vinyloxonium (**12**) is indicated to be a relatively low-energy species separated from **11** by a substantial barrier to intramolecular rearrangement and is therefore an attractive prospect for experimental observation.

(iii) The only stable form of protonated oxirane is the O-corner-protonated isomer (**7**).

(iv) Although the 2-hydroxyethyl cation (**10**) is stable with respect to cyclization to O-protonated oxirane (**7**) and proton migration to vinyloxonium (**12**), it collapses without activation energy to the 1-hydroxyethyl cation (**11**).

(v) The ethoxy cation (**16**) is also indicated to be an unstable species, collapsing without activation to **9** or **11**.

(vi) STO-3G optimized structures are found to provide a reasonable basis for calculating activation energies at higher levels of theory.

(vii) Both polarization functions and electron correlation are found to be important in providing an accurate description of the $C_2H_5O^+$ potential energy surface.

Acknowledgment. We thank Mr. M. A. Ballard for assistance with some of the calculations. We are indebted to Dr. Dudley Williams for helpful and stimulating discussions.

An Investigation of the Mechanism of Phosphine Photolysis

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Abstract: Photolysis of PH_3 gives P_2H_4 as an initial photoproduct. The concentration of P_2H_4 increases to a maximum and then decreases during the course of the photolysis. Disproportionation of PH_2 was eliminated as a reaction by the observation that the ratio of $4n_{P_4}/n_{P_2H_4}$ extrapolates to near zero at zero reaction time. The yield of P_2H_4 increases with increasing PH_3 concentration, but it is only slightly affected by the addition of SF_6 or N_2. The absence of an effect with the added inert gases eliminates the possibility of termolecular reactions and hot atom reactions in the formation of P_2H_4. P_2H_4 formation from PH_2 was shown to be a gas phase and not a wall reaction by flash photolysis studies. The pseudo-second-order rate constant determined for the formation of P_2H_4 ($(5.4 \pm 2.4) \times 10^9\ M^{-1}\ s^{-1}$) is diffusion controlled and close to the rate constant for the formation of N_2H_4 from NH_2. That the rate constants are comparable suggests both hydrides are formed by the same reaction pathway. Initial quantum yields are Φ_{PH_3} (PH_3 loss) $= 1.78 \pm 0.18$, $\Phi_{H_2} = 0.43 \pm 0.23$, $\Phi_{P_2H_4} = 0.80 \pm 0.08$, and $\Phi_{4P_4} = 0.04 \pm 0.16$. The value of Φ_{PH_3} close to 2 indicates the formation of PH_2 by reaction of H and PH_3 (reaction 3) is an important reaction pathway in PH_3 photolysis. A new mechanism is proposed for PH_3 photolysis, and the significance of these findings to the atmospheric chemistry of Jupiter is discussed.

Phosphine (PH_3) photochemistry has been studied sporadically since the initial work of Melville in 1932,[2] but these limited studies are dwarfed by the extensive investigations of NH_3, the corresponding group 5 hydride.[3] The apparent lack of interest in PH_3 may reflect the hazardous nature of the compound[4] as well as the experimental problem of having a solid photoproduct, P_4, coat the walls of the photolysis cell; neither of these problems complicates the study of NH_3 photochemistry. The discovery of PH_3 in the atmospheres of Jupiter and Saturn by Ridgway,[5] a result which has subsequently been confirmed by airborne observations,[6] ground-based studies,[7] and the Voyager II mission,[8] has prompted increased interest in PH_3 photochemistry. The discovery of PH_3 led to the suggestion that the red coloration of the Great Red Spot of Jupiter is due to the photolysis of PH_3 to red phosphorus (P_4).[9] The PH_3 may be formed from phosphorus in the lower, hotter levels of the Jovian atmosphere or by reaction with H atoms in the upper atmosphere or with the NH_3–H_2O clouds in the upper troposphere.[10]

The primary process in the photolysis of PH_3 between 160 and 210 nm is predissociation to PH_2 and H atoms (eq 1)[11] which is

$$4PH_3 \xrightarrow{h\nu} P_4 + 6H_2 \qquad (1)$$

reflected in the featureless UV spectrum of PH_3 from 240 nm down to the vacuum ultraviolet.[12] Red phosphorus and H_2 are the only photoproducts that have been reported (eq 1).[2,13]

The quantum yield for PH_3 loss (Φ_{PH_3}) was reported to be 0.5[2] and was not affected by pressure variations of 10–760 torr and temperature variations of 15–300 °C. The Φ_{PH_3} increased with an increase in the surface to volume ratio of the reaction cell. This finding suggests that the secondary reactions of H and PH_2 occurred on the wall of the reaction vessel and that their activation energies were small. One of the proposed secondary reactions, the recombination of H and PH_2 (reaction 8), would account for a value of Φ_{PH_3} less than 1.

H atoms have been demonstrated to have an important role in the decomposition of PH_3.[14] They react with PH_3 to give the same products, H_2 and P_4, as are observed in the photolysis of PH_3. The rate constant for the reaction of H atoms with PH_3

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Table I. Variation in Yield of P_2H_4 and P_4 with Time of Irradiation

time, h	$10^7P_2H_4$, mol	10^8P_4, mol
0.5	1.87	0.55
1.0	2.72	1.6
2.0	3.79	3.8
3.0	3.81	6.5
4.0	4.52	6.2
5.0	4.72	10.0
6.0	3.99	12.2
7.4	3.78	16.7
15.5	1.54	37.2
24.8	0.97	26.8
48.0	0.61	29.3

(eq 3) has been found to be $2.72 \times 10^{10} \exp(-1470/RT)$ and is close to diffusion controlled at 20 °C ($k = 2.2 \times 10^9$ M^{-1} s^{-1}).[15] This rapid rate implied that the H atoms formed by the photolysis of PH_3 should effect the decomposition of other PH_3 molecules and is also the basis for the postulate that the H atoms produced by the photolysis of NH_3 in the Jovian atmosphere will accelerate the decomposition of PH_3.[16]

The transients PH_2, PH, and P_2 were reported in flash photolysis studies of PH_3.[13] All of these intermediates reached their maximum concentration levels 15 μs after the flash, indicating they were formed in the gas phase. Reactions 4 and 5 were proposed to account for the observation of PH and P_2. A reaction pathway consistent with the steady-state and flash photolysis data in the literature is given in reactions 2–8. Reactions 7 and 8 probably occur mainly on the wall of the reaction vessel.

$$PH_3 \xrightarrow{h\nu} PH_2 + H \tag{2}$$

$$H + PH_3 \rightarrow PH_2 + H_2 \tag{3}$$

$$2PH_2 \rightarrow PH + PH_3 \tag{4}$$

$$2PH \rightarrow P_2 + H_2 \tag{5}$$

$$2P_2 \rightarrow P_4 \tag{6}$$

$$2H \rightarrow H_2 \tag{7}$$

$$H + PH_2 \rightarrow PH_3 \tag{8}$$

$$2PH_2 \xrightarrow{M} P_2H_4 \tag{9}$$

In reviewing the studies published on PH_3 photolysis, we were surprised that its photochemistry did not more closely parallel that of NH_3. In particular there was no report of the formation of diphosphine (reaction 9) as a product even though hydrazine (N_2H_4) is a central photoproduct in the photolysis of NH_3 to N_2.[3] It was also puzzling that the quantum yield for PH_3 loss was only 0.5 especially since the large value for the rate constant of eq 3[15] suggested that the initial quantum yield for the photolysis of PH_3 should be greater than 1 and may even approach 2. We undertook this investigation to clarify the mechanism of PH_3 photolysis and to better understand the possible role of this compound in the atmospheric chemistry of Jupiter.

Results and Discussion

Diphosphine (P_2H_4) was observed as a photoproduct on short-term irradiation of 87 torr of PH_3 with a low-pressure mercury lamp (253.7 and 184.9 nm) or iodine lamp (206.2 nm).[17] It was detected by an increased UV absorption in the photolysate extending from about 250 nm down to that of PH_3 at 210 nm. On prolonged irradiation this absorption disappeared and only that of PH_3 remained.

A sample of the photochemically formed P_2H_4 was obtained by repeated short-term irradiations of PH_3 followed by condensation of the P_2H_4 at −116 °C. Its identity as P_2H_4 was established by comparison of its IR spectrum,[18] UV spectrun (Figure 1), and gas chromatographic retention time with those of an authentic sample.[19]

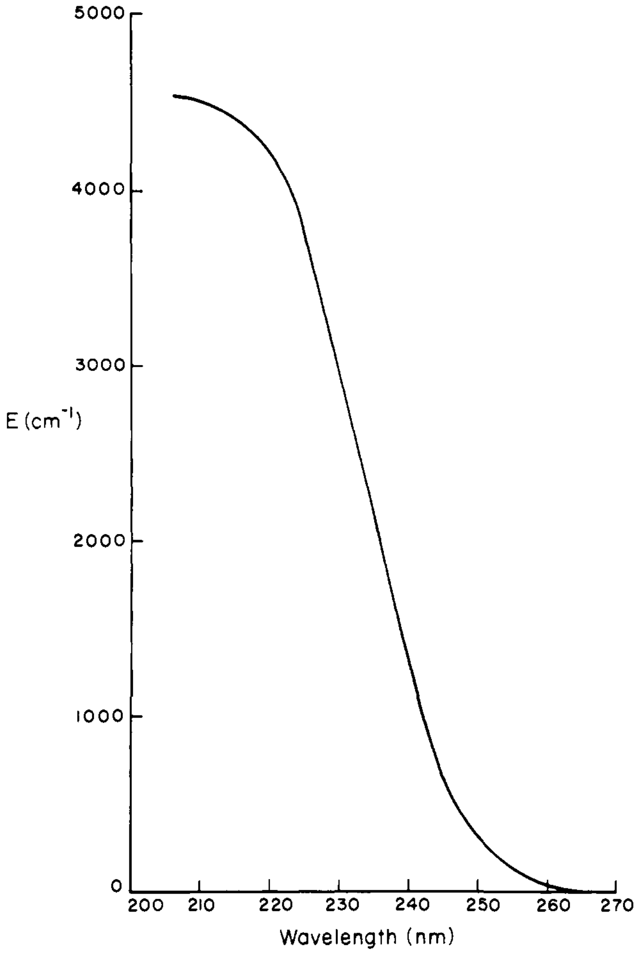

Figure 1. Absorption spectrum of P_2H_4.

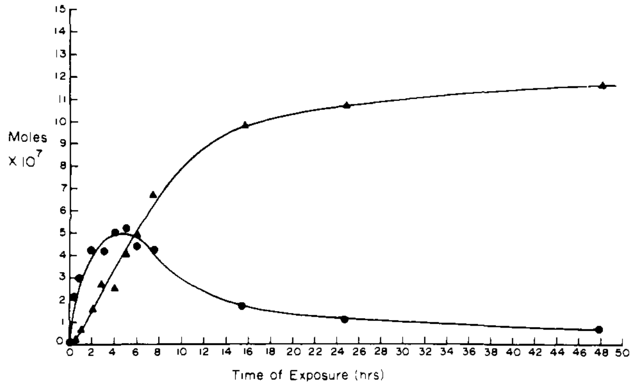

Figure 2. P_2H_4 (●) and P_4 (▲) yields with time of irradiation.

Our observation that the P_2H_4 concentration decreased on prolonged irradiation prompted an investigation of the variation in P_2H_4 yield with the extent of irradiation (Table I). The P_2H_4 was determined from the UV absorbance of the photolysate at 235 nm corrected for the absorbance of the P_4 layer on the window of the irradiation cell. The yield of phosphorus was determined after its oxidation to phosphate,[20] and the amount of PH_3 decomposed was determined from the stoichiometry given in eq 1.

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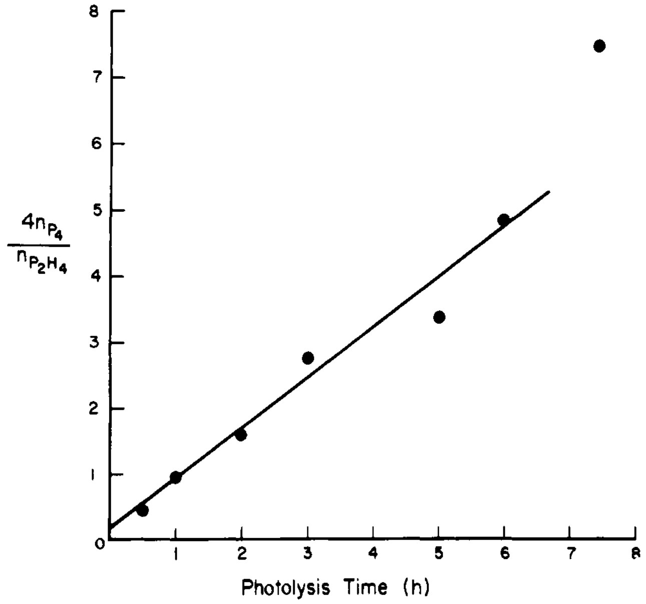

Figure 3. Ratio $4n_{P_4}/n_{P_2H_4}$ with time of irradiation.

The yield of P_4 levels off after 16 h (Figure 2), a result which reflects the attenuation of the incident radiation by the P_4 on the cell window. The yield of P_2H_4 reaches a maximum after 4 h and then decreases to about 20% of that maximum value (Figure 2). The diminished yield of P_2H_4 on extended irradiation explains why it was not detected in previous studies[2,13] since the early workers had performed their analyses after prolonged irradiation when the P_2H_4 yield was low.

The variation in the yield of P_2H_4 with time of irradiation (Figure 2) is not understood. A similar time variation of the N_2H_4 yield during NH_3 photolysis was reported without comment.[21] One postulate which would explain the P_2H_4 variation but not the N_2H_4 variation, is an effect due to the diminished light intensity resulting from the buildup of the P_4 layer on the cell window. P_2H_4 formation is a second-order reaction with respect to PH_2 (eq 9) while P_2H_4 decomposition is first order with respect to PH_2 or H (eq 10 and 11). Decomposition of P_2H_4 becomes more important with decreasing light intensity than its formation. This explanation of the variation in P_2H_4 yield and other explanations based on effects due to the P_4 layer were excluded by observing that comparable yields of P_2H_4 were obtained when fresh samples of PH_3 were irradiated in a clean cell or in a cell which had a P_4 coating the window from a prior 3-h photolysis of PH_3. Another explanation of the decrease in P_2H_4 and N_2H_4 concentrations on prolonged photolysis may be an undetermined autocatalytic process which results in the production of H atoms. These H atoms (or other radical species) would be expected to readily attack P_2H_4 (eq 10) and N_2H_4,[22] thereby accelerating the decomposition of these molecules to phosphorus and nitrogen, respectively.

Disproportionation of the initially formed PH_2 was proposed for the formation of P_2 on photolysis of PH_3 (eq 4–6).[2,13] Our discovery of P_2H_4 as a reaction intermediate suggests an alternative pathway for PH_2 disappearance, namely, combination of PH_2 to form P_2H_4. If disproportionation of PH_2 (reaction 4) is a competitive pathway for PH_2 disappearance, then both P_4 and P_2H_4 will be formed concurrently at short times. It is shown in the Experimental Section that

$$\lim_{t \to 0} (4n_{P_4}/n_{P_2H_4}) = k_4/k_9$$

An extrapolation to zero irradiation time of plot of $4n_{P_4}/n_{P_2H_4}$ vs. time of irradiation (Figure 3) gives an intercept close to zero indicating that disproportionation of PH_2 is not a significant pathway for the formation of P_4.

Table II. Variation in P_2H_4 and P_4 Yield with PH_3 Pressure

irradiation time, h	10^7(PH_3 pressure), torr	10^7(P_2H_4 yield), mol	10^7(P_4 yield), mol	10^7(PH_3 decomposed),[a] mol
0.5	28.7	1.36		
	57.6	1.59		
	103.6	1.70		
	196.7	2.62		
	398.5	2.86		
	596.7	3.46		
24.67	49.9	0.55	4.0	17.1
	87.2	0.87	3.3	14.8
	188.6	1.31	4.5	20.5
	340.5	1.83	3.7	18.6
	416.8	2.42	2.8	15.8
	491.8	2.83	2.3	14.9

[a] $n_{PH_3} = 4n_{P_4} + 2n_{P_2H_4}$.

Table III. Variation in P_2H_4 Yield with N_2 and SF_6 Pressure[a]

PH_3, torr	added gas	added gas pressure, torr	10^8(P_2H_4 yield), mol
0.5			6.0
0.5	N_2	147	4.1
0.5	N_2	481	6.5
30.2			12.2
30.2	SF_6	177	13.6
30.2	N_2	320	16.6
30.2	N_2	534	16.2
30.2	N_2	538	15.1
30.2	SF_6	574	15.0

[a] A 0.5-h irradiation time.

Table IV. Flash Photolysis of PH_3

PH_3, torr	H_2, torr	λ, nm	A[a]	A_{235}[b]	A/A_{235}	normalized absorbance ratio[c]
1.33	180	235	0.0495	0.0256	1.93	1
1.33	180	240	0.0360	0.0258	1.34	0.69
1.33	180	245	0.0193	0.0202	0.96	0.50
1.33	180	260	0.0133	0.0300	0.44	0.23
1.33	180	280	0.0065	0.0266	0.24	0.12
0.94	220	235	0.0261	0.0148	1.76	1
0.94	220	232.5	0.0453	0.0172	2.63	1.49
0.94	220	230	0.0412	0.0160	2.58	1.47
0.94	220	225	0.0642	0.0222	2.89	1.64

[a] Absorbance measured 300 μs after the flash. [b] Absorbance measured 1 h after the flash on Cary 219 after the P_4 settled. [c] Absorbance ratio normalized to $A = 1$ at 235 nm.

The effect of pressure on the conversion of PH_3 to P_4 and P_2H_4 was investigated to probe the mechanism of the photolysis. When the PH_3 pressure is increased, the yield of P_2H_4 increases and the yield of P_4 decreases (Table II); however, if the pressure of PH_3 remains constant and the total pressure is altered by the addition of an inert gas such as N_2 or SF_6, there is little or no effect on the yield of P_2H_4 (Table III). This increase in P_2H_4 concentration with PH_3 pressure may be due to an increase in the rate of reaction 9 because the light is absorbed in a smaller volume resulting in concentrating of PH_2 near the cell window. An alternative explanation is there is an increase in the rate of reaction 3 because of the greater concentration of PH_3 and a corresponding decrease in the rate of destruction of P_2H_4 (reaction 10). Termolecular processes and hot atom reactions are eliminated at PH_3 pressures ≥ 0.5 torr by the absence of an effect of N_2 or SF_6 pressure on the formation of P_2H_4.

The absence of wall effects on the formation of P_2H_4 was shown by flash photolysis studies. Our detection of P_2H_4 by flash photolysis conflicts with earlier studies where it was concluded that little or none is formed.[13] The P_2H_4 was identified in the present work by its UV absorption spectrum (Figure 4) which was obtained by measuring the absorbance at different wavelengths 300 μs after the flash. This spectrum correlates well with the

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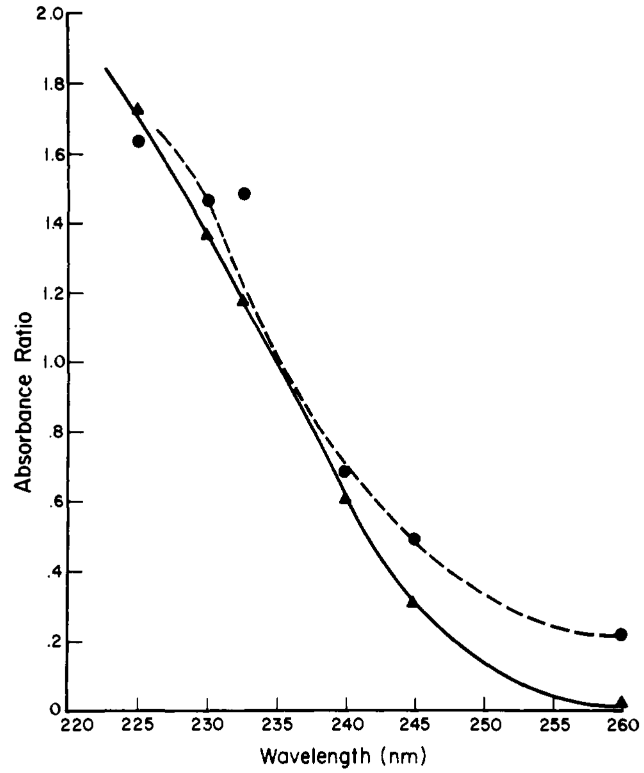

Figure 4. Normalized absorption spectra of P_2H_4 determined from flash photolysis results (●) and a pure sample (▲).

Table V. Quantum Yields as a Function of Quanta Absorbed by PH_3

$10^7 Q_{PH_3}$, einstein	quantum yield			
	PH_3[a]	H_2	P_2H_4	$4P_4$
3.58	1.63	0.75	0.72	0.19
3.64	1.57	0.74	0.72	0.13
5.64		0.56	0.52	
5.67	1.03	0.58	0.50	0.03
9.04		0.76	0.41	
11.9	0.97	1.13	0.38	0.22
13.2	0.87	1.14	0.31	0.25
14.0	0.76	1.14	0.18	0.39
14.2	0.81	1.30	0.20	0.41
15.4	0.84	1.13	0.16	0.52
17.4	0.67	1.59	0.097	0.49
19.8	0.65	1.27	0.054	0.54

[a] Moles of PH_3 decomposed calculated from $n_{PH_3} = 2n_{P_2H_4} + 4n_{P_4}$.

spectrum of pure P_2H_4 with the exception in the longer wavelength region. That P_2H_4 is formed in the gas phase was established by the observation that it is formed in less than 300 μs after the flash. The P_2H_4 cannot be formed on the cell wall because this time interval is too short for PH_2 radicals to diffuse to the cell wall and combine to form P_2H_4 and for the P_2H_4 to then diffuse to the path of the analyzing beam passing through the center of the photolysis cell. A pseudo-second-order rate constant of $(5.4 \pm 2.4) \times 10^9$ M^{-1} s^{-1}, consistent with a near diffusion-controlled reaction, was calculated from the flash data (Table V) for the combination of PH_2 to P_2H_4 (reaction 9). A comparable pseudo-second-order rate constant of 2.5×10^9 M^{-1} s^{-1} was reported for the combination of NH_2 to N_2H_4 at 10 torr of NH_3,[23,24] a result which lends support to the rate constant for P_2H_4 formation measured in the present study.

The large rate constant for reaction 3 (2.3×10^9 M^{-1} s^{-1})[15] suggests that hydrogen atoms formed by photolysis of PH_3 should effect the decomposition of another molecule of PH_3. The quantum yield for PH_3 loss could then be greater than 1 and will have a limiting value of 2. Since the value of 0.5 reported for Φ_{PH_3} by Melville[2] appeared to be inconsistent with the mechanistic conclusions of this study, we decided to determine Φ_{PH_3} from the quantum yields for the formation of H_2, P_4, and P_2H_4. A difficulty with these quantum yield measurements is the attenuation of the incident light by the photochemically formed phosphorus which means a correction factor must be determined to calculate the amount of light absorbed by the PH_3 (Q_{PH_3}) from the light incident on the cell. Melville measured the cell transmittance before and after irradiation and used an average value of the transmittance as a measure of the decreased light intensity.[2] This calculation is based on the erroneous assumption that the P_4 transmittance decreases linearly with time. Actually the rate of photolysis decreases exponentially as the P_4 layer increases. Consequently Melville overestimated the value of Q_{PH_3}, and the quantum yield he calculated was too low. In the present study a series of measurements of the light absorbed by the NH_3 actinometer (Q_{NH_3}) and the transmission of the phosphorus layer (T_{P_4}) were made at different exposure times. A plot of T_{P_4} vs. Q_{NH_3} permitted the calculation of Q_{PH_3} from $\sum_i T_{P_4} Q^i_{NH_3}$ at equal intervals on the Q_{NH_3} axis; $Q^i_{NH_3}$ is a constant and $T^i_{P_4}$ is the average value of T_{P_4} in the ith interval. A plot of quanta of light absorbed by PH_3 (Q_{PH_3}) vs. Q_{NH_3} is obtained from which Q_{PH_3} can be obtained for any value of Q_{NH_3}. The procedure must be repeated at each pressure of PH_3 investigated. The values of the quantum yields for the loss of PH_3 and the formation of H_2, P_2H_4, and $4P_4$ vs. Q_{PH_3} are listed in Table V.

Extrapolation of the data in Table V to zero reaction time provides insight into the mechanism of the reaction at the initial stage of the reaction. The quantum yields at zero reaction time are Φ_{PH_3} (PH_3 loss) $= 1.78 \pm 0.18$, $\Phi_{H_2} = 0.43 \pm 0.23$, $\Phi_{P_2H_4} = 0.80 \pm 0.08$, and $\Phi_{4P_4} = 0.04 \pm 0.16$. The significance of reaction 3 in the decomposition of PH_3 is shown by the quantum yield for PH_3 loss (1.78) which is close to 2 at zero reaction time. The quantum yield for P_2H_4 formation (0.80) which is close to 1 also reflects the importance of reaction 3 in forming PH_2 in addition to its formation in the initial photochemical step (reaction 2). The one surprising observation is the low value of Φ_{H_2} (0.43) since values closer to 1 would be expected due to the formation of H_2 by the reaction of H with PH_3 (reaction 3).

The complexity of the reaction mechanism at longer reaction times is reflected in the decrease in the quantum yield for PH_3 loss (Table V). The value for Φ_{PH_3} decreases to 0.8 after 5 h. This decrease from 1.78 may reflect the competing reaction of $PH_2\cdot$ with other photoproducts such as P_2H_4 to regenerate PH_3.

If Melville's method of the average P_4 transmittance is used to correct for the buildup of the P_4 layer during the course of the reaction,[2] the calculated quantum yield for PH_3 loss is 0.5 after 10-h irradiation. This significantly lower value of Φ_{PH_3} underlines the differences in the methods used to correct for P_4 transmittance. An extent of irradiation comparable to ours is indicated by Melville's calculations of 0.5 for Φ_{PH_3}, and this exposure time may account for his failure to detect P_2H_4 since the concentration is half the maximum value.

Our findings require substantial modification of the previous mechanism of PH_3 photolysis: (1) Values of Φ_{PH_3} greater than unity at short exposure time indicate that hydrogen abstraction by hydrogen atoms from PH_3 (reaction 3) is an important reaction and (2) Φ_{4P_4} of 0.04 ± 0.16 compared to $\Phi_{P_2H_4}$ of 0.80 ± 0.08 at zero reaction time indicates that combination of PH_2 radicals (reaction 9) is much more important than disproportionation (reaction 3).

The mechanism of the conversion of P_2H_4 to P_4 was not investigated in detail in the present study, but plausible reaction pathways can be suggested by analogy with the reactions known for the photolysis of NH_3 to N_2 via N_2H_4.[3,22,25,26] Hydrogen abstraction from P_2H_4 by PH_2 (eq 11) and H (eq 10) would

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$$P_2H_4 + H \rightarrow P_2H_3 + H_2 \quad (10)$$

$$P_2H_4 + PH_2 \rightarrow P_2H_3 + PH_3 \quad (11)$$

$$2P_2H_3 \rightarrow P_2H_2 + P_2H_4 \quad (12)$$

$$P_2H_3 + PH_2 \rightarrow P_2H_2 + PH_3 \quad (13)$$

$$2P_2H_3 \rightarrow P_4H_6 \quad (14)$$

$$P_4H_6 \rightarrow 2PH_3 + P_2 \quad (15)$$

$$P_2H_2 \rightarrow P_2 + H_2 \quad (16)$$

generate P_2H_3 which is converted to P_2 via P_2H_2 (eq 12, 13, and 16) or P_4H_6 (eq 14 and 15). The final conversion of P_2 to P_4 (eq 6) is a well-established reaction.[1] This mechanism is still incomplete since it does not explain the maximum in the P_2H_4 yield shown in Figure 2.

None of the reactions proposed for P_4 formation account for the observation of PH by flash photolysis.[13] It is possible that the PH observed is formed by the low level of PH_2 disproportionation indicated in Figure 3. Alternatively the PH may be formed by photochemical processes (e.g., P_2H_2 photolysis) in the flash photolysis studies which are not observed in the continuous illumination experiments where a lower intensity light source is used.

These studies indicate that P_2H_4 would be expected to be a minor constituent of the atmosphere of the Jovian planets since it is formed efficiently in the gas phase ($\Phi_{P_2H_4} = 0.8$) by PH_3 photolysis. Most of it may be converted to P_4; however there should be a steady-state concentration sufficient to be detected either by ground-based IR measurements[7] or during the Galileo orbiter and probe of the Jovian atmosphere. The recent report of the effect of acetylene on PH_3 photolysis[27] suggests that the other constituents of the Jovian atmosphere may have a significant effect on its photochemistry. The photolysis of PH_3–NH_3 mixtures under the conditions where they absorb light on Jupiter (150 K (760 torr)) especially merit investigation because NH_3 and PH_3 are probably present in the same regions of the Jovian atmosphere,[9] both compounds absorb in the same spectral range and their photolyses proceed by similar reaction pathways. It has already been suggested that NH_3 photolysis may accelerate the decomposition of PH_3 on Jupiter.[16] The present studies indicate that PH_2NH_2[28] may be formed by the combination of the photochemically formed PH_2 and NH_2. Further decomposition of PH_2NH_2 to phosphorus paranitride $(PN)_x$ may also take place. Phosphorus paranitride, a reddish brown polymer,[29] may also be responsible for some of the coloration in the atmosphere of Jupiter.

Experimental Section

General Data. IR spectra were determined on a Perkin-Elmer 621 spectrophotometer and UV spectra on a Unicam SP 800A or a Cary 219 spectrophotometer. H_2 analysis was performed by gas chromatography on an Aerograph A-700 gas chromatograph (thermal conductivity detector) using a 6-ft molecular sieve 5A column operating at 100 °C using argon as the carrier gas. PH_3 was removed before injecting the H_2 into the gas chromatograph. Diphosphine was analyzed by gas chromatography on a Varian 2400 flame ionization gas chromatograph equipped with a phosphorus-nitrogen detector using a 6-ft OV-1 column operating at 30 °C using nitrogen as the carrier gas. P_4 was analyzed by oxidation by 1 or 5 mL of concentrated HNO_3 at 150 °C for 7 h (1 mL of acid for 0.5-1-h irradiation, 5 mL for longer times).[20] An additional 5 or 15 mL of 5 M HNO_3 was added, and heating was continued for 2 h at 140 °C. The solutions were transferred to 25- or 100-mL volumetric flasks, the cells were rinsed with double-distilled water, and the pH of the combined solutions was adjusted to 7 ± 2 by using NH_4OH. A 15-mL aliquot of this solution was mixed with 10 mL of sodium molybdate solution (7.6 g of $Na_2MoO_4 \cdot 2H_2O$ in 100 mL of concentrated HCl diluted to 500 mL with water) in a separatory funnel. The solution was shaken twice with 10 mL of 4:1 $CHCl_3$–*n*-butyl alcohol for 1 min. The combined organic extracts were diluted to 25 mL, and the absorbance was measured at 310 nm. A reagent blank was performed in exactly the same way on an empty cell. The estimated error is ±5%. Pressure measurements were performed by using an oil manometer containing dibutyl phthalate or with an MKS Baratron Type 77 pressure meter. No mercury was used in the vacuum system.

Irradiation Experiments. Most photolysis were performed at room temperature by using an iodine discharge lamp.[17,30] The wavelengths less than 206.2 nm were filtered with 1 cm of distilled water. In a few initial experiments a low-pressure mercury lamp was used.[31] Samples were irradiated in 10 × 2.8 cm cylindrical quartz cells of volume 67.5-75 mL. Quantum yield measurements were performed by using a merry-go-round apparatus using cells containing 100 torr of ammonia as an actinometer ($\Phi = 0.31$).[32]

Materials. PH_3 (Matheson electronic, 99.999%) was purified by three distillations from an ether slush bath at −116 °C. Ammonia (Matheson, anhydrous 99.999%) and SF_6 (Matheson, instrument purity 99.999%) were subjected to freeze–pump–thaw cycles, to remove noncondensable gases, before use. Hydrogen (Ultra High Purity 99.999%) was obtained from Matheson and used without further purification.

Photochemical Synthesis of P_2H_4. PH_3 (87 torr) was photolyzed with the low-pressure mercury lamp for 15 min at which time the UV absorption at 270 nm due to P_2H_4 reached a maximum, the P_2H_4 was separated by condensation at −116 °C, and the entire process was repeated 20 additional times. The IR and UV spectra of the material condensing at −116 °C were identical with that of an authentic sample of P_2H_4.[18] The photoproduct and authentic materials exhibited the same retention time (2.2 min) by gas chromatography. A peak with the retention time of PH_3 (1.2 min) was also present in both the authentic and photochemically synthesized P_2H_4. It persisted even after extensive purification of the authentic P_2H_4 and probably results from decomposition of the P_2H_4 in the gas chromatography. No other products were detected in the photolysate. P_2H_4 was analyzed spectrophotometrically (Figure 1) by its absorbance at 235 nm (ϵ 2.74 M^{-1} cm^{-1}) or 250 nm (ϵ 304 M^{-1} cm^{-1}) after correcting for the absorbance of P_4. The estimated error in P_2H_4 analysis is ±10%.

Irradiation of PH_3 at Different Time Intervals. PH_3 (87 torr) was irradiated with the iodine lamp (206 nm) at room temperature for different time intervals. The results are given in Table I and plotted in Figure 2. The ratio of the rate constants for the disproportionation to combination for $PH_2(k_4/k_9)$ were calculated by considering reactions 4–6 and 9.

$$d(P_2H_4)/dt = k_9(PH_2)^2$$

$$d(P_4)/dt = k_6(P_2)^2$$

Assuming

$$\frac{d(P_2)}{dt} = 0 = k_5(PH)^2 - 2k_6(P_2)^2$$

$$(P_2)^2 = k_5((PH)^2/2k_6)$$

$$d(PH)/dt = 0 = k_4(PH_2)^2 - 2k_5(PH)^2$$

$$(PH)^2 = k_4(PH_2)^2/2k_5$$

$$d(P_4)/dt = k_6(P_2)^2 = k_6\frac{k_5}{2k_6}\,\frac{k_4}{2k_5}(PH_2)^2 = \frac{k_4}{4}(PH_2)^2$$

$$\lim_{t\to 0}\frac{d(P_4)/dt}{d(P_2H_4)/dt} = \lim_{t\to 0}\frac{n_{P_4}}{n_{P_2H_4}} = \frac{k_4}{4k_9}$$

Effect of Pressure on PH_3 Photolysis. The effect of variation in PH_3 pressure on the yields of P_2H_4 and P_4 is given in Table II. The photolyses were performed at room temperature by using a 206-nm light source. Similar experiments performed on N_2 and SF_6 as the added gas are given in Table III.

Flash Photolysis of PH_3. The flash photolysis studies were performed by Professor R. Strong[33] on a sample containing about 1 torr of PH_3 and 200 torr of H_2. The variation in transmittance with time was measured at single wavelengths at both 100 and 500 μs/cm. A long-lived species was formed which absorbed in the 225–280-nm region. An aerosol of P_4 formed after about 10 ms. The normalized absorption spectrum given in Figure 4 was determined from the absorbances measured at various wavelengths 300 μs after the flash, which were corrected for the variation

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in the intensity of the flash lamps by dividing by the absorbance of the sample at 235 nm measured on the Cary 219 1 h after the flash, the 1-h interval allowing the aerosol of P_4 to settle. The results are given in Table IV.

It was possible to estimate the pseudo-second-order rate constant for the combination of PH_2 to P_2H_4 (reaction 9) from the rate of formation of P_2H_4. With the assumption that the only reaction PH_2 is recombination of P_2H_4, then at time t

$$(PH_2)_t = 2[(P_2H_4)_\infty - (P_2H_4)_t]$$

For a second-order reaction

$$\frac{1}{(PH_2)_t} - \frac{1}{(PH_2)_{t_0}} = 2k_9(t - t_0)$$

$$(P_2H_4)_t = \frac{A_{t,\lambda}}{\epsilon_\lambda 10}$$

$$(PH_2)_t = \frac{A_{\infty,\lambda} - A_{t,\lambda}}{5\epsilon_\lambda}$$

where $A_{t,\lambda}$ = absorbance of P_2H_4 at λ and time t and ϵ_λ = exctinction coefficient of P_2H_4 at λ.

A plot of $1/(PH_2)_t - 1/(PH_2)_{t_0}$ vs. $t - t_0$ gave a straight line with slope of $2k$. The rate constants were evaluated at 225, 232.5, 235, and 245 nm. The plots were strongly dependent on the A_∞ values which were difficult to measure accurately. A value of $(5.4 \pm 2.4) \times 10^9$ M^{-1} s^{-1} was calculated from the rate constants determined at the above wavelengths.

Quantum Yields. Quantum yields were determined from the product yields and the quanta absorbed on the basis of NH_3 actinometry. The quantum yields for zero time of irradiation were determined from least-squares analyses[34] of quantum yields plotted against time of irradiation (Table V). A value of $\Phi_{PH_3} = 1.65 \pm 0.26$ was calculated by using all the data. If the results in Table V at 5.67 einsteins are omitted, then $\Phi_{PH_3} = 1.78 \pm 0.18$. Values of Φ_{4P_4} of 0.013 ± 0.15 and 0.041 ± 0.156 were calculated from the data with and without the result at 5.67 einsteins, respectively. Initial quantum yield for H_2 is 0.43 ± 0.23 and for P_2H_4 is 0.80 ± 0.08.

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The Molecular Structure of the Cubanelike Compound, $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$, and a Description of Its Bonding

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Abstract: The tetramer, $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 24.179$ (5) Å, $b = 14.413$ (3) Å, $c = 12.590$ (3) Å, $\alpha = 75.78$ (1)°, $\beta = 59.65$ (1)°, and $\gamma = 58.35$ (1)° at −170 °C. The structure was solved by using 5893 unique reflections having $F > 2.33\sigma(F)$. Full-matrix, least-squares refinement converged to final residuals of $R_F = 0.085$ and $R_{wF} = 0.070$. The symmetry of the elongated $[MoN(\mu_3\text{-}S)]_4$ moiety is adequately described by the D_{2d} point group. Two Mo–Mo bonds are present. Both Mo–N bond distances and Mo–N–C(aryl) bond angles point to triple-bond character in this linkage. A molecular orbital treatment accounts for the binding of the ligands to the core including four Mo≡N bonds, the metal–metal bonds, and the observed diamagnetism. The molecular orbital treatment is also able to account for the formation of a tetramer when $[MoO(\mu\text{-}S)(S_2CNEt_2)]_2$ is reduced electrochemically.

Cubane-like Fe_4S_4 clusters have become increasingly well-known in recent years.[1] Even more recently, double cubane-like molecules containing two $MoFe_3S_4$ clusters have been obtained and structurally characterized.[2] The isolation of a tetramer of Mo(V), which we have suggested[3] to be $[Mo(N(tol))(\mu_3\text{-}S)(S_2P(OEt)_2)]_4$ (tol = $p\text{-}CH_3C_6H_4$) with a cubane-like Mo_4S_4 cluster, is one of the more unusual results from our recent studies of arylimido complexes of molybdenum.[4] Since we made that suggestion, the structure of another tetrameric Mo(V) complex with an authenticated cubane-like Mo_4O_4 cluster, $[MoO(\mu_3\text{-}O)(\mu\text{-}O_2PMe_2)_{1/2}(\mu\text{-}OSPMe_2)_{1/2}]_4$, has also appeared[5] and lends further credence to our original suggestion.

This paper reports the structural characterization of our tetramer and shows that the suggested structure is correct. Moreover, this paper examines the bonding within the tetramer and also accounts in a reasonable fashion for the formation of a tetramer, proposed to be $[MoO(\mu_3\text{-}O)(S_2CNEt_2)]_4^-$, after the reduction of $[MoO(\mu\text{-}O)(S_2CNEt_2)]_2$.[6]

Experimental Section

Crystals of $[Mo(N(tol))(\mu_3\text{-}S)(S_2P(OEt)_2)]_4$ from the original preparation were employed in this structural study. Unit-cell dimensions and

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