

methyl resonance (not shown) is a doublet at 1.37 ppm *vs.* DSS and has a spacing of 6.0 Hz. Of the three protons remaining on the propylenediamine backbone, it appears that H_a produces the triplet-like resonance at highest field, and that H_b and H_c are almost coincident at lowest field. The triplet-like resonance of H_a results from spin coupling to H_b and H_c with nearly equal magnitudes ($J_{ab} \approx -12.5$ and $J_{ac} \approx 11.0$ Hz).^{6,7} Simultaneous irradiation of cobalt-59 and the methyl doublet leads to changes in the low-field portion of Figure 2B which are consistent with the assignment of H_c. The approximate chemical shifts are $\delta_a \sim 2.48$, $\delta_b \sim 2.93$, and $\delta_c \sim 3.05$ ppm *vs.* DSS. Use of solvent shifts and a higher spectrometer frequency spreads out the spectrum sufficiently for a complete analysis, now in progress.

The sharpness of the H_a lines compared to the H_b lines tends to indicate that the Co-N-C-H coupling constant is greater for equatorial protons than for axial protons. A similar result is evident for Co(en)₃³⁺ in Figure 1C.²¹ This finding, in addition to the fact that $\delta_b > \delta_a$ in L-[Co((-)pn)₃]³⁺ supports the assignment of $\delta_{axial} \sim 2.75$ ppm and $\delta_{equatorial} \sim 2.93$ ppm in Co(en)₃³⁺.

Acknowledgments. We thank the United States Public Health Service (Grant No. 9-R01ES00477) for its support of this work. The Varian HA-100 nmr spectrometer was provided through a National Science Foundation Grant to the department.

(21) The same trend is observed for Pt-N-C-H coupling constants: L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 6371 (1968).

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The Chemistry of Trifluoramine Oxide. VI. Formation of Trifluoramine Oxide in the Fluorine-Nitric Oxide Flame¹

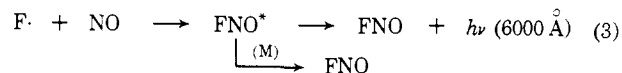
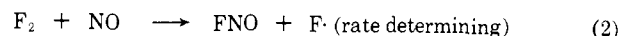
Sir:

Recent interest in the spontaneous, exothermic reaction of fluorine and nitric oxide as an energy source for chemical lasers² prompts us to describe an unexpected and chemically useful observation in the course of our own studies of the fluorine-nitric oxide flame.

Earlier workers had shown that the fluorination of nitric oxide proceeds according to the equation³



Through studies of the dilute diffusion flame and its emission spectrum, others measured the kinetics of the reaction and proposed the following mechanism^{4,5}



(1) Presented in part at the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., Aug 1967. The properties of trifluoramine oxide are summarized by W. B. Fox, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2604 (1966).

(2) T. A. Cool, *Chem. Eng. News*, **47** (52), 58 (1969).

(3) A. V. Faloon and W. B. Kenna, *J. Amer. Chem. Soc.*, **73**, 2937 (1951).

(4) D. Rapp and H. S. Johnston, *J. Chem. Phys.*, **33**, 695 (1960).

(5) H. S. Johnston and H. J. Bertin, *J. Mol. Spectrosc.*, **3**, 683 (1959).

In this mechanism, the FNO* is essentially a metastable triplet-state molecule. The 6000-Å chemiluminescence is ascribed to the small fraction of FNO* which undergoes the spin-forbidden transition to the ground state, with the remainder of the FNO molecules simply undergoing collisional deactivation (M).

In our examination of this system, however, we observed that the effluent from the nitric oxide-fluorine flame contained traces of trifluoramine oxide, F₃NO, suggesting that the very exothermic initial reaction provided the energy necessary for further fluorination of nitrosyl fluoride. Rapidly quenching the energy-rich gas mixture in the flame (by impinging on a cold surface) increased the yield of F₃NO, and further enhancement resulted when fluorine in excess of that required for FNO formation was used. These observations led to the development of a convenient, continuous-flow process for F₃NO synthesis in yields up to 20% using the empirically optimized reactor geometry, reactant ratio, gas flow rates, and quench temperature described below.

Materials. Nitric oxide (Matheson Co.) was freed of traces of NO₂ and N₂O by passage through a -78° trap packed with silica gel. Fluorine (Allied Chemical Corp.) was passed over NaF pellets to remove traces of HF.

Apparatus and Procedure. Figure 1 is a schematic representation of the "jet"-type reactor used. The entire assembly, constructed of nickel, was immersed in a stirred coolant bath which could be maintained at any desired temperature over the range -125 to 25°. A pump was used to circulate coolant through the 3/8-in. o.d. cold-finger insert. Flows of gaseous fluorine and nitric oxide at atmospheric pressure were metered into the reactor through calibrated Fisher-Porter rotameters. The nitric oxide nozzle and cold finger were movable so that the volume and geometry of the flame zone could be altered as needed. Products leaving the reactor were led at ambient temperature through an infrared cell to permit continuous on-stream monitoring of F₃NO concentration. The yields of F₃NO estimated by infrared analysis were periodically confirmed by collection of the condensable reactor effluent and recovery of the F₃NO (bp -87.5°) by distillation in an all-nickel low-temperature still.

In the course of around 80 runs it was established that the optimum yield of F₃NO (15% at production rate 37.5 ml/min) for the reactor shown was reproducibly obtained in continuous operation with the NO nozzle positioned 0.5 in. above the quenching section, the cold finger 0.5 in. below the flame zone, a coolant temperature of -125°, total (NO + F₂) flow rate of 1000 ml/min, and reactant ratio NO:F₂ = 1.0.

Better yields of F₃NO (~20%) and higher production rates were obtained by modifying the reactor of Figure 1 as follows. The modified reactor incorporated a nitric oxide inlet with a 0.0135-in. orifice positioned 0.5 in. above a larger cold finger (0.5-in. o.d.), the latter fitting closely in the quenching section of the outer tube (0.516-in. i.d.). With this configuration, the annular space for product flow around the cold finger was only 0.008 in. wide, thus providing high-velocity flow in the quenching section. In addition, the cold-finger insert was squared off at the top, as was the shoulder of the flame zone, and the top of the cold finger was po-

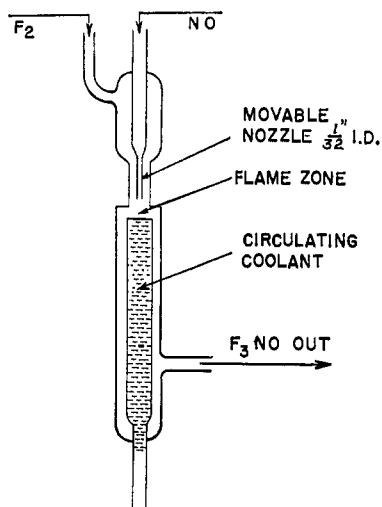
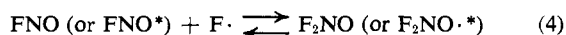


Figure 1. Flame reactor for continuous F_3NO production.

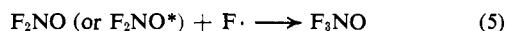
sitioned 0.005 in. below the shoulder. With F_2 and NO inputs of 500 ml/min each and coolant at -125° , 20% yields of F_3NO were produced at a continuous rate of 50 ml/min. As was the case with the previous reactor system, the residence time between generation of the $NO-F_2$ reaction mixture and product quenching for optimum operation was 15 msec.

Caution! Trifluoramine oxide is highly toxic and a powerful oxidant. All operations should be conducted in properly shielded hoods, and contact of reactants or products with organic materials must be avoided.

The mechanism of F_3NO formation probably involves the initial reaction of excess fluorine in the very hot ($\sim 2000^\circ K$) flame with FNO to produce an $F_2NO\cdot$ radical in either the ground or first excited state.



Reaction with a second fluorine would then produce the observed F_3NO .



We suggest that the intermediate radical is more likely to be the excited-state F_2NO^* on the following grounds. The ground-state $F_2NO\cdot$ radical (Figure 2) is, as predicted by Walsh⁶ and verified in our own low-temperature spin resonance work,⁷ slightly bent with the unpaired electron localized in a p orbital on the oxygen atom. Attack of fluorine on this radical would then occur on oxygen to yield a "hypofluorite" product, F_2NOF , which has never been observed, although its formation and subsequent rearrangement to F_3NO cannot be ruled out. On the other hand, the excited-state $F_2NO\cdot^*$, which should be energetically attainable at the $2000^\circ K$ flame temperature, would be planar (Figure 2) with the unpaired electron localized on nitrogen

(6) A. D. Walsh, *J. Chem. Soc.*, 2306 (1953).

(7) Photolysis of F_3NO at -196° produces the $F_2NO\cdot$ radical which exhibits a nine-line esr spectrum consisting of a fluorine-split triplet ($a_F = 142.2$ G), each component of which is further split by nitrogen into a triplet ($a_N = 94.3$ G). The fluorine hyperfine splitting is remarkably close to that observed for the isoelectronic, bent $CF_3\cdot$ radical [144.7 G: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 43, 2704 (1965)]. On the other hand, the nitrogen hyperfine splitting of $F_2NO\cdot$ is more than ten times that of the planar $(CF_3)_2NO\cdot$ radical [8.2 G: W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, 87, 802 (1965)]. A more complete account will be published separately by N. Vanderkooi, J. S. MacKenzie, and W. B. Fox.

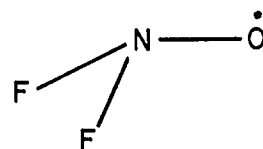
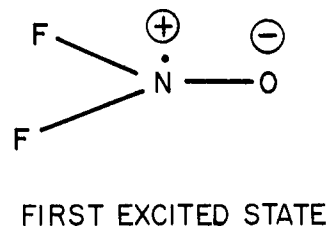


Figure 2. Configurations of the F_2NO radical.

to about the same extent as in NO .⁶ Fluorination of this radical would then occur on nitrogen to give F_3NO directly.

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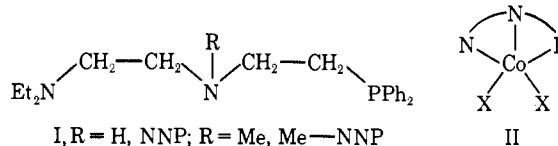
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Received May 18, 1970

Spin-State Equilibrium in a Five-Coordinate Complex of Cobalt(II) Thiocyanate with an NNP Tridentate Ligand

Sir:

It has been found that in five-coordinate cobalt(II) and nickel(II) complexes the spin-pairing tendency parallels the nucleophilic reactivity constant (n^0) of the donor atoms,¹ as defined by Basolo and Pearson.² It has been shown for complexes of the type $Co(L)_2X_2$ (L = tridentate ligand; X = halogen, pseudohalogen) that the magnetic cross-over point occurs when the overall nucleophilic reactivity constant (Σn^0) is in the range 29–31.¹ In this range are the values for the donor sets NP_2X_2 in the spin-state isomeric complexes recently reported.³

With the "hybrid" ligands of general formula I we



- (1) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).
(2) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 75.
(3) S. M. Nelson and W. S. J. Kelly, *Chem. Commun.*, 94 (1969).