leading to chlorine atoms, also plays a role, albeit minor. Addition of benzene to a sample of ClO_2 in trichlorofluoromethane led, upon laser excitation, to a transient with $\lambda_{max} \sim 490$ nm, readily characterized as the π-complex between chlorine atoms and benzene.[20] Given the known excitation coefficients of the π-complex and of ClO_2, it is possible to estimate that ~8% of the initial (fast) bleaching is due to reaction 4.

$$ClO_2 \rightarrow Cl^{\bullet} + O_2 \qquad (4)$$

Our results indicate rapid (within the laser pulse) formation of $Cl^{\bullet}$. This tends to eliminate the ClO + O reaction as a possible source of $Cl^{\bullet}$, unless the process was to occur in a geminate fashion before the products of reaction 1 leave the solvent cage.

Thus in solution, ClO remains as the most likely intermediate to combine with ClO_2 (reaction 5).

$$ClO + ClO_2 \rightarrow Cl_2O_3 \qquad (5)$$

This appears to be the first time that formation of Cl_2O_3 in ClO_2 photolysis has been clearly demonstrated although McHale and von Elbe[11] and Lipscomb et al.[12] have previously reported circumstantial evidence supporting its existence.

Considering the small solvent-induced red shift (~8 nm) in the UV spectrum of ClO_2 in Cl_3CF[21] as due to the different conditions, the results agree well with the gas-phase spectra obtained by Cox and Hayman in the photolysis of ClO_2[3] and by Molina and Molina in the $Cl^{\bullet} + ClO_2$ system.[4] In all cases maxima are observed at 270–280 nm, and therefore, on the basis of both spectral and chemical evidence, it appears reasonable to conclude that they can be attributed to Cl_2O_3.[22] Further work will be reported elsewhere.[23,24]

Registry No. ClO_2, 10049-04-4; Cl_2O_3, 17496-59-2; TME, 27416-06-4.

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Reaction between the Amidogen Radical, $\dot{N}H_2$, and Molecular Oxygen in Low-Temperature Matrices

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The reaction between $\dot{N}H_2$ and O_2 has been examined in a low-temperature matrix for the first time. Results from a series of experiments employing isotopically substituted ammonia and oxygen indicate that the primary reaction products are HONO and H atoms. A reaction mechanism is proposed that involves the intermediacy of the aminoperoxy radical, $NH_2O\dot{O}$, which is stabilized by the low-temperature/high-pressure environment of the matrix before undergoing intramolecular decomposition or reaction with oxygen.

Introduction

The reaction between the amidogen radical, $\dot{N}H_2$, and oxygen is a potential source of NO_x species in the troposphere and has therefore stimulated a considerable amount of research. Despite this, neither the end products nor the rate coefficients or mechanism involved in the overall photooxidation of ammonia is well characterized.[1]

Channels 1–7 have been suggested to follow the primary reaction between NH_3 and $\dot{O}H$ radicals in the atmosphere.[2] Early

$$\dot{N}H_2 + O_2 \longrightarrow \left\{ \begin{array}{llr} \rightarrow NO + H_2O & \Delta H_f/kJ\ mol^{-1} = -347 & (1) \\ \rightarrow NO_2 + H_2 & \Delta H_f/kJ\ mol^{-1} = -167 & (2) \\ \rightarrow HONO + H & \Delta H_f/kJ\ mol^{-1} = -50 & (3) \\ \rightarrow HNO + \dot{O}H & \Delta H_f/kJ\ mol^{-1} = -42 & (4) \\ \rightarrow NH_2O\dot{O} & \Delta H_f/kJ\ mol^{-1} = -21 & (5) \\ \rightarrow H_2NO + O & \Delta H_f/kJ\ mol^{-1} = +125 & (6) \\ \rightarrow NH + H\dot{O}_2 & \Delta H_f/kJ\ mol^{-1} = +188 & (7) \end{array} \right.$$

experiments in which mixtures of NH_3 and O_2 were photolyzed by 213.9-nm light at room temperature led to the proposal of the so-called Gesser mechanism[3,4] in which channel 1 is most important. A secondary reaction between $\dot{N}H_2$ and NO was thought to account for the observation of N_2 product in these experiments. Jayanti[5] conducted similar experiments and, by adding CO to the reaction mixture, was able to show that channel 4 which produces HNO and $\dot{O}H$ radicals was not important because CO_2 was not observed. Instead a mechanism involving $NH_2O\dot{O}$, the addition product of $\dot{N}H_2$ and O_2, was proposed to account for the formation of N_2O and N_2:

$$\dot{N}H_2 + O_2 \rightarrow NH_2O\dot{O} \qquad (5)$$

$$NH_2O\dot{O} + NH_2O\dot{O} \rightarrow 2NH_2\dot{O} + O_2 \qquad (8)$$

$$NH_2O\dot{O} + NH_2\dot{O} \rightarrow N_2O + 2H_2O \qquad (9)$$

$$NH_2\dot{O} + NH_2\dot{O} \rightarrow N_2 + 2H_2O \qquad (10)$$

Flash photolysis of NH_3/O_2 mixtures was found to lead to a

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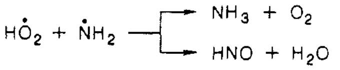
different set of products, and accordingly channel 2 was favored by Hussain and Norrish.[6] In this case, it was suggested that the observed N_2O product arose from HNO self-reaction:

$$HNO + HNO \rightarrow N_2O + H_2O \qquad (11)$$

Two further flash photolysis studies[7,8] concluded that the measured rapid production of $\dot{H}O_2$ results only from reaction between H atoms and O_2. This step is followed by $\dot{H}O_2$ reaction with $\dot{N}H_2$ and accounts for $\dot{N}H_2$ loss in the system rather than its direct removal by O_2:



$$\dot{H}O_2 + \dot{N}H_2 \rightarrow \begin{cases} NH_3 + O_2 & (12) \\ HNO + H_2O & (13) \end{cases}$$

The previously observed N_2 and N_2O products may then be reached via reaction 11 (for N_2O) or by the unimolecular dissociation of HNO to give NO which may then react with $\dot{N}H_2$ to form N_2. A series of shock-tube experiments also leads to inconsistent conclusions. Bradley[9] and Bull[10] suggested that channel 4 provides the initial products whereas Takeyama[11] was able to analyze the results in terms of $\dot{H}O_2$ and NH formation (via channel 7). In contrast, Fujii[12] proposed that the reaction proceeded with the intermediacy of a vibrationally excited $NH_2O\dot{O}^\dagger$ radical that was able to collisionally deactivate to $NH_2O\dot{O}$ or dissociate to HNO plus $\dot{O}H$. These results confirmed the high-temperature work of MacLean[13] in which HNO and $\dot{O}H$ were shown to be formed.

For all gas-phase experiments in which NH_3 is directly photolyzed in the presence of O_2 it is possible that $\dot{H}O_2$ radicals participate in the overall mechanism. However, Hack[14] and Patrick[15] have eliminated the intermediacy of hydroperoxyl radicals in the chemistry by use of H-atom abstraction reactions using F or $O(^1D_2)$ atoms. In the experiments of Hack[14] the reaction between F atoms and NH_3 was used to produce $\dot{N}H_2$ in the presence of O_2 at various pressures and temperatures. The measured rate coefficient was found to have a negative temperature dependence and the results were interpreted in terms of the formation of an $NH_2O\dot{O}$ radical intermediate. In contrast, Patrick[15] produced $\dot{N}H_2$ radicals from $O(^1D_2)$ atom reaction with ammonia but found no evidence for the formation of $NH_2O\dot{O}$. The same conclusions were drawn from the pulse radiolysis work of Pagsberg.[16]

Other experiments involving the photolysis of NH_3/O_2 mixtures by a high-power pulsed CO_2 laser[17,18] and the reaction between $\dot{N}H_2$ and electronically excited molecular oxygen[19] have also failed to provide unambiguous conclusions regarding the true nature of the end products for $\dot{N}H_2$ reaction with O_2.

Several theoretical papers concerning the product analysis for $\dot{N}H_2 + O_2$ reaction also fail to agree. The computer simulation of Levine[20] suggests that the formation of $NH_2O\dot{O}$ is possible but concludes that the Gesser mechanism (channel 1) best explains the results of Jayanti.[5] By computing the enthalpies of formation for $NH_2O\dot{O}$ and $NH_2O\dot{O}^\dagger$, Pouchan and Chaillet[21] calculate that the reaction forming $NH_2O\dot{O}$ is endothermic by 42 kJ mol^{-1} and that the aminoperoxy radical does not exist. The calculations of Melius[2] on the other hand found the same reaction to be exothermic by 21 kJ mol^{-1}. Melius[2] was also able to propose reaction pathways to final products that all pass through a $NH_2O\dot{O}$ intermediate: H_2, NO, and O atoms being the favored end products in this case.

The above discussion reveals little consistency in the cited final products at either high or low temperature. The high-temperature results, including both flash photolysis and shock-tube experiments, can be divided into early reports where HNO and $\dot{O}H$ are thought to provide chain propagation, and later reports where it is suggested that products arise through $\dot{H}O_2$ reaction with $\dot{N}H_2$. At low temperatures the literature is divided between the Gesser and Jayanti type mechanisms with little direct evidence for either. In experiments where $\dot{H}O_2$ participation is avoided the results still disagree: one study favoring $NH_2O\dot{O}$ formation, and the other indicating no involvement for this species.

The underlying problem in analysis of the $\dot{N}H_2 + O_2$ reaction is the fact that it is extremely slow. The recommended rate coefficient is $<3.0 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} [1] at room temperature compared with a value of 3.4×10^{-11} cm^{-1} $molecule^{-3}$ s^{-1} for the reaction between $\dot{N}H_2$ and $\dot{H}O_2$.[1]

In an attempt to identify the primary reaction products and intermediates in the photooxidation of ammonia, a task seemingly impossible in the gas phase, experiments were performed in low-temperature matrices where secondary chemistry can be eliminated and unstable and intermediate species are trapped in an inert environment.

Experimental Section

The experimental procedure is described in detail elsewhere[22] and is only briefly outlined here. Matrices were prepared by the pulsed deposition of gas mixtures containing NH_3 and O_2 in argon. The matrix was deposited over a period of approximately 1 h onto a CsI window held at 4.2 K by an Air-Products Heliplex Model CS-308 closed-cycle cryogenic refrigeration system. Infrared spectra of the matrices were obtained on a Digilab FTS-20V FTIR spectrometer using an MCT detector. The spectra shown in Figures 1 and 2 are the result of the coaddition of 1000 scans with box-car apodization and were recorded with 0.5 cm^{-1} resolution.

Accurate measurement of partial pressures of the gases was obtained from an MKS Instruments Inc. Baratron capacitance manometer (Model 310, 0–1 Torr) and a Wallace Tiernan precision dial manometer (Model FA 141, 0–1000 Torr), both attached to a mercury-free vacuum line fitted with Youngs greaseless stopcocks. The total pressure in the bulbs was 150 Torr in each experiment and between 50 and 100 pulses of approximately 10 cm^3 were deposited.

Photolysis of the matrix at 184.9/253.7 nm was carried out with a Philips Model 93109 E low-pressure mercury lamp. The lamp and immediate environment were flushed with nitrogen to prevent absorption of the 184.9-nm line by atmospheric oxygen.

Argon (Messer Griesheim GmbH 99.999% stated purity) was passed through a glass spiral immersed in liquid nitrogen before use. Oxygen (Messer Griesheim GmbH 99.998% stated purity) was passed through a spiral immersed in a solid CO_2/acetone bath. Ammonia (B.D.H. Chemicals Ltd. 99.98% stated purity) was thoroughly degassed at 77 K by a repeated freeze–pump–thaw cycle to remove noncondensables at this temperature. The isotopic species, ($^{18}O_2$, 99% atom purity, $^{15}NH_3$, 99.5% atom purity, and ND_3, 99.1% atom purity) were all supplied by The British Oxygen Co. and used without further purification.

Results

Argon matrices containing ammonia and oxygen in a range of matrix ratios from 1/0.2/200 to 1/5/200 were subjected to 184.9/253.7-nm photolysis for up to 8 h. As oxygen absorbs light

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TABLE I: Products from the 184.9/253.7-nm Photolysis of NH_3/O_2Ar Matrices

freq/cm^{-1}	assignment	lit. value, cm^{-1}
3725.2	H_2O	3722
3634.0	H_2O	3639
3514.6	HO_2	3414.0
3216.5	NH_2	3220
1879.5/1871.7	NO	1876
1688.0	HONO (trans)	1690
1632.6	HONO (cis)	1633
1609.9/1606.6	NO_2	1610
1593.5	H_2O	1591.4
1497.1/1495.2	NH_2	1499.0
1388.6	HO_2	1389.4
1263.3/1259.4	HONO (cis)	1265
1118.6	NH_2OH	1115
1100.8	HO_2	1101.3
1032.8	O_3	1033.5/1039.6
849.6/843.8	HONO (cis)	850
795.1/785.4	HONO (trans)	800
698.6		
639.9/636.0	HONO (cis)	637
608.0/605.1	HONO (cis)	610
549.2		

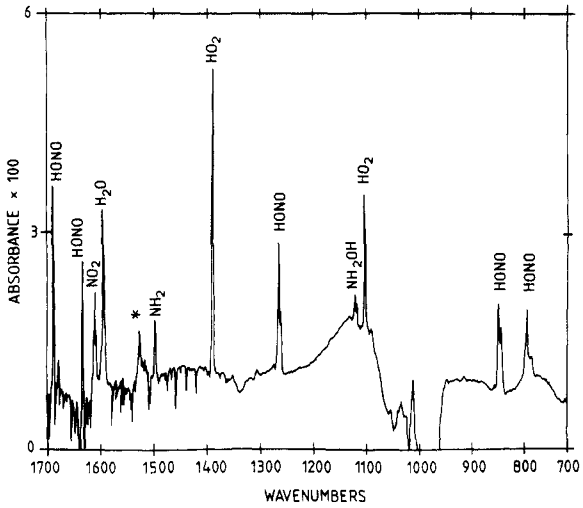

Figure 1. Products arising from 184.9/253.7-nm photolysis of a $NH_3/O_2/Ar$ matrix with MR = 1/5/200.

only weakly at 184.9 nm compared to ammonia, concentrations of oxygen up to 5 times that of ammonia could be utilized without unduly affecting the primary process (photolysis of ammonia) but ensuring reaction between $\dot{N}H_2$ and O_2. Above this concentration level, increasing amounts of $(O_2)_2$ dimer in the matrix results in increasing O_3 formation:

$$(O_2)_2 \xrightarrow{h\nu} O_3 + O(^3P) \qquad (14)$$

$$O(^3P) + O_2 \xrightarrow{\text{matrix}} O_3 \qquad (15)$$

Gas-phase photolysis of similar mixtures would result in the formation of $H\dot{O}_2$ which would rapidly consume $\dot{N}H_2$ radicals. However, in the matrix, competition between O_2 and $H\dot{O}_2$ for $\dot{N}H_2$ is less important because cage-pairing rather than random reactive collisions determines which reaction dominates. In the present experiments the certain excess of O_2 over $H\dot{O}_2$ ensures that any $\dot{N}H_2$ radical produced has a very high chance of being next to an oxygen molecule in the matrix.

The product bands from an experiment in which a matrix containing $NH_3/O_2/Ar$ (MR = 1/5/200) was photolyzed as described above, are shown in Table I. Two bands, at 698.6 and 549.2 cm^{-1}, left unassigned at this stage are discussed later. The detected products are HONO, $\dot{N}H_2$, $H\dot{O}_2$, H_2O, NO, NO_2, NH_2OH, and O_3, these assignments being made by comparison with literature values for each species, and unambiguously confirmed by complementary experiments using isotopically substituted ammonia ($^{15}NH_3$ or ND_3) and oxygen ($^{18}O_2$). Figure 1 shows the FTIR spectrum of the $NH_3/O_2/Ar$ matrix obtained after 9 h of photolysis. This is referenced against the prephotolysis spectrum; bands pointing upwards therefore represent product formation and those pointing down depletion of ammonia or miscancelled water vapor lines. The NO spectrum obtained in these experiments is interesting as it always appears as a well-separated doublet (see Figure 2). The reason for this splitting may be associated with a site perturbation, which is considered in the Discussion section.

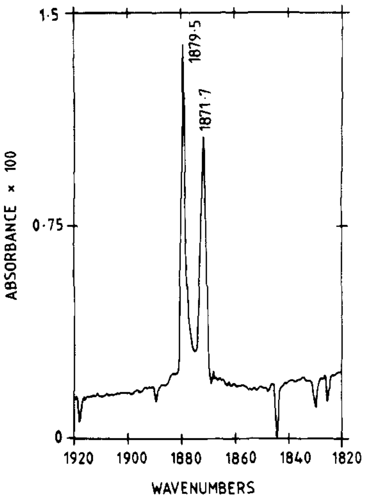

Figure 2. Infrared spectrum of NO product in two distinct matrix sites.

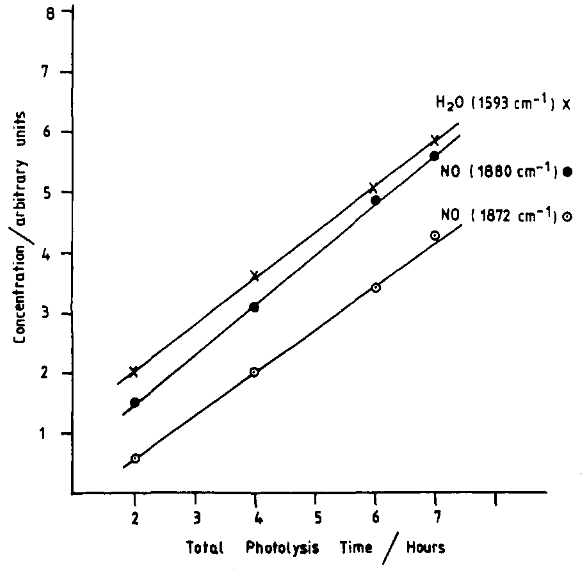

Figure 3. Linear concentration–photolysis time behavior of H_2O and NO products.

In order to determine which of the observed species are primary products of the $\dot{N}H_2 + O_2$ reaction, and which are the result of secondary chemistry initiated by photolysis of primary products, serial photolysis experiments were carried out. In these, the matrix was photolyzed for short periods in between which the infrared spectrum was obtained as usual. In such experiments, an intermediate species will display a nonlinear concentration/time dependence whereas the concentration of an end product will increase uniformly with time. The results of an experiment in which an $NH_3/O_2/Ar$ matrix was photolyzed for periods of 2, 2, 2, and 1 h are summarized in Figures 3 and 4. In each case the plot is absorbance peak height of the strongest band of that molecule versus total photolysis time.

Experiments were also carried out with different oxygen concentrations in the matrix. Products from experiments where the $NH_3/O_2/Ar$ ratio was 1/0.2/200, 1/0.4/200, 1/1/200, 1/3/200, and 1/5/200 are listed in Table II.

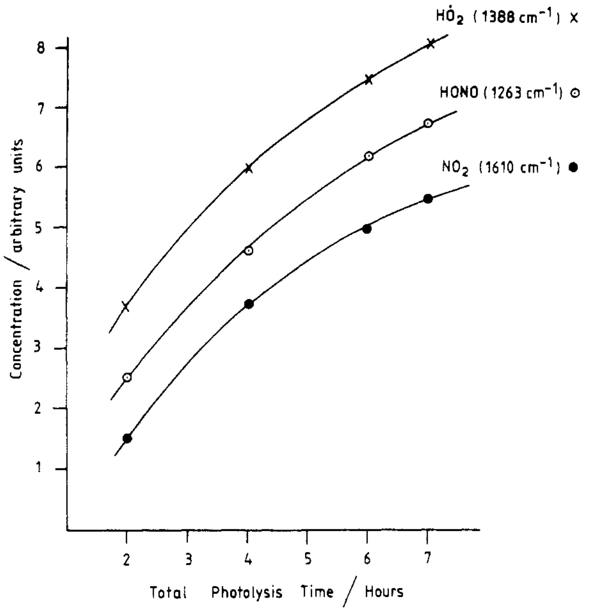

Figure 4. Nonlinear concentration–photolysis time behavior of $H\dot{O}_2$, HONO, and NO_2 products.

TABLE II: Products Formed in Matrices Containing Varying Amounts of Oxygen

matrix ratio ($NH_3/O_2/Ar$)				
1/0.2/200	1/0.4/200	1/1/200	1/3/200	1/5/200
$\dot{N}H_2$ $H\dot{O}_2$	$\dot{N}H_2$ $H\dot{O}_2$ HONO	$\dot{N}H_2$ $H\dot{O}_2$ HONO NO NO_2 H_2O NH_2OH	$\dot{N}H_2$ $H\dot{O}_2$ HONO NO NO_2 H_2O NH_2OH	$\dot{N}H_2$ $H\dot{O}_2$ HONO NO NO_2 H_2O NH_2OH O_3

Discussion

The experiments carried out, including use of isotopic ammonia and oxygen, serial photolysis, and variation of matrix oxygen concentration, enable the compilation of a large data base concerning the reaction between the amidogen radical and oxygen. In the case of the high O_2 content experiments the large number of products suggests that the aim of reducing secondary chemistry is not achieved. Despite this, an important conclusion can be drawn from this result, i.e., that HNO is not a primary product of $\dot{N}H_2 + O_2$ reaction in the inert matrix. This also implies that at low temperatures reaction 13 is inefficient. A number of reaction pathways exist by which the observed products may arise:

HONO:

$$OH + NO \rightarrow HONO \tag{16}$$

$$NH + O_2 \rightarrow HONO \tag{17}$$

$$H + NO_2 \rightarrow HONO \tag{18}$$

$$\dot{N}H_2 + O_2 \rightarrow HONO + H \tag{3}$$

NO_2:

$$NO + O(^3P) \rightarrow NO_2 \tag{19}$$

$$HONO \xrightarrow{h\nu} NO_2 + H \tag{20}$$

$$\dot{N}H_2 + O_2 \rightarrow NO_2 + H_2 \tag{2}$$

NO:

$$HONO \xrightarrow{h\nu} NO + OH \tag{21}$$

$$NO_2 \xrightarrow{h\nu} NO + O \tag{22}$$

$$\dot{N}H_2 + O_2 \rightarrow NO + H_2 \tag{1}$$

H_2O:

$$\dot{O}H + H \rightarrow H_2O \tag{23}$$

$$\dot{N}H_2 + O_2 \rightarrow NO + H_2 \tag{1}$$

NH_2OH:

$$NH_3 + O_3 \rightarrow NH_2OH + O_2 \tag{24}$$

O_3:

$$(O_2)_2 \xrightarrow{h\nu} O_3 + O(^3P) \tag{14}$$

$$O(^3P) + O_2 \rightarrow O_3 \tag{15}$$

Both the serial photolysis experiments and those where the oxygen concentration was varied enable secondary end products to be differentiated from the primary ones.

Serial Photolysis Experiments. The linear concentration/time dependence displayed by NO and H_2O (see Figure 3) show that they are end products that neither undergo further reactions nor are photolyzed. Both H_2O and NO will not be photolyzed in the present experiments as all 184.9-nm light will be absorbed by the considerable excess of ammonia in the matrix. The fact that NO is a final product does, however, rule out the possibility that reaction 16 is the source of HONO.

The rates of growth of bands from species that absorb visible light, e.g., NO_2 and $H\dot{O}_2$, decrease with photolysis time. However, the behavior of HONO is less straightforward due to the existence of two isomers, the cis and trans forms. The infrared photoisomerization of HONO in low-temperature matrices is an example of photochemistry initiated by infrared light and was first observed by Pimentel[23] when near-IR light was found to cause cis to trans isomerization, and UV radiation the reverse process. An important observation of the present study is that HONO is formed initially in the cis form and isomerizes to the trans form, which is the more stable by approximately 130 cm^{-1}.[25] The production of the least stable HONO isomer may yield some information regarding the mechanism by which it is formed.

It was also observed in the serial photolysis experiments that the ratio of HONO concentration to NO and NO_2 concentration decreased with increasing photolysis time. This behavior effectively rules out the possibility that HONO is formed from either $H + NO_2$ (reaction 18) or $\dot{O}H + NO$ (reaction 16).

Variation of Oxygen Content. Several trends were observed when the O_2 concentration was varied. In experiments where the O_2 concentration is low only $\dot{N}H_2$ and $H\dot{O}_2$ radicals are formed. In this case $H\dot{O}_2$ is the product of $H + O_2$ reaction which may occur when a hydrogen atom migrates to a site containing an oxygen molecule. Raising the O_2 concentration results in the formation of only one additional infrared detectable product, namely HONO. The important observation here is that neither NO nor NO_2 is formed at this stage.

The intensity of the $H\dot{O}_2$ absorptions did not increase linearly with O_2 concentrations as would be expected if the sole route to $H\dot{O}_2$ was $H + O_2 \rightarrow H\dot{O}_2$. Instead the rise was apparently exponential, increasing rapidly at higher O_2 concentrations. This suggests that another reaction may also be responsible for $H\dot{O}_2$ formation.

The Proposed Reaction Sequence in a Matrix. Any reaction sequence proposed to describe the reaction between $\dot{N}H_2$ and O_2 in low-temperature matrices must account for all the above observations. The Gesser mechanism, producing both NO and H_2O directly from $\dot{N}H_2 + O_2$ reaction, clearly does not apply as these products are found to arise through secondary chemistry. The Hussain mechanism is ruled out because HNO is not detected at all. For the same reason, the reaction between $\dot{N}H_2$ and $H\dot{O}_2$ is not important as it should give HNO and H_2O. The production of HONO via NO or NO_2 has already been ruled out in the above

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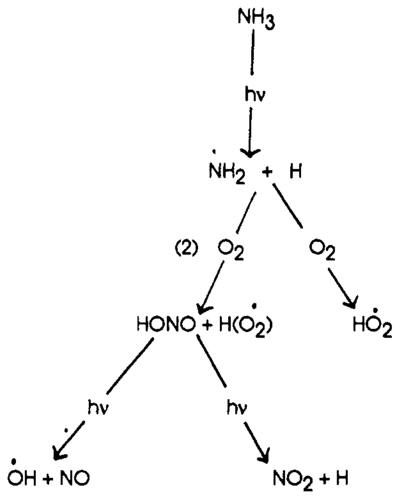


Figure 5. Proposed reaction scheme showing routes to products observed in 184.9/253.7-nm photolysis of a $NH_3/O_2/Ar$ matrix at 4.2 K.

discussion. This leaves only channels 3 and 17 by which nitrous acid may be formed.

Reaction 17 involves the NH radical, which cannot be generated directly from NH_3 by 184.9-nm photolysis.[26] However, the possibility that NH was formed from the photolysis of $\dot{N}H_2$ radicals must be considered. One can rule out 184.9-nm photolysis of NH_2 as this light will be absorbed entirely by the ammonia present in the matrix. Furthermore, the overall efficiency of NH_3 photolysis is only ca. 1%; the secondary photolysis of $\dot{N}H_2$ can be expected to be no more efficient under the same conditions. $\dot{N}H_2$ does have an absorption band between 390 and 830 nm where NH_3 does not absorb. However, even the highest energy radiation that may be absorbed (390 nm) is not sufficiently energetic to dissociate $\dot{N}H_2$ to NH + H, as the NH–H bond strength is ca. 84 kJ mol^{-1} in excess of that available at 390 nm. These conclusions are consistent with those of Schnepp[27] who found that NH was not a product of $\dot{N}H_2$ photolysis by the light from an unfiltered medium-pressure mercury arc lamp and with results from this laboratory that indicate that NH is not formed by the prolonged photolysis of a N_2/NH_3 matrix at 184.9/253.7 nm. Finally, the infrared absorption band of NH was not seen in any experiment and its participation is therefore discounted.

Reaction 3 therefore appears to be the only possible source of HONO in these experiments:

$$\dot{N}H_2 + O_2 \rightarrow HONO + H \tag{3}$$

Once HONO has been established as the primary product in a matrix it remains to propose routes for the other observed species. The 253.7-nm photolysis of HONO results in the formation of both NO_2 and NO as shown in reactions 20 and 21. Nitric oxide is seen in two energetically distinct sites in the matrix which is consistent with its production from secondary photolysis of HONO. One band is thus proposed to be due to NO in close proximity to the other photofragment, $\dot{O}H$; the other is due to NO neighboring either a water molecule formed by $\dot{O}H$ + H reaction (where the H atom from the primary reaction 3 remains in the site) or NO neighboring a $H\dot{O}_2$ molecule. An alternative source of H_2O may be the reaction between NH_3 and O_3 which also accounts for the small amount of NH_2OH seen.

The complete reaction sequence proposed is shown in Figure 5.

The Mechanism for HONO Production. The mechanism by which the primary HONO product is obtained from primary reaction 3 must now be considered. In particular the fact that HONO is formed in the least stable of its isomeric forms requires some consideration. Experiments by other research workers have utilized the in situ reaction between NO_2 and photolytically produced H atoms[24] to produce nitrous acid.

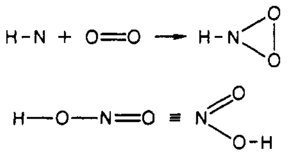
$$H + O\text{-}N\text{-}O \rightarrow HONO \tag{18}$$

The reaction between NH and O_2 has also been shown to provide a source of HONO. Thus the photolysis of matrices containing HN_3 and O_2 results in the following processes[24]

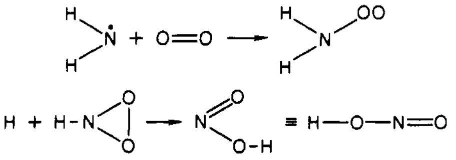
$$HN_3 \xrightarrow{h\nu} N_2 + NH \tag{25}$$

$$NH + O_2 \rightarrow HONO \tag{17}$$

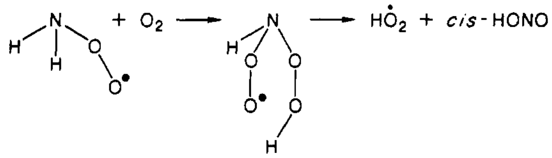
HONO produced in these reactions is formed as a mixture of both trans and cis isomers. Clearly, reaction 18 is a simple addition reaction requiring only the formation of an OH bond, whereas reaction 17 is more complex and must involve the breaking of an O–O bond and the formation of two N–O bonds and an O–H bond. This may proceed via a cyclic intermediate as shown below:



This mechanism is similar to one which can be proposed to occur for the $NH_2 + O_2$ reaction:



The participation of the aminoperoxy radical is invoked in this scheme as predicted by the calculations of Melius.[2] The radical may then break down intramolecularly to form an H atom and the cyclic "HNOO", which then rearranges to HONO as shown above. However, if this represented the exact process then one would expect HONO to be produced initially in both the trans and cis forms rather than solely in the cis form as is observed in these experiments. The question also arises as to why the aminoperoxy radical should decompose to an H atom plus a cyclic oxirene. The matrix observations show that, at very low oxygen concentrations, HONO is not produced but that a higher oxygen content is required. It is therefore suggested that a second oxygen molecule is indeed required to react with the aminoperoxy radical but it must be in a specific conformation which leads exclusively to *cis*-HONO. One possibility is



This reaction may be the additional source of HO_2 radicals that was discussed previously. Having involved the aminoperoxy radical in this mechanism, the possibility exists that it is stabilized sufficiently in the matrix environment for detection by FTIR. Indeed the matrix represents the ideal environment in which to examine an association reaction that may display a negative temperature dependence. The low temperature of the matrix encourages adduct formation, and the solid cage ensures very efficient stabilization by transfer of vibrational energy that in the gas phase may force the adduct to break apart to reactants.

The only experimental vibrational spectrum of $NH_2O\dot{O}$ to have been measured to date is in liquid ammonia where it is thought to be stabilized by hydrogen bonding.[28] Raman bands at ca. 680, 1500, 980, and 820 cm^{-1} were observed to have a doublet structure due to the existence of both *cis*- and *trans*-NH_2OO and were assigned as NOO bend, NH_2 bend, NH_2 wag, and NO stretch,

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respectively. The theoretical infrared spectrum of NH_2OO has been calculated[22] and bands are predicted at 3483/3568, 3389/3443, 1340/1370, 1261/1335, 1032/1002, 822/896, 558/576, and 500/475 cm^{-1}, where the first of each pair corresponds to the trans conformer and the second to the cis conformer.

In the present experiments, bands are indeed seen in approximately the correct positions but are assigned to species such as HONO and $H\dot{O}_2$. Two weak bands, however, remain unassigned and display isotopic shifts as shown below:

experiment	$^{14}NH_3/^{16}O_2$	$^{15}NH_3/^{16}O_2$	$^{14}NH_3/^{18}O_2$
wavenumber/cm^{-1}	549.2, 698.6	548.2, 690.9	546.8, 677.9

The band at 698.6 cm^{-1} is close to the wavenumber of the strongest Raman band in the solution-phase work[28] and the isotopic shifts are close to what might be expected if the vibration were associated with the bending of the NOO chain in the $NH_2O\dot{O}$ molecule. The 549.2-cm^{-1} band is close to the calculated band at 558 cm^{-1} but the small isotopic shifts suggest that this vibration would be associated with the NH_2 grouping if it were a $NH_2O\dot{O}$ band rather than with the NOO chain, as predicted. It is of course impossible to make a positive assignment to $NH_2O\dot{O}$ on the basis of two weak spectral bands and the isotopic counterparts in such a complex system without the detection of other absorption bands, and the assignment of these bands to $NH_2O\dot{O}$ in the matrix must be regarded as very tentative.

It remains to be considered why the matrix product of $\dot{N}H_2$ + O_2 reaction, HONO, has never been detected in the gas-phase studies of this reaction. The detection of HONO has in most instances been excluded because of (i) the highly specific detection techniques employed to monitor the kinetic behavior of the participating species and (ii) the formation of $H\dot{O}_2$, which rapidly removes $\dot{N}H_2$ from the system. Conversely, no gas-phase work has been carried out under sufficiently low-temperature/high-pressure conditions so that the formation and stabilization of $NH_2O\dot{O}$ is possible. In the matrix environment, cage pairing ensures that $\dot{N}H_2$ and O_2 react, and the low-temperature (4.2 K) and high-pressure (solid cage) ensure that $NH_2O\dot{O}$ is able to form and undergo rapid collisional deactivation before either breaking apart intramolecularly to form HONO + H or reacting with O_2 to form HONO + $H\dot{O}_2$.

Conclusion

The primary products of the reaction between $\dot{N}H_2$ and O_2 in a low-temperature matrix are HONO and H atoms. The reaction mechanism by which these products arise involves the aminoperoxy radical, the formation and deactivation of which are favored by the matrix conditions. The aminoperoxy radical subsequently either breaks down intramolecularly or reacts with O_2 to form the HONO product. The fact that HONO is produced exclusively in the cis form is one of several factors which effectively rules out the participation of NH in the matrix photochemistry. HNO is not observed in this study in contrast to experiments performed with $\dot{N}H_2$ + NO.[29]

Registry No. $\dot{N}H_2$, 13770-40-6; O_2, 7782-44-7.

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Production of NF($a^1\Delta$) by Dissociation of Fluorine Azide

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The reactions of vibrationally excited HF or DF molecules with FN_3 were found to dissociate the azide, but not to yield metastable NF fragments. Thermal dissociation of FN_3, on the other hand, yielded metastable NF($a^1\Delta$) with near-unit efficiency. Concentrations of NF($a^1\Delta$) approaching 3 × $10^{16}/cm^3$ were obtained at temperatures near 1000 K, and the decay of NF($a^1\Delta$) was found to be dominated by self-annihilation. The activation energy for production of NF($a^1\Delta$) by thermal dissociation of FN_3 was found to agree with ab initio calculations by Michels.

Introduction

Fluorine azide (FN_3) was first synthesized in 1942 by Haller, upon gas-phase reaction of HN_3 with F_2. In preliminary studies, Haller found that FN_3 reacted by fracture of the azide group which he attributed to a weak central bond. Haller also found that FN_3 was highly explosive when condensed and the gaseous material was slowly but efficiently converted to N_2F_2 and N_2 upon mild heating.[1] Later, Gipstein and Haller[2] obtained an ultraviolet absorption spectrum of FN_3, while Pankratov et al.[3] demonstrated that FN_3 could be obtained by the reaction of F_2 with NaN_3. Also, Milligan and Jacox[4] obtained the infrared absorption spectrum of FN_3 in an Ar matrix. More recently, we studied the ArF laser photolysis of FN_3 and determined the heat of formation as 125–135 kcal/mol, sufficient to allow the molecule to dissociate to electronically excited NF radicals by an exothermic reaction.[5] Moreover, analysis of the direct products in this experiment suggested that FN_3 had a singlet ground state; therefore, upon dissociation, only metastable NF($a^1\Delta$,$b^1\Sigma$) should be formed if spin is conserved. Similar results were obtained for ClN_3 and BrN_3 by Coombe et al.[6] and Coombe and Lam,[7] respectively. On the basis of these findings, we began an investigation of FN_3 dissociation in hopes of developing an efficient and chemically clean (scalable) source of singlet NF. Since Hartford[8] had demonstrated analogous production of ND($a^1\Delta$) upon CO_2 laser multiphoton dissociation of DN_3, we decided to concentrate on methods to add thermal or vibrational energy to the FN_3 ground state. In parallel with our study, Michels[9] performed ab initio calculations of the FN_3 potential energy surfaces which yielded vibrational frequencies in good agreement with infrared absorption data[4,10] and which demonstrated a 0.5–0.7-eV barrier to dissociation of the electronic ground state by central bond rupture. A substantially larger

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