4 and SOF_4 by salt formation. The use of CsF also helps to remove Br_2 and converts NO_2 into FNO. Some of these side products are almost impossible to remove by distillation from SF_5NO_2 without such treatment with CsF. The crude SF_5NO_2 was then purified by low-temperature trap-to-trap distillation.

The ^{19}F NMR spectrum of SF_5NO_2 revealed an AB_4 pattern. The simulated NMR data are $\delta = 46.79$ ppm (F_{ax}), $\delta = 43.02$ ppm (F_{eq}), and coupling constant $^2J(F_{ax}–F_{eq}) = 144.3$ Hz. In addition, the ^{14}N NMR spectrum of SF_5NO_2 was recorded and is shown in Figure 1. The spectrum does not reveal perfect quintet splitting because of the quadrupolar effects of the ^{14}N nucleus (^{14}N NMR (versus external reference NO_3^- at $\delta = 383$ ppm): $\delta = 283.8$ ppm; $^2J(F–N) = 8$ Hz).

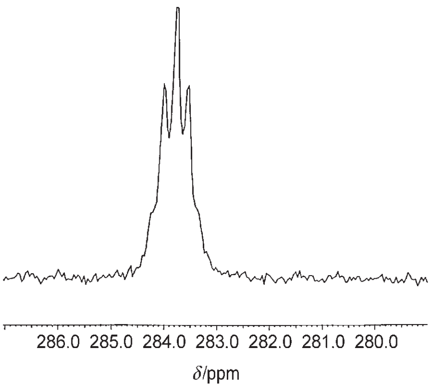

Figure 1. ^{14}N NMR spectrum of SF_5NO_2.

The IR spectrum of SF_5NO_2 is shown in Figure 2. In Table 1, the $\tilde{\nu}_{as}NO_2$ and $\tilde{\nu}_sNO_2$ vibrational frequencies of NO_2 are compared to XNO_2 (X = F, CF_3, and SF_5). As a result of the inductive effects of the strong electron-withdrawing substituents (F, CF_3, and SF_5), the $\tilde{\nu}_{as}NO_2$ and $\tilde{\nu}_sNO_2$ stretching frequencies of these three compounds are all shifted to higher frequencies relative to those for the NO_2 molecule.

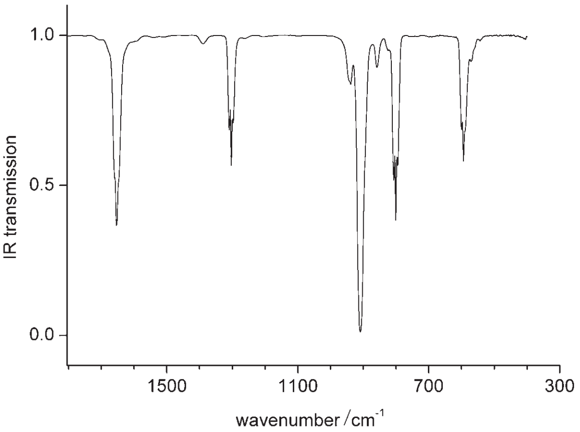

Figure 2. IR spectrum of SF_5NO_2.

Table 1: IR spectral data for the NO_2 moiety in XNO_2 (X = F, CF_3, SF_5) versus the NO_2 molecule.[a]

Compound	$\tilde{\nu}_{as}NO_2$ [cm^{-1}]	$\tilde{\nu}_sNO_2$ [cm^{-1}]	δNO_2 [cm^{-1}]
NO_2	1613	1261	751
FNO_2[16]	1792	1310	822
SF_5NO_2[b] (this work)	1654	1303	801
CF_3NO_2[17,18]	1627	1310	751

[a] $\tilde{\nu}_{as}$ asymmetric stretch; $\tilde{\nu}_s$ symmetric stretch; δ bending mode. [b] For $SF_5{}^{15}NO_2$, the $^{15}NO_2$ frequencies are $\tilde{\nu}_{as}NO_2 = 1618$, $\tilde{\nu}_sNO_2 = 1287$, and $\delta NO_2 = 793$ cm^{-1}.

A mass spectrum of SF_5NO_2 was obtained and shows the fragmentation pattern, m/z 127 (SF_5^+, 100%), 108 (SF_4^+, 6.7%), 89 (SF_3^+, 51.0%), 81 ($SFNO^+$, 1.5%), 70 (SF_2^+, 11.5%), 64 (SO_2^+, 12.1%), 51 (SF^+, 5.9%), 46 (NO_2^+, 69.3%). Although the molecular ion was not observed, the mass spectrum did reveal fragments at m/z 46 and 127 that indicate the presence of NO_2^+ and SF_5^+, respectively. In addition, the peak at m/z 81, which corresponds to $SFNO^+$, provided evidence that the two previously mentioned fragments are originally bonded together. By gas density measurements, the relative molecular mass was determined as $M_r = 173.0 \pm 0.5$. The equation derived from the vapor pressure curve is $\ln(p/p_o) = -3788/T + 13.33$. The normal extrapolated boiling point for SF_5NO_2 was determined as 9 °C, its heat of vaporization is approximately 29.3 $kJ\,mol^{-1}$, and it melts at -78 ± 2 °C. Thermal studies of SF_5NO_2 indicate that it mainly decomposes to SOF_4 and FNO at a rate of 3% a day at room temperature, but when heated at 80 °C total decomposition took place within minutes.

A gas-phase electron diffraction study of SF_5NO_2 was carried out. The preliminary data, as shown in Figure 3, reveal the longest reported $S^{VI}–N$ bond at 1.903(7) Å, which is some 0.2 Å longer than a normal $S^{VI}–N$ single bond. Quantum chemical calculations (HF/6-31 G* and B3LYP/6-311 + G*) predict rather different values for the $S^{VI}–N$ bond from 1.844 Å to 2.049 Å. Further details of this structure[19] will be reported at a later date.

The goal of this research was to synthesize both SF_5NO_2 and SF_5NO. Here, SF_5NO_2 was successfully prepared by two independent methods but SF_5NO remains unknown. Of the two routes used to prepare SF_5NO_2, one employed the novel amine $(SF_5)_3N$ as a starting material while the other started from SF_5Br. Because $(SF_5)_3N$ is extremely difficult to prepare, the second route was the preferred method for preparing gram quantities of SF_5NO_2. Along the way, a modified procedure for preparing SF_5Br on a 500-gram scale was developed.

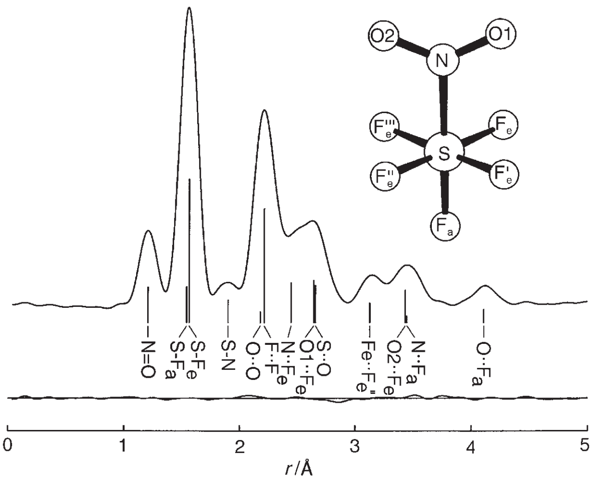

Figure 3. The structure of SF_5NO_2 obtained from gas-phase electron diffraction studies.

The success of the photochemical preparative method for SF_5NO_2 is based on the use of blue light from a diazo lamp ($\lambda_{max} = 420$ nm), as the molecule NO_2 photodissociates at wavelengths shorter than 395 nm as associated with the use of a mercury immersion lamp. The former source of irradiation excites the NO_2 molecule, and the excited NO_2 molecule is believed to further participate in the formation of SF_5 radicals. The molecule SF_5NO_2 has also been studied as a ^{15}N-labeled compound. The IR spectrum of $SF_5{}^{15}NO_2$ shows the expected mass effects of the ^{15}N isotope. The ^{15}N NMR spectrum of $SF_5{}^{15}NO_2$ shows a clear quintet splitting (^{15}N NMR (vs external reference NO_3^- at $\delta = 383$ ppm): $\delta = 283.4$ ppm (quintet), $^2J(F\text{–}N) = 11.6$ Hz), and its ^{19}F NMR spectrum shows additional multiplicities in the equatorial fluorines (AB_4X spin system). The structural data obtained from gas-phase electron diffraction studies indicate the longest S^{VI}-N single bond reported. Further details concerning this study will appear in due course.

Experimental Section

Preparation of SF_5NO_2: Method A: The amine $(SF_5)_3N$ (0.36 g, 0.90 mmol) was transferred under vacuum into a fluorinated ethylene propylene (FEP) tube equipped with a metal valve. Nitrogen dioxide (0.12 g, 2.60 mmol) was then condensed into the FEP tube at −196 °C, and the reaction vessel was allowed to gradually warm to room temperature. After 4 h, all of the $(SF_5)_3N$ crystals had disappeared. The volatile products were subjected to a series of distillations through −105, −130, and −196 °C traps. The −130 °C trap stopped the crude SF_5NO_2. The percentage yield was not calculated owing to the difficult purification of the product.

Method B: SF_5Br (3.9 g, 18.8 mmol) and NO_2 (0.9 g, 19.6 mmol) were transferred to a 4-L or 20-L pyrex reactor. A photolysis chamber with 12 diazo lamps (TL40W/03; each 40 W, 48 inches (ca. 122 cm) long) was used to photolyze this mixture. After 12 h irradiation, the resulting products were condensed into a 300-mL stainless-steel cylinder held at −196 °C. This cylinder was then warmed to dry-ice temperature (−78 °C), and all the materials that are volatile at this temperature were then transferred under vacuum into another cylinder cooled to −196 °C containing 400 grams (large excess) of CsF, which was used to easily remove Br_2, SOF_4, and SF_4 and also to convert NO_2 into FNO. Then, a trap-to-trap distillation through traps at −78 °C, −130 °C, and −196 °C was carried out to separate SF_5NO_2 from impurities such as FNO and SF_6. The product SF_5NO_2 (0.09 g, 0.56 mmol; 3 % yield) was recovered in the trap at −130 °C.

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