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The Reaction $NH_2 + PH_3 \rightarrow NH_3 + PH_2$: Absolute Rate Constant Measurement and Implication for NH_3 and PH_3 Photochemistry in the Atmosphere of Jupiter

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(NASA-TM-85063) THE REACTION NH2 + PH3 YIELDS NH3 + PH2: ABSOLUTE RATE CONSTANT MEASUREMENT AND IMPLICATION FOR NH3 AND PH3 PHOTOCHEMISTRY IN THE ATMOSPHERE OF JUPITER (NASA) 28 p HC A03/MF A01 CSCL 03B G3/91 N84-23430 Unclas 13113

THE REACTION $NH_2 + PH_3 \rightarrow NH_3 + PH_2$: ABSOLUTE RATE CONSTANT MEASUREMENT AND IMPLICATION FOR NH_3 AND PH_3 PHOTOCHEMISTRY IN THE ATMOSPHERE OF JUPITER

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Introduction

The abundance of ammonia (NH_3) in the atmosphere of Jupiter [Wildt, 1937] stands in marked contrast to the ready photolysis: $NH_3 + h\nu \rightarrow NH_2 + H$ by solar radiation in the 160 to 230 nm region [Calvert and Pitts, 1966]. In the absence of recycling mechanisms, all of the Jovian NH_3 should have been irreversibly converted to hydrazine (N_2H_4) and molecular nitrogen (N_2) over the relatively short period of 60 million years [Strobel, 1973; Atreya and Donahue, 1979]. Although some NH_3 is regenerated in the upper atmosphere by the reaction:

$$NH_2 + H + M \rightarrow NH_3 + M \qquad (1)$$

substantial amounts are converted to hydrazine via combination of NH_2 free radicals:

$$NH_2 + NH_2 + M \rightarrow N_2H_4 + M \qquad (2)$$

Hydrazine loss processes in the upper atmosphere include photolysis to form N_2 and H_2 [Strobel, 1973; Atreya and Donahue, 1979; Houston and Hawkins, 1982], reaction with atomic hydrogen [Stief and Payne, 1976] and condensation from the cold upper atmosphere [Strobel, 1973]. Ammonia is ultimately regenerated by conversion of N_2H_4 and N_2 to NH_3 in the planet's hotter interior with upward convection of the product NH_3 [Strobel, 1973]. If ground state NH_2 is promoted by solar radiation to the electronically excited A state, it could then react with H_2 to form NH_3 [McNesby, 1969]. However, electronically excited NH_2 could be deactivated in collision with H_2 rather than chemically react to form NH_3. Nicodem and Ferris [1973] presented experimental evidence against any significant contribution from electronically excited NH_2 and Strobel [1975] and Atreya and Donahue [1979] argue that the average absorption cross section of NH_2 in the visible is about three orders of magnitude too small for this process to be significant in the region where most NH_3 is photochemically destroyed. There is also the possibility of regenerating NH_3 if the initial ammonia photoproduct, NH_2, would react with another trace species, abstracting an H atom.

The discovery of phosphine (PH_3) as a minor component of the Jovian atmosphere [Ridgeway, 1974; Ridgeway et al., 1976; Larson et al., 1977] has led to a great deal of speculation by planetary modelers regarding the role of PH_3 in the complex atmospheric chemistry of that planet. Since the flash photolysis experiments of Norrish and Oldershaw [1961] show that elemental phosphorus (P_n) is the end photoproduct of the decomposition of PH_3, Prinn and Lewis [1975] have suggested that the red colorations in the Jovian atmosphere, in particular the Great Red Spot, are a result of the photochemical production of red phosphorus particles. The more recent product analysis experiments of Ferris and Benson [1981] suggest that the initial stable product of the photodecomposition of PH_3 is P_2H_4 which may yield P_n upon further reaction.

Strobel [1977] has proposed that the photochemistries of NH_3 and PH_3 are linked since both PH_3 and NH_3 are present in the Jovian stratosphere and upper troposphere, absorb solar radiation in the same UV region, and undergo the same photolysis scheme. Specifically, the reaction

$$NH_2 + PH_3 \rightarrow NH_3 + PH_2 \qquad (3)$$

would, if the rate were fast enough at Jovian stratospheric temperatures, regenerate ammonia in the upper atmosphere while at the same time accelerating the decomposition of PH_3. Regeneration of NH_3 was shown to be the more significant effect. For reaction (3) to be competitive with reaction (2), the dominant NH_2 loss process, Strobel [1977] estimates that its rate would have to be comparable to the rate for the reaction:

$$H + PH_3 \rightarrow H_2 + PH_2 \qquad (4)$$

which also contributes to the decomposition of Jovian PH_3. At room temperature, both reactions (3) and (4) are exothermic, the former by about 24 and the latter by about 25.5 kcal/mole [Okabe, 1978]. There has been only one study of reaction (4) while no measurements of the rate of reaction (3) have been reported. The $H + PH_3$ reaction was examined in our laboratory [Lee et al., 1976] and we found $k_4 = (4.52 \pm 0.39) \times 10^{-11} \exp(-740 \pm 50/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 209-495 K. Buchanan and Hanrahan [1970], in radiolysis studies of PH_3-NH_3 mixtures, found that PH_3 was a very

good scavenger of H and NH_2 and set an upper limit of 2-3 kcal/mole for the activation energies of reactions (3) and (4). Ferris and Bossard [1982] photolyzed PH_3-NH_3 mixtures and suggested that reaction (3) proceeds at room temperature.

Since there have been no direct or indirect studies of the rate of reaction (3) and because of this reaction's possible importance in understanding the regeneration of NH_3 and decomposition of PH_3 in the Jovian atmosphere, we have measured the absolute rate constant for this reaction over as wide a range of temperature and pressure as experimentally possible. The technique employed was flash photolysis coupled with detection of NH_2 via laser induced fluorescence.

Experimental

The experiments described in this study were conducted using the flash photolysis-laser induced fluorescence (FP-LIF) technique. Our original flash photolysis-resonance fluorescence apparatus [Klemm and Stief, 1974; Michael and Lee, 1979] and the modifications to it for radical-molecule reactions [Stief et al., 1980; Michael et al., 1982] have been described in detail previously. Details of temperature measurement and control are given in Klemm and Stief [1974] and Stief et al. [1980]. Specific modifications for the detection and monitoring of the NH_2 radical, as well as operational procedures, have also been recently discussed [Stief et al., 1982]. Thus, only changes specific to this study will be described.

NH_2 radicals were generated by the flash photolysis of ammonia highly diluted in argon. To spectrally isolate the photoflash, a 175.0 nm interference filter (Ditric Optics, Inc., skewed FWHM of -13 and +25 nm) was mounted over the flashlamp. In later experiments, a 206.0 nm interference filter (Acton Research Corp., skewed FWHM of -15 and +25 nm) was used to minimize photolysis of PH_3. Both filter combinations yielded identical rate data.

Detection and monitoring of NH_2 was accomplished via laser induced fluorescence [Hancock et al., 1975]. The previously described [Stief et al.,

1982] CW dye laser system and tuning technique were utilized to precisely adjust output wavelength to either 570.3 nm or 568.2 nm, wavelengths which correspond to strong NH_2 absorptions by populations of rotational levels of the (0,10,0)π vibronic state [Kroll, 1975]. Use of either wavelength produced identical NH_2 decay constants. A 577.0 nm interference filter (Ditric Optics, Inc., FWHM ± 9.8 nm) was placed in front of the detector to discriminate against scattered laser radiation. The detector was at right angles to both the flashlamp and the laser systems. A Melles-Griot sheet polarizer was also mounted in front of the detector with its plane of polarization perpendicular to that of the laser system. Thus, the isotropically scattered fluorescent photons were selectively passed to the detector and not the polarized scattered laser light. The combination of the polarizer and 568.2 nm excitation wavelength resulted in a much improved signal-to-noise ratio compared to our previous work on NH_2 kinetics [Stief et al., 1982].

Gas handling techniques have been described in detail in previous reports from this laboratory [Klemm and Stief, 1974; Michael and Lee, 1979; Stief et al., 1980; Michael et al., 1982]. Ammonia (Air Products, 99.99%) and phosphine (Ideal Gas Products, 99.998%) were purified by bulb-to-bulb distillation at 168 K and 123 K respectively, the middle fraction being retained in both instances. Typical impurities in the ammonia and in the phosphine are trace quantities, respectively, of oxygen, nitrogen and water and hydrogen, nitrogen, and hydrocarbons. Most of these were readily removed by distillation, but, in any event, these species are known to be virtually unreactive with the NH_2 radical. Argon (Matheson, 99.9995%) was used as a diluent in gas mixtures without further purification. Fresh gas mixtures were prepared daily.

Unlike previous reports from this laboratory, in which gas mixtures were continuously flowed through the reaction cell, for this study the experiments were carried out under static conditions. Initial experiments showed that an aerosol of particulate matter was formed on flash photolysis of reaction mixtures containing phosphine, ammonia, and argon but not on photolysis of mixtures containing ammonia and argon only. Mixtures containing phosphine and argon only did not result in aerosol formation upon exposure to the flash, but this is as expected if phosphine photolysis was minimized or eliminated by the

interference filter on the flashlamp. This phenomenon caused intense laser light scattering within the reaction cell and resulted in saturation of the detecting photomultiplier tube. The effect was reduced significantly by the use of the polarizer described above. Tests indicated that the onset of particulate formation was directly related not only to flash energy but also to $[PH_3]$ and total pressure. It was also inversely related to temperature. In order to further minimize this phenomenon, it was necessary to limit total pressure, partial pressure of PH_3 and flash energy. Because low total pressures were used and had to be accurately regulated, static conditions were necessary. Even so, all experimental conditions were varied substantially. Gas mixtures were completely replenished frequently within the reaction cell and routine diagnostic tests, carried out on first-order decay plots, indicated that there were no contributions from secondary reactions.

Results

In the experiments reported here, $[PH_3]$ was $\sim 6 \times 10^{14}$ molecules/cm^3 or greater while $[NH_2]_o$ was of the order of 5×10^{11} radicals/cm^3 or less. Thus pseudo-first-order conditions were achieved with $[PH_3] \gg [NH_2]$ and the decay of NH_2 radicals is given by:

$$\ln[NH_2] = -k_{observed}\, t + \ln[NH_2]_o \qquad (5)$$

The observed pseudo-first-order decay constant is represented by:

$$k_{observed} = k_3\,[PH_3] + k_d \qquad (6)$$

where k_3 is the bimolecular rate constant for reaction (3) and k_d is the first order rate constant for the diffusional loss of NH_2 radicals from the reaction volume viewed by the detector. Accumulated fluorescent counts are proportional to $[NH_2]$ and plots of $\ln$ (counts-background) vs time were linear as required by equation (5). Typical examples are shown in Fig. 1. $k_{observed}$ was determined from linear-least-squares analyses of such plots.

Experiments were carried out on a series of reaction mixtures, each set of mixtures having a constant $[NH_3]$ and a varying $[PH_3]$ and run at the same total pressure and temperature. For each $[PH_3]$ in the set, experiments were performed over a range of flash intensity. Under such conditions, equation (6) predicts that a plot of the measured $k_{observed}$ values vs $[PH_3]$ will yield a straight line having a slope of k_3 and an intercept of k_d. Linear-least-squares analysis was used to determine k_3 in this manner. An example of such a set of experiments is shown in Fig. 2. It was found that experiments with $[PH_3] = 0$ (included for the determination of k_3) agreed within experimental error with the intercepts of such plots (k_d).

Rate data for the reaction of NH_2 with PH_3 at the various experimental conditions employed in this study are presented in Table 1. The error limits quoted are at the one standard deviation level. The rate constant is invariant with $[PH_3]$, total pressure and flash intensity (i.e., initial $[NH_2]$) and increases with increasing temperature. A plot of $\ln k$ vs $1/T$ is shown in

Fig. 3, and the best representation for the data over the temperature range 218-456 K is given by:

$$k_3 = (1.52 \pm 0.16) \times 10^{-12} \exp(-928 \pm 56/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors are given at the one standard deviation level. This expression is shown as a solid line in Fig. 3.

Discussion

Comparison with previous measurements is not possible since this study represents the first determination of the rate constant for the reaction $NH_2 + PH_3 \rightarrow NH_3 + PH_2$ (3). However, there is an estimate available which was made in order to account for the results of the radiolysis of $NH_3 - PH_3$ mixtures.

Buchanan and Hanrahan [1970] estimated that reactions (3) and (4) would have an upper limit of 2-3 kcal/mole for their activation energies. Further, they postulated that neither reaction would have a substantial steric factor and concluded that the rates of reactions would be within one or two orders of magnitude of collisional frequency at room temperature. Our determination of 1.84 kcal/mole for the activation energy of reaction (3) and that of 1.47 kcal/mole for that of reaction (4) by Lee et al. [1976] are in moderate agreement with Buchanan and Hanrahan's estimate. The agreement with their further estimate is less satisfactory. For reaction (4), Lee et al. obtained a pre-exponential factor of 4.52×10^{-11} cm^3 molecule^{-1} s^{-1} and found $k_4 = 3.45 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K, a factor of 10^2 slower than collisional frequency. We find that the pre-exponential factor for reaction (3) is 1.52×10^{-12} cm^3 molecule^{-1} s^{-1}, a factor of 30 smaller than that for reaction (4), and $k_3 = 6.11 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K, a factor of 5×10^3 slower than collisional frequency. Clearly, the prediction of Buchanan and Hanrahan regarding the steric factor (and hence the Arrhenius pre-exponential factor) for reaction (3) is much larger than the experimental result. This results in a considerable over-estimate of k_3 at all temperatures.

Since there have been no previous studies of this reaction with which to compare our results, we thought it instructive to consider reaction (3) from a theoretical standpoint. In order to determine if our measured activation energy is reasonable, we carried out a Bond-Energy-Bond Order (BEBO) calculation according to the methods of Johnston [1966] and incorporating recent modifications [Jordan and Kaufman, 1975; Gilliom, 1976]. Known values for the internuclear distances and bond energies of NH_2 and PH_3 [Herzberg, 1966] as well as for an N-P single bond (1.67 Å and 70 kcal/mole, respectively) [Goldwhite, 1981] were used. In order to evaluate the Morse parameter, β, it was necessary to estimate the frequency of single bond N-P and the reasonable value of 700 cm^{-1} was chosen. The selected value is consistent with the assignment of the N-P stretching frequency to the 680-820 cm^{-1} region [Rao, 1963]. Using these parameters, the BEBO calculation predicts a barrier height of 2.05 kcal/mole at $n_{PH} = 0.904$ and $n_{NH} = 0.096$. This result implies $R_{NH} = 1.673$ Å and $R_{PH} = 1.449$ Å, meaning that the complex is very close to the reactants.

These results led us to construct an abstraction activated complex model with N-H-P colinear, all HPH angles at 93.3° (the bond angle in PH_3) and the angle of the abstracted hydrogen with either of the NH_2 hydrogens approximating that in NH_3. The pre-exponential factor for the reaction was then estimated by using Activated Complex Theory [Laidler, 1969], where:

$$A = \frac{KT}{h} \frac{Q^{\neq}}{Q_{NH_2} Q_{PH_3}}$$

with $Q^{\neq}$ being the partition function of the activated complex. Evaluation of the translational, rotational, and electronic partition functions for the reactants and the activated complex and inclusion of one free internal rotation (consistent with the activated complex model chosen) leads to:

$$A = 1.18 \times 10^{-8}\ T^{-3/2} \frac{q_v^{\neq}}{q_v^{NH_2} q_v^{PH_3}}$$

with q_v being the vibrational partition function of a species. Use of the known vibrational frequencies for NH_2 and PH_3 [Nakamoto, 1978] allowed the evaluation of those vibrational partition functions as a function of temperature. The only important vibrations for the activated complex should be the PH_2 twist and wag (which were taken as 878 and 636 cm^{-1}, respectively, by analogy with P_2H_4 [Durig, 1975]) and the two N-H-P bends (which were taken as 860 and 820 cm^{-1} by analogy with $C\ell HF^-$ [Nakamoto, 1978]). These values were used to evaluate $q_v^{\ddagger}$ as a function of temperature.

The resulting pre-exponential factor is temperature dependent and is tabulated as a function of temperature in Table 2. Using the 2.05 kcal/mole activation energy predicted by the BEBO calculation, our theoretical bimolecular rate constant is also tabulated in Table 2, along with the experimentally determined rate constant at that particular temperature. While this theoretical treatment is at best a crude approximation of the actual reaction dynamics, it is in very good agreement with our experimental results.

Our results for $NH_2 + PH_3$ may be contrasted with those for the $H + PH_3$ reaction as mentioned above and also with the reaction

$$OH + PH_3 \rightarrow H_2O + PH_2 \qquad (8)$$

Fritz et al. [1982] have recently studied this reaction and obtained the result

$$k_8 = (2.7 \pm 0.6) \times 10^{-11} \exp(-155/T)\ cm^3\ molecule^{-1}\ s^{-1} \qquad (9)$$

The reactions of isoelectronic NH_2 and OH radicals with PH_3 provide an interesting contrast. Reaction (8) is almost twice as exothermic as reaction (3) (40.3 kcal/mole vs. 24.0 kcal/mole [Okabe, 1978]), has a much smaller activation energy (308 cal/mole vs. 1.84 kcal/mole) and an order of magnitude higher pre-exponential factor. The Arrhenius parameters and room temperature rate constants for the reaction of H, OH and NH_2 with PH_3 are summarized in Table 3 to facilitate comparison.

Our observations of the formation of a particulate aerosol in extreme experimental conditions may be compared with the results of Norrish and Oldershaw [1961]. They observed a similar phenomenon in their PH_3 flash photolysis experiments and attributed it to the formation of small phosphorus particles produced from the secondary reactions of their primary initial photoproduct PH_2, which would remain suspended in the gas phase if the total pressure of their system were high enough. Our flashlamp-filter combination was chosen specifically to minimize PH_3 photolysis and experiments carried out on PH_3-Ar gas mixtures showed that no particles were being formed from PH_3 photolysis. However, in NH_3-PH_3-Ar gas mixtures particulate aerosols could be formed. If the aerosol was of phosphorus particles, then the PH_2 necessary for a P_n formation sequence such as that of Norrish and Oldershaw [1961] or Ferris and Benson [1981] would have had to have come mostly from reaction (4), reaction (3) being fifty times slower at 298 K (Table 3). Since we observed that the formation of particles was directly related to high flash energies (e.g., high initial [H] from NH_3 photolysis), high [PH_3], and high total pressures (to suspend the particles in the gas phase), we argue that the particles formed were indeed phosphorus and that their formation was primarily due to the reactions of PH_2 radicals formed via the reaction $H + PH_3 \rightarrow PH_2 + H_2$ (4). This occurred only under extreme experimental conditions. Under our normal operating conditions, no particulate formation was observed and, because we were directly following [NH_2] as a function of time, our kinetic data was not perturbed by secondary reactions. It is clear that more investigation is needed to determine the mechanism of how PH_2 is converted to P_n, both in the laboratory and possibly on Jupiter.

Conclusions

The potential role of the reactions $NH_2 + PH_3 \rightarrow NH_3 + PH_2$ (3) and $H + PH_3 \rightarrow PH_2 + H_2$ (4) in models of the aeronomy or photochemistry of the atmosphere of Jupiter was outlined in the Introduction. Thus the extrapolation of our present results for reaction (3) and our previous study [Lee et al., 1976] of reaction (4) to Jovian temperatures is of considerable interest. At 150 K, $k_3 = 3.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} and $k_4 = 3.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Strobel [1977] has argued that for reaction (3) to be competitive with the dominant NH_2 loss process, i.e., combination to form hydrazine (N_2H_4), k_3

should be comparable to k_4. Since we now find k_3 to be two orders of magnitude slower than k_4, it appears that reaction (3) can make only a negligible contribution to both the recycling of NH_3 and the decomposition of PH_3 in the upper atmosphere of Jupiter as Kaye and Strobel [1983] confirm in a photochemical model of the Jovian tropopause region.

The recycling or inhibition of the photochemical destruction of NH_3 in the Jovian atmosphere is therefore probably best accounted for at the present time by a combination of the reaction $NH_2 + H \overset{M}{\rightarrow} NH_3$ (1) and the reaction $NH_2 + NH_2 \overset{M}{\rightarrow} N_2H_4$ (2) [Strobel, 1973; Atreya and Donahue, 1979]. The latter is followed by condensation of N_2H_4, convection to the hot interior, thermal decomposition of N_2H_4 to NH_2 and finally reaction of NH_2 with abundant H_2 at the high temperature required to overcome the considerable activation energy for this reaction. If sufficient N_2H_4 remains in the vapor phase such that photolysis or reaction with atomic hydrogen are significant loss processes, the resulting product N_2 can similarly be transported to the hot interior where the overall reaction $N_2 + 3H_2 \rightarrow 2NH_3$ becomes important.

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Table 1. Rate Data for the Flash Photolysis - Laser Induced Fluorescence Study of the Reaction $NH_2 + PH_3$

T,K	[Ar] torr	$[NH_3]$ mtorr	$[PH_3]$ mtorr	Flash Energy[a]	No. of expts.	$k_{obs}(s^{-1})$		k_{bi}/[b] $10^{-14}cm^3molecule^{-1}s^{-1}$	
218	2.5	342	34.2	24 - 62	4	99	9	2.56	0.59
			68.3	24 - 62	4	127	9		
	2.5	342	27.3	24 - 62	4	150	3	2.71	0.72
			54.7	24 - 47	3	138	7		
			82.0	35 - 62	5	196	15		
	5.0	342	23.2	35 - 62	4	61	3	1.96	0.45
			46.5	35 - 62	4	75	6		
					28			2.14	0.40[c]
247	2.5	302	60.3	35 - 62	5	124	8	3.78	0.52
			90.5	47 - 62	3	159	7		
	2.5	302	0	16 - 47	4	112	7	2.39	0.12
			24.1	16 - 47	4	132	3		
			48.3	16 - 47	4	150	4		
			72.4	16 - 47	4	168	4		
	2.5	302	0	16 - 47	4	101	3	3.09	0.22
			30.2	9 - 35	4	122	4		
			60.3	4 - 62	6	145	12		
			90.5	24 - 62	4	193	8		
	2.5	302	0	16 - 47	4	124	15	3.78	0.31
			24.1	16 - 47	5	156	8		
			48.3	16 - 47	5	191	14		
			72.4	16 - 47	5	212	7		
	5.0	302	0	16 - 47	4	65	5	2.66	0.19
			24.1	24 - 62	4	89	8		
			48.3	24 - 62	4	109	5		
			72.4	24 - 62	4	128	8		
	5.0	302	0	35 - 62	6	37	3	3.93	0.13
			20.5	35 - 62	4	63	5		
			41.0	35 - 62	4	87	4		
			61.5	35 - 62	3	117	4		
					94			3.27	0.65[c]

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298	2.5	250	0	11 - 47	4	83	7	7.12	0.30
			50.0	9 - 47	5	203	6		
			75.0	16 - 47	6	272	14		
			100.0	9 - 47	5	308	18		
	4.0	200	0	35 - 62	8	52	8	5.46	0.19
			40.0	35 - 62	4	124	10		
			60.0	35 - 62	4	157	14		
			80.0	35 - 62	4	294	5		
	4.0	280	0	37	1	120		5.95	0.41
			48.0	24,37	2	196	2		
			72.0	24,37	2	260	5		
			96.0	37	1	298			
	5.0	244	0	37 - 110	4	47	4	6.55	0.40
			30.1	9 - 47	6	148	17		
			45.4	9 - 47	5	179	13		
			60.0	9 - 47	5	206	9		
	7.5	366	0	9 - 47	6	36	4	6.30	0.22
			4.52	16 - 47	3	131	11		
			68.1	16 - 55	4	168	12		
			90.0	24 - 47	3	229	10		
	7.5	750	0	16 - 62	5	58	3	5.54	0.16
			39.4	16 - 62	5	139	7		
			80.8	16 - 62	5	205	8		
			120.0	16 - 62	5	276	17		
	10.0	208	0	9,16	2	29	2	5.78	0.12
			25.0	9,16	3	80	1		
			50.0	9,16	2	121	1		
			75.0	16	1	172			
					107			6.11	0.60 [c]
363	2.5	205	0	24 - 62	5	137	19	10.4	0.7
			41.0	24 - 62	6	359	40		
			82.0	24 - 62	6	444	26		
			120.0	24 - 62	6	564	38		
	2.5	144	0	47	1	210		15.0	1.1
			24.6	47 - 62	3	310	17		
			36.9	47 - 62	3	353	6		
			49.3	47 - 62	6	440	16		
	5.0	205	0	24 - 47	5	187	23	12.2	0.9
			41.0	35 - 62	4	296	9		
			61.6	35 - 62	7	383	17		
			82.1	35 - 62	5	528	54		

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	5.0	287	0	47	2	194	4	12.5	1.3
			49.3	47 - 62	3	322	9		
			73.9	47 - 62	3	428	58		
			110.8	47,62	2	647	23		
					67			12.5	1.9 [c]
456	5.0	204	0	4 - 16	3	106	4	22.6	1.0
			20.5	9 - 16	3	217	7		
			40.8	9 - 16	3	384	1		
			61.1	16	2	553	43		
	10.0	408	0	4 - 16	3	70	2	20.0	0.5
			41.0	4 - 16	3	312	8		
			81.9	4 - 16	3	559	20		
			122.4	4 - 16	3	871	36		
	20.0	408	0	4 - 16	3	62	3	21.5	0.6
			33.0	4 - 16	3	296	33		
			65.0	4 - 16	3	503	16		
			97.0	16	2	747	23		
					34			21.4	1.3 [c]

a. Effective flash energy through a 175.0 nm interference filter except for the 10 torr experiments at 298 K and all experiments at 456 K

b. error limit is one standard deviation

c. average k at that temperature

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Table 2. Calculated Temperature Dependent Pre-Exponential Factor A(T) and Bimolecular Rate Constant k for the Reaction $NH_2 + PH_3 \quad NH_3 + PH_2$

T(K)	A(T)[a]	k_{calc}[a]	$k_{expt'l}$[a]
218	3.76×10^{-12}	3.30×10^{-14}	$(2.41 \quad 0.40) \times 10^{-14}$
247	3.18×10^{-12}	4.87×10^{-14}	$(3.27 \quad 0.65) \times 10^{-14}$
298	2.53×10^{-12}	7.93×10^{-14}	$(6.11 \quad 0.60) \times 10^{-14}$
363	2.07×10^{-12}	1.20×10^{-13}	$(1.25 \quad 0.19) \times 10^{-13}$
456	1.74×10^{-12}	1.81×10^{-13}	$(2.14 \quad 0.13) \times 10^{-13}$

a. units are cm^3 $molecule^{-1}$ s^{-1}.

Table 3. Comparison of Room Temperature Rate Constant and Arrhenius Parameters for Reactions of H, OH and NH_2 with PH_3

Reactant	k(298 K) cm^3 $molecule^{-1}$ s^{-1}	A cm^3 $molecule^{-1}$ s^{-1}	E k cal/mole	Reference
H	3.45×10^{-12}	4.52×10^{-11}	1.47	a
OH	1.6×10^{-11}	2.7×10^{-11}	0.31	b
NH_2	6.11×10^{-14}	1.52×10^{-12}	1.84	c

a. Lee et al., 1976.

b. Fritz et al., 1982.

c. this work.

Figure Captions

Fig. 1. Decay plots of NH_2 fluorescent counts vs time at four temperatures. 218 K: P_{PH_3} = 27.3 mtorr, P_{NH_3} = 342 mtorr, $k_{observed}$ = 146 ± 12 s^{-1}; 247 K: P_{PH_3} = 72.4 mtorr, P_{NH_3} = 302 mtorr, $k_{observed}$ = 219 ± 4 s^{-1}; 298 K: P_{PH_3} = 75.0 mtorr, P_{NH_3} = 250 mtorr, $k_{observed}$ = 270 ± 7 s^{-1}; 363 K: P_{PH_3} = 49.3 mtorr, P_{NH_3} = 144 mtorr, $k_{observed}$ = 417 ± 11 s^{-1}. Total pressure is 2.5 torr for all four experiments.

Fig. 2. Plot of $k_{observed}$ vs P_{PH_3} at 298 K and 4 torr total pressure. Individual points denote experiments performed at different flash intensities, i.e., different values of $[NH_2]_o$. The linear least squares line is given by $k_{observed} = (5.46 \pm 0.19) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} $[PH_3] + (52.2 \pm 3.0)$ s^{-1}.

Fig. 3. Arrhenius plot of rate data for the reaction $NH_2 + PH_3$. The linear least squares line is given by $k_3 = (1.52 \pm 0.16) \times 10^{-12} \exp(-928 \pm 56/T)$ cm^3 $molecule^{-1}$ s^{-1}.

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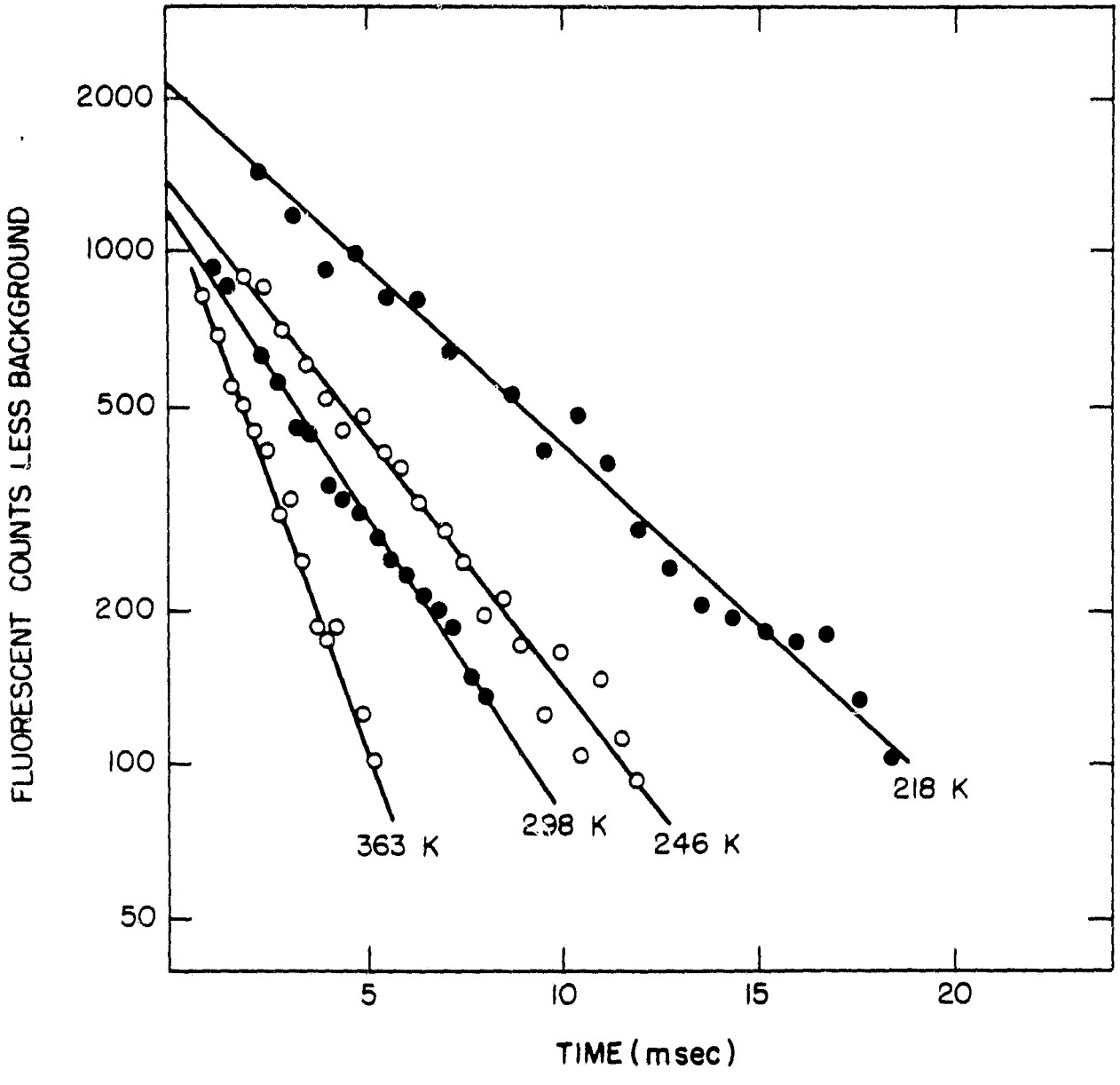

Figure 1

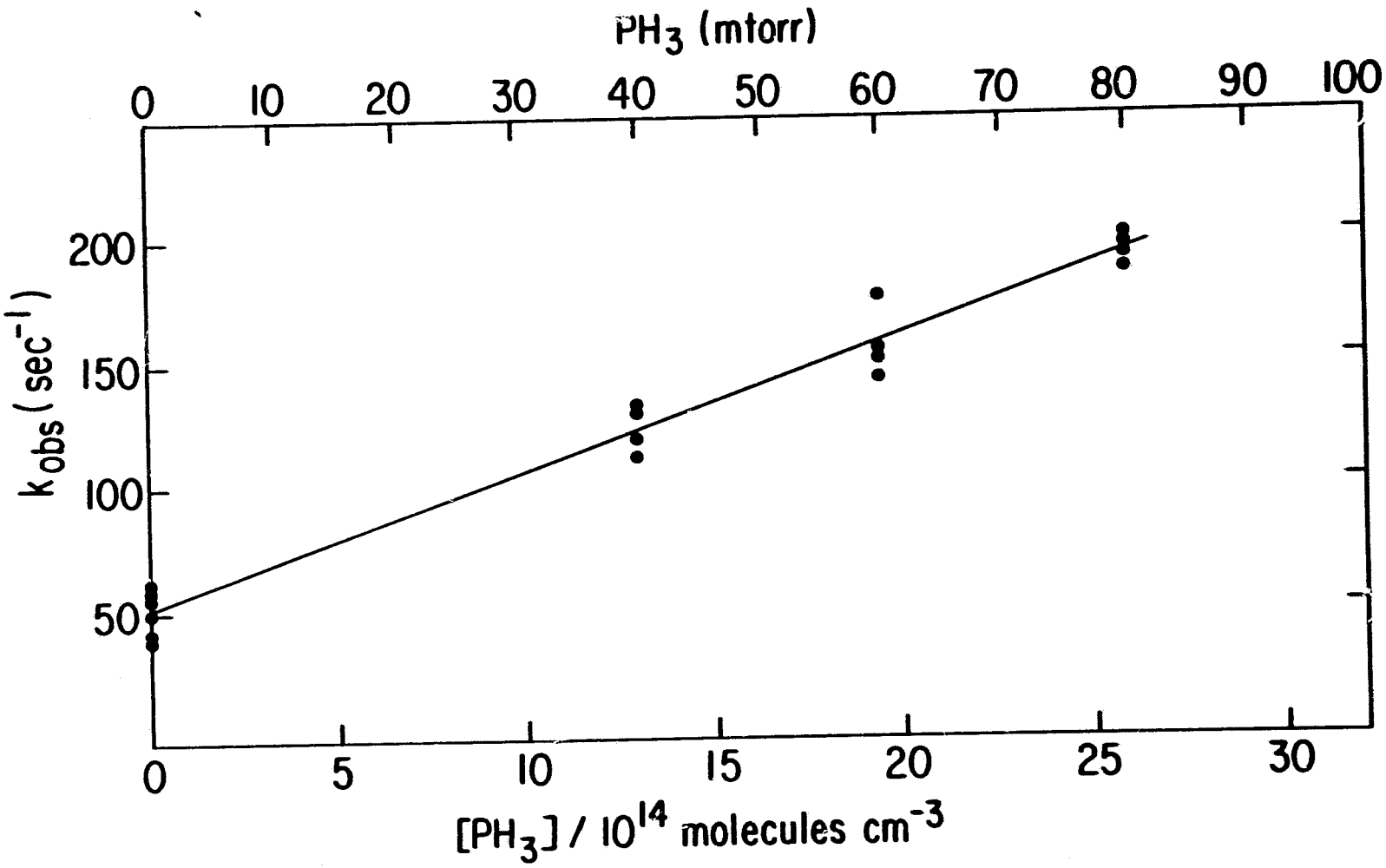

Figure 2

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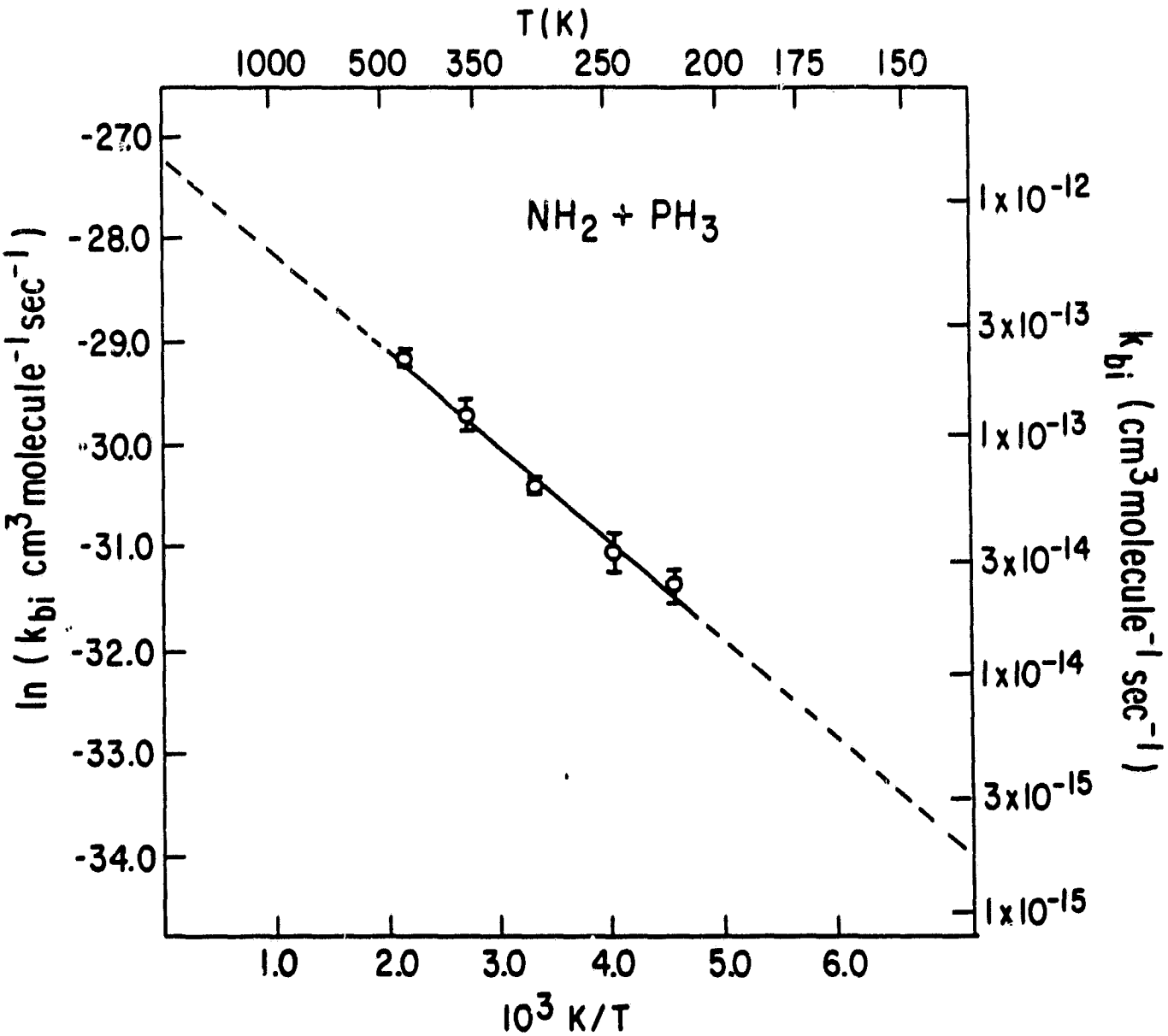

Figure 3