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Oxidative Chemical Oxygenation of NF_3 and Novel Synthesis of NF_3O

Karl O. Christe

Hughes STX, Edwards Air Force Base, California 93524
Loker Institute, University of Southern California
Los Angeles, California 90089

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Nitrogen trifluoride oxide, NF_3O, is a fascinating molecule[1−8] which is isoelectronic with NF_4^+. Its N−O bond possesses a high degree of double-bond character ($r_{N-O} = 1.159$ Å),[1] 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_3O molecule is best described as an $NF_2O^+F^-$ 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 Å)[1] and polar N−F bonds observed for NF_3O.

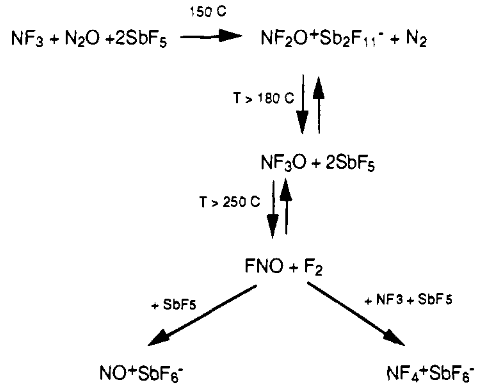
Since NF_3O possess a N(+V) central atom, its synthesis is difficult and has been achieved either by the fluorination of an NO-containing molecule, such as FNO, or by oxygenation of NF_3. The oxidative fluorination of FNO has been accomplished using the powerful fluorinating agents IrF_6,[9] elemental fluorine at temperatures in excess of 260 °C,[10] or N_2F^+ or XeF^+ salts.[11] The oxygenation of NF_3 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.[12,13] No evidence could be found in the literature for a purely chemical oxygenation of NF_3 to NF_3O. In a recent paper,[14] Cacace and coworkers have reported the formation of gaseous NF_2O^+ ions from the chemical ionization of NF_3/N_2O mixtures in a mass spectrometer. On the basis of their observations, they suggested eq 1, where XF_5 represents a strong Lewis acid, as an alternate route to salts containing the NF_2O^+ cation. Whereas the

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

formation of free gaseous NF_2^+ cations in a mass spectrometer is facile, their formation in bulk on a preparative scale presents a major problem. Thus, previous studies from other[15] and our[16] laboratories had shown that, even at low temperatures, NF_3 does not form stable adducts with the strong Lewis acids SbF_5, AsF_5, or BF_3. In spite of these dire prospects, the possibility of chemically oxygenating NF_3 was explored.

Attempts were unsuccessful to prepare the known[17,18] $NF_2O^+AsF_6^-$ salt from NF_3, N_2O, and AsF_5 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_3 and N_2O and reaction times of about 3 days. Only unreacted starting materials were recovered from these experiments. When AsF_5 was replaced by SbF_5, 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_3 and N_2O being recovered unchanged. Raising the reaction tempreature to 190 °C resulted in the formation of a mixture of $NF_2O^+SbF_6^-$ and $NF_2O^+Sb_2F_{11}^-$ which contained small amounts of NO^+ [20] and NF_4^+ [21−24] 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_3 and N_2O were again recovered unchanged.

The observed products can be readily explained by the scheme depicted in eq 2. The tendency of NF_3O and SbF_5 to form a salt containing the $Sb_2F_{11}^-$ polyanion at 150 °C is in accord with a previous report.[17] With increasing temperature, the formation of $NF_2O^+SbF_6^-$ is favored, followed by its dissociation 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_3O is well-known[10] to form an equilibrium with FNO and F_2 which, in the presence of SbF_5, is continuously shifted to the FNO and F_2 side by the formation of the stable $NOSbF_6$[26] and NF_4SbF_6[25] salts.



(2)

The mechanism of the first step of eq 2 is not as clear-cut. On the basis of the ion−molecule experiment of Cacace[14] and the requirement for SbF_5 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[15,16] had shown no evidence for NF_3 forming an adduct with either BF_3, AsF_5, or SbF_5, further

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(19) The $NF_2O^+Sb_2F_{11}^-$ 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.

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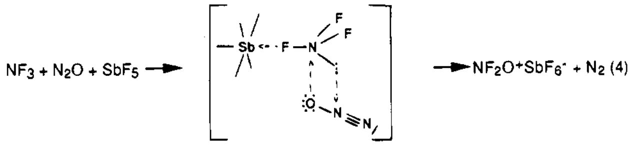
experiments were carried out on the SbF_5-NF_3, SbF_5-N_2O, and $SbF_5-NF_3-N_2O$ systems. Liquid SbF_5 was pressurized with 2 atm of either NF_3, N_2O, or an equimolar mixture of NF_3 and N_2O, and its Raman spectra were recorded. The spectra of the liquid phase showed no detectable frequency shifts 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[27] for the free molecules in the gas phase; hence, liquid SbF_5 does not interact with either NF_3 or N_2O at room temperature.

Since NF_3 and N_2O do not react with each other in the absence of SbF_5 at temperatures as high as 260 °C, as shown by the recovery of the unreacted excess NF_3 and N_2O in our reactions, one might argue that at 150 °C NF_3 and N_2O are in equilibrium with NF_3O and N_2 and that this equilibrium (3), which in the absence of SbF_5 must lie far to the left, is continuously shifted to the right by trapping of the NF_3O as solid $NF_2O^+SbF_6^-$.

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

Thermodynamically, eq 3 is feasible because the $NF_3 + N_2O$ reaction is calculated[28] to be exothermic by about 27 kcal mol^{-1}, and the lattice energy of solid $NF_2O^+SbF_6^-$ 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_3O should react with N_2 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 SbF_5 does not interact with NF_3 but at 150 °C it does. This might be possible because at room temperature liquid SbF_5 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_5 might be able to interact in the gas phase with NF_3 and polarize it sufficiently to allow its attack by N_2O with the resulting ternary intermediate then undergoing an exothermic intramolecular N_2 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 ^{18}F radio tracer study.

In order to provide a convenient synthesis for free NF_3O, it was necessary to convert the $NF_2O^+Sb_2F_{11}^-$ salt in an efficient manner to pure NF_3O. This was achieved by vacuum pyrolysis of $NF_2O^+Sb_2F_{11}^-$ 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,[29] can act as a powerful, oxidative oxygenating agent. Using N_2O as the oxygenating agent, the first purely chemical oxygenation of NF_3 to NF_3O has been achieved. This reaction affords a new, simple, high-yield synthesis of NF_3O from commercially available starting materials.

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