An HTP kinetics study of the reaction between ground-state H atoms and NH₃ from 500 to 1140 K

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The H + NH₃ reaction has been investigated using the high-temperature photochemistry (HTP) technique. H(1²S) atoms were generated by flash photolysis of NH₃ and monitored by time-resolved atomic resonance fluorescence with pulse counting. The rate coefficient for 660 ≤ T ≤ 1140 K is given by $k(T) = (5.7 \pm 2.8) \times 10^{-10} \exp[(-8650 \pm 410)K/T]$ cm³ molecule⁻¹ s⁻¹, where the uncertainties represent one standard deviation based on a propagation of error treatment including systematic errors. The Arrhenius plot reveals curvature between 500 and 660 K which follows the results of quantum mechanical tunneling calculations based on transition state theory and an Eckart potential.

INTRODUCTION

The reaction of ground-state hydrogen atoms with ammonia

has recently been investigated by Michael *et al.* using the flash-photolysis/shock tube (FP-ST) method.^{1,2} The results obtained with this isolated elementary reaction technique over the range 900 to 1800 K differ considerably from earlier determinations.^{3,4} Reaction (1) is known to be important in the thermal decomposition of NH₃.^{5,6} and one aim of the present work is to employ a second technique which isolates this reaction. Combining their data with a determination of k at 750 K from a flash-photolysis/resonance fluorescence (FP-RF) apparatus Michael *et al.*² noted slight curvature in the Arrhenius plot; another goal of the present work is to investigate this non-Arrhenius behavior using a single technique. Because NH₃ is thermodynamically unstable with respect to decomposition it is easily lost by heterogeneous pyrolysis, which prevents extension of conventional FP-RF measurements above 750 K.² Accordingly we employ a wider temperature range modification of the FP-RF technique, the HTP method. This method allows injection of NH₃ through a cooled inlet into an effectively wall-less reactor whose temperature can be varied from 300 to 1800 K.⁷ The technique has already been applied to the study of, for example, O + CH₄,⁷ O + C₂H₄,⁸ and OH + CH₄.⁹

TECHNIQUE

Experimental

The general principles and an early version of the HTP reactor have been described previously.⁷ A brief outline is given here, together with some modifications to the earlier design. Figure 1 illustrates the present apparatus. A slow flow of argon bath gas passes along the heated alumina reaction tube while thermally unstable reactants, NH₃ in this case, are injected from the air-cooled inlet. This inlet can be maintained below 500 K when the reactor is above 1700 K. The reaction tube has four 2 cm diameter holes facing the side-arms of the vacuum housing. An essentially wall-less reaction zone is defined by the intersection of the cones of

light from the flash lamp and the cw resonance lamp, and is observed by the photomultiplier tube (PMT). Heterogeneous decomposition of reactants is avoided by cooling the inlet and using a wide reaction tube (internal diameter 5 cm) so that diffusion times to the walls are relatively long. Reactants are heated by mixing with much larger quantities of bath gas and homogeneous pyrolysis is minimized by reducing the residence time before reaching the reaction zone. Transient species, H in this case, are generated photolytically and react on a time scale short compared to flow past the PMT, i.e., the HTP reactor is kinetically equivalent to a static system. Detection of the transient species is by resonance fluorescence with pulse counting. An advantage of this type of apparatus is that reactant concentrations, total pressure, and temperature are independently variable.

One major construction difference from the earlier design⁷ is that spiral silicon carbide heating elements replace the previously used platinum/rhodium resistance wire. Gas flows are measured using Teledyne-Hastings electronic flow gauges and gas pressures with a Fluid Precision capacitance manometer. For temperature measurements a Pt/Rh thermocouple is lowered into the reaction zone before and after kinetic runs. The thermocouple is doubly shielded to reduce radiation errors.¹⁰

The gases used in the reactor are Linde 99.998% Ar and 99.99% NH₃ and Matheson 99.998% NH₃, all from the liquid. No difference in results from the two grades of NH₃ is observed. A small part (about 10%) of the Ar flow into the reactor is injected via the observation ports, to minimize heating of the lenses and windows. H atoms are generated by the pulsed photolysis of a small fraction of the NH₃ using a conventional nitrogen-filled flash lamp (pressure about 200 Torr) at energies from 12 to 50 J per pulse. An EG&G TM-11A trigger module fires the lamp at around 0.8 Hz. A lens or flat window, plus a concave mirror behind the flash electrodes,¹¹ provides the optical coupling between the flash lamp and the reactor. Photolysis conditions are varied by changing the power input to the flash lamp and by employing either Suprasil quartz or magnesium fluoride as the window material. Suprasil photolysis of NH₃ at $\lambda > 165$ nm yields mainly NH₂ + H, whereas MgF₂ photolysis with $\lambda > 110$ nm also generates a significant fraction of NH.¹²

FIG. 1. Schematic of the HTP reactor.

Furthermore, because the absorption coefficient¹² of NH₃ increases strongly below $\lambda = 165$ nm, photolysis at a given power through MgF₂ delivers actinic intensity equivalent to a higher flash power through quartz. A microwave discharge flow lamp containing a 1% mixture of H₂ in He at 1.5 Torr is the source of resonance radiation at $\lambda = 121.6$ nm [$H(2^2P) \rightarrow H(1^2S)$], which is focused with an MgF₂ lens. Fluorescence is detected at right angles to the flow lamp by a solar-blind EMR 541 G-0917 PMT, operated at 2.9 kV with a gain of about 10^7 . Careful collimation of the optics reduces scattered light from both lamps, permitting the use of an ungated PMT. The H-atom fluorescence signals are spectrally isolated by means of a gas filter comprising 2.5 cm of dry air at atmospheric pressure.¹³ Output signals from the PMT pass via an EG&G model 1121A amplifier/discriminator to a Nicolet LAS 12/70 multichannel scaler (256 channels used). Data collection is initiated by a trigger photodiode close to the flash lamp. Depending on the pulse counting rate, signals from 50 to 1000 flashes are accumulated to yield initial total counts of typically 250 per channel. A range of time bases of approximately 2.5×10^{-3} to 2.5×10^{-1} s are employed, corresponding to times of 10^{-5} to 10^{-3} s per channel. After capture the data are transferred to an IBM PC microcomputer for storage and analysis.

A difficulty, peculiar to reaction (1), which did not occur during earlier HTP investigations, arises because the reactant-in-excess and the photolyte are identical. When k is large, decays of [H] are fast and thus fluorescence signals (counts per channel) are weak. Previously the concentration of photolyte could be increased to compensate,⁷ but in the present case this also speeds up removal of H and further weakens the signal. The lack of independent control over reactant and photolyte concentrations here limits suitable k values to those below 1140 K, which is nevertheless a consid-

erably higher temperature limit than for conventional FP-RF work.²

Data handling

Following their generation H atoms are lost from the reaction zone primarily by reaction with NH₃ and diffusion. For suitable boundary conditions the latter process is first-order with respect to [H],¹⁴ thus

$$-\frac{d[H]}{dt} = k[NH_3][H] + k_D[H] = k_{ps1}[H], \quad (2)$$

where k_D represents essentially diffusional loss. k_{ps1} is the pseudo-first-order decay coefficient describing the overall reduction of [H] as a function of time. Note that loss of H by flow out of the observation zone has not been included explicitly in k_{ps1} since this loss is not a first-order process. Experimentation showed that when loss by flow is significant compared to k_{ps1} , i.e., when pseudostatic conditions are not closely approximated, erroneous k_{ps1} values result.

Since the resonance fluorescence intensity is proportional to [H] the observed signal at time t , I_t in arbitrary units, is given by

$$I_t = I_0 \exp(-k_{ps1}t) + B, \quad (3)$$

where I_0 represents $I(t=0)$ and B a steady background from scattered light from the microwave lamp. I_t data are analyzed using a curve-fitting routine developed for the present work. For any one decay B is estimated by averaging I_t values at long times, then I_0 and k_{ps1} are fitted iteratively to minimize

$$\chi^2 = \sum \{I_t - I_0 \exp(-k_{ps1}t) - B\}^2 w_t, \quad (4)$$

w_t is a statistical weighting factor,¹⁵ equal to $1/\sigma_t^2$, where the variance σ_t^2 of the count for each channel I_t is estimated assuming the counts follow a Poisson distribution.¹⁵ The ad-

vantage of this curve-fitting method over the frequently used simple plots of $\ln(I_t - B)$ vs t is that I_t data may be analyzed at longer times (typically $4/k_{\text{ps1}}$), when random fluctuations cause some individual I_t values to lie below B . Calculation of the reduced χ^2 value permits a statistical check that Eq. (3) is indeed a suitable fit to the signal. Typical uncertainties of the fit are $\sigma_{k_{\text{ps1}}}/k_{\text{ps1}} \lesssim 5\%$.

Figure 2 shows that plots of k_{ps1} against $[\text{NH}_3]$ are linear with slope $k(T)$, cf. Eq. (2). The algorithm of Irvin and Quickenden,¹⁶ which takes account of uncertainties in both $[\text{NH}_3]$ and k_{ps1} , is employed to derive k together with its standard deviation σ_k from such plots. This procedure averages out uncertainties in $[\text{NH}_3]$ which are of the order of 1%–10% for an individual decay. Small systematic errors in k are also included in σ_k . Radiation errors in thermocouple temperature measurements have been discussed previously: the use of the doubly shielded thermocouple leads to a maximum error due to radiation of 2.5%.¹⁰ Assigning the standard deviation as half the limit of error we estimate a contribution to σ_T/T of 1.25%. Combining this vectorially with estimates of possible temperature gradients across the reaction zone and a calibration uncertainty yields $\sigma_T/T \approx 2\%$. There is additionally a much smaller contribution to σ_T from any drift in T during a run, assessed from the scatter in T measurements taken between each decay. The uncertainty in T slightly affects the values of σ_k derived, since a 2% error in T propagates as a 2% error in $[\text{NH}_3]$ and thus k . This effect is small compared to the scatter observed in k_{ps1} vs $[\text{NH}_3]$ plots (normally of the order of 10%–

20%), but has been included in final estimates of σ_k . All quoted uncertainties and error limits given here represent one standard deviation.

RESULTS AND DISCUSSION

Interpretation of data

Table I summarizes the rate coefficients obtained as a function of temperature, together with the experimental conditions. $[M]$ represents the total concentration. $\bar{v}$ is the average linear gas velocity calculated for the purpose of allowing estimates of the flow time of NH₃ from the cooled inlet which is at a distance l from the reaction zone. F is the energy dissipated in the flash lamp.

It may be seen that, within the experimental scatter of k , there is no consistent variation of k with $[M]$ which changes by a factor of 15, indicating that k is independent of pressure. There is also no dependence of k on the implicit parameters $\bar{v}$, l , and effective F , which vary by factors of 35, 4.5, and more than 4, respectively. This confirms that gas flows are well mixed, that thermal equilibration is achieved, and that no significant fraction of NH₃ has decomposed thermally.

Thirty-six measurements of k were made from 500 to 1140 K, spanning a range of rate coefficients of approximately 2×10^{-16} to 3×10^{-13} cm³ molecule⁻¹ s⁻¹. These k values are plotted in Arrhenius form in Fig. 3. The data for $T \geq 660$ K may be fitted to a simple Arrhenius expression, $k(T) = (5.7 \pm 2.8) \times 10^{-10} \exp[(-8650 \pm 410) \text{ K}/T]$ cm³ molecule⁻¹ s⁻¹, where the error limits represent $\pm 1\sigma$.

Figure 3 shows clear curvature for $T \leq 660$ K and to explain this result we use transition state theory (TST) calculations based on an *ab initio* calculation by Melius.¹⁷ Employing the same parameters as Michael *et al.*, and similarly assuming that electronic degeneracies cancel and that no hindered rotors are involved,² TST gives curve (a) in Fig. 4. Applying Wigner's expression for the correction factor Γ^* arising from quantum mechanical tunneling¹⁸ yields curve (b), cf. Michael *et al.*² Figure 4 indicates that k deviates from curve (b) at low temperatures. Such deviations could result if k were overestimated at $T \leq 660$ K because of reaction of H with secondary species. However the invariance of k with $[M]$ rules out recombination processes with photolysis products of NH₃. Similar independence of k from the flash energy, and thus the initial $[\text{NH}_2]$, demonstrates the absence of any significant bimolecular reactions other than (1).

An alternative approach to calculating tunneling is to fit an Eckart potential along the reaction coordinate.¹⁸ Combining the parameters² for NH₃ and NH₂⁺ with the enthalpies of formation of NH₂ and H gives¹⁹ the energies of the transition state above reactants and products. Including zero-point energies^{2,20} these barrier heights are both approximately 67 kJ mol⁻¹. Combined with the "vibrational" frequency along the reaction coordinate² $\omega^* = 2476$ cm⁻¹ the Eckart parameters are calculated to be $\alpha = 14$ and $u^* = 3565$ K/ T . Johnston has presented numerical solutions for Γ^* as a function of these parameters,¹⁸ which show that the factor to account for tunneling rises from approximately 1.5 at 1200 K to approximately 26 at 450 K. These

FIG. 2. Plots of the pseudo-first-order decay coefficient for loss of H atoms against $[\text{NH}_3]$, yielding k at 860 and 975 K.

TABLE I. Summary of rate coefficient measurements on H + NH₃.

$T \pm \sigma_T$ (K)	P (Torr) ^a	[M] (10 ¹⁸ cm ⁻³)	[NH ₃] (10 ¹⁶ cm ⁻³)	$\bar{v}$ (cm s ⁻¹)	l (cm)	F (J)	$k \pm \sigma_k$ (cm ³ molecule ⁻¹ s ⁻¹)
1136 ± 23	85	0.72	0.05 to 0.35	43	8	Q40 W ^b	2.6 ± 0.6 (−13) ^c
1061 ± 21	100	0.93	0.07 to 0.41	34	8	Q40	1.4 ± 0.2 (−13)
1044 ± 21	38	0.35	0.01 to 0.30	32	16	M40 W	2.1 ± 0.2 (−13)
1032 ± 21	460	4.3	0.04 to 0.86	7.2	16	M40 W	1.2 ± 0.1 (−13)
997 ± 20	41	0.40	0.09 to 1.01	77	3.5	M40 W	1.2 ± 0.1 (−13)
975 ± 20	250	2.5	0.15 to 2.33	34	8	Q40	7.8 ± 0.2 (−14)
962 ± 20	130	1.3	0.17 to 1.87	25	12	Q50	1.6 ± 0.2 (−13) ^d
952 ± 19	210	2.1	0.21 to 0.89	15	8	Q40 W	8.0 ± 0.8 (−14)
952 ± 19	210	2.1	0.03 to 1.51	6.1	3.5	M40 W	4.1 ± 0.4 (−14)
949 ± 19	540	5.5	0.07 to 2.36	4.0	3.5	M40 W	3.3 ± 0.4 (−14)
914 ± 18	250	2.6	0.17 to 2.39	33	8	Q40	3.7 ± 0.1 (−14)
899 ± 18	93	1.0	0.08 to 0.68	4.1	8	Q40	3.1 ± 0.3 (−14)
860 ± 17	240	2.7	0.17 to 2.52	31	8	Q40	1.77 ± 0.05 (−14)
854 ± 17	110	1.2	0.13 to 2.98	22	11	M40 W	3.6 ± 0.4 (−14)
845 ± 17	81	0.93	0.25 to 2.41	33	8	Q40 W	3.3 ± 0.1 (−14)
812 ± 16	82	0.98	0.61 to 2.45	32	8	Q40	1.44 ± 0.04 (−14)
781 ± 16	110	1.4	0.10 to 0.98	6.0	15	Q18	8.1 ± 1.8 (−15)
779 ± 16	130	1.6	0.07 to 1.76	8.3	8	Q40	9.7 ± 0.4 (−15)
757 ± 15	220	2.8	0.24 to 2.80	2.7	8	Q40	4.4 ± 0.1 (−15)
740 ± 15	200	2.6	0.11 to 1.28	12	12	Q50	7.2 ± 0.3 (−15) ^d
728 ± 15	75	1.0	0.11 to 1.52	4.0	8	Q40	3.0 ± 0.3 (−15)
723 ± 14	210	2.8	0.28 to 2.82	10	8	Q40	3.2 ± 0.2 (−15)
705 ± 14	66	0.90	0.06 to 1.43	2.9	8	Q40	1.6 ± 0.4 (−15)
688 ± 14	200	2.8	0.22 to 3.30	2.7	8	Q40	1.9 ± 0.1 (−15)
688 ± 14	110	1.6	0.10 to 2.57	5.3	15	Q40	3.0 ± 0.1 (−15)
660 ± 14	51	0.74	0.08 to 1.82	40	8	Q40	1.2 ± 0.2 (−15)
628 ± 13	160	2.5	0.11 to 3.29	4.3	8	Q40	7.9 ± 0.6 (−16)
591 ± 12	110	1.8	0.12 to 3.18	4.5	15	Q18	7.8 ± 1.3 (−16)
591 ± 12	120	2.0	0.17 to 3.26	4.5	4.5	Q40	8.1 ± 1.4 (−16)
574 ± 12	120	2.0	0.16 to 4.80	9.3	11.5	Q50	5.3 ± 0.9 (−16)
558 ± 12	230	3.9	0.30 to 4.78	3.1	4.5	Q40	3.2 ± 0.2 (−16)
540 ± 11	250	4.5	0.18 to 3.16	4.4	12	Q50	3.4 ± 0.7 (−16) ^d
531 ± 11	300	5.5	0.16 to 6.56	2.2	7.5	Q40	4.1 ± 0.7 (−16)
519 ± 11	240	4.5	0.59 to 6.51	4.3	8	Q12	2.3 ± 0.7 (−16)
502 ± 10	380	7.3	0.22 to 3.61	4.0	12	Q50	1.9 ± 0.2 (−16) ^d
502 ± 10	180	3.4	0.44 to 6.78	5.4	11.5	Q40	1.8 ± 0.2 (−16)

^a 1 Torr = 133.3 Pa.^b The prefix "Q" or "M" indicates that photolysis is through suprasil quartz or magnesium fluoride, respectively. The suffix "W" indicates that a flat window is employed. In the other experiments an $f/1.5$ or $f/2.0$ lens is used.^c Should be read as $(2.6 \pm 0.6) \times 10^{-13}$.^d Obtained using Matheson 99.998% NH₃. Linde 99.99% NH₃ is used for the other experiments.

corrections have been incorporated in curve (c), Fig. 4, which fits the low-temperature data best. Considering that no adjustable parameters are involved in this theoretical analysis and given the considerable uncertainties when attempting to quantify tunneling¹⁸ the agreement with experiment is good. A conventional fit to $k(T)$ of the form $A T^B \exp(-C/T)$ is unsuitable for this reaction: at low temperatures the effect of tunneling increases sharply, distorting the fit that would be expected to a purely TST expression.

Comparison with earlier results

The simple Arrhenius expression for $T \geq 660$ K can be compared to the flash-photolysis/shock tube results of Michael *et al.*,²

$$k(T) = (3.02 \pm 0.30) \times 10^{-10} \exp[(- 8067 \pm 117) \text{K}/T] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

which are shown in Fig. 5. In the region of overlapping temperatures the results from the two different techniques agree,

although slightly different temperature trends are suggested. The present results are somewhat lower than the single flash-photolysis/resonance fluorescence point² of Michael *et al.* The FP-ST and HTP methods may be considered complementary techniques as the former is useful for temperatures around 800–2500 K,²¹ whereas the latter is in general suitable for 300–1800 K.⁷ The present technique permits independent variation of pressure, over a wider range than can be achieved with the FP-ST method, and temperature; both P and T in the reaction zone are measured directly rather than inferred. On the other hand the FP-ST technique is totally wall-less and avoids preheating of the reactants.¹ Another difference is that the FP-ST technique employs resonance absorption, while resonance fluorescence is used for HTP experiments.

While our results thus do not differ sharply from those of Michael *et al.*,^{1,2} we confirm their disagreement with data from earlier experiments, all of which implied smaller values of k . Some of these earlier results are plotted in Fig. 5. For

FIG. 3. Summary of the rate coefficients obtained for the reaction $\text{H} + \text{NH}_3$, showing the fit for $T \geq 660$ K. Error bars represent one standard deviation for T and k .

example, the shock tube measurements of Dove and Nip⁵ gave $k(T) = (4.6 \pm 1.7) \times 10^{-11} \exp[(8760 \pm 650)\text{K}/T]$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and those of Yamura and Asaba²² yielded $k(T) = 2 \times 10^{-10} \exp(-10\,800 \text{ K}/T)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with wide error limits (an order of magnitude in the pre-exponential factor and 50% in the activation energy). From discharge flow experiments Kurylo *et al.*²³ found $k < 2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 750 K and Albers *et*

*al.*²⁴ gave upper limits of 2×10^{-17} and $2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 500 and 800 K, respectively. It is not clear why the limit determinations from these discharge flow systems^{23,24} are lower than the HTP and FP-ST measurements, but often observations on multireaction media such as in shock tubes yield results that are not confirmed by isolated reaction determinations.

As a test of these data we compare the Arrhenius param-

FIG. 4. Comparison of transition state theory calculations with experimental data for $\text{H} + \text{NH}_3$. Error bars represent $\pm \sigma_T$ and $\pm \sigma_k$. Curve (a): no tunneling included. Curve (b): Wigner tunneling correction included. Curve (c): tunneling calculated for Eckart potential.

FIG. 5. Comparison of various experimental determinations of $k(T)$ for the reaction $\text{H} + \text{NH}_3$. (—) present work, HTP. (---) Michael *et al.* (Ref. 2), FP-ST. (— · —) Dove and Nip, (Ref. 5) shock tube. (---) Yamura and Asaba, (Ref. 22) shock tube. (●) single FP-RF point by Michael *et al.* (Ref. 2). (□) upper limit by Kurylo *et al.* (Ref. 23), discharge flow reactor. (○) upper limits by Albers *et al.* (Ref. 24), discharge flow reactor.

eters for reaction (1) with those for the analogous H-atom reactions with CH₄ and H₂O, which are molecules isoelectronic with NH₃. We estimate the parameters for CH₄ and H₂O by fitting a straight line to the slightly curved Arrhenius plots over the same temperature range as for NH₃, namely 660 to 1140 K, using the expressions recommended by Warnatz.²⁵ The results are shown in Table II. The activation energy for reaction (1) is seen to form part of a consistent trend, while the A factors are similar and of the order expected for simple atom-molecule reactions. This should be contrasted to some of the earlier determinations of k which as seen above suggest either smaller A factors or larger activation energies than fit this sequence.

CONCLUSION

Considering data from HTP and FP-ST systems reaction (1) has now been studied directly from 500 to almost 1800 K, revealing that $k(T)$ is greater than previously thought. Indeed, some experiments where this reaction has been assumed to be slow or negligible will have to be reevaluated. An example is a recent study of the removal of NH₃ by OH in flames,²⁶ where the rate coefficients for the reaction

OH + NH₃ may have been overestimated because NH₃ is also lost through reaction (1).

Note added in proof: Hack *et al.*²⁷ have just measured R from 673 to 1003 K in a discharge flow reactor. Their expression for $k(T)$ agrees with ours within the quoted uncertainty limits.

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TABLE II. Comparison of Arrhenius parameters for the temperature range 660–1140 K.

Reaction	A ($10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	E_a/R (K)	Reference
$\text{H} + \text{CH}_4$	5	7 000	25
$\text{H} + \text{NH}_3$	6 ± 3	$8\,650 \pm 410$	This work
$\text{H} + \text{H}_2\text{O}$	2	10 700	25

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