Nitrosodifluoroamine, F_2N_2O[†,‡]

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Nitrous oxide, N_2O, was observed to react with F_2 under UV irradiation at −196 °C to form initially F_2N_2O which in accord with earlier reports from the literature decomposes above −140 °C to form N_2F_4 and NO. The apparently different reaction behavior of N_2O toward H radicals ($\rightarrow H_2O + N_2$) and F radicals ($\rightarrow F_2N_2O \rightarrow N_2F_4 + NO$) can be accounted for by thermodynamic considerations [average bond energies (kcal mol^{-1}): O−H (114.2) > N−H (93.3); N−F (66.4) > O−F (44.7)]. A reaction mechanism for the formation and decomposition of F_2N_2O from N_2O and F_2 (present study) and from N_2F_4 and NO has been suggested using valence bond considerations. The structure of F_2N_2O was fully optimized at the electron correlated MP2(FULL)/cc-pVTZ level of theory and was shown to possess C_1 symmetry. A frequency analysis clearly shows the C_1 structure to represent a true minimum (NIMAG = 0), whereas the earlier reported planar C_s structure was shown to represent a first-order transition state (NIMAG = 1).

Introduction

It is well-known that compared to other oxides of nitrogen, nitrous oxide, N_2O, is relatively unreactive and inert toward halogens and alkali metals at room temperature.[5−7] With hydrogen, however, the main reaction that occurs at high temperature is the formation of N_2 and H_2O (eq 1). The

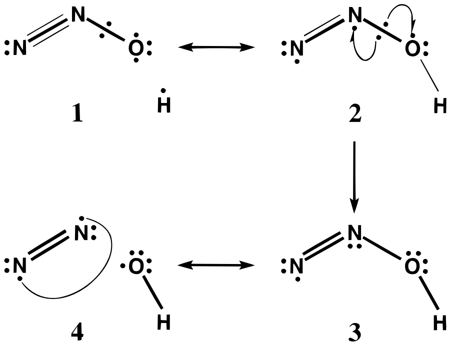
$$N_2O + H_2 \rightarrow N_2 + H_2O \qquad (1)$$

mechanism of this reaction is not simply dependent on the dissociation of nitrous oxide, and for the propagation, the following mechanism which is based on the presence of H radicals has been suggested (eqs 2 and 3).[7−9] More recently, ab initio studies have been performed for the reaction of H radicals with N_2O (eq 2) for which a direct mechanism was calculated to proceed via an NNOH transition state.[10] The calculated structure for this transition state (NN, 1.13 Å; NO, 1.23 Å; OH, 1.52 Å; NNO, 1.48°; NOH, 113°)[10] is in accord with that which is implied by resonance between the increased-valence structures **1** and **2** (Scheme 1). At the transition state, the potential energy curves for structures **1** and **2** cross. Therefore the valence bond (VB) description of the transition state involves equal contributions from these two structures. The electronic reorganization indicated in **2** leads to **3**, which participates in resonance with **4**, thereby generating N_2 and OH as products.[11]

$$H + N_2O \rightarrow OH + N_2 \qquad (2)$$

$$OH + H_2 \rightarrow H_2O + H \qquad (3)$$

SCHEME 1: Valence bond structures 1−4



In the present contribution we want to report on an experimental study concerning the reactivity of N_2O with fluorine radicals at low temperature. In the theoretical study we analyze the observed reaction behavior of N_2O with F radicals and compare it with the reactivity of N_2O toward H radicals.

Results and Discussion

After an equimolar mixture of N_2O and F_2 is irradiated at −196 °C with UV radiation, a dark blue liquid was observed to form in small amounts. This liquid was observed to decompose at temperatures above −140 °C. The high thermal instability and dark blue color identified this compound as being the known compound nitrosodifluoroamine, F_2NNO.[1a,b] The main reported route to forming F_2NNO in the literature is the reaction of N_2F_4 with a 10-fold excess of NO at 310 °C followed by quenching at −196 °C (eq 4).[1,2] To investigate the decomposition products of the thermally highly unstable dark blue liquid, a room temperature gas-phase IR spectrum was recorded

$$^1/_2\, N_2F_4 + NO \rightarrow F_2NNO \qquad (4)$$

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[‡] We dedicate this paper to Professor Dr. Paul v. R. Schleyer on the occasion of his 70th birthday.

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which showed unreacted N_2O (2260, 2230, 1300, 1150, 600 cm^{-1}; cf. refs 12a,b) starting material and small amounts of N_2F_4 (1025, 1015, 998, 738, 540 cm^{-1}; cf. refs 12c−e) and NO (1960 cm^{-1}, cf. ref 12f), which correspond to the decomposition products as were observed in the literature. In addition traces of SiF_4, NO_2, and HF (IR) as well as traces of N_2 but no F_2 were identified by gas discharge (*Note*: A very small leak, i.e. traces of air could also have caused the appearance of O_2/N_2). Therefore, from our observations, in contrast to the literature, N_2O does indeed react with fluorine at low temperature (eq 5), however, only if the reaction mixture is irradiated

$$F_2 + N_2O \rightarrow F_2NNO \qquad (5)$$

with UV; without UV irradiation no reaction was observed to occur. Whereas N_2O does not react with fluorine under ambient conditions (atmospheric pressure at room temperature), we found that at −196 °C F_2 does indeed react with N_2O to form initially F_2N_2O (eq 5), which above −140° decomposes to yield N_2F_4 and NO (see above) (eq 6; note, eq 6 is the reverse of eq 4).

$$F_2N_2O \rightarrow {}^1/_2\ N_2F_4 + NO \qquad (6)$$

Since reaction 5 was only observed under UV irradiation, the presence of F radicals can be assumed to be essential for the reaction to occur. This can be seen in analogy to the reaction mechanism proposed for the reaction of N_2O with H_2 which requires the presence of H radicals. However, the products formed (H_2O and N_2 vs N_2F_4 and NO) indicate different reaction mechanisms for the hydrogen and fluorine reaction, where in one case the H radicals attack the oxygen atom of N_2O whereas in the other reaction the F radicals apparently attack the terminal N atom of the N_2O. This different reaction behavior is surprising at a first glance; however, if the average bond energies of the binary molecules H_2O, NH_3, OF_2, and NF_3 are compared, it becomes apparent the O−H bond (114.2 kcal mol^{-1}) is stronger than the N−H bond (93.3 kcal mol^{-1}), whereas the N−F bond (66.4 kcal mol^{-1}) is much stronger than the O−F bond (44.7 kcal mol^{-1}).[7] So the initial attack of the H radical at the O atom of N_2O can well be explained by the fact that the average O−H bond is ca. 20 kcal mol^{-1} stronger than the average N−H bond, whereas in the case of an F radical attacking the N_2O molecule it is exactly the other way around with the average N−F bond being ca. 20 kcal mol^{-1} stronger than the average O−F bond. (For a comparative ab initio study at configuration interaction (CI) level including polarization functions of the systems ONH_3 vs ONF_3, see ref 13.)

Note: The reliability of this crude average bond energy approach is nicely demonstrated by a comparison of the experimental reaction enthalpy ΔH^{exp} and the reaction enthalpy which has been calculated using a simple Born−Haber cycle ΔH^{abe} with the above *a*verage *b*ond *e*nergies for the following reaction: $3H_2O + 2NF_3 \rightarrow 2NH_3 + 3OF_2$; $\Delta H^{exp} = +195.5$,[6] $\Delta H^{abe} = +255.6$ kcal mol^{-1}. This (average bond energy) method only represents a crude estimate since the bond energies in radicals often differ significantly from those in closed shell molecules. For example, the N−H bond energy in N_2H is much weaker than in N_2H_2.[5,6]

Since the F_2N_2O molecule which is formed in reaction 4 is stable at low temperatures only ($T < -140$ °C; it decomposes according to eq 6 to form N_2F_4 and NO), this finding is nicely in agreement with an earlier study which reports on the formation of the thermally highly unstable F_2N_2O from a thermolysis reaction of N_2F_4 and NO followed by subsequent quenching of the F_2N_2O formed at −196 °C (eq 6).[1−3] Also in this study it was observed that F_2N_2O decomposes at temperatures above −140 °C to form N_2F_4 and NO (eq 6).[1,2]

TABLE 1: F_2N_2O Molecule in C_s vs C_1 Symmetry

method/ basis set	C_s[a] −*E*/au	imag freq/ cm^{-1}	C_1[b] −*E*/au	Δ*E*($C_s - C_1$)/ (kcal mol^{-1})
PM3/VSTO-3G*		−464*i*		+8.4
HF/4-31G	381.783 563	−464*i*	381.812 534	+18.2
HF/6-31G*	382.330 612	−552*i*	382.366 103	+22.3
MP2/6-31G*	383.185 934	−483*i*	383.223 029	+23.3
MP2(FULL)/ cc-pVTZ	383.685 778	−451*i*	383.716 675	+19.4

[a] For all C_s type structures NIMAG = 1. [b] For all C_1 type structures NIMAG = 0.

TABLE 2: Structural Parameters Calculated for F_2NNO (C_1 Symmetry) at MP2(FULL)/cc-pVTZ Level of Theory

bond type	*d*/Å	angle	∠/deg	mode	ν/cm^{-1} (rel int)[a]
N3−F1	1.387	F1−N3−F2	103.1	ν_1	95 (1)
N3−F2	1.369	F1−N3−N4	94.9	ν_2	260 (11)
N3−N4	1.769	F2−N3−N4	99.1	ν_3	306 (14)
N4−O5	1.149	N3−N4−O5	109.6	ν_4	398 (20)
				ν_5	539 (1)
		F1−N3−N4−O5	−115.7	ν_6	709 (21)
		F2−N3−N4−O5	−11.5	ν_7	950 (132)
				ν_8	1033 (72)
				ν_9	1817 (233)

[a] Relative IR intensities in kilometers per mole; zpe = 8.7 kcal mol^{-1}.

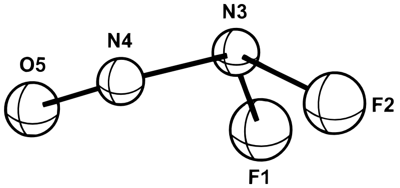
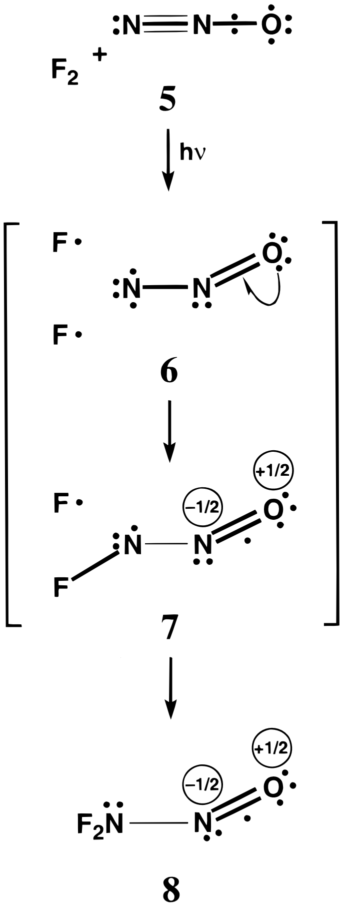


Figure 1. Structure of F_2NNO (C_1 symmetry) calculated at the MP2(FULL)/cc-pVTZ level of theory.

The structure of F_2NNO calculated using quantum chemical calculations (HF/4-31G) is wrongly reported in the literature as being planar with C_s symmetry.[3,4] As a frequency analysis of this planar structure (HF/4-31G, MP2/6-31+G*, MP2(FULL)/cc-pVTZ) shows NIMAG = 1, this structure merely represents a transition state (Table 1). Recalculation of this compound as the more likely nonplanar structure (C_1 symmetry) [14] at MP2(FULL)/cc-pVTZ generates a structure of F_2NNO which does represent a true minimum for this compound (Figure 1, Tables 1 and 2), therefore, we here report on the structure of F_2NNO as predicted by quantum chemical calculations.

The bonding situation in the nonplanar F_2N_2O was also investigated with the help of an NBO analysis.[15a−c] In view of the high thermal instability of this molecule and its ready dissociation into NF_2 and NO radicals, it was interesting to investigate whether the natural bond orbital (NBO) analysis would give insight into the bonding situation. The *RESONANCE* keyword was activated to permit strongly delocalized structures. The NBO analysis nicely accounts for the rather long and weak N−N bond in F_2N_2O. The standard Lewis structure to which the NBO analysis corresponds is in agreement with that shown in Scheme 2 (**7**) (see below). This resonance structure has reasonably well-localized σ NBOs (1.982−1.999 electrons), but one severely depleted π lone pair centered at the oxygen atom

SCHEME 2: Valence bond structures 5−7



(π-LP(O5), 1.778 electrons) and corresponding high occupancy in one σ* antibond (σ*(N3−N4), 0.260 electrons). Therefore, the most significant type of donor−acceptor interaction (negative hyperconjugation, anomeric effect)[15d−f] in F_2N_2O that is responsible for the non-Lewis contributions is π-LP(O5) ⇒ σ*(N3−N4) (Figure 2). This intramolecular donor−acceptor interaction causes the NO bond to be stronger than a double bond and the N−N bond to be weaker than a single bond. This finding is also nicely in accord with VB structure **10** (Scheme 3, see below) which contains an N−O bond with a bond order greater than 2 and a fractional N−N bond ($b < 1$). Structure **10** is obtained by spin-pairing the odd electron of F_2N with the odd electron of NO. The latter electron occupies an antibonding MO. Moreover, it is also in agreement with the decomposition of the F_2N_2O molecule occurring at the long and weak N−N bond forming NF_2 and NO.

The formation of F_2N_2O from both (i) N_2F_4 and NO and from (ii) N_2O and F_2 can also be rationalized from the valence bond point of view.[11,23b,24] The best VB structure for N_2O is structure **5** in Scheme 2. Electronic excitation of N_2O and dissociation of F_2 leads to the formation of F_2NNO with VB structure **8**, via VB structures **6** and **7**.

The formation and decomposition of F_2NNO from N_2F_4 (which is known to dissociate easily into radicals) and ground-state NO (VB structure **9**)[24b] can on the other hand easily be described by the spin-pairing mechanism shown in Scheme 3 (cf. F + NO → FNO).[24b]

Experimental Methods

Caution: Many N−F compounds are highly explosive and often are very toxic. Fluorine, F_2, is a strong oxidizer. Although no explosion was observed in our studies, all covalent N−F compounds and high oxidizers should be handled with respect, and fully protective clothing should be warn at all times.

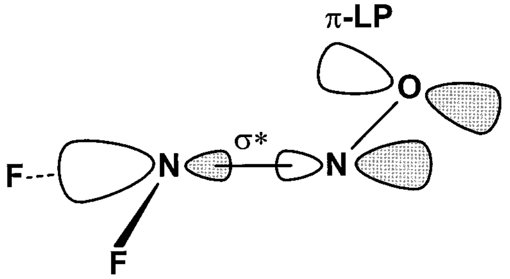
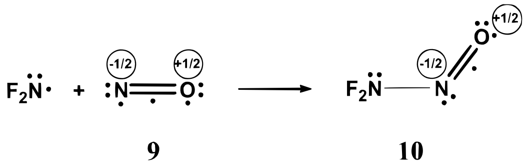


Figure 2. Negative hyperconjugation in F_2N_2O: π-LP(O5) ⇒ σ*(N3−N4). (For an alternative formulation of negative hyperconjugation, see ref 26).

SCHEME 3: Valence bond structures for NF_2 + NO → F_2NNO



F_2 (Solvay) and N_2O (Aldrich) were used as obtained. The experimental techniques and apparatus used in this study have been described elsewhere.[16]

Using a Monel vacuum line, 2.0 mmol of N_2O were condensed at −196 °C into a prepassivated (ClF_3, 100 °C, 2 atm, 2 h) 15 mL glass one-bulb vessel fitted with a Young valve. At −196 °C 2.0 mmol of F_2 was condensed into the reaction vessel. The reaction vessel was then irradiated at −196 °C for 2 h using a Hg high-pressure 1000 W UV lamp (254 nm) which was submerged together with the reaction vessel in a large steel Dewar vessel containing liquid nitrogen. All glass parts were made of quartz glass, and the distance between the UV lamp and the reaction vessel was no more than 1 cm. A gas cell IR spectrum was recorded at room temperature after all volatile materials had been removed under vacuum at −196 °C.

Computational Methods

The calculations were performed with the program package Gaussian 98.[17] The structure of F_2N_2O, its energy and zero point energy (zpe), and the vibrational data were calculated at the electron correlated MP2(FULL) level of theory[18] using a polarized standard triple-ζ cc-pVTZ basis set.[19]

The usually very poor agreement between experiment and uncorrelated HF calculation for fluorine containing nonmetal molecules clearly shows the great importance of electron correlation for accurate predictions for fluorine containing nonmetal compounds.[20] (*Note*: The F_2 molecule is unbound if electron correlation is not taken into account.[21]) Whereas the CCSD(T) method has generally been shown to be reliable for covalently bound nonmetal compounds,[22,23] often the less expensive MP2 method in combination with a double-ζ basis set gives very good structural results and vibrational frequencies.[22,23] Since the contribution of the core orbitals to the binding energy is structure-dependent,[25] the frozen core approximation was assumed not to allow sufficient variational freedom in the calculations in order to correctly determinate the energy and structure for F_2N_2O, for which we expected to have a relatively flat potential energy surface. Therefore we applied the more expensive MP2(FULL) method, where all electrons are included in a correlation calculation.

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