## Oxidative Chemical Oxygenation of NF<sub>3</sub> and Novel Synthesis of NF<sub>3</sub>O

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Nitrogen trifluoride oxide, NF<sub>3</sub>O, is a fascinating molecule<sup>1-8</sup> which is isoelectronic with  $NF_4^+$ . Its N-O bond possesses a high degree of double-bond character ( $r_{\rm N-O} = 1.159$  Å),<sup>1</sup> and therefore, it is not a typical amine oxide with a long, semipolar N-O bond and a negative charge on the oxygen atom. To avoid exceeding eight valence electrons on nitrogen and to satisfy the high electronegativity of fluorine, the NF<sub>3</sub>O molecule is best described as an NF<sub>2</sub>O<sup>+</sup>F<sup>-</sup> type structure in which the negative charge is evenly distributed over all three fluorine ligands. This description is supported by the unusally long  $(1.432 \text{ Å})^1$  and polar N-F bonds observed for NF<sub>3</sub>O.

Since NF<sub>3</sub>O possess a N(+V) central atom, its synthesis is difficult and has been achieved either by the fluorination of an NO-containing molecule, such as FNO, or by oxygenation of NF<sub>3</sub>. The oxidative fluorination of FNO has been accomplished using the powerful fluorinating agents  $IrF_{6}$ ,<sup>9</sup> elemental fluorine at temperatures in excess of 260 °C,10 or N<sub>2</sub>F<sup>+</sup> or XeF<sup>+</sup> salts.11 The oxygenation of NF<sub>3</sub> is much more difficult and has been achieved only by the use of O atoms which were generated by electric glow discharge at low temperatures.<sup>12,13</sup> No evidence could be found in the literature for a purely chemical oxygenation of NF<sub>3</sub> to NF<sub>3</sub>O. In a recent paper,<sup>14</sup> Cacace and coworkers have reported the formation of gaseous NF<sub>2</sub>O<sup>+</sup> ions from the chemical ionization of NF<sub>3</sub>/N<sub>2</sub>O mixtures in a mass spectrometer. On the basis of their observations, they suggested eq 1, where XF<sub>5</sub> represents a strong Lewis acid, as an alternate route to salts containing the  $NF_2O^+$  cation. Whereas the

$$NF_3 + XF_5 + O\text{-donor} \rightarrow NF_2O^+ XF_6^- + donor$$
 (1)

formation of free gaseous NF2<sup>+</sup> cations in a mass spectrometer is facile, their formation in bulk on a preparative scale presents a major problem. Thus, previous studies from other<sup>15</sup> and our<sup>16</sup> laboratories had shown that, even at low temperatures, NF3 does not form stable adducts with the strong Lewis acids SbF<sub>5</sub>, AsF<sub>5</sub>,

- (1) Plato, V.; Hartford, W. D.; Hedberg, K. J. Chem. Phys. 1970, 53, 3488
- (2) Curtis, E. C.; Pilipovich, D.; Moberly, W. H. J. Chem. Phys. 1967, 46, 2904.
- (3) Kirchhoff, W. H.; Lide, D. R., Jr. J. Chem. Phys. 1969, 51, 467.
   (4) Abramowitz, S.; Levin, I. R. J. Chem. Phys. 1969, 51, 463.
   (5) Hirschmann, R. P.; Harnish, D. F.; Holmes, J. R.; MacKenzie, J. S.;
   W. B. And Schutzer, 1960, 232223
- Fox, W. B. Appl. Spectrosc. 1969, 23, 333.
   (6) Frost, D. C.; Herring, F. G.; Mitchell, K. A. R.; Stenhouse, I. R. J.
- (7) Grein, F.; Lawlor, L. J. Theor. Chim. Acta 1983, 63, 161
   (7) Grein, F.; Lawlor, L. J. Theor. Chim. Acta 1983, 63, 161
- (8) Brumm, M.; Frenking, G.; Breidung, J.; Thiel, W. Chem. Phys. Lett. 1992. 197. 330
- (9) Bartlett, N.; Passmore, J.; Wells, E. J. J. Chem. Soc., Chem. Commun. 1966, 213.
- (10) Bougon, R.; Chatelet, J.; Desmoulin, J. P.; Plurien, P. C. R. Seances Acad. Sci., Ser. C 1968, 266, 1760.
- (11) Minkwitz, R.; Bernstein, D.; Preut, H.; Sartori, P. Inorg. Chem. 1991, 30. 2157.
- (12) Maya, W. U.S. Patent 3,320,147, 1967.
- (13) Fox, W. B.; MacKenzie, J. S. U.S. Patent 3,323,866, 1967. Fox, W. B.; MacKenzie, J. S.; Vanderkooi, N.; Sukornick, B.; Wamser, C. A.; Holmes, J. R.; Eibeck, R. E.; Stewart, B. B. J. Am. Chem. Soc. 1966, 88, 2684
- (14) Cacace, F.; Pepi, F.; Grandinetti, F. J. Phys. Chem. 1994, 98, 8009.
- (15) Craig, A. D. Inorg. Chem. 1964, 3, 1628.
  (16) Christe, K. O.; Wilson, R. D.; Goldberg, I. B. Inorg. Chem. 1979, 18, 2572.

or BF<sub>3</sub>. In spite of these dire prospects, the possibility of chemically oxygenating NF3 was explored.

Attempts were unsuccessful to prepare the known<sup>17,18</sup> NF<sub>2</sub>O<sup>+</sup>AsF<sub>6</sub><sup>-</sup> salt from NF<sub>3</sub>, N<sub>2</sub>O, and AsF<sub>5</sub> in a Monel cylinder at autogeneous pressures of about 80 atm at temperatures ranging from 100 to 190 °C using a 7-fold excess of NF<sub>3</sub> and N<sub>2</sub>O and reaction times of about 3 days. Only unreacted starting materials were recovered from these experiments. When AsF5 was replaced by SbF<sub>5</sub>, no reaction was observed at 100 °C. When, however, the reaction temperature was raised to 150 °C, a quantitative formation of  $NF_2O^+Sb_2F_{11}^{-17,19}$  was obtained with the excess NF<sub>3</sub> and N<sub>2</sub>O being recovered unchanged. Raising the reaction tempreature to 190 °C resulted in the formation of a mixture of NF<sub>2</sub>O<sup>+</sup>SbF<sub>6</sub><sup>-</sup> and NF<sub>2</sub>O<sup>+</sup>Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> which contained small amounts of NO<sup>+ 20</sup> and NF<sub>4</sub><sup>+ 21-24</sup> salts as byproducts. When the reaction was carried out at 260 °C,  $NO^+SbF_6^-$  and  $NF_4^+SbF_6^-$  became the main products, and the excess NF<sub>3</sub> and N<sub>2</sub>O were again recovered unchanged.

The observed products can be readily explained by the scheme depicted in eq 2. The tendency of NF<sub>3</sub>O and SbF<sub>5</sub> to form a salt containing the  $Sb_2F_{11}^-$  polyanion at 150 °C is in accord with a previous report.<sup>17</sup> With increasing temperature, the formation of  $NF_2O^+SbF_6^-$  is favored, followed by its dissocia-tion to  $NF_3O$  and  $SbF_5$ . This is analogous to our previous observations for  $NF_4^+Sb_2F_{11}^{-.25}$  At temperatures above 250



°C, NF<sub>3</sub>O is well-known<sup>10</sup> to form an equilibrium with FNO and F<sub>2</sub> which, in the presence of SbF<sub>5</sub>, is continuously shifted to the FNO and  $F_2$  side by the formation of the stable NOSb $F_6^{26}$ and NF<sub>4</sub>SbF<sub>6</sub><sup>25</sup> salts.

The mechanism of the first step of eq 2 is not as clear-cut. On the basis of the ion-molecule experiment of Cacace<sup>14</sup> and the requirement for SbF<sub>5</sub> in this reaction, it would seem logical to postulate  $NF_2^+SbF_6^-$  as an intermediate in the formation of  $NF_2O^+$ . Since previous studies<sup>15,16</sup> had shown no evidence for NF<sub>3</sub> forming an adduct with either BF<sub>3</sub>, AsF<sub>5</sub>, or SbF<sub>5</sub>, further

- (17) Christe, K. O.; Maya, W. Inorg. Chem. 1969, 8, 1253.
  (18) Wamser, C. A.; Fox, W. B.; Sukornik, B.; Holmes, J. R.; Stewart, B. B.; Juurik, R.; Vanderkooi, N.; Gould, D. Inorg. Chem. 1969, 8, 1249.
  (19) The NF<sub>2</sub>O<sup>+</sup>Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> salt was identified by its infrared and Raman spectra (ref 17). Single crystals were grown from anhydrous HF solution.
- Attempts by Prof. R. Bau to solve the crystal structure were unsuccessful due to the poor quality of the crystals.
- (20) Geichman, J. R.; Smith, E. A.; Trond, S. S.; Ogle, P. R. Inorg. Chem. 1962, 1, 661.
- (21) Christe, K. O.; Guertin, J. P.; Pavlath, A. E. Inorg. Nucl. Chem. Lett. 1966, 2, 83.
- (22) Guertin, J. P.; Christe, K. O.; Pavlath, A. E. Inorg. Chem. 1966, 5, 1921
- (23) Christe, K. O.; Guertin, J. P.; Pavlath, A. E.; Sawodny, W. Inorg. Chem. 1967, 6, 533 (24) Tolberg, W. E.; Rewick, R. T.; Stringham, R. S.; Hill, M. E. Inorg.
- Chem. 1967, 6, 1156. (25) Christe, K. O.; Wilson, R. D.; Schack, C. J. Inorg. Chem. 1977,
- 16, 937 (26) Griffith, J. E.; Sunder, W. A.; Falconer, W. E. Spectrochim. Acta, Part A 1975, 31A, 1207.

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experiments were carried out on the SbF<sub>5</sub>-NF<sub>3</sub>, SbF<sub>5</sub>-N<sub>2</sub>O, and SbF<sub>5</sub>-NF<sub>3</sub>-N<sub>2</sub>O systems. Liquid SbF<sub>5</sub> was pressurized with 2 atm of either NF<sub>3</sub>,  $N_2O_3$ , or an equimolar mixture of NF<sub>3</sub> and N<sub>2</sub>O, and its Raman spectra were recorded. The spectra of the liquid phase showed no detectable frequency shifts for the  $SbF_5$  bands. In addition, weak signals were observed for  $NF_3$  and  $N_2O$  dissolved in the liquid  $SbF_5$ . The frequencies of these dissolved species were identical to those reported<sup>27</sup> for the free molecules in the gas phase; hence, liquid SbF<sub>5</sub> does not interact with either  $NF_3$  or  $N_2O$  at room temperature.

Since NF<sub>3</sub> and N<sub>2</sub>O do not react with each other in the absence of SbF5 at temperatures as high as 260 °C, as shown by the recovery of the unreacted excess NF<sub>3</sub> and N<sub>2</sub>O in our reactions, one might argue that at 150 °C NF<sub>3</sub> and N<sub>2</sub>O are in equilibrium with  $NF_3O$  and  $N_2$  and that this equilibrium (3), which in the absence of SbF<sub>5</sub> must lie far to the left, is continuously shifted to the right by trapping of the NF<sub>3</sub>O as solid NF<sub>2</sub>O<sup>+</sup>SbF<sub>6</sub><sup>-</sup>.

$$NF_3 + N_2O \rightleftharpoons NF_3O + N_2 \xrightarrow{+SbF_5} NF_2O^+SbF_6^-$$
 (3)

Thermodynamically, eq 3 is feasible because the  $NF_3 + N_2O$ reaction is calculated<sup>28</sup> to be exothermic by about 27 kcal mol<sup>-1</sup>. and the lattice energy of solid NF<sub>2</sub>O<sup>+</sup>SbF<sub>6</sub><sup>-</sup> should provide an additional driving force. If these assumptions were correct and equilibrium 3 does indeed exist and at 150-250 °C is shifted far to the left, NF<sub>3</sub>O should react with N<sub>2</sub> at these temperatures to produce  $NF_3$  and  $N_2O$  in high yield. This, however, is not the case, and a more plausible mechanism is required for explaining the role of  $SbF_5$  in the first step of eq 2.

A more appealing, although unprecedented, explanation is that at room temperature SbF5 does not interact with NF3 but at 150 °C it does. This might be possible because at room temperature liquid SbF5 is highly polymeric and self-associated through fluorine bridges, while above its boiling point (141 °C) in the gas phase it is largely depolymerized. Thus, SbF<sub>5</sub> might be able to interact in the gas phase with NF<sub>3</sub> and polarize it sufficiently to allow its attack by N<sub>2</sub>O with the resulting ternary intermediate then undergoing an exothermic intramolecular N<sub>2</sub> elimination reaction with simultaneous formation of solid  $NF_2O^+SbF_6^-$  eq 4.



The concept of a Lewis acid-Lewis base pair interacting in the gas phase but not in the condensed liquid phase is highly unusual and will be the subject of a forthcoming <sup>18</sup>F radio tracer study.

In order to provide a convenient synthesis for free NF<sub>3</sub>O, it was necessary to convert the  $NF_2O^+Sb_2F_{11}^-$  salt in an efficient manner to pure NF<sub>3</sub>O. This was achieved by vacuum pyrolysis of NF<sub>2</sub>O<sup>+</sup>Sb<sub>2</sub>F<sub>11</sub><sup>-</sup> at 190–230 °C in the presence of excess NaF eq 5. This process affords pure  $NF_3O$  in high yield.

$$NF_2O^+Sb_2F_{11}^- + 2NaF \rightarrow 2Na^+SbF_6^- + NF_3O \quad (5)$$

In summary, it has been demonstrated that  $N_2O$ , in spite of its high kinetic stability and concomitant unreactivity,<sup>29</sup> can act as a powerful, oxidative oxygenating agent. Using  $N_2O$  as the oxygenating agent, the first purely chemical oxygenation of NF<sub>3</sub> to NF<sub>3</sub>O has been achieved. This reaction affords a new, simple, high-yield synthesis of NF<sub>3</sub>O from commercially available starting materials.

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(29) Greenwood, N. N.; Earnshaw, A. Chemistry of the Elements; Pergamon Press: Oxford, U.K., 1986.

<sup>(27)</sup> Shimanouchi, T. Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)

<sup>1972, 39, 1.</sup> (28) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochem. Tables, Third Edition, J. Phys. Chem. Ref. Data 1985, 14, Suppl. 1.