

Journal of The Chemical Society, Chemical Communications

NUMBER 7/1974

3 APRIL

Formation of Anomalous "Hypofluorite" Tautomers of Nitrosyl Fluoride and Nitryl Fluoride by Addition of Fluorine to Nitric Oxide and Nitrogen Dioxide in Cryogenic Matrices

By RICHARD R. SMARDZEWSKI and W. B. FOX*

(*Naval Research Laboratory, Code 6130, Washington, D.C. 20375*)

Summary Reaction of photolytically generated fluorine atoms with NO and NO₂ molecules at 8–20 K produces, in addition to nitrosyl fluoride (FNO) and nitryl fluoride (FNO₂), the new hypofluorite tautomers, NOF and ONOF.

THE exothermic gas-phase reaction of nitric oxide and fluorine, of recent interest as a source of fluorine atoms to initiate chemical lasers,¹ has been reported to produce quantitative yields of nitrosyl fluoride, FNO, in which the fluorine atom is bound to nitrogen.² In a similar manner, NF-bonded nitryl fluoride, FNO₂, is the primary product of the gas-phase reaction of fluorine and nitrogen dioxide.³ These observations are consistent with the generally accepted thesis that if two points of attachment are possible, the highly electronegative fluorine atom will bond to the more electropositive site.

We have found, however, that simultaneous deposition of molecular fluorine and nitric oxide (from separate sources) in nitrogen or argon matrices (*M/R* = 250) at 8 K produces, in addition to the "normal" FNO, substantial quantities of the previously unknown "hypofluorite" tautomer, NOF, in which fluorine is bound to oxygen. In an argon matrix, for example (Ar:F₂:NO = 500:1:1), i.r. analysis shows both the "normal" FNO absorptions at 1852.1 (N–O stretch), 751.4 (FNO bend), 509.9 (N–F stretch) cm⁻¹, and the NOF "hypofluorite" isomer bands at 1886.6 (N–O

stretch), 734.9 (NOF bend), and 492.2 (O–F stretch) cm⁻¹. Frequencies were shifted slightly in nitrogen matrices, but approximately the same relative separations between FNO and NOF frequencies were maintained. Though the relative amounts of FNO and NOF could be varied as described below, the relative intensities of the absorptions within each species' three-band system remained unaltered. In experiments involving ¹⁵N and ¹⁸O enrichment and mixed isotopic substitution, the observation of single isotopic counterparts of these frequencies is consistent with the presence of one nitrogen and one oxygen atom in the NOF species.

It seems likely that the normal FNO isomer arises from attack of both molecular and atomic fluorine on nitric oxide, but the anomalous "hypofluorite" form appears to derive mainly from reaction of photolytically generated fluorine atoms with NO. This tentative conclusion arises from the observation that the photolytic generation of significant (though relatively immobile) fluorine atoms at 8 K using filtered 360 nm radiation, followed by cessation of photolysis and warming to 21 K to enhance F· atom migration, produced an order-of-magnitude increase in intensities of the NOF bands, while the FNO bands increased only slightly. (To ensure that the three new i.r. features were not a result of aggregate formation, a warmup to 22 K was performed on a similar matrix sample without prior u.v. irradiation; no significant changes in the i.r.

spectrum were observed after the warmup.) Upon resumption of photolysis, the FNO concentration increased as that of NOF decreased, suggesting both photochemical decomposition of NOF and its conversion into the more stable FNO.

In the case of nitrogen dioxide, the initial codeposition of separate samples of $N_2:F_2 = 250$ and $N_2:NO_2 = 500$ at 8 K provided no evidence of any reaction, and subsequent photolysis (360 nm) at 8 K resulted only in the formation of FNO_2 . However, after this photolysis, a warmup to 20 K in the absence of photolytic radiation produced the new ONOF isomer as well as additional FNO_2 . I.r. absorptions at 1716.4 (asym. N-O stretch), 1199.9 (sym. N-O stretch), 702.3 (NOF bend) and 411.9 (OF torsion) cm^{-1} were assigned to this species which was shown from ^{15}N and ^{18}O isotopic studies to contain one nitrogen and two

nonequivalent oxygen atoms [*i.e.*, the observation of a quartet structure for the 1199.9 cm^{-1} band in the mixed (^{16}O , ^{18}O) experiments].

Continued photolysis of matrices containing ONOF resulted in a decrease in the ONOF concentration and an increase in FNO_2 , again suggesting photoisomerization to the more stable FNO_2 form. These observations call to mind a recent claim by Schumacher that carefully controlled heterogeneous fluorination of nitrogen dioxide affords, in addition to the normal nitryl fluoride FNO_2 , a new substance thought to be the "hypofluorite" tautomer ONOF.⁴

One of us (R.R.S.) thanks the National Research Council for support of this research under the auspices of an NRC-NRL Resident Research Associateship.

(Received, 13th August 1973; Com. 1164.)

¹ T. A. Cool and R. R. Stephens, *J. Chem. Phys.*, 1969, **51**, 91.

² H. S. Johnston and H. J. Bertin, *J. Amer. Chem. Soc.*, 1959, **81**, 6402; H. S. Johnston and H. J. Bertin, *J. Mol. Spectroscopy*, 1959, **3**, 683; R. Schmutzler, *Angew. Chem. Internat. Edn.*, 1968, **7**, 440.

³ O. Ruff, *Angew. Chem.*, 1929, **42**, 807; R. L. Perrine and H. S. Johnston, *J. Chem. Phys.*, 1953, **21**, 2202.

⁴ P. J. Bruna, J. E. Sicre, and H. J. Schumacher, *Chem. Comm.*, 1970, 1542.