

REACTION OF NH($a^1\Delta$) WITH HN₃*

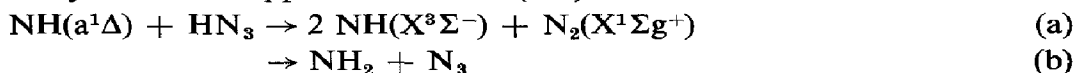
RICHARD J. PAUR and EDWARD J. BAIR

Department of Chemistry, Indiana University, Bloomington, Ind. 47401 (U.S.A.)

(Received June 19, 1972; in revised form July 31, 1972)

SUMMARY

This research is a preliminary survey to explore a possible analogy between the chemistry of the NH singlet radical and its electronic isomer, O(1D). The flash decomposition of HN₃ forms NH($a^1\Delta$) as the predominant observable primary product. The time dependence of the absorption by NH($X^3\Sigma^-$), NH($a^1\Delta$), NH₂, N₃, the emission by NH($^3\Pi$), NH($^1\Pi$), and the initial and final absorbance by HN₃ were observed and correlated. The decomposition appears to result from the electrical disturbance which accompanies the photolysis flash rather than (or in addition to) photolysis. The disappearance of NH($a^1\Delta$) is consistent with the mechanism



The combined rate of disappearance of NH($a^1\Delta$) by all processes, $2.5 \pm 1.0 \times 10^{-11}$ cm³/molecule sec, is independent of inert gas pressure, although the product distribution is not. The implications of this result are discussed.

I. INTRODUCTION

Reactions of biradicals are less well characterized kinetically than other kinds of gas phase reactions. This is true partly because experiments forming them generally yield both ground state and metastable excited radicals which have quite different reactivity. Considerable attention has been directed to distinguishing this singlet and triplet reactive character. However, there is abundant evidence that reactions of singlet biradicals are complex in themselves. The present research is directed towards better understanding the isolated, gas phase reactions of metastable singlet biradicals.

The photochemical decomposition of HN₃ has been studied by many workers¹⁻⁶ over a number of years. A recent experiment by Darwent and coworkers⁷

* Contribution 2103, Chemistry Department, Indiana University. This research was supported by the Chemistry Division of the United States Air Force Office of Scientific Research under Project No. 70-1903.

used monochromatic 2139 Å radiation to investigate the steady state photolysis of HN_3 in the presence of CO_2 and various hydrocarbons. They account for their results using the following mechanism:



where the primes denote non-electronic excitation. The purpose of the present research is to test the Darwent mechanism by direct observation of the appearance and disappearance of the observable species which are involved.

The $\text{O}({}^1\text{D}) + \text{O}_3$ reaction has been studied intensively and warrants comparison with $\text{NH}({}^1\Delta) + \text{HN}_3$ as a simpler analog. The reaction proceeds by two alternative modes,



Reaction mode (3a) was first suspected owing to its subsequent contribution to the quantum yield⁸⁻¹⁰ and to the rapid relaxation^{10,11} of vibrationally excited $\text{O}_2\ddagger$, which is characteristic of systems containing $\text{O}({}^3\text{P})$ ¹². Very recently, Giachardi and Wayne¹³ have confirmed that reaction (3a) is significant by direct observation of $\text{O}({}^3\text{P})$ using resonance fluorescence under conditions which identify the $\text{O}({}^3\text{P})$ as the product of reaction (3a). Reaction mode (3b) is well known¹⁴ from direct observation of $\text{O}_2\ddagger$ in levels higher than those permitted by the energy of reaction (3a). This $\text{O}_2\ddagger$ has been tied by kinetic analysis¹⁰ to reaction (3b).

Reaction path (3a) is significant at moderate total pressures but only reaction (3b) is observed when the photolysis is carried out in liquid argon solutions¹⁵.

The emerging concept of this reaction, which has been partly tested¹⁶, is that the *overall rate of the $\text{O}({}^1\text{D}) + \text{O}_3$ reaction is relatively independent of environment, but the distribution of the products is not*. This is as if the reaction proceeds through a *single O_4^* intermediate* which can dissociate in a variety of ways, the relative probability of these modes of dissociation depending on the inert gas environment. In particular, the probability of reaction modes which break two bonds of the intermediate is smaller at higher pressures of inert gas.

The present research is a qualitative preliminary survey to determine the extent to which reactions of $\text{NH}({}^1\Delta)$ might be analogous with those of $\text{O}({}^1\text{D})$.

2. EXPERIMENTAL

The experimental apparatus, a 3 m double beam grating spectrometer with photomultiplier detectors and a 68 cm multiple reflection cell, has been described previously^{17,18}. For the photographic work the photolysis lamp was powered by 30 μF capacitor bank charged to 18,000 V (4860 J); the kinetic measurements were

carried out using a 7 μ F capacitor bank charged to 18,000 V (1130 J) as the photolysis flash power source. The HN₃ was prepared by dropping solid NaN₃ into an 85% H₃PO₄ solution, then drying the gas by passing it through a trap in a dry ice-acetone bath.

Kinetic data for the NH singlet were obtained by observing the Q₃ line of the $c^1\Pi \leftrightarrow a^1\Delta$ transition at 30,728.10 cm⁻¹.¹⁹ Triplet NH was observed by monitoring the band head of the $A^3\Pi \leftrightarrow X^3\Sigma$ system at 29,761 cm⁻¹.²⁰ The N₃ band head² at 36,761 cm⁻¹ was used to monitor N₃ concentrations while NH₂ was observed by following the lines at 16,725.70 cm⁻¹.²¹ Hydrazoic acid was monitored at 46,500 cm⁻¹ using a Garton-Wheaton lamp and at 36,600 cm⁻¹ using the normal broad-flash apparatus.

3. RESULTS

A preliminary photographic survey of the absorption spectrum following flash photolysis of various mixtures of HN₃ with rare gases showed that all of the species predicted by the Darwent mechanism which have observable spectra are, in fact, observed. These include the following:

NH- $A^3\Pi \leftrightarrow X^3\Sigma^-$ system: 0,0; 1,1; 2,2; 3,3; 1,0; 2,1 bands

$c^1\Pi \leftrightarrow a^1\Delta$ system: 0,0; 1,1; (2,1?) bands

NH₂- $A^2A_1 \leftarrow X^2B_1$ system

N₃-2700 Å system: 0,0 band

In the absence of a background continuum source some of the above bands also appear in emission. These bands include the 0,0 band of the $c^1\Pi \rightarrow a^1\Delta$ system of NH and the 0,0 and 1,1 bands of the $A^3\Pi \rightarrow X^3\Sigma^-$ system of NH. The term designations are abbreviated $^1\Pi$, $^1\Delta$, $^3\Pi$, and $^3\Sigma$ in the description which follows.

3.1 Formation and disappearance of NH($^1\Delta$)

Singlet NH appears both in emission and absorption. Furthermore, the initial rise in both emission and absorption precedes the rise in the intensity of the photolysis flash, and coincides instead with the initial current to the flash lamps. The origin of the spectrum was further investigated by wrapping the flash lamps with opaque foil. In this case the duration of the electrical discharge is increased, but characteristics of the reaction, such as emission by NH($^1\Pi$) are qualitatively similar to the normal flash behavior. There is no clear evidence that any of the features which are observed result from photolysis. For the present purpose we have considered it to be sufficient that the process, however complex, be a source of NH($^1\Delta$) which can be characterized empirically.

Measurements of the HN₃ absorbance before and after photolysis show that the overall fraction of HN₃ decomposed is about 0.05. The accuracy with which the fraction of HN₃ decomposed can be determined at various intermediate

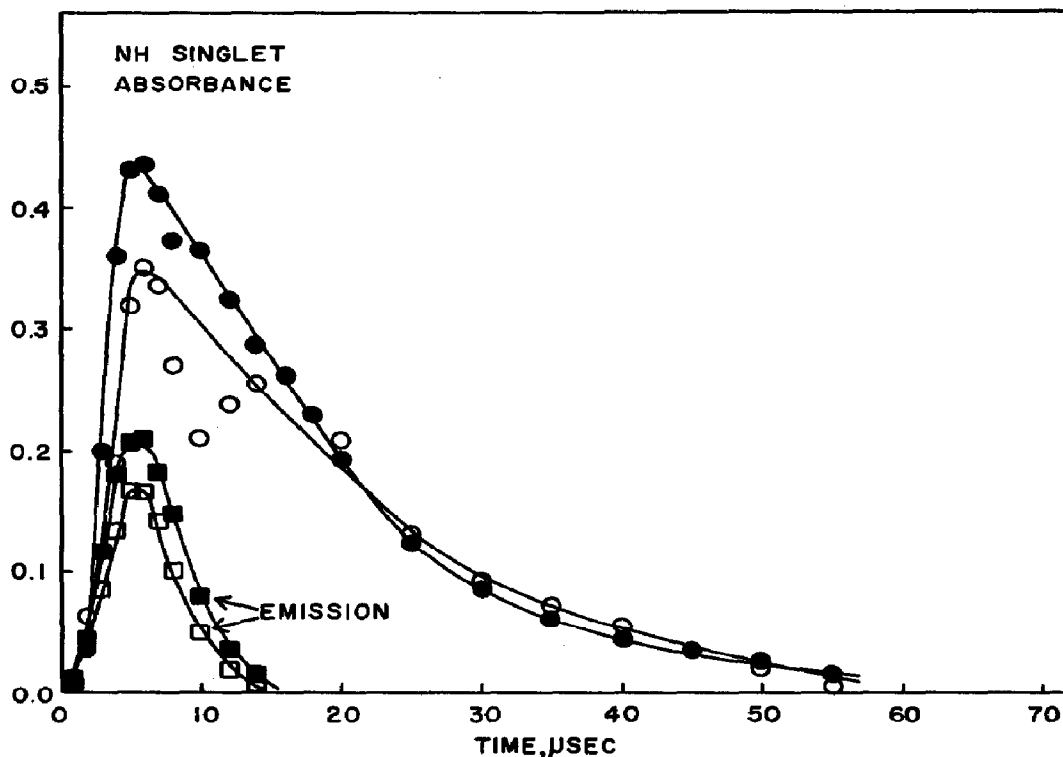


Fig. 1. Absorption by $\text{NH}(^1\Delta)$ following decomposition of HN_3 compared with emission of $\text{NH}(^1\Pi)$. \circ \square , 0.1 Torr HN_3 + 10 Torr Ar; \bullet \blacksquare , 0.1 Torr HN_3 + 100 Torr Ar.

times *during* the reaction is therefore marginal. The qualitative knowledge that the total fraction of HN_3 decomposed is small is nevertheless useful in interpreting the data.

There are minor technical problems involved in correcting the $\text{NH}(^1\Delta)$ absorbance data for emission by $\text{NH}(^1\Pi)$. Although this radiant flux appears significant in comparison with the absorption background source, its absolute intensity indicates that the fraction of HN_3 decomposed to form $\text{NH}(^1\Pi)$ is less than 0.0001 of the HN_3 initially present. It is therefore less than 0.01 of the $\text{NH}(^1\Delta)$ produced. The NH singlet emission and absorption data are given in Figs. 1 and 2 for two different HN_3 concentrations. The apparent oscillation in the $\text{NH}(^1\Delta)$ concentration may be a real consequence of the complex mode of formation but is more likely an artifact of the method used to correct the absorption data for emission. The important points to be noted are these: (i) $\text{NH}(^1\Delta)$ and $\text{NH}(^1\Pi)$ are formed earlier than any other species that was observed; (ii) the rate of disappearance of $\text{NH}(^1\Delta)$ is fast enough for it to be the precursor of $\text{NH}(^3\Sigma)$, NH_2 , and N_3 ; (iii) the rate of disappearance of $\text{NH}(^1\Delta)$ increases with increasing concentration of HN_3 ; (iv) the $\text{NH}(^1\Delta)$ formation and disappearance are not greatly affected by the addition of excess Ar.

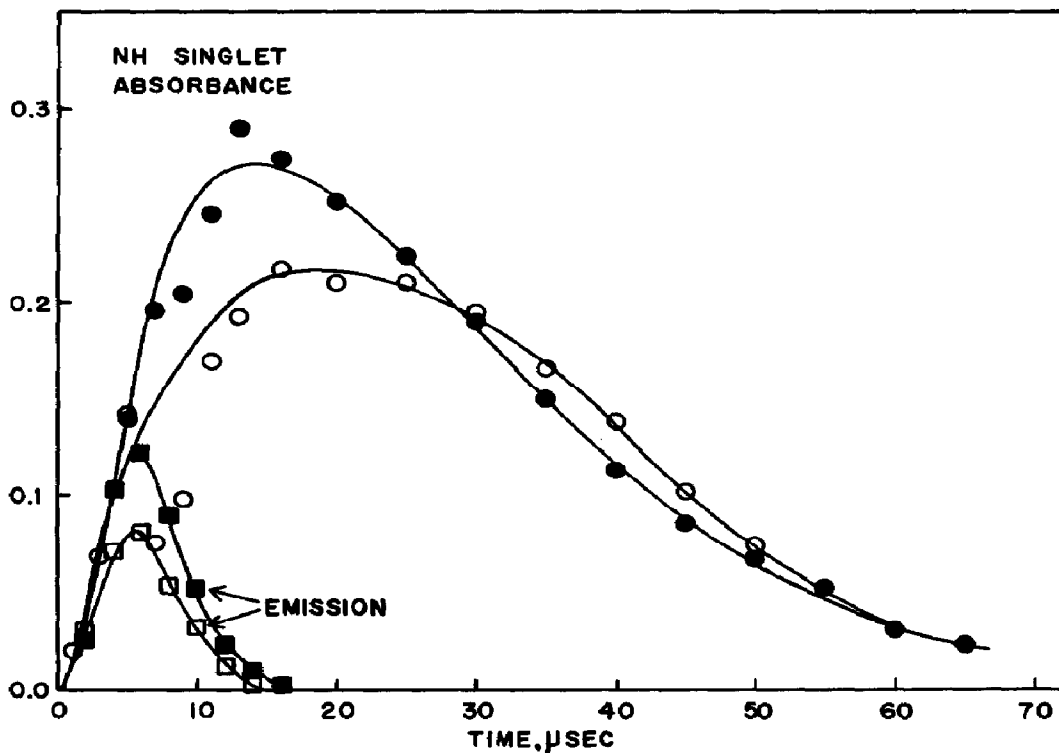


Fig. 2. Absorption by $\text{NH}(a^1\Delta)$ following decomposition of HN_3 compared with emission by $\text{NH}(c^1\Pi)$. \circ \square , 0.02 Torr HN_3 + 2.0 Torr Ar; \bullet \blacksquare , 0.02 Torr HN_3 + 20.0 Torr Ar.

3.2 Absorption and emission by triplet NH

Data for the formation and disappearance of triplet NH are shown in Fig. 3. Both emission by $\text{NH}(^3\Pi)$ and absorption by $\text{NH}(^3\Sigma)$ are observed. The concentrations of both species depend similarly on Ar concentration. However, the timing of their formation and disappearance is not similar. The formation of $\text{NH}(^3\Pi)$ lags behind the formation of $\text{NH}(^1\Pi)$, but precedes the formation of $\text{NH}(^3\Sigma)$. The formation of $\text{NH}(^3\Sigma)$ correlates closely with the disappearance of the $\text{NH}(^1\Delta)$. Its disappearance is slow on the time-scale of these experiments, in no way competitive with $\text{NH}(^1\Delta)$ reactions. Although no attempt was made to determine absolute values, absorption by $\text{NH}(^3\Sigma)$ is weak in comparison with $\text{NH}(^1\Delta)$ as they are ordinarily observed. Under the conditions of Fig. 2, $\text{NH}(^3\Sigma)$ absorption was barely detectable, while the usually weak $\text{NH}(^1\Delta)$ could be seen easily.

3.3 Formation and disappearance of NH_2

The appearance of NH_2 also has a close correlation with the disappearance of $\text{NH}(^1\Delta)$, as shown in Fig. 4. Its rate of disappearance is at least an order of magnitude slower than the rate of disappearance of $\text{NH}(^1\Delta)$ and it disappears

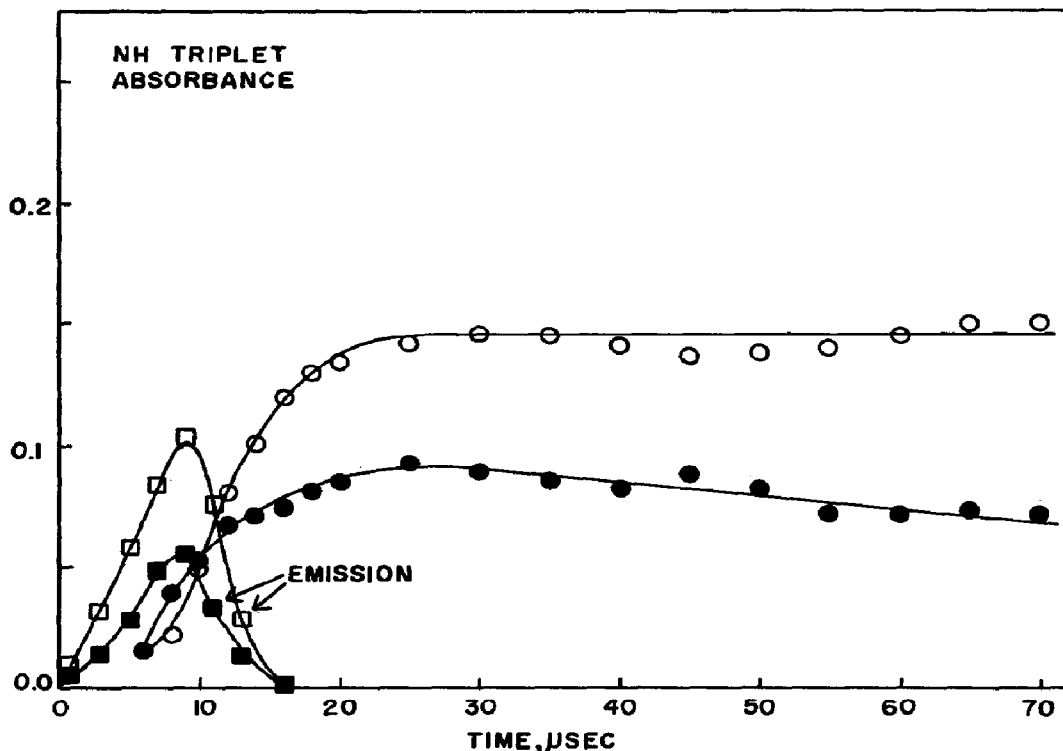


Fig. 3. Absorption by $\text{NH}(X^3\Sigma^-)$ following decomposition of HN_3 compared with emission by $\text{NH}(A^3\Pi)$. $\circ \square$, 0.1 Torr HN_3 + 10 Torr Ar; $\bullet \blacksquare$, 0.1 Torr HN_3 + 100 Torr Ar.

considerably faster at high pressure (500 Torr added argon) than at low pressure (12 Torr added argon). The pressure dependence of the rate of formation of NH_2 is small, if present at all. Using the estimates of the NH_2 absorption coefficient at $16,725.70\text{ cm}^{-1}$ by Hanes and Bair²², the maximum concentration of NH_2 compares favorably with the amount of HN_3 believed to be decomposed by primary decomposition processes. Formation of NH_2 therefore appears to be a major secondary reaction path, possibly more important than $\text{NH}(^3\Sigma)$ formation under the conditions used. The disappearance of NH_2 is slow enough to be attributable to radical-radical reactions and has an inert gas pressure dependence consistent with a combination process near its high pressure limit.

3.4 Formation and disappearance of N_3

The N_3 absorption data are shown in Fig. 5. The formation of N_3 is assumed to be delayed with respect to the formation of $\text{NH}(^1\Delta)$ in much the same way as $\text{NH}(^3\Sigma)$ and NH_2 . Scattered photolysis radiation at the long paths required makes the formation of N_3 difficult to measure. $\text{NH}(^3\Sigma)$, NH_2 , and N_3 all appear to be products of secondary reactions rather than primary decomposition of HN_3 . The possibility that some N_3 is formed by the primary process cannot be ruled out.

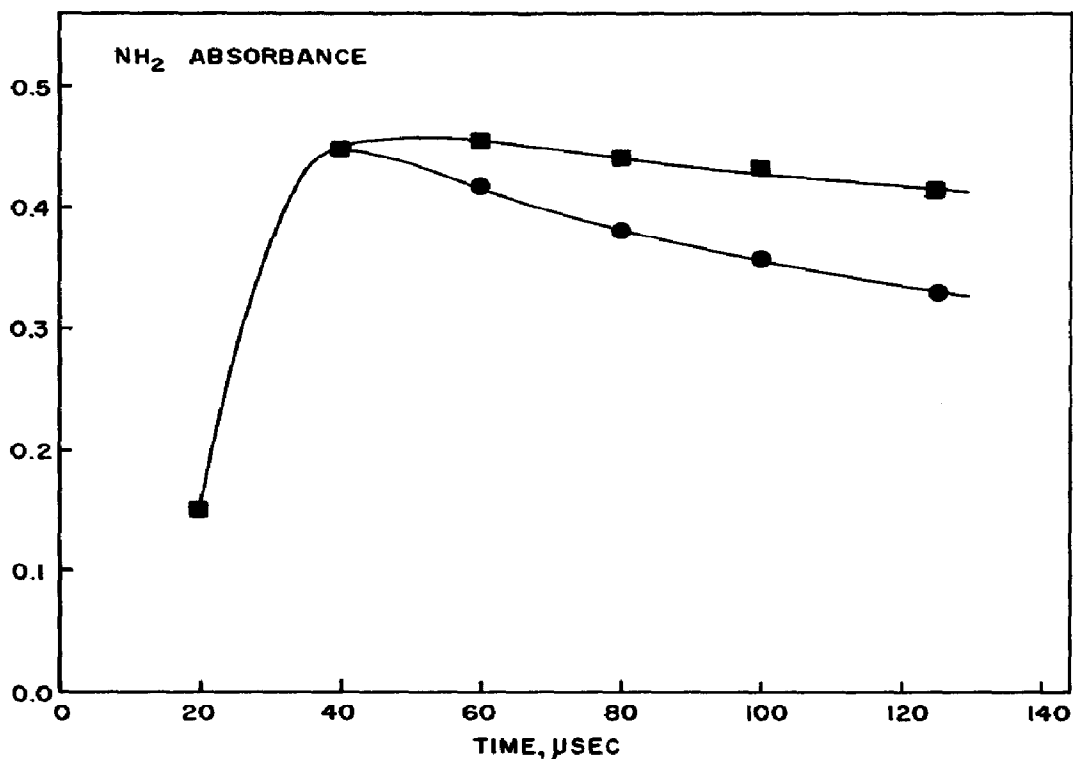


Fig. 4. NH_2 absorbance following decomposition of HN_3 . ■, 0.127 Torr HN_3 + 12.7 Torr Ar; ●, 0.127 Torr HN_3 + 500 Torr Ar.

N_3 disappears with an initial time constant of about 3×10^{-5} sec. Being faster than expected for reaction with other radical intermediates at concentrations present in this system, this rate most likely represents reaction with HN_3 . After about 80–100 μsec the rate of disappearance decreases. If the initial rate of disappearance is correctly interpreted as reaction with HN_3 , the decreased rate of disappearance may indicate that some additional source of N_3 becomes more important in this time range.

Measurements of the pressure dependence of the formation of N_3 were considered beyond the scope of the present preliminary investigation. This is a non-trivial measurement because the extinction coefficient and Beer's law exponent both depend on pressure.

4. DISCUSSION AND CONCLUSIONS

Since the decomposition is obviously complex, this preliminary investigation has been largely a qualitative survey of spectroscopic features which might lend themselves to a more quantitative investigation of the specific questions discussed

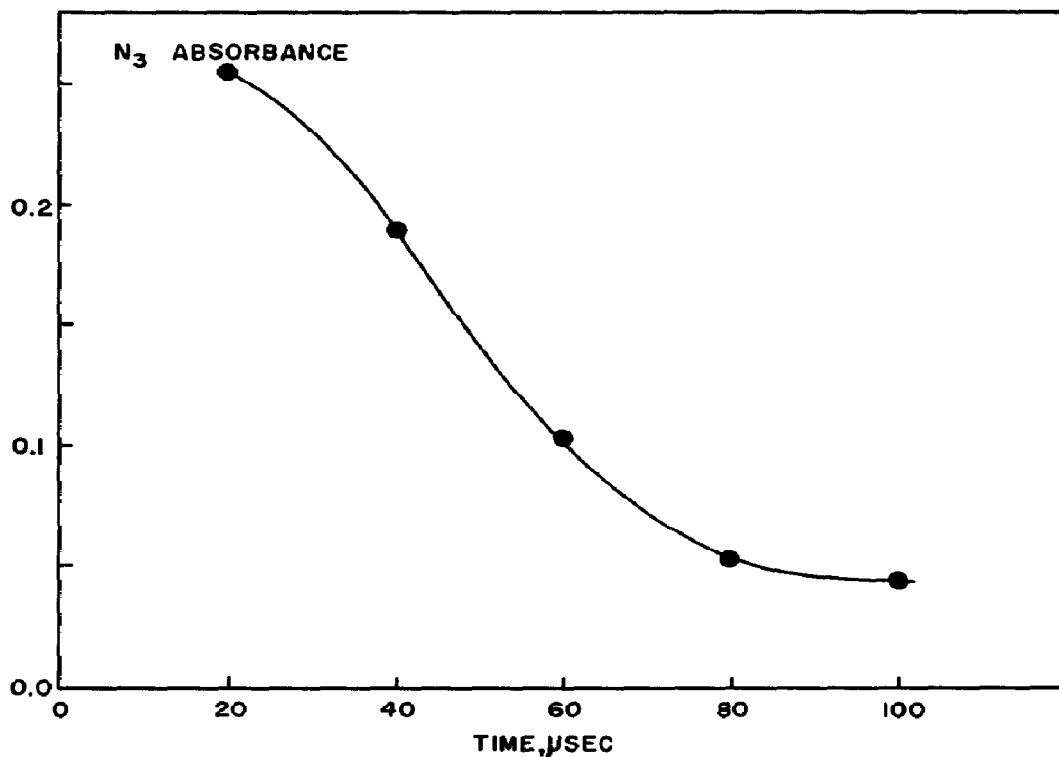


Fig. 5. N₃ absorbance following decomposition of HN₃. ●, 0.283 Torr HN₃ + 28.3 Torr Ar.

in the introduction. The discussion is largely limited to identifying observed spectroscopic features with the phenomenological process causing them.

4.1 Spectroscopic features of the $NH(^1\Delta) + HN_3$ reaction

The primary decomposition, whatever its exact nature might be, has the property, in common with ultra-violet photolysis of ozone or diazomethane, that it provides an observable quantity of singlet biradicals which precedes the formation of other observable intermediates. $NH(^1\Delta)$ is the only reactive intermediate known to precede the formation of $NH(^3\Sigma)$, NH_2 , and N_3 (accepting the estimated emission intensity as an indication that $NH(^1\Pi)$ is unimportant, either as an intermediate in the formation of $NH(^1\Delta)$ or as a reactant in its own right). The effect of the flash is therefore taken to be:



In the absence of reason to believe otherwise, it is convenient to assume that this is the only primary process.

Since the rate of disappearance of $NH(^1\Delta)$ is fast, its numerical value must be determined by a modeling procedure which takes simultaneous account of the rate

of formation and decay. Taking note of the correlation between HN₃ concentration and the rate of NH($^1\Delta$) disappearance, the data give a value for the overall disappearance, $k_2 = 2.5 \pm 1.0 \times 10^{-11}$ cm³/molecule sec, assuming that the reaction is with HN₃. It should be noted that since the extent of decomposition of HN₃ is small, there is no alternative bimolecular process except simple deactivation by Ar which could account for the observed rate of disappearance using rates below the collision limit. The Ar pressure dependence suggests that simple deactivation is relatively unimportant.

The mechanism by which NH($^3\Pi$) is formed is not obvious. Both NH($^1\Pi$) and NH($^3\Pi$) have radiative lifetimes of about 0.5 μ sec²³. Their emission intensity is therefore essentially proportional to and coincident with their rate of formation. Although NH($^1\Pi$) is energetic enough to form NH($^3\Pi$), the timing is wrong. According to Okabe²⁴, photolysis of HN₃ in the vacuum ultra-violet produces some N₂($^3\Pi_g$), which reacts with HN₃ to produce NH($^3\Pi$). Since the lifetime of N₂($^3\Pi_g$) is $\tau \approx 10 \mu$ sec²⁵ this mechanism accounts satisfactorily for the timing of the observed emission. In any case, the total quantity of NH($^3\Pi$) is small and it has no appreciable influence on the other observable components.

The formation of NH($^3\Sigma$) correlates kinetically with the disappearance of NH($^1\Delta$) within the accuracy of the data. On the basis of the substances which are observed its formation is most reasonably attributed to the reaction:



In contrast with its behavior in ammonia photolysis, the disappearance of NH($^3\Sigma$) is slow enough to be the result of radical-radical processes. This supports our previous conclusion²⁶ that NH($^3\Sigma$) reacts rapidly with NH₃. Its reaction with HN₃ is apparently slow.

The formation of NH₂ also has the correct time-dependence to be a result of the NH($^1\Delta$) + HN₃ reaction, in which case N₃ could also be a product. Although the timing of the N₃ formation was not observed in detail, the observed component is consistent with the NH₂ data, so these products are attributed to:

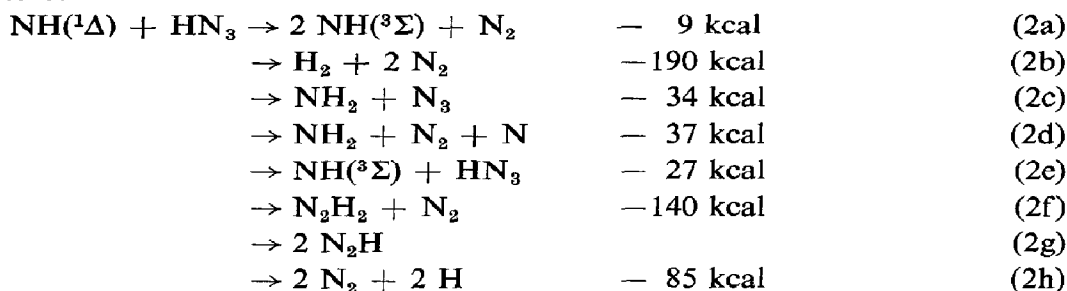


These results are in agreement with the mechanism used to explain the steady state photolysis⁷ and support the O(1D) + O₃ analogy.

4.2 Pressure dependence of the product distribution

The previous section showed that NH($^1\Delta$) disappears primarily by reaction with HN₃ and that deactivation by Ar is relatively unimportant ($k \ll 10^{-14}$ cm³/molecule sec). In fact, Ar concentration has very little effect on either the formation or disappearance of NH($^1\Delta$), although it has a marked effect on the formation of NH($^3\Sigma$). Inert gas appears to alter the distribution of reaction products without affecting the overall rate.

A comprehensive consideration of the reaction would include the following processes:



The experimental results support the view that all processes occur on the same potential energy hyper-surface with independent, or group-wise independent, probability, subject to constant total probability of reaction in the forward direction. The effect of added inert gas can be regarded as removal of energy from the active intermediate. An alternative view¹⁶ is that inert gas inhibits certain modes of dissociation by decreasing the density of energy levels characteristic of those modes. This has the greatest effect on incipient translational modes of separating products, in which added inert gas preferentially inhibits those modes of dissociation in which more than one bond is broken.

The data of these experiments give two relevant experimental facts: (i) the formation of $\text{NH}({}^3\Sigma)$ is inhibited by the addition of Ar; (ii) the formation of NH_2 is essentially independent of Ar concentration.

Since the $\text{NH}({}^3\Sigma)$ is inhibited by Ar without affecting the overall rate of $\text{NH}({}^1\Delta)$ disappearance, some other mode(s) of reaction must be simultaneously enhanced. If the various modes of dissociation are independent, reaction mode (2c) is expected to be one of these enhanced modes. This is not observed, although it is possible that the decrease in reaction mode (2a) corresponds to an undetectable increase in reaction mode (2c).

Alternatively, if the various modes of dissociation are only group-wise independent, reactions (2a), (2b), and (2f) are a group in which N_2H_2 acts as a sub-intermediate. Normal N_2H_2 is stable with respect to forming 2 NH but not with respect to $\text{N}_2 + \text{H}_2$. Since the products of reaction (2b) are observed as products of photolysis⁷, it will be of interest to learn whether they are favored at higher inert gas pressure.

Similarly, reactions (2c) and (2d) might constitute a sub-group in which N_3 is the sub-intermediate. Since NH_2 is a product of both reactions of the group its independence of pressure would be expected. It will be of interest to learn whether N_3 is enhanced by inert gas pressure, as predicted.

Reactions (2g) and (2h) are a sub-group analogous to the reaction $\text{O}({}^1\text{D}) + \text{N}_2\text{O} \rightarrow 2 \text{NO}$ which accounts for about 0.67 of the reaction of $\text{O}({}^1\text{D})$ with N_2O under certain conditions²⁷. There is no evidence that reactions (2g) and (2h) are important in the present experiments.

ACKNOWLEDGEMENT

The authors acknowledge helpful suggestions about the manuscript by Dr. M. Pilling.

REFERENCES

- 1 A. O. Beckman and R. G. Dickenson, *J. Am. Chem. Soc.*, 52 (1930) 124.
- 2 B. A. Thrush, *Proc. R. Soc. (A)*, 235 (1956) 143.
- 3 D. W. Cornell, R. S. Berry and W. Lwowski, *J. Am. Chem. Soc.*, 88 (1966) 544.
- 4 D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 41 (1964) 2838.
- 5 K. H. Welge, *J. Chem. Phys.*, 45 (1966) 4373.
- 6 H. Okabe, *J. Chem. Phys.*, 49 (1968) 2726.
- 7 R. S. Konar, S. Matsumoto and B. De B. Darwent, *Trans. Faraday Soc.*, 67 (1971) 1698.
- 8 H. A. Webster, *Ph. D. Dissertation*, Indiana University, Bloomington, Ind., 1972.
- 9 H. A. Webster III and E. J. Bair, *J. Chem. Phys.*, 53 (1970) 4532.
- 10 V. D. Baiamonte, L. G. Hartshorn and E. J. Bair, *J. Chem. Phys.*, 55 (1971) 3617.
- 11 H. A. Webster III and E. J. Bair, *J. Chem. Phys.*, 56 (1972) 6104.
- 12 J. H. Kiefer and R. W. Lutz, *11th Combustion Symp. Berkeley, Calif.*, 1966, p. 67.
- 13 D. J. Giachardi and R. P. Wayne, *Proc. R. Soc. (A)*, in press.
- 14 W. C. McGrath and R. G. W. Norrish, *Proc. R. Soc.*, A247 (1957) 265; A254 (1960) 317.
- 15 W. B. DeMore and O. F. Raper, *J. Chem. Phys.*, 37 (1962) 2048.
- 16 H. A. Webster III and E. J. Bair, *J. Chem. Phys.*, in press.
- 17 D. R. Snelling, V. D. Baiamonte and E. J. Bair, *J. Chem. Phys.*, 44 (1966) 4137.
- 18 D. R. Snelling and E. J. Bair, *J. Chem. Phys.*, 47 (1967) 228.
- 19 G. H. Dieke and R. W. Blue, *Phys. Rev.*, 45 (1934) 395.
- 20 R. N. Dixon, *Can. J. Phys.*, 37 (1959) 1171.
- 21 K. Dressler and D. A. Ramsay, *Phil. Trans. R. Soc.*, 251 (1959) 553.
- 22 M. H. Hanes and E. J. Bair, *J. Chem. Phys.*, 38 (1963) 672.
- 23 W. H. Smith, *J. Chem. Phys.*, 51 (1969) 520.
- 24 H. Okabe, *J. Chem. Phys.*, 49 (1968) 2726.
- 25 M. Jeunehomme, *J. Chem. Phys.*, 45 (1966) 1805.
- 26 K. A. Mantei and E. J. Bair, *J. Chem. Phys.*, 49 (1968) 3248.
- 27 C. S. Goldman, R. I. Greenberg and J. Heicklen, *Int. J. Chem. Kinet.*, 3 (1971) 501.