

**DETECTION OF NH ($X^3\Sigma^-$) BY RESONANCE FLUORESCENCE
IN THE PULSED VACUUM UV PHOTOLYSIS OF NH₃
AND ITS APPLICATION TO REACTIONS OF NH RADICALS**

I. HANSEN, K. HÖINGHAUS, C. ZETZSCH and F. STUHL
Ruhr-Universität, Physikalische Chemie I, 4630 Bochum, Germany

Received 24 May 1976

Using resonance fluorescence the kinetics of NH ($X^3\Sigma^-$) was studied in the pulsed vacuum UV photolysis of mixtures of NH₃ and NO. The rate constant of the reaction NH + NO was determined to be $(4.7 \pm 1.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

In the course of an investigation of the kinetics of imino radicals we have recently studied the quenching of metastable NH and ND radicals in their ($b^1\Sigma^+$) states [1,2]. In the present paper we would like to describe a method to study the kinetics of ground state NH ($X^3\Sigma^-$) radicals.

Kinetic data on reactions of NH ($X^3\Sigma^-$) radicals is sparse. Only a few estimates on rate constants are reported which are based on experimental work such as those for the reactions with NH₃ [3], NH, O₂, C₃H₆ [4], C₂H₄ [4,5], NO [6], HN₃ [7] and N₂H₄ [8]. None of these rate constants have been obtained from more than one experiment. In the most direct studies, NH ($X^3\Sigma^-$) has been generated either by electron bombardment or flash photolysis of NH₃ or HN₃ and was detected by time resolved absorption spectroscopy. With these techniques concentrations of NH in the approximate range of 3×10^{13} cm⁻³ to 2×10^{15} cm⁻³ were produced and lifetimes $\tau_{1/2} \leq 0.2$ ms were usually observed. In the presence of NH₃ it was concluded that NH is removed efficiently by NH₃ [3,9] and even more efficiently by NH [4].

The apparatus used in the present study consisted of a pulsed light source, a reaction chamber, an NH emission lamp and a resonance fluorescence detection system. A similar photolysis apparatus for the study of the kinetics of OH radicals has been described previously [10]. Vacuum UV light pulses ($\tau_{1/2} = 1.5$ μ s) were generated by discharging a capacitor with a repetition frequency of about 0.2 Hz. NH ($X^3\Sigma^-$)

radicals were produced by photolysing mixtures of NH₃, inert gas and reactive gas through a LiF window ($\lambda > 105$ nm).

The approximate range of the initial concentration of NH was conservatively estimated to be from 2×10^{11} cm⁻³ to 2×10^{12} cm⁻³ for the corresponding storage energies of the capacitor (5 to 60 J). At these low concentrations of NH, the resonance fluorescence intensity can be expected to depend linearly on the concentration, since the electronic transition probability for NH is relatively small.

The NH resonance emission was generated by passing a small flow of a mixture of NH₃ at 0.35 torr and Ar at 1.6 torr through a microwave discharge. The spectrum of the NH ($A^3\Pi \rightarrow X^3\Sigma^-$)-emission is shown in fig. 1. The dominant feature of this spectrum is the Q-branch of the (0;0)-band. Furthermore the R- and P-branches of this band and the Q-branch of the (1;1)-band are clearly observed in this spectrum. Care had to be taken to avoid generation of the N₂ ($C^3\Pi; v' = 0 \rightarrow B^3\Pi; v'' = 0$) emission at 337 nm in the discharge. It should be noted also that under the present conditions the emission intensity from NH ($c^1\Pi \rightarrow a^1\Delta$) at 324 nm is very small.

The resonance fluorescence from NH radicals was monitored at right angles to the incident flash light and to the NH resonance light. It was detected by a photomultiplier through an interference filter, the transmission of which is included in fig. 1 (dashed line). The signal of the photomultiplier was fed to a multi-

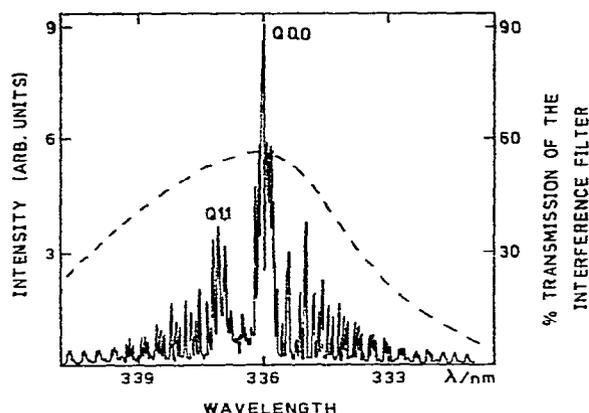


Fig. 1. Emission spectrum of the NH lamp produced by a microwave discharge in a mixture of 0.35 torr NH_3 and 1.6 torr Ar. The transmission of the interference filter used is included (dashed line, right ordinate).

channel scaler where up to 64 single runs were accumulated and averaged.

The gases under study were mixed in the reaction chamber. Different methods were used to add desired amounts of NO to this system such as premixing at pressures 2 to 10 times higher than subsequently used. Pressures in the reaction chamber ranging from 10^{-5} torr to 10^3 torr were measured by capacitance manometers. The minimum purities of the gases used were as follows: NH_3 , 99.999% (Linde); ND_3 , 95% D-atoms; NO, 99.8% (Messer-Griesheim); He, 99.996% (Air Products).

Several experiments were performed to show that the observed fluorescence signal indeed originated from the presence of NH ($X^3\Sigma^-$) radicals. With the discharge lamp off no signal was detected showing that chemiluminescence plays a negligible role in this system. In one experiment the interference filter was tilted resulting in a decrease of the fluorescence intensity. This is in agreement with another experiment in which the wavelength distribution of the resonance fluorescence intensity was investigated using a monochromator (8 nm resolution). The maximum intensity was found to be at 336 nm in agreement with the position of the Q-branch of the NH ($A^3\Pi$; $v' = 0 \rightarrow X^3\Sigma^-; v'' = 0$) emission. Since NH_3 forms NH ($X^3\Sigma^-$) at photolysis wavelengths < 155 nm [11] in one experiment a quartz window was used to cut off the photolysis light below 160 nm. With this window the resonance fluorescence intensity was reduced by more than a factor of 50. In another experiment

ND_3 was photolysed resulting in a decrease of the NH resonance fluorescence signal corresponding to the H-atom content of the ND_3 sample used.

It has been previously observed by absorption spectroscopy that vibrationally excited NH ($v = 1$) radicals are formed in the vacuum UV flash photolysis ($\lambda > 105$ nm) of NH_3 [12]. The absorption spectra showed that the concentration of the excited radicals was about a factor of 10 smaller than that of NH ($v = 0$). Furthermore, NH ($v = 1$) disappeared much faster than NH ($v = 0$) in these flash photolysis experiments [12]. According to the spectral analysis of fig. 1 the present resonance fluorescence method is expected to be able to detect NH ($v = 1$), however, with less sensitivity than NH ($v = 0$). It is therefore likely that resonance fluorescence from NH ($v = 1$) and/or relaxing processes NH ($v = 1 \rightarrow v = 0$) play only a minor role in the present study.

In this system NH radicals can be observed up to more than 1 s after the light pulse. In the presence of NH_3 with and without inert gas added, the removal of NH ($X^3\Sigma^-$) appears to be rather complex. As an example fig. 2, curve A, shows the decay of NH in the

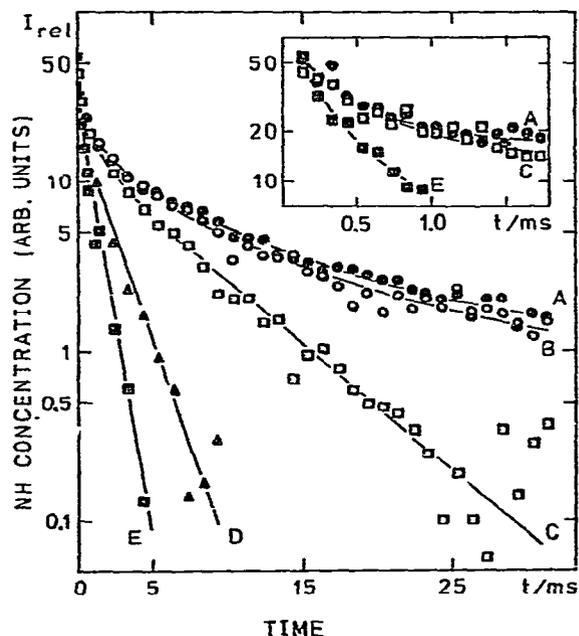


Fig. 2. Semilogarithmic plot of the resonance fluorescence intensity I_{rel} (arbitrary units) versus time. NH was generated by photolysing mixtures of 0.1 torr NH_3 and 30 torr He (discharge energy 25 J). Curve A: no NO added; curves B, C, D and E: 10^{-5} , 10^{-4} , 3.6×10^{-4} and 10^{-3} torr NO added. The insert shows the decay curves at short reaction times.

presence of 0.1 torr NH_3 and 30 torr He in a semi-logarithmic plot. Decays like that shown by curve A can neither be represented by a single first order nor by a single second order reaction. This behavior of NH in the presence of its parent molecule NH_3 will be described elsewhere in detail.

Upon the addition of small amounts of NO to this system the lifetime of NH ($X^3\Sigma^-$) decreased noticeably. Fig. 2 shows for example the decays of NH in the absence of NO (curve A) and in the presence of 10^{-5} , 10^{-4} , 3.6×10^{-4} and 10^{-3} torr NO (curves B, C, D and E, respectively). It should be noted in this figure that exponential decays are approached for increasing pressures of NO. Furthermore, at small amounts of NO added, the removal of NH was found to correspond to first order decays after several ms, hence defining a lifetime τ . In the reaction



this lifetime, τ , of NH can thus be approximated by

$$\tau^{-1} = (\tau_0)^{-1} + k_1 [\text{NO}], \quad (2)$$

where τ_0 is the (approximate) lifetime of NH at long reaction times in the absence of NO and k_1 is the rate constant for reaction (1). To minimize uncertainties τ was kept small compared to τ_0 . Thus the slope of a linear plot of τ^{-1} versus $[\text{NO}]$ determines the value for k_1 . Fig. 3 shows such a linear plot yielding a value of $k_1 = (4.7 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The given uncertainty represents three times the standard deviation of the slope.

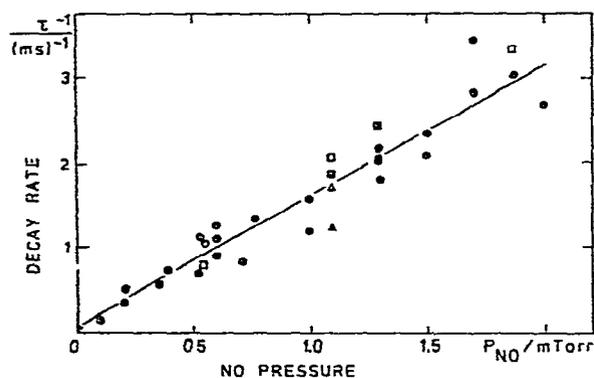


Fig. 3. Decay rates of the NH resonance fluorescence intensity, τ^{-1} , as a function of NO pressure. The pressure of NH_3 was constant at 0.1 torr. \bullet 30 torr He, discharge energy 25 J; \blacktriangle 30 torr He, 60 J; \blacksquare 30 torr He, 12 J; \triangle 700 torr He, 25 J; \square 100 torr He, 25 J.

According to eq. (2), the decay rate, τ^{-1} , does not depend on the total pressure or on the concentration of the NH radicals. As fig. 3 shows this was verified for He pressures ranging from 30 to 700 torr and for various initial concentrations of NH produced by different discharge energies. A presumption for the validity of eq. (2) is the presence of NO in large excess over the concentration of NH. This presumption is certainly fulfilled for NO pressures greater than 5×10^{-4} torr. At smaller pressures of NO, NH first reacts with constituents of the NH_3 -photolysis system (including radicals). After the concentration of NH has decreased by about a factor of 10, NO appears to be the dominant reactive species for NH. Regarding all the approximations discussed we estimate the overall uncertainties of k_1 to be $\pm 25\%$.

Previously, Gordon et al. [6] have determined a value of $k_1 = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by irradiating NH_3 with pulses of 2-MeV electrons. The rate of disappearance of NH radicals was followed by measuring the decrease in absorption at 336 nm. No detailed experimental data regarding reaction (1) is given in their paper. The reported value for k_1 is in good agreement with that determined in the present study.

References

- [1] C. Zetzsch and F. Stuhl, Chem. Phys. Letters 33 (1975) 375.
- [2] C. Zetzsch and F. Stuhl, Ber. Bunsenges. Physik. Chem. 79 (1975) 1156.
- [3] K.A. Mantei and E.J. Bair, J. Chem. Phys. 49 (1968) 3248.
- [4] G.M. Meaburn and S. Gordon, J. Phys. Chem. 72 (1968) 1592.
- [5] D.W. Cornell, R.S. Berry and W. Lwowski, J. Am. Chem. Soc. 88 (1966) 544.
- [6] S. Gordon, W. Mulac and P. Nangia, J. Phys. Chem. 75 (1971) 2087.
- [7] H. Okabe, J. Chem. Phys. 49 (1968) 2726.
- [8] I.J. Eberstein and I. Glassman, Tenth Symposium on Combustion, 1964 (The Combustion Institute, Pittsburgh, 1965) p. 365.
- [9] R.J. Paur and E.J. Bair, J. Photochem. 1 (1972/73) 255.
- [10] F. Stuhl and J. Niki, J. Chem. Phys. 57 (1972) 3671.
- [11] J.G. Calvert and J.N. Pitts, Photochemistry (Wiley, New York, 1966) p. 203, and references therein.
- [12] F. Stuhl, Ph.D. Thesis, Rhein. Friedr. Wilh. University, Bonn, Germany, Sept. 1966.