

## REACTIONS OF THE $(CF_3)_2NO$ RADICAL WITH STRONG OXIDIZERS

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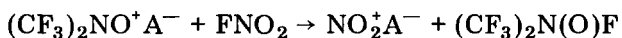
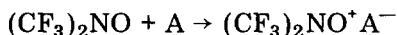
### Summary

The reactions of  $(CF_3)_2NO$  with  $PtF_6$ ,  $MoF_6$ ,  $ReF_6$ ,  $O_2^+SbF_6^-$  and  $O_2^+AsF_6^-$  have been studied. The reaction of  $(CF_3)_2NO$  with  $O_2^+SbF_6^-$  presents a new method of producing  $CF_3$  radicals chemically at low temperature. This was demonstrated by a new and high yield synthesis of  $(CF_3)_2NOCF_3$ . In addition, the novel compound  $[(CF_3)_2NO]_2CF_2$  has been isolated as a by-product from this reaction and was characterized.

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### Introduction

The bis(trifluoromethyl) nitroxide radical was discovered [1,2] in 1964. Since then, the physical and chemical properties of this unusually stable radical have been studied extensively and were summarized in two recent reviews [3,4]. In its reaction chemistry,  $(CF_3)_2NO$  behaves as a pseudo-halogen with an oxidizing power similar to or higher than that of  $Cl_2$  [3]. Due to this high oxidizing power, the previously reported studies [3,4] appear to have been limited to combinations with other radicals, additions across double bonds, and reactions with reducing agents. In view of the well-known stability of the  $F_2N=O^+$  cation [5,6] and of hexafluoroacetone which are isoelectronic with  $COF_2$  and the hypothetical  $(CF_3)_2N=O^+$  cation, respectively, it seemed interesting to study the behavior of  $(CF_3)_2NO$  towards strong oxidizers. If the oxidation could be limited to a simple one-electron transfer from  $(CF_3)_2NO$  to an oxidizing species A, the following reaction series would allow not only the synthesis of the  $(CF_3)_2N=O^+$  cation, but also that of the novel bis(trifluoromethyl)-substituted  $NF_3O$  molecule:



Although we could not limit the oxidation of  $(CF_3)_2NO$  to a one-electron transfer without breakage of chemical bonds, several interesting results were obtained which we report in this paper.

## Experimental

### Materials

Rhenium hexafluoride and  $\text{MoF}_6$  (Ozark Mahoning) and  $\text{CF}_3\text{NO}$  (PCR) were purchased. Platinum hexafluoride was prepared by burning Pt wire in an  $\text{F}_2$  atmosphere at  $-196^\circ\text{C}$  [7]. The  $\text{O}_2^+$  salts of  $\text{AsF}_6^-$  and  $\text{SbF}_6^-$  were synthesized by the methods of Beal [8] and Shamir [9], respectively. Bis(trifluoromethyl) nitroxide was prepared [10] from  $\text{Ag}_2\text{O}_2$  and  $(\text{CF}_3)_2\text{NOH}$ , with the latter being synthesized as previously described [1]. Prior to use, all volatile starting materials were purified by fractional condensation and their purity was verified by spectroscopic techniques.

### Apparatus

The materials used in this work were manipulated in a well-passivated (with  $\text{ClF}_3$ ) 304 stainless-steel vacuum line equipped with Teflon FEP U traps and 316 stainless-steel bellow-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise-Bourdon tube type gauge (0 - 1500 mm  $\pm$  0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Model 337 and 457 spectrophotometers in the range 4000 - 250  $\text{cm}^{-1}$ . The spectra of gases were obtained using 304 stainless-steel cells of 5 cm path length fitted with AgCl or AgBr windows. The spectra of solids were obtained by pressing two small single-crystal platelets of either AgCl or AgBr into a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line and a Claassen filter [11] for the elimination of plasma lines. Glass melting point capillaries were used as sample containers in the transverse-viewing-transverse-excitation technique.

Mass spectra were recorded on a Quad 300 (Electronic Associates Inc.) quadrupole mass spectrometer using a passivated all-stainless-steel inlet system.

The  $^{19}\text{F}$  NMR spectra were recorded at 56.4 MHz on a Varian DA60 NMR spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique.

### The $(\text{CF}_3)_2\text{NO}-\text{MoF}_6$ system

Molybdenum hexafluoride (0.90 mmol) and  $(\text{CF}_3)_2\text{NO}$  (1.44 mmol) were combined at  $-196^\circ\text{C}$  in a passivated 25  $\text{cm}^3$  sapphire stainless-steel reaction tube (Varian Model CS-4250-3). After warming the mixture to  $29^\circ\text{C}$  for 1 h, only unreacted starting materials were recovered.

### *The (CF<sub>3</sub>)<sub>2</sub>NO-ReF<sub>6</sub> system*

Rhenium hexafluoride (2.01 mmol) and (CF<sub>3</sub>)<sub>2</sub>NO (1.88 mmol) when kept at 29 °C for 1 h in a sapphire reactor produced a small amount of a non-volatile white solid. To increase the yield of this solid, the starting materials were recombined in the reactor and kept at 29 °C for 100 h. The volatile products were removed, separated by fractional condensation, measured by PVT and identified by spectroscopic techniques. They consisted of (CF<sub>3</sub>)<sub>2</sub>NOCF<sub>3</sub> (0.29 mmol), (CF<sub>3</sub>)<sub>2</sub>NO (1.61 mmol) and ReF<sub>6</sub> (1.92 mmol). The white solid residue (8 mg) was mainly NO<sup>+</sup>ReF<sub>6</sub><sup>-</sup>, but its infrared spectrum also indicated the presence of a new rhenium oxyfluoride anion having strong absorptions at 1059, 1022 and 971 cm<sup>-1</sup>.

### *The (CF<sub>3</sub>)<sub>2</sub>NO-PtF<sub>6</sub> system*

Platinum hexafluoride (1.78 mmol) and (CF<sub>3</sub>)<sub>2</sub>NO (3.56 mmol) were combined at -196 °C in a sapphire reactor. The mixture was slowly warmed up until the (CF<sub>3</sub>)<sub>2</sub>NO started to melt and react. The reaction with PtF<sub>6</sub> was very violent (caution!) and the reaction was immediately quenched by cooling to -196 °C. This procedure was repeated several times until the reaction was essentially complete when the reactor was kept at 25 °C for 1 day. The volatile products consisted of COF<sub>2</sub> and CF<sub>4</sub> (4.04 mmol), (CF<sub>3</sub>)<sub>2</sub>NOCF<sub>3</sub> (0.54 mmol) and (CF<sub>3</sub>)<sub>2</sub>NO (0.73 mmol). The dark-grey solid residue (570 mg) was identified by vibrational spectroscopy as NO<sup>+</sup>PtF<sub>6</sub><sup>-</sup>.

### *The (CF<sub>3</sub>)<sub>2</sub>NO-O<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> system*

In a Teflon-FEP ampoule, (CF<sub>3</sub>)<sub>2</sub>NO (0.86 mmol) and O<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> (0.95 mmol) were combined at -196 °C. The mixture was slowly warmed up to 25 °C and a smooth reaction occurred with gas evolution. The volatile products consisted of O<sub>2</sub> (0.90 mmol), (CF<sub>3</sub>)<sub>2</sub>NO (0.32 mmol) and CF<sub>4</sub> and COF<sub>2</sub> (0.98 mmol). The white solid residue consisted of NO<sup>+</sup>AsF<sub>6</sub><sup>-</sup> (0.48 mmol) indicating that some O<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> had decomposed irreversibly during the reaction, with the free AsF<sub>5</sub> being absorbed by the metal fluoride surface of the passivated metal line.

### *The (CF<sub>3</sub>)<sub>2</sub>NO-O<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> system*

In a 30 cm<sup>3</sup> stainless-steel cylinder, (CF<sub>3</sub>)<sub>2</sub>NO (1.92 mmol) and O<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> · 0.73SbF<sub>5</sub> (0.70 mmol) were combined at -196 °C. The mixture was allowed to warm to -21 °C and kept at this temperature for 1 day. The volatile products consisted of O<sub>2</sub> (0.70 mmol), CF<sub>4</sub> and COF<sub>2</sub> (0.74 mmol), (CF<sub>3</sub>)<sub>2</sub>NOCF<sub>3</sub> (0.73 mmol) and [(CF<sub>3</sub>)<sub>2</sub>NO]<sub>2</sub>CF<sub>2</sub> (0.16 mmol). The white solid residue consisted of NO<sup>+</sup>SbF<sub>6</sub><sup>-</sup> · 0.73SbF<sub>5</sub> (0.70 mmol).

### *The CF<sub>3</sub>NO-O<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> system*

When mixtures of CF<sub>3</sub>NO and O<sub>2</sub><sup>+</sup>SbF<sub>6</sub><sup>-</sup> · 0.73SbF<sub>5</sub> with either component in excess were kept for several days at ambient temperature, little interaction occurred. Heating to 80 °C was required for NO<sup>+</sup>SbF<sub>6</sub><sup>-</sup> formation and O<sub>2</sub> evo-

TABLE 1

Mass spectrum\* of  $[(CF_3)_2NO]_2CF_2$ 


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|  |
|--|
| 367, $(CF_3)_2NOCF_2ONC_2F_5^+$ , (6); 279, $C_2F_5NOCF_2ONCF_2^+$ , (7);                                |
| 234, $(CF_3)_2NOCF_2O^+$ , (0+); 218, $(CF_3)_2NOCF_2^+$ , (38); 191, $C_2F_4NOCFON^+$ , (0.7);          |
| 168, $(CF_3)_2NO^+$ , (2.8); 149, $C_2F_5NO^+$ , (1.4); 133, $C_2F_5N^+$ , (2.8);                        |
| 130, $C_2F_4NO^+$ , (90); 127, $CF_3NOCO^+$ , (0.7); 114, $C_2F_4N^+$ , (29); 111, $C_2F_3NO^+$ , (0.7); |
| 108, $CF_2NOCO^+$ , (0+); 99, $CF_3NO^+$ , (1.2); 95, $C_2F_3N^+$ , (0.2); 92, $C_2F_2NO^+$ , (1);       |
| 83, $CF_3N^+$ , (0.3); 80, $CF_2NO^+$ , (0.2); 76, $C_2F_2N^+$ , (0+); 70, $CNOCO^+$ , (20);             |
| 69, $CF_3^+$ , (1000); 66, $CF_2O^+$ , (32); 64, $CF_2N^+$ , (60); 61, $CFNO^+$ , (3);                   |
| 57, $C_2FN^+$ , (0.2); 50, $CF_2^+$ , (104); 47, $CFO^+$ , (195); 45, $CFN^+$ , (14);                    |
| 44, $CO_2^+$ , (54); 31, $CF^+$ , (106); 30, $NO^+$ , (340); 26, $CN^+$ , (3); 19, $F^+$ , (46);         |
| 16, $O^+$ , (120); 14, $N^+$ , (135); 12, $C^+$ , (11).  |

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\* Measured at 70 ev. Results quoted as *m/e*, ion, relative intensity.

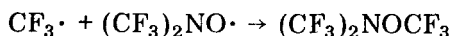
lution. No evidence was obtained for the formation of any species containing more than one carbon atom. The main products were  $COF_2$ ,  $CF_4$  and  $CF_3NO_2$ .

#### Properties of $[(CF_3)_2NO]_2CF_2$

The compound is a stable, colorless liquid having vapor pressures of 3 and 16 mmHg at  $-31.2^\circ C$  and  $0^\circ C$ , respectively. During fractional condensation, it slowly passed a  $-64^\circ C$  trap and was retained at  $-78^\circ C$ . Its mass spectrum is given in Table 1 and its infrared and Raman spectrum in Fig. 1 and Table 2. The  $^{19}F$  NMR spectrum showed a 1:2:1 triplet at 67.96 ppm ( $CF_3$ ) and a multiplet ( $\sim 13$ ) at 69.77 ppm ( $CF_2$ ) above the internal standard  $CFCl_3$  with  $J(FF) = 6.0$  Hz and an area ratio slightly larger than 6:1. Three additional weak signals were observed at 66.2, 66.9 and 73.6 ppm which were broad singlets. The relative peak area of the low-field signal increased for the neat compound and increased further with increasing temperature. In addition, the  $CF_3$  signal started to show a low-field component with increasing intensity of the low-field  $CF_2$  signals at  $\sim 66$  ppm. Analysis: Found: C, 15.7; F, 68.1%.  $C_5F_{14}N_2O_2$  requires C, 15.54; F, 68.39%.

#### Results and discussion

Of the strong oxidizers studied,  $PtF_6$  and  $O_2^+$  salts are capable of oxidizing the  $(CF_3)_2NO$  radical under the given conditions whereas  $MoF_6$  is not. Rhenium hexafluoride with an electron affinity  $> 90$  kcal mol $^{-1}$  [12] appears capable of slowly oxidizing  $(CF_3)_2NO$  at room temperature. These results are in excellent agreement with the apparent [3] high electronegativity of the  $(CF_3)_2NO$  radical. This requirement of a strong oxidizing reagent may also explain the lack of  $(CF_3)_2NO^+$  formation. Instead of a simple one-electron transfer reaction, an oxidative fission of the N—C bond was observed resulting in the formation of  $CF_4$ ,  $NO^+$  salts and significant amounts of  $CF_3$  radicals. In the presence of unreacted  $(CF_3)_2NO$  radicals, the  $CF_3$  radical undergoes the following reaction



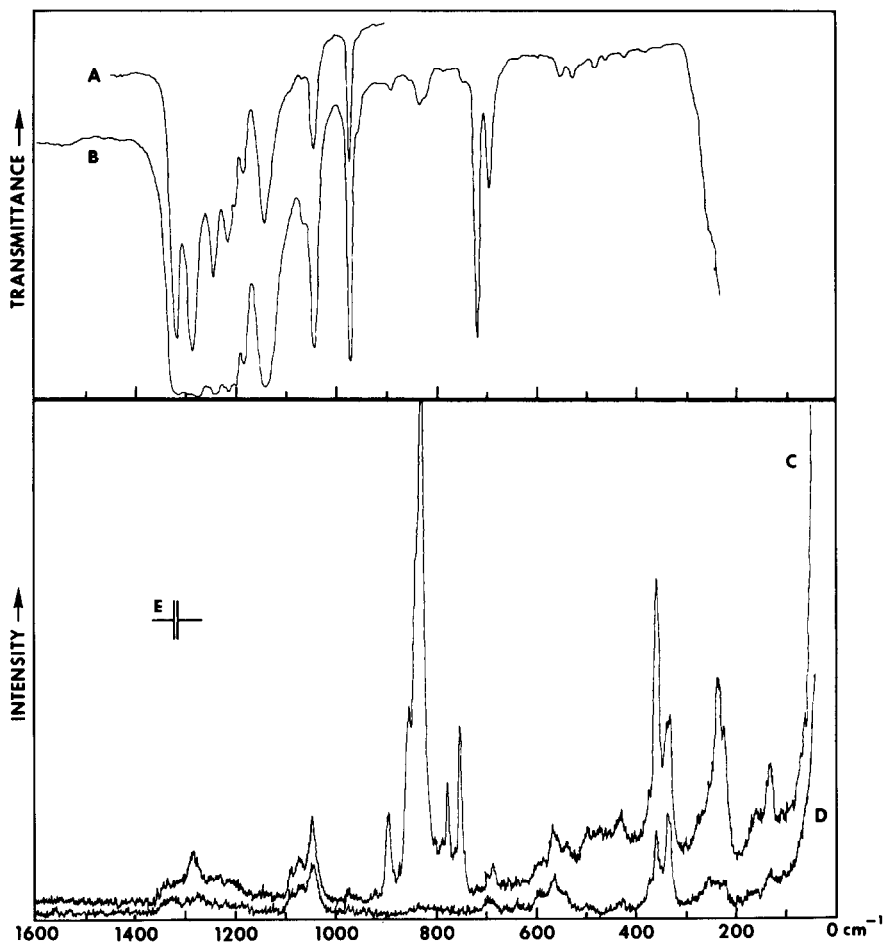


Fig. 1. Vibrational spectrum of  $((\text{CF}_3)_2\text{NO})_2\text{CF}_2$ . A and B: IR spectrum of the gas at 10 and 3 mm, respectively, path length 5 cm, window material AgBr. C and D: Raman spectrum of the liquid with the polarization parallel and perpendicular, respectively. E indicates the spectral slit width.

Thus, these reactions present a new high yield synthesis of  $(\text{CF}_3)_2\text{NOCF}_3$ . However, owing to the commercial availability of  $\text{CF}_3\text{NO}$ , the catalytic fluorination of  $\text{CF}_3\text{NO}$  yielding  $(\text{CF}_3)_2\text{NOCF}_3$  in 55% yield [13] appears to be a more attractive synthetic route. A brief study to substitute  $(\text{CF}_3)_2\text{NO}$  by  $\text{CF}_3\text{NO}$  in its reaction with  $\text{O}_2^+$  salts did not result in the formation of any two carbon atom species but only  $\text{CF}_3\text{NO}$  oxidation products. This observation agrees with the above postulate that in  $(\text{CF}_3)_2\text{NO}$  an N-C bond is attacked first with  $\text{CF}_4$  formation resulting in an excited  $\text{CF}_3\text{NO}$  species which can readily lose a  $\text{CF}_3$  radical. The interaction between  $(\text{CF}_3)_2\text{NO}$  and  $\text{O}_2^+\text{SbF}_6^-$  when carried out under suitable conditions (such as gas phase reaction, use of a carrier gas, etc.) may have potential for producing  $\text{CF}_3$  radicals under mild

TABLE 2

| Vibrational spectrum ( $\text{cm}^{-1}$ ) of $[(\text{CF}_3)_2\text{NO}]_2\text{CF}_2$ and its assignment compared to those of $[(\text{CF}_3)_2\text{NO}]_2\text{CO}$ and $[(\text{CF}_3)_2\text{N}]_2$ |                                  | Tentative assignment for $(\text{CF}_3)_2\text{NOCF}_2\text{ON}(\text{CF}_3)_2$ |   |  |  |                |             |              |                |  |
|--|----------------------------------|---|---|--|--|----------------|-------------|--------------|----------------|--|
| $\text{F}_3\text{C}$<br>$\text{F}_3\text{C}$   | $\text{CF}_3^a$<br>$\text{CF}_3$ | $\text{F}_3\text{C}$<br>$\text{F}_3\text{C}$                                    | $\text{NO}-\text{C}(=\text{O})-\text{ON}$<br>$\text{CF}_3$<br>$\text{CF}_3^b$ | $\text{F}_3\text{C}$<br>$\text{F}_3\text{C}$ | $\text{NOCF}_2\text{ON}$<br>$\text{CF}_3$<br>$\text{CF}_3$ | Raman (liquid) | IR (gas)    | IR (gas)     | Raman (liquid) |  |
| 1333 (s)   | 1334(4)                          | 1317 (vs)   | 1322 (vs)   | 1322 (vs)                                    | 1325(4)  |                | 1322 (vs)   | 1322 (vs)    | 1325(4)        |  |
| 1310 (s)   | 1295(3)                          | 1269 (vs)   | 1291 (vs)   | 1291 (vs)                                    | 1285(10) (p)   |                | 1291 (vs)   | 1291 (vs)    | 1285(10) (p)   |  |
| 1292 (s)   | 1278(2)                          | 1237 (vs)   | 1249 (vs)   | 1249 (vs)                                    |  |                | 1249 (vs)   | 1249 (vs)    |                |  |
| 1232 (s)   | 1239(9) (p)                      | 1218 (vs)   | 1220 (vs)   | 1220 (vs)                                    |  |                | 1220 (vs)   | 1220 (vs)    |                |  |
| 1205 (s)   | 1203(4)                          | 1132 (vs)   | 1205 (m)  | 1205 (m)                                     |  |                | 1205 (m)    | 1205 (m)     |                |  |
| 1180 (s)   | 1176(3)                          |   | 1189 (m)  | 1189 (m)                                     |  |                | 1189 (m)    | 1189 (m)     |                |  |
|  |                                  |   | 1145 (vs)   | 1145 (vs)                                    |  |                | 1145 (vs)   | 1145 (vs)    |                |  |
|  |                                  |   | 1096 (m)  | 1096 (m)                                     |  |                | 1070 (w)    | 1070 (w)     |                |  |
|  |                                  |   | 1038 (s)  | 1038 (s)                                     |  |                | 1047 (s)    | 1046(18) (p) |                |  |
|  |                                  |   | 975 (s)   | 975 (s)                                      |  |                | 976 (s)     | 975(2)       |                |  |
| 987 (vs)   | 987(2) (dp)                      |   | 960 (w)   | 960 (w)                                      |  |                | 960 (w)     | 960 (w)      |                |  |
| 886 (s)  | 889(1) (dp)                      |   | 893 (vw)  | 893 (vw)                                     |  |                | 893 (vw)    | 895(14) (p)  |                |  |
|  | 864(1) (p)                       |   | 852 (sh,vw)   | 852 (sh,vw)                                  |  |                | 852 (sh,vw) | 850(20) (p)  |                |  |
|  | 832(2) (p)                       |   | 835 (w)   | 835 (w)                                      |  |                | 835 (w)     | 835 (sh,p)   |                |  |
|  |                                  |   | 825 (sh)  | 825 (sh)                                     |  |                | 825 (sh)    | 826(100) (p) |                |  |
| 785 (sh)   | 764(2) (p)                       |   | 777 (w)   | 777 (w)                                      |  |                | 775(13) (p) | 775(13) (p)  |                |  |
| 741 (s)  | 752(1) (p)                       |   | 748 (w)   | 748 (w)                                      |  |                | 750 (w)     | 750(28) (p)  |                |  |
| 722 (s)  | 724(2) (p)                       |   | 713 (s)   | 713 (s)                                      |  |                | 719 (s)     | 718(1)       |                |  |
|  |                                  |   | 699 (m)   | 699 (m)                                      |  |                | 699 (m)     | 693(4)       |                |  |
|  |                                  |   | 668 (w)   | 668 (w)                                      |  |                | 640 (vw)    | 681(5)       |                |  |
| 652 (w)  | 652(3) (p)                       |   |   |  |  |                |             | 635(0+)      |                |  |
|  | 592(6) (p)                       |   |   |  |  |                |             | 599(5) (dp)  |                |  |
|  | 582(6)                           |   |   |  |  |                |             |              |                |  |

$\text{CF}_3$  stretch  
 $\text{CF}_2$  stretch

$\nu_{\text{as}}(\text{CO}_2)$

$\nu_{\text{sym}}(\text{CO}_2)$

$\nu(\text{N}-\text{O})$

$\nu_{\text{as}}(\text{NC}_2)$

$\nu_{\text{sym}}(\text{NC}_2)$

$\text{CF}_3$  deformation

$\text{CF}_3$  deformation

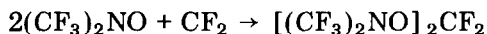
|          |              |          |              |                             |
|----------|--------------|----------|--------------|-----------------------------|
| 561 (m)  | 566(7) (dp)  | 555 (w)  | 562(12) (dp) | CF <sub>3</sub> deformation |
| 536 (m)  | 538(2) (dp)  | 531 (w)  | 538(4)       |                             |
| 485 (sh) | 489(5) (p)   | 487 (w)  | 490(3) (p)   |                             |
|          |              | 427 (vw) | 429(6) (p)   |                             |
|          | 365 (sh,dp)  |          | 368 (sh,dp)  | NC <sub>2</sub> deformation |
|          | 378(28) (p)  |          | 357(55) (p)  |                             |
| 250 (m)  | 323(90) (p)  |          | 338(34) (dp) |                             |
|          | 352(34) (dp) |          | 253 (sh,dp)  | CF <sub>3</sub> rock        |
|          | 252(4) (dp)  |          | 239(32) (p)  |                             |
|          | 237(7) (dp)  |          | 225(4)       |                             |
|          | 202(2) (dp)  |          | 156(5)       |                             |
|          | 153(6) (dp)  |          | 130(12) (p)  |                             |
|          | 108(3) (dp)  |          | 105(0+) (dp) |                             |
|          | 69 (dp)      |          |              |                             |

<sup>a</sup> Values from ref. 15.

<sup>b</sup> Values from ref. 16.

conditions by chemical means. However, further experiments in this direction were beyond the scope of the present study.

In addition to  $(\text{CF}_3)_2\text{NOCF}_3$  a new compound,  $[(\text{CF}_3)_2\text{NO}]_2\text{CF}_2$ , was formed in about 20% yield based on  $\text{O}_2^+$  salt. This indicates that significant amounts of the  $\text{CF}_2$  diradical are also formed which interact  $(\text{CF}_3)_2\text{NO}$  according to:



The formation of a carbon species with only two fluorine atoms attached to it, such as  $\text{CF}_2$  or  $\text{COF}_2$ , is not unreasonable since the formation of  $\text{CF}_4$  in the first step will create a fluorine deficiency in the system.

The  $[(\text{CF}_3)_2\text{NO}]_2\text{CF}_2$  molecule may be considered as a derivative of the previously reported  $(\text{F}_2\text{NO})_2\text{CF}_2$  molecule [14] in which the fluorines attached to the nitrogen atom are replaced by  $\text{CF}_3$  groups. The observed mass spectrum (Table 1), vibrational spectrum (Table 2) and  $^{19}\text{F}$  NMR data are in excellent agreement with the suggested structure. Tentative assignments for the more important vibrational modes are given in Table 2. These were made by comparison with the previously reported spectra for  $(\text{CF}_3)_2\text{N}-\text{N}(\text{CF}_3)_2$  [15] and  $[(\text{CF}_3)_2\text{NO}]_2\text{CO}$  [16]. The general agreement between the vibrational spectra of the three compounds is excellent except for the difference in the relative Raman intensities of  $\nu_{\text{sym}}(\text{NC}_2)$  between  $(\text{CF}_3)_2\text{N}-\text{N}(\text{CF}_3)_2$  and  $[(\text{CF}_3)_2\text{NO}]_2\text{CF}_2$ . As pointed out previously [15], the Raman intensities observed for these modes in  $(\text{CF}_3)_2\text{N}-\text{N}(\text{CF}_3)_2$  are much lower than those usually found for related  $(\text{CF}_3)_2\text{N}$ -type molecules. A more detailed analysis is not warranted due to the size of the molecule and to the possible existence of different rotational isomers as indicated by the NMR spectral data.

The  $^{19}\text{F}$  NMR chemical shifts and coupling constant observed for  $[(\text{CF}_3)_2\text{NO}]_2\text{CF}_2$  are in excellent agreement with those reported for the related  $(\text{CF}_3)_2\text{NOCF}_2\text{X}$ -type compounds [17,18]. The chemical shift of the  $\text{CF}_2(\text{OX})_2$  group appears to decrease with decreasing electronegativity of X resulting in the following order for X: F(84.2) [19],  $\text{NF}_2$ (84) [14],  $\text{OCF}_3$  and  $\text{OOCF}_3$ (79.2) [20],  $\text{N}(\text{CF}_3)_2$ (69.8),  $\text{SO}_2\text{F}$ (53.6) [21]. The fact that in addition to the 69.8 ppm  $\text{CF}_2$  signal, three other weak signals having similar chemical shifts were observed for  $[(\text{CF}_3)_2\text{NO}]_2\text{CF}_2$  indicates the possible existence of rotational isomers which would not be surprising for this bulky molecule.

## Acknowledgements

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