

Nitrogen Oxide Trifluoride

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THE synthesis of OCF_3^- salts by Willis and his co-workers¹ suggested the probability of making the isoelectronic molecule, nitrogen oxide trifluoride.

Although the new oxyfluoride is formed, in low yield, by interaction of nitric oxide with fluorine at -196° , it is not formed from nitrosyl fluoride and fluorine at room temperature and pressures of ~ 1 atm. Such a mixture does produce the oxyfluoride when it is heated in a nickel vessel at 220° with fluorine at higher pressures (~ 120 p.s.i.), although under these conditions there is extensive corrosion of the container. The highly corrosive nature of the basic ONF, however, is largely overcome by exploiting the fluorinating and oxidizing properties of the more powerfully oxidizing transition-metal fluorides. Thus the compound has been made in good yield by (a) the pyrolysis of nitrosyl hexafluoronickelate(IV) in fluorine and (b) the interaction of nitrosyl fluoride with iridium hexafluoride. In (a), nickel fluoride was treated with a mixture of fluorine (~ 60 p.s.i.) and an excess of nitrosyl fluoride (50 p.s.i.), in a nickel vessel held at $\sim 200^\circ$. The red complex nickel fluoride so formed, was pyrolysed in fluorine (70 p.s.i.) at $\sim 350^\circ$. The volatile product was an approximately equimolar mixture of ONF and ONF_3 : $(\text{ON})_2\text{NiF}_6 \rightarrow \text{ONF} + \text{ONF}_3 + \text{NiF}_2$. The oxyfluoride has been obtained in high purity

by route (b), with the reactants brought together in the 3:2 stoichiometry for the ideal equation: $3\text{ONF} + 2\text{IrF}_6 \rightarrow 2\text{ONIrF}_6 + \text{ONF}_3$. In a typical preparation, iridium hexafluoride (2.43 mmoles) was mixed with ONF (3.31 mmoles) in a nickel vessel at -196° and the mixture was brought to $\sim 20^\circ$. Apart from a small amount of fluorine gas, which was identified by its vapour pressure at -196° , the absence of infrared absorption and its complete uptake with liquid mercury, the gaseous product was nitrogen oxide trifluoride (0.84 mmoles). The pale yellow solid product, identified by X-ray powder-photography, was nitrosyl hexafluoroiridate(V) (2.40 mmoles).²

High-purity nitrogen oxide trifluoride has been obtained by fluorolysis of the nickel salt. By first forming this compound, troublesome impurities such as carbon tetrafluoride (from the fluorine) and nitrous oxide (from the nitric oxide) are avoided. The mixture, with nitrosyl fluoride and some nitryl fluoride, is purified chemically by titrating the gas with boron trifluoride, when both of the strongly basic oxyfluorides are removed as fluoroborates:

$\text{ONF} + \text{O}_2\text{NF} + 2\text{BF}_3 \rightarrow \text{ONBF}_4 + \text{O}_2\text{NBF}_4$
Nitrogen oxide trifluoride prepared and purified in this way is colourless. The vapour pressure of the solid at -121° is 97 mm. Hg and is ~ 1 atm. at -90° .

The chemical identity of the compound has been established by its synthesis, chemical properties, molecular weight (Found 84; ONF_3 required 87), and its ^{19}F n.m.r. spectrum. A solution of ONF_3 in carbon trichloride fluoride, with which ONF_3 does not interact, gave a ^{19}F n.m.r. 1,1,1, triplet, symmetrical in intensity but not in line-width, at -82° . The spectrum, obtained at 94.1 Mc./sec., gave a low-field shift centred at 365.7 ± 0.2 p.p.m. from CFCl_3 , the line-width of the central line being 6 c./sec., the width of the outer lines being 8 c./sec., $J_{\text{N-F}}$ was found to be 135.5 ± 0.5 c./sec. No other fluorine resonance was detected. The occurrence of a triplet at such a low temperature is indicative of a symmetrical electric field gradient at the nitrogen nucleus,³ the spectrum being fully consistent with the pseudo-tetrahedral environment of the oxide trifluoride. A hypofluorite formulation $\text{F}_2\text{N-O-F}$ should possess two fluorine resonances and such a molecule would probably possess considerable electric field asymmetry at the nitrogen nucleus.

The infrared spectrum of the gas is simple and requires no more than six fundamentals for complete assignment. A hypofluorite, FONF_2 , molecule, could not have higher than C_s symmetry (since F-O-N would be bent) and this would require nine distinct infrared-active fundamentals.⁴ Evidently the molecular symmetry of the new oxyfluoride is close to T_d , since the band contours of the degenerate fundamentals, of species e (\perp bands), of which there are three in C_{3v} symmetry,⁴ are not readily distinguished from the three a_1 modes (\parallel bands). Tentative assignments based on C_{3v} symmetry, are as follows (in cm^{-1}):

527 s, $\nu_6(e)$; 739 s, $\nu_3(a_1)$; 744 s, $\nu_5(e)$; 804 w, $\nu_2(a_1) - \nu_4(e)$; 883 vs, $\nu_4(e)$; 935 vw, ?; 1050 w, $2\nu_6(e)$; 1263 w, $\nu_6(e) + \nu_3(a_1)$; 1280 w, (CF_4 imp.);

1412 w, $\nu_4(a_1) + \nu_6(e)$; 1475 vw, $2\nu_3(a_1)$; 1505 vw, $2\nu_5(e)$; 1598 vvw, $?\nu_2(a_1)$ (^{18}O); 1624 w, $\nu_3(a_1) + \nu_4(e)$; 1690 vs, $\nu_2(a_1)$; 1773(Q) s, 1766(Q) s, $2\nu_4(e)$ and $2\nu_1(a_1)$?; 2210 vw, $\nu_2(a_1) + \nu_6(e)$; 2340 vw, (imp. ?); 2430 vw, $\nu_2(a_1) + \nu_3(a_1)$, $\nu_2(a_1) + \nu_5(e)$; 3378 w, $2\nu_2(a_1)$; 3475 vw, $2\nu_4(e) + \nu_2(a_1)$. It is possible that the value of $\nu_1 \approx \nu_4$. The assignments ν_3 (ON stretch) = 1690 and ν_4 (NF stretch) = 883 cm^{-1} are the most certain in the list.

The compound shows some of the chemical inertness of related carbon tetrafluoride. It interacts with nitric oxide according to the equation $2\text{ON} + \text{ONF}_3 \rightarrow 3\text{ONF}$, but the reaction requires several days to proceed to completion. The gas reacts only very slowly with water vapour, a gas mixture in an infrared-spectrometer cell having shown only slight interaction over a period of 12 hr. Liquid water hydrolyses it more rapidly and it is completely hydrolysed by base in a short time (< 1 min.). The gas does not attack mercury at 20° nor does it attack glass or quartz at temperatures up to 100° , and the interaction is slow even at 400° . It forms an adduct, $\text{ONF}_3 \cdot \text{AsF}_5$ (possibly $\text{ONF}_2^+[\text{AsF}_6]^-$) which is slightly dissociated at 20° into the component molecules, but there is no solid adduct with BF_3 under normal temperatures and pressures. The infrared spectrum of the solid shows bands centred at 745, 895, 1150, and 1850 cm^{-1} , consistent with an ONF_2^+ ion, and a broad intense band at 695 cm^{-1} indicative of the hexafluoroarsenate(v) ion.⁵

Nitrogen oxide trifluoride is undoubtedly of some theoretical interest; there is however no difficulty in formulating the bonding in a conventional way, with the oxygen joined to NF_3 by a semi-ionic bond $\equiv \text{N}^+ - \text{O}^-$.

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