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THE CHEMISTRY OF TRIFLUORAMINE OXIDE. VII. PHOTOLYTIC GENERATION AND ELECTRON SPIN RESONANCE SPECTRA OF F_2NO RADICALS

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SUMMARY

Photolysis of solid F_3NO at -196° produces the F_2NO radical identified by its 9-line ESR spectrum consisting of a fluorine-split 1:2:1 triplet ($a_F = 143.0$ G), each component of which is further split by ^{14}N into 1:1:1 triplets ($a_N = 94.5$ G), with $g = 2.0093$. Trifluoramine oxide enriched with ^{15}N provided the expected 6-line spectrum of $F_2{}^{15}NO$ comprised of the fluorine triplet ($a_F = 142.6$ G) each component of which is further split by ^{15}N into doublets ($a_N = 132.3$ G), with $g = 2.0094$. The data are best interpreted in terms of a pyramidal structure for F_2NO.

INTRODUCTION

The physical and chemical properties of F_3NO have been described in some detail [1-7], and spectroscopic studies [8-10] have shown that the molecule possesses C_{3v} symmetry, with N-F

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bonds substantially weaker than the N-O bond, a view that is consistent with chemical studies indicating a predominance of N-F bond cleavage over N-O cleavage [4]. In an early account of the chemistry of F_3NO [1], we cited preliminary evidence for the generation and detection of the F_2NO radical by photolysis of F_3NO, and we present herewith a more detailed account of the photochemical experiments and the ESR spectral characterization of the F_2NO radical.

EXPERIMENTAL

The preparation of F_3NO by photochemical fluorination of nitric oxide has been described elsewhere [7]. Isotopically enriched F_3NO containing 97% of the ^{15}N-isotope was prepared using ^{15}NO and fluorine. Since preliminary experiments showed that even traces of NO_2 impurity proved detrimental in obtaining good spectral data, the F_3NO was always pumped *in vacuo* from a -110° trap immediately before use. Samples were condensed *via* conventional vacuum line techniques onto the surface of a 4 mm. o.d., quartz cold finger located in the cavity of the ESR spectrometer and filled with liquid nitrogen. In most experiments, F_3NO served as the matrix for the photolytically generated radicals, although xenon or C_2F_6 matrices were used in several experiments. In these cases, F_3NO and the matrix material were co-deposited on the cold finger from a homogeneous gas mixture.

Photolysis was accomplished with ultraviolet light from a 550 watt Hanovia high pressure mercury lamp equipped with a quartz lens to concentrate the output on the sample area of the cold finger.

The ESR spectra were recorded with a Varian V4500-10A Spectrometer equipped with a six-inch magnet. Microwave frequencies were measured with a Sperry Model 14X1 Cavity Frequency Meter with an accuracy of ± 0.01%, and magnetic field strength was determined by a Varian F-8 Fluxmeter with crystal-controlled oscillator having an accuracy of ± 0.005%. The procedure yielded magnetic field markers accurate to ± 0.2 gauss.

RESULTS

Irradiation of pure, solid F_3NO at -196° for 10 minutes produced a strong, symmetrical ESR spectrum of $F_2NO\cdot$ radical which consisted essentially of a 1:2:1 triplet of 1:1:1 triplets. The 1:2:1 triplet splitting is attributable to the unpaired electron interaction with two equivalent fluorine nuclei ($I = 1/2$), and the 1:1:1 splitting of each of these lines arises from interaction with the ^{14}N nucleus ($I = 1$). The measured splittings were $a_F = 142.2$ G and $a_N = 94.3$ G, with $g = 2.0093$. Three of the spectral lines, corresponding to the center-field fluorine line and its sub-components, (i.e., corresponding to the magnetic state where the spins of the two fluorine atoms are opposed), displayed an additional small second-order doublet splitting of 9.2 G. That this additional sub-component splitting is a second order effect, rather than a matrix-induced perturbation, was confirmed in subsequent experiments which reproduced the same effect for F_2NO radicals generated in xenon and C_2F_6 matrices. Similar second-order effects have been observed in other fluorinated radicals such as CF_3 [11] and PF_4 [12].

Unequivocal verification of the F_2NO radical assignments was provided through an experiment conducted as described above but employing $F_3{}^{15}NO$ of 97% ^{15}N-isotopic purity. The resultant ESR spectrum was, as predicted, comprised basically of six lines in the form of the ^{19}F triplet (two equivalent fluorines of $I = 1/2$) split into ^{15}N doublets (^{15}N has $I = 1/2$), with essentially the same second-order splitting of the fluorine center line components (8.3 G) as before. The $F_2{}^{15}NO$ g-value (2.0094) and fluorine hyperfine interaction ($a_F = 143.6$ G) were virtually identical with those noted earlier for $F_2{}^{14}NO$, while a_N was increased to 132.3 G, in close agreement with the calculated value of 132.0 G which would be dictated by the change in spectroscopic splitting factor in going from ^{14}N to ^{15}N.

In other experiments, it was determined that, after a steady-state concentration of F_2NO radicals was obtained (10 to 15 min) and the ultraviolet lamp was extinguished, the radicals decayed by an approximately second-order rate process with a half-life of 15-20 minutes, suggesting the possibility that

F_2NO decays by reaction with other F_2NO radicals through a dimer intermediate.

When matrices containing F_3NO in xenon were irradiated, precisely the same F_2NO spectral lines and coupling parameters as observed in pure F_3NO were recorded, though intensities were much reduced. A mixture of 1% F_3NO in Xe gave a steady-state concentration of F_2NO only one-tenth that in pure F_3NO, and the concentration of F_2NO from 33% F_3NO in Xe was only twice that of the 1% mixture. Moreover, the decay of F_2NO in the 33% F_3NO-Xe matrix followed a first-order rate, indicating spontaneous decomposition or reaction of F_2NO with the matrix. In a solid mixture of 1% F_3NO in C_2F_6, the same F_2NO spectrum as before was observed, though a much longer irradiation period was required and the outer lines of the spectrum showed considerable broadening.

An attempt was made to observe F_2NO radicals in the gas phase by passing a gaseous F_3NO-N_2 mixture at 1-2 torr through a quartz tube externally heated to 650° before passage through the microwave cavity. Intense ESR signals for fluorine and oxygen atoms [13] were observed, indicating extensive decomposition of the F_3NO, but no evidence for gas-phase F_2NO was obtained.

DISCUSSION

The fluorine hyperfine splitting of F_2NO ($a_F = 143.0$ G) is remarkably close to that reported for the bent, isoelectronic CF_3 radical ($a_F = 144.7$ G) [11], suggesting that the bond hybridizations involving the fluorines and the central atom (C or N) in each case are similar. The most compelling evidence for non-planar F_2NO, however, is the magnitude of the coupling with the ^{14}N nucleus ($a_N = 94.3$ G), indicating that the unpaired electron is in a nitrogen orbital with substantial s-character (we calculate 17.3% 2s spin population at the N atom). Walsh [14] has predicted on theoretical grounds that species with 25 valence electrons should be non-planar; in the Walsh model applied to F_2NO, the unpaired electron would be in an $a_1S_A\text{-}\bar{a}_2''$ orbital and the N would be pyramidal with the unpaired electron having appreciable 2*s*-character at the nitrogen atom. Finally, it should be noted that the nitrogen hyperfine splitting of F_2NO is more than ten times that of the planar $(CF_3)_2NO$ radical (8.2 G) [15], in keeping with a pyramidal form for F_2NO.

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