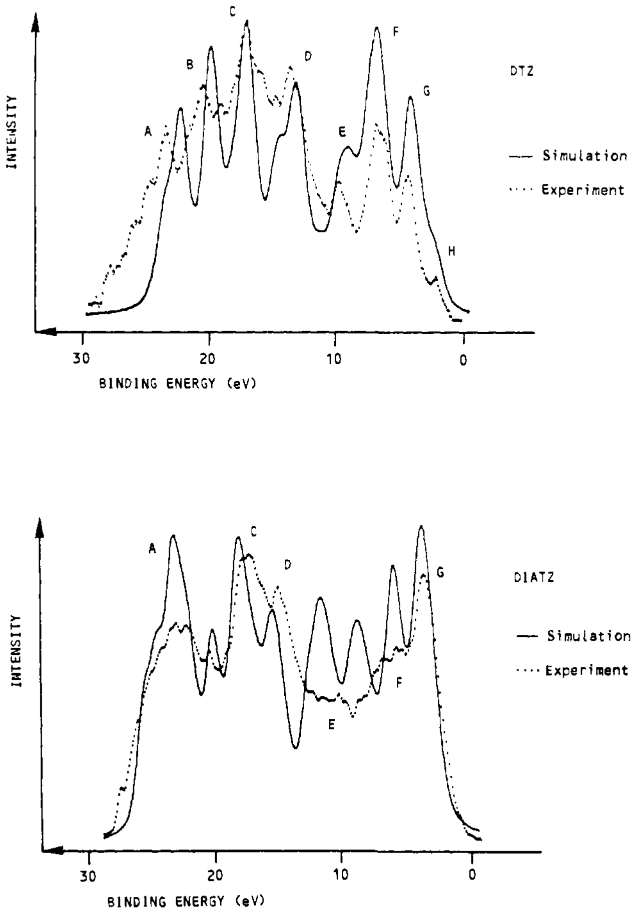

Figure 6. Experimental and simulated valence-band spectra of DTZ and DIATZ.

C1s and S2p lines and their absence in the neighborhood of the N1s core level, combined with the rather low amplitude (at 3.7 eV) of the transition, may suggest that the transition has its origin in the HOMO, which exhibits significant electron densities on the S_1 and C_3 atoms. The broadness of the satellite line at 290.3 eV is probably due to the simultaneous existence of the well-known[18] $\pi \rightarrow \pi^*$ shake-up of the phenyl rings occuring in the same energy range, i.e., at 5.9 eV from the main C1s line.

The N1s level is also followed by a satellite at 403.0 eV, 4.3 eV higher in binding energy than the main peak. From the MO diagram in Figure 2, this shake-up process could originate from the π $2a_{1u}$ level. The absence of such a feature in the vicinity of the C1s and S2p peaks agrees with the electron density map of this π orbital.

In the case of DIATZ we only observe structure at 5.8 eV after the S_{2p} peak, but the impurities detected in the spectrum do not allow the assignment of this feature to a shake-up transition involving an MO of DIATZ.

Concluding Remarks

The electronic structure of diphenyl- and bis(dimethylamino)dithiatetrazocines as revealed by XPS and ab initio results shed some light on the origin of the conformational differences exhibited by two closely related compounds. The dithiatetrazocine heterocycle alone obeys the $4n + 2$ Hückel rule and per se should be planar. Strong electron donor groups increase the electron density on the $S_2N_4C_2$ framework, thereby inducing structural stresses and a destabilization of the heterocycle. As a consequence, the geometry of the whole molecule changes by developing a bonding interaction between the ring sulfurs, in order to lower the total energy at the price of a loss in the aromatic character.

Participation of the S3d orbitals must be discussed with caution. It is indeed difficult to estimate their involvement in the regulation of the structures. In each compound, they induce a significant reduction of the S–N bond polarity. They seem, however, to play a minor role in the shape of the occupied molecular orbitals. Their somewhat more pronounced participation in the unoccupied MO's suggests a more active contribution in properties related to excited states.

Registry No. DTZ, 76843-75-9; DIATZ, 76843-76-0.

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Mechanism of Phosphine Photolysis. Application to Jovian Atmospheric Photochemistry

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Abstract: PH_3 is photolyzed to H_2 and P_2H_4 and the P_2H_4 in turn is converted to red phosphorus. The initial quantum yield of H_2 formation was redetermined and found to be 0.93 ± 0.07. Red phosphorus was identified by its chemical properties and by the absence of P–H stretching bands in its infrared spectrum. The reaction pathway was not changed by lowering the PH_3 partial pressure from 90 to 11 torr or by performing the photolysis in a 70-fold excess of H_2. The initial quantum yields at 11 torr of PH_3 are $\Phi_{P_2H_4} = 0.40 \pm 0.02$ and $\Phi_{H_2} = 0.74 \pm 0.08$. The initial rate of P_2H_4 formation was not affected by lowering the PH_3 temperature to 227 or 157 K. The yield was greater at 157 K because the P_2H_4 condensed and was protected from further destruction. The initial quantum yields for the formation of P_2H_4 and H_2 in PH_3–NH_3 mixtures were comparable to those observed for PH_3 alone. Photolysis of mixtures in which NH_3 was absorbing 90% of the light resulted in the rapid formation of P_2H_4. No N_2 was formed when PH_3–NH_3 mixtures were photolyzed, suggesting that the destruction of NH_3 is quenched by PH_3. The application of these findings to Jovian atmospheric chemistry is discussed.

Our initial studies on the mechanism of phosphine (PH_3) photolysis with a 206.2-nm light established that diphosphine (P_2H_4) was the initial stable photoproduct and intermediate in the formation of red phosphorus.[1,2] Comparable findings for 147-nm light sources were reported subsequently.[3,4] It has been proposed that the color of the Great Red Spot on Jupiter is due

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Table I. Photolysis of PH_3 at 298 K[a]

	90 torr of PH_3			11 torr of PH_3			26 torr of PH_3		
time, h	P_2H_4, mol × 10^7	H_2, mol × 10^7	P_n, OD at 206 nm	P_2H_4, mol × 10^7	H_2, mol × 10^7	P_n, OD at 206 nm	P_2H_4, mol × 10^7	H_2, mol × 10^7	P_n, OD at 206 nm
0.05				0.43		0			
0.1				0.84		0.005	1.3		0.02
0.12	2.0		0.02						
0.15	2.4		0.03				1.8		0.03
0.2	3.4		0.05	1.5		0.01	2.3		0.04
0.25	3.5		0.06	1.7	2.2	0.02			
0.3							3.1		0.05
0.5	4.3	5.0	0.12	2.6		0.06			
1	5.6	11	0.24	3.2	9.2	0.16			
2	6.1	14	0.47	2.7	19	0.33			
4	5.6	21	0.77	1.7	22	0.59			
6	4.7	26	0.87						
9.5				0.7	36	0.93			
10	2.9	31	1.14						

[a] Experiments were performed by using a merry-go-round with an iodine lamp with a photon flux of (2.0–3.2) × 10^{14} photons s^{-1}.

Table II. Photolysis of PH_3 in the Presence of H_2 and Ar at Room Temperature[a]

PH_3, torr	H_2, torr	P_2H_4, mol × 10^7	P_n, OD at 206 nm
88.5	0	5.5	0.21
88.5	100	5.8	0.24
88.5	302	5.3	0.21
88.5	649	6.1	0.20
89.8	197	5.4	0.21
89.8	404	6.0	0.22
89.8	654	5.2	0.22
10.9	0	3.5	0.17
10.9	302	3.8	0.13
10.9	702	3.6	0.12
10.8	713	3.2	0.12
11.2[b]	0	0.9	0.008
11.2[b]	64 (Ar)	0.9	0.009
11.2[c]	0	1.5	0.013
11.2[c]	64 (Ar)	1.5	0.013

[a] 1 h of irradiation time with an average photon flux of (2.0 ± 0.5) × 10^{14} photons s^{-1} at 89 torr and (2.5 ± 1) × 10^{14} photons s^{-1} at 11 torr. [b] 5 min of irradiation time with a photon flux of 3.4 × 10^{14} photons s^{-1}. [c] 10 min of irradiation time with a photon flux of 3.4 × 10^{14} photons s^{-1}.

to the photolysis of PH_3, which is being rapidly transported to the stratosphere from below the layers of NH_3 clouds.[5] We undertook an investigation of PH_3 photochemistry to provide an experimental basis for postulates concerning its role in Jovian atmospheric chemistry.[6] In this paper we report the photolysis of PH_3 in the presence of H_2 and NH_3 and at temperatures down to 157 K, conditions comparable to those at the cloud tops of Jupiter where PH_3 photolysis occurs.

The structure of red phosphorus has been improperly represented as P_4 in previous papers by ourselves[1,2] and others[5,7] concerned with its postulated role as a chromophore in the atmosphere of Jupiter. It was noted that red phosphorus really has an ill-defined structure[8] and not the repeating tetrahedral units present in the white allotrope of phosphorus.[9] Therefore we refer to the red allotrope as P_n in this paper.

Results and Discussion

Photolysis of PH_3 Alone. The initial values for the quantum yields for the formation of P_2H_4 [$\Phi_{P_2H_4}$] (0.92 ± 0.17) and H_2 [Φ_{H_2}] (0.93 ± 0.07) with 90 torr of PH_3 and a 206.2-nm source were redetermined in the course of the present study. The value for $\Phi_{P_2H_4}$ is comparable with that reported previously[1,2] while the value of Φ_{H_2} of 0.93 ± 0.07 is greater than our previously reported value of 0.42 ± 0.23. An improved sampling procedure in the gas chromatographic analyses of the H_2 formed by PH_3 photolysis (Table I) resulted in a more accurate determination of the H_2 quantum yield. The value of approximately 1 for Φ_{H_2} and $\Phi_{P_2H_4}$ is consistent with eq 1–3 (Scheme I) proposed for the mechanism of the photolysis of PH_3 to P_2H_4. These values of the initial quantum yields establish that the radical recombination reactions 4–6 make little or no contribution to the initial photochemical processes. Φ_{H_2} is constant for irradiation times of up to 10 h, indicating that the reaction of hydrogen atoms with PH_3 (eq 2) or other phosphorus hydrides predominates over their recombination to molecular hydrogen (eq 4–6).

Scheme I

$$PH_3 \xrightarrow{h\nu} PH_2 + H \tag{1}$$

$$PH_3 + H \rightarrow PH_2 + H_2 \tag{2}$$

$$PH_2 + PH_2 \xrightarrow{M} P_2H_4 \tag{3}$$

$$H + H \xrightarrow{\text{wall}} H_2 \tag{4}$$

$$H + H \xrightarrow{M} H_2 \tag{5}$$

$$PH_2 + H \xrightarrow{M} PH_3 \tag{6}$$

$$P_2H_4 + H \rightarrow P_2H_3 + H_2 \tag{7}$$

$$NH_3 \xrightarrow{h\nu} NH_2 + H \tag{8}$$

$$PH_3 + NH_2 \rightarrow PH_2 + NH_3 \tag{9}$$

$$NH_2 + H \xrightarrow{M} NH_3 \tag{10}$$

$$2NH_2 \xrightarrow{M} N_2H_4 \tag{11}$$

$$PH_2 + NH_2 \xrightarrow{M} PH_2NH_2 \tag{12}$$

Previous analyses of the solid deposit formed on the window of the photolysis cell indicated that it consisted principally of phosphorus but did not eliminate the possibility of the presence of P–H linkages. The infrared spectrum of the solid precipitate did not exhibit absorption in the 2457–2270-cm^{-1} range characteristic of the P–H stretching frequency,[10] a finding consistent

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with the conclusion that red phosphorus was formed. It has been suggested from the material balance that photolysis of PH_3 at 147 nm gives a product that contains P–H linkages.[3] The absence of a P–H stretching frequency in the solid formed at 206.2 nm suggests that the presence of P–H bonds in the product formed at 147 nm should be investigated further.

The photolysis of PH_3 was studied at 11, 26, and 90 torr to determine if PH_3 pressure affected the course of the photolysis. Light absorption at 206.2 nm is essentially complete (>96%) in a 10-cm cell at 11 torr. Qualitatively the time course for P_2H_4 formation and destruction was the same for 90 and 11 torr of PH_3 (Table I).[1,2] The initial quantum yield for P_2H_4 formation at 11 torr PH_3 is 0.40 ± 0.02, a value that is about half that observed at 90 torr (0.92 ± 0.17). The initial quantum yields were evaluated by determining the quantum yields at different times, in particular at shorter times within the limitation of our experimental setup, and then extrapolation to zero time. Least-squares fit of the data to a straight line was obtained in all cases. The straight line extrapolated to near the origin (0,0) even though the origin was not included in the least-squares plot. It is concluded that the differences obesred in $\Phi_{P_2H_4}$ at 90 and 11 torr are real and are not due to secondary reactions involving P_2H_4 decomposition because the plots of P_2H_4 yield vs. photon flux were linear for 0.2 h of irradiation time.

The quantum yield for P_2H_4 formation was measured with 26 torr PH_3 to determine if there was an abrupt change in the photochemistry between 11 and 90 torr. The quantum yield at 26 torr is 0.49 ± 0.03, a value between that observed at 11 and 90 torr. This suggests there are only gradual changes in the reaction pathway as the pressure is varied between 11 and 90 torr.

The initial quantum yield for H_2 formation was only slightly lower at 11 (0.74 ± 0.08) than at 90 torr of PH_3 (0.93 ± 0.07). The value of Φ_{H_2} was constant for up to 10 h of irradiation time with both 11 and 90 torr of PH_3.

The lower values of $\Phi_{P_2H_4}$ at 11 torr of PH_3 are not due to the lower total pressure since no effect was observed when up to 700 torr of H_2 or 64 torr of Ar was added (Table II). Initially, we concluded that the lower $\Phi_{P_2H_4}$ was due to an increase in the relative rates of the recombination reactions 4 and 6 (M = wall) as is observed when NH_3 is photolyzed at pressures less than 100 torr.[14] But the competing reaction of hydrogen atoms with PH_3 (eq 2) is about 10^4 times faster than their diffusion to the cell wall where they can recombine (eq 4).

The lower value of $\Phi_{P_2H_4}$ must be due to its slower rate of formation (eq 3). The steady-state concentration of PH_2 is lower at 11 torr because a 10-cm path length is required to absorb the 206.2-nm light. At 90 torr the light is completely absorbed in the first few millimeters so the effective PH_2 concentration is much greater and reaction 3 proceeds at a faster rate than at 11 torr, where the gradient of PH_2 radicals extends the length of the cell. This explanation is also consistent with the small variation in Φ_{H_2} that was observed. The main process by which H_2 is formed is given in eq 2. Even though the effective concentration of H is also lower at 11 torr because of the extended zone of photolysis, the concentration of PH_3 is only decreased 8-fold so that the product $[H][PH_3]$ is much greater than $[PH_2]^2$. Consequently, there is a much greater effect of PH_3 pressure on $\Phi_{P_2H_4}$ (eq 3) than on Φ_{H_2} (eq 2).

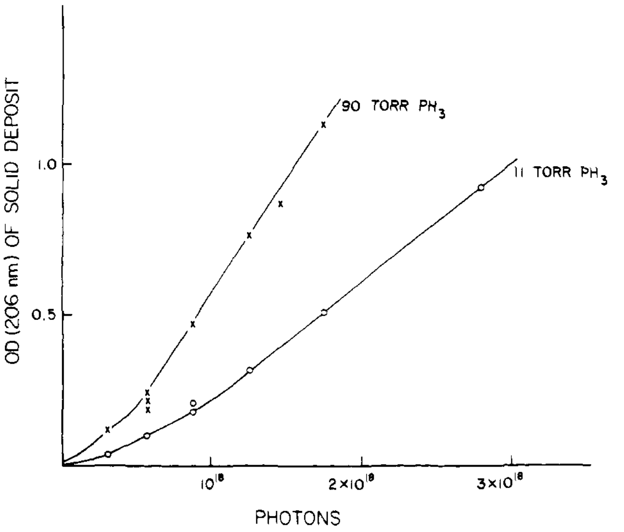

Figure 1. Formation of red phosphorus at different PH_3 pressures.

The deposition of red phosphorus on the cell as a function of the photon flux was determined from the decrease in light transmission and is given in Figure 1. There is an induction period at both 90 and 11 torr due to the formation of intermediates such as P_2H_4 before P_n is formed. The slower decrease in the transmission when the 11-torr sample is photolyzed is mainly due to the deposition of P_n on the sides of the cells as well as the cell window because, as noted above, the reaction zone extends the length of the cell at 11 torr.

PH_3 Photolysis in the Presence of Hydrogen. Although no major change in the reaction mechanism was observed when the PH_3 pressure was changed 8-fold, PH_3 photolysis was performed in the presence of varying amounts of H_2 since this permitted even greater changes in total pressure of the system, while keeping the PH_3 pressure constant. The large partial pressure of hydrogen was used to model Jovian atmospheric conditions, where hydrogen is the principal component.[11] If the observed reaction pathway is due to the presence of hot hydrogen atoms, then these should be thermalized by the high partial pressure of hydrogen present.

No effect was observed on the amount of P_2H_4 formed when either 90 or 11 torr of PH_3 was photolyzed in the presence of increasing amounts of hydrogen up to 700 torr (Table II). This result is consistent with previous studies where we observed no effect on the rate of P_2H_4 formation by the addition of N_2 or SF_6 to the PH_3 being photolyzed.[2] The H_2:PH_3 ratio was varied incrementally from 0 to 70. Although it was impossible to attain the H_2:PH_3 ratio of 10^7 observed on Jupiter, the absence of a significant effect with ratios ranging from 0 to 70 indicates it is highly unlikely that the course of PH_3 photolysis will be changed on further dilution of the PH_3 with hydrogen.

The absence of a hot-atom effect on the course of the reaction is consistent with the central role of reaction 2 in PH_3 photochemistry. The large magnitude of the rate constant for reaction 2 (3.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K)[12] indicates the rate is close to the diffusion-controlled limit, and there will be only a small increase in $\Phi_{P_2H_4}$ if thermalized hydrogen atoms are replaced by hot hydrogen atoms. Other reactions of hydrogen atoms do not compete effectively with reaction 2. For example, the second-order rate constant for reaction 5 is 2×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 300 K and 760 torr of H_2,[13] a value that is about 0.05 times the rate constant for reaction 2. Since the PH_3:H ratio is approximately 10^6, then the rate of reaction 2 will be about 2×10^7 times greater than the rate of reaction 5 in the presence of 1 atm of hydrogen.

Effect of Temperature on PH_3 Photolysis. Since the photolysis of PH_3 on Jupiter proceeds in the stratosphere, where the temperature ranges from 110 to 160 K,[6] we investigated PH_3 photochemistry at temperatures of 227 and 157 K for comparison with our previous studies at 298 K. The amount of P_2H_4 present at different irradiation times was identical at 298 and 227 K over the total photolysis time while almost three times as much was present when the photolysis was performed at 157 K (Table III, Figure 2). Since the initial quantum yields of P_2H_4 formation were identical at the three temperatures, the increased amounts of P_2H_4 present at 157 K cannot be due to an increased rate of

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Table III. Photolysis of PH_3 at Different Temperatures[a]

	297 K		227 K		157 K	
time, min	P_2H_4, mol × 10^7	P_n, OD at 206 nm	P_2H_4, mol × 10^7	P_n, OD at 206 nm	P_2H_4, mol × 10^7	P_n, OD at 206 nm
1	2.6	0.06			2.4	0.08
1	3.1	0.08			2.6	0.06
2	6.0	0.16			5.5	0.16
2	5.0	0.14				
5	6.7	0.47	7.4	0.41	9.1	0.36
5	6.5	0.43	6.4	0.31	8.3	0.41
5	6.0	0.29				
15	5.9	0.84	6.9	1.0	17.2	0.81
15	6.7	0.92			13.0	0.79

[a] PH_3 pressure 88.3-90.5 torr. Direct irradiation with an average photon flux of $(5.4 \pm 1.0) \times 10^{15}$ photons s^{-1}.

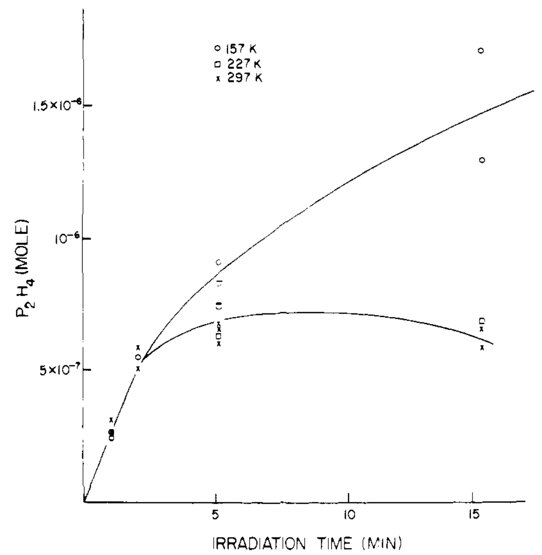

Figure 2. Formation of P_2H_4 from PH_3 at different temperatures.

formation at this lower temperature. The enhanced yield must reflect the condensation of P_2H_4 at 157 K. Its melting point is 174 K[15] and therefore it should have a very low vapor pressure at 157 K. The P_2H_4 is protected from hydrogen abstraction reactions when it is condensed on the cell wall and consequently its concentration is greater (on warming the photolysis cell to room temperature for analysis) at longer irradiation times even though its rate of formation is the same.

The absence of a temperature effect in the photolysis of PH_3 to P_2H_4 is consistent with the proposed reaction pathway. The rate of formation of P_2H_4 is decreased only slightly at lower temperatures because the activation energies for reactions 2 and 3 are low. The chemical processes leading to phosphorus formation are also dominated by hydrogen abstraction from P_2H_4 and other phosphorus hydrides. The activation energies for these processes should also be low so the principal effect of lower temperatures on P_n formation will be due to the condensation of these intermediates from the gas phase.

Table IV. Photolysis of PH_3-NH_3 Mixtures at 100-torr Total Pressure[a]

PH_3, %	irrad time, h	P_2H_4, mol × 10^7	H_2, mol × 10^7	P_n, OD at 206 nm
1	1	0.9	7.8	0.27
1	1	1.0	8.2	0.30
1	2.5	1.2	14.5	0.62
1[b]	2.5	1.3		0.53
1[b]	2.5	1.3		0.55
1[b]	10	0.8		1.08
5	1	2.6		0.29
5[b]	2.5	2.9		0.52
5[b]	5	3.0		0.68
5[b]	10	2.1		0.92
10	1	3.8	9.3	0.24
10	1	3.7		0.20
10	2.5	4.4		0.55
10	2.5	4.2	18	0.58
10[b]	2.5	4.1		0.62
10	5	3.9	25	0.67
10[b]	5	4.5		0.69
10[b]	10	3.3		1.02
50	1	7.1	13	0.24
50	1	6.2		0.23
50	2.5	8.1		0.63
50	2.5	8.7	21	0.60
50[b]	2.5	8.0		0.58
50	5	7.3	26	0.79
50[b]	5	7.7		0.86
50[b]	10	6.0		1.12
100[b]	1	6.1		0.27
100	2.5	7.1	19	0.63
100[b]	2.5	5.9		0.63
100	5	4.8		0.97
100[b]	10	2.5		1.36

[a] Photolyses at room temperature with a photon flux of $(1.9\text{-}2.6) \times 10^{14}$ photons s^{-1}. [b] Less than 10^{-8} mol of N_2 formed; 2.9×10^{-7} to 1.36×10^{-6} mol detected when 100 torr of NH_3 was irradiated under the same conditions.

Table V. Photolysis of PH_3-NH_3 Mixtures at 11-torr Total Pressure[a]

PH_3, %	H_2, torr	irrad time, h	P_2H_4, mol × 10^7	H_2, mol × 10^7	P_n, OD at 206 nm
10	0	0.5	0.79	5.4	0.05
10	0	0.5	0.80	3.9	0.04
10	0	1	0.79	6.6	0.07
10	0	1	0.79	6.8	0.09
10[b]	0	2	0.74		0.18
10	0	4	0.46	19	0.26
10[b]	0	9.5	0.39		0.45
10	300	1	1.0		0.15
10	300	1	0.93		0.13
10	700	1	0.88		0.20
10	700	1	0.92		0.11
50	0	0.5	2.3	5.9	0.07
50	0	0.5	2.0	5.0	0.06
50	0	1	2.6	7.3	0.10
50	0	1	2.8	8.1	0.13
50[b]	0	2	2.8		0.31
50	0	2	2.6	13	0.28
50	0	4	2.6		0.38
50	0	4	2.9	22	0.50
50[b]	0	9.5	2.0		0.67
100	0	1	2.9	6.7	0.11

[a] Photolysis at room temperature with a photon flux of $(2.1\text{-}3.0) \times 10^{14}$ photons s^{-1}. [b] Less than 2×10^{-8} mol of N_2 formed.

Photolysis of PH_3-NH_3 Mixtures. The photolysis of PH_3-NH_3 mixtures was investigated because there is about 200 times as much NH_3 as PH_3 present in the atmosphere of Jupiter.[11,16] Since these gases have almost identical absorption wavelengths and absorption coefficients at those wavelengths,[17,18] it has been suggested that the extent of their photolysis on Jupiter depends on the proportion of light absorbed by each.[5] In another theoretical consideration of this problem it was concluded that the rapid rate of reaction of NH_2 with PH_3 (eq 9)[19,20] is of greater significance

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Table VI. Initial Quantum Yields for P_2H_4 and H_2 Formation in PH_3-NH_3 Mixtures[a]

PH_3, %	total pressure, torr	$\Phi_{P_2H_4}$	Φ_{H_2}
1	100	0.18	0.80
5	100	0.40	
10	100	0.57	0.90
50	100	0.85	1.1
100	100	0.87	1.0
10	11	0.2	0.54
50	11	0.4	0.66
100	11	0.5	0.75

[a] The absolute error in each measurement is about ±30% and the relative error is about ±10% on the basis of the observed variation in the lamp flux.

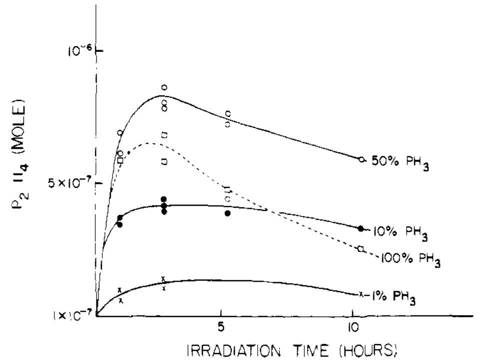

Figure 3. Formation of P_2H_4 from PH_3-NH_3 mixtures at a total pressure of 100 torr.

to the photochemical processes than the NH_3:PH_3 ratio.[21] Our experimental study was undertaken to determine if there was coupling in the NH_3 and PH_3 photoprocesses when a mixture of these gases was irradiated.[6,21]

In our initial studies mixtures of PH_3 and NH_3 were irradiated in which the total pressure was 100 torr (Table IV). The quantum yields in Table IV are based on the total light absorption by both NH_3 and PH_3 because of the rapid reaction of NH_2 and H, the initial photoproducts of NH_3, with PH_3. The formation of P_2H_4 was monitored by the increase in absorption at 235 nm.[2] The possibility that this absorption is also due to the formation of PH_2NH_2 and N_2H_4 is eliminated in arguments to be discussed later. The initial quantum yields for P_2H_4 formation from pure PH_3 and a 1:1 PH_3-NH_3 mixture are identical (Table VI). The invariance of $\Phi_{P_2H_4}$ reflects the reaction of the NH_3 photoproducts with PH_3 (eq 2 and 9). Consequently, even though about 50% of the light is absorbed by NH_3 in a 1:1 PH_3-NH_3 mixture because the absorption coefficients of NH_3 and PH_3 are comparable, the final results is the same as if PH_3 were absorbing all the light because of the efficiency of reactions 2 and 9.[19]

The lower values of $\Phi_{P_2H_4}$ (Table VI), when PH_3:NH_3 ratios are 1:99, 1:19, or 1:9, reflect the effect of the lower partial pressures of PH_3 in these mixtures. The initial quantum yields for P_2H_4 formation are directly proportional to the PH_3 partial pressure (compare the $\Phi_{P_2H_4}$ values in Table VI for 100 torr of NH_3-PH_3 with 1, 5, and 10% PH_3 with those for 11 torr of NH_3-PH_3 with 10, 50, and 100% PH_3, respectively). The reactions are independent of the NH_3 partial pressure because of the very efficient reaction of PH_3 with the NH_2 and H formed by NH_3 photolysis.

Irradiation of PH_3-NH_3 mixtures for an extended period of time gives a greater steady-state concentration of P_2H_4 than irradiation of PH_3 alone (Figure 3). Less red phosphorus is formed from the PH_3-NH_3 mixtures when irradiation times greater than 2.5 h are used (Figure 4). These results indicate a slower conversion of P_2H_4 to P_n in the presence of NH_3. It is not clear why the P_2H_4 should be more stable in the presence of NH_3 since the same H-abstraction processes that result in the conversion of PH_3 to P_2H_4 should also be operative in the conversion of P_2H_4 to P_n.

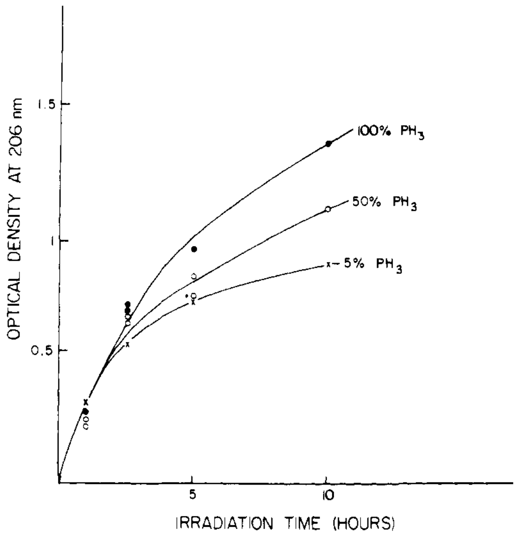

Figure 4. Formation of red phosphorus from PH_3-NH_3 mixtures at a total pressure of 100 torr. The induction period of P_n formation (Figure 1) is apparent from the corresponding plot of P_n vs. photon flux.

The formation of N_2H_4 in the PH_3-NH_3 mixtures could account for both the decreased yield of P_n and an apparent increase in the yield of P_2H_4. N_2H_4 absorbs at 235 nm[22] and it would not be distinguishable from P_2H_4 by UV analysis. However, N_2H_4 formation is unlikely because N_2 could not be detected as a reaction product. N_2 is formed readily by the reaction of N_2H_4 with H-abstracting radicals.[23] The limit of detection of N_2 was 10^{-8} mol, yet none was detected when PH_3-NH_3 mixtures containing 1, 5, 10, and 50% PH_3 were irradiated for 10 h. The photolysis of pure NH_3 for comparable time periods yields 30×10^{-8} mol of N_2.

We conclude from the absence of N_2 formation that the reaction of NH_2 with PH_3 is a dominant factor in the photolysis of PH_3-NH_3 mixtures, but there are smaller and yet-unexplained other factors due to the proportion of NH_3 in the mixture which affect the amount of P_2H_4 formed on prolonged irradiation. The initial formation of P_2H_4 by irradiation of PH_3-NH_3 mixtures may be explained by the reaction sequence in Scheme II. This reaction scheme is consistent with the observation of an initial quantum yield of H_2 formation that was close to 1 with pure PH_3 or 1:99 PH_3:NH_3 (Table VI). The quantum yield for H_2 formation from 100 torr of NH_3 is 0.3 so the 1% PH_3 markedly enhances the rate of H_2 formation. This result provides additional confirmation of the ease of hydrogen abstraction from PH_3 and other phosphorus hydrides.

Scheme II

$$PH_3 \xrightarrow{h\nu} PH_2 + H \quad (1)$$

$$NH_3 \xrightarrow{h\nu} NH_2 + H \quad (8)$$

$$PH_3 + H \rightarrow PH_2 + H_2 \quad (2)$$

$$PH_3 + NH_2 \rightarrow PH_2 + NH_3 \quad (9)$$

$$PH_2 + PH_2 \xrightarrow{M} P_2H_4 \quad (3)$$

The preponderance of P_2H_4 and the absence of N_2H_4 are consistent with the rate constants for the reactions in Scheme II. The steady-state concentrations of NH_2, H, and PH_2 may be

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approximated from the following expressions derived from the reactions given in Scheme II.

$$[\mathrm{H}] = \frac{I_a\Phi_{\mathrm{PH_3}} + I_a\Phi_{\mathrm{NH_3}}}{k_2[\mathrm{PH_3}]}$$

$$[\mathrm{NH_2}] = \frac{I_a\Phi_{\mathrm{NH_3}}}{k_9[\mathrm{PH_3}]}$$

$$[\mathrm{PH_2}] = \left(\frac{I_a\Phi_{\mathrm{PH_3}} + I_a\Phi_{\mathrm{NH_3}}}{k_3}\right)^{1/2}$$

Assuming a mixture of 1 torr of PH_3 and 99 torr of NH_3 ($[PH_3] = 3.5 \times 10^{16}$ molecules cm^{-3}), a lamp flux (I_a) of 2.3×10^{14} photons s^{-1}, a cell volume of 70 cm^3, quantum yields for the dissociation of NH_3 and PH_3 of 1, and the rate constants (molecules^{-1} cm^3 s^{-1}) $k_2 = 3.8 \times 10^{-12}$,[12] $k_3 = 9.0 \times 10^{-12}$,[2] and $k_9 = 5.7 \times 10^{-14}$,[24] the following approximate values can be calculated (molecules cm^{-3}): $[H] = 2.5 \times 10^7$, $[NH_2] = 1.7 \times 10^9$, and $[PH_2] = 6 \times 10^{11}$.

It is apparent from these calculations why P_2H_4 would be expected to predominate as a reaction product over PH_2NH_2 and N_2H_4 when PH_3–NH_3 mixtures are irradiated. The rate constants for the formation of these molecules should be comparable and therefore the relative amounts of P_2H_4, PH_2NH_2, and NH_2NH_2 produced should be proportional to the product of the concentrations of each of the radical species from which they are formed.[2] From the values of $[NH_2]$ and $[PH_2]$ it can be shown that the ratio of P_2H_4:PH_2NH_2:N_2H_4 should decrease in the order 18×10^4:360:1. From this we conclude that there may be very small amounts of PH_2NH_2 formed but the amount of NH_2NH_2 present should be negligible.

The photolysis of PH_3–NH_3 mixtures was performed at 11-torr total pressure to detect pressure effects on the reaction pathway. The same trends in P_2H_4, H_2, and P_n formation were observed in these mixtures as were observed when 90 and 11 torr of pure PH_3 were irradiated (Table V). The initial values of $\Phi_{P_2H_4}$ and Φ_{H_2} decrease at the lower partial pressure of PH_3 as was observed when the irradiation of pure PH_3 was investigated (Table VI). The time course of the formation of P_2H_4 is comparable with that observed with 100-torr PH_3–NH_3 mixtures. The levels of P_2H_4 are greater in the PH_3–NH_3 mixtures than when 11 torr of PH_3 is irradiated alone for extended time periods. No N_2 was detected among the reaction products, indicating that reaction 9 makes an important contribution to the reaction pathway when NH_3 is present.

The presence of H_2 had no affect on the course of the photolysis of the 11-torr PH_3–NH_3 mixtures. Mixtures of 10% PH_3 in NH_3 were irradiated for 1 h in the presence of 0, 300, and 700 torr of H_2 without affecting $\Phi_{P_2H_4}$. This finding confirms our previous conclusions that the course of PH_3 decomposition proceeds equally as efficiently with thermalized hydrogen atoms or the hot hydrogen atoms, which are the initially formed products of reactions 1 and 8. The findings at 11 torr are completely in accord with the reaction mechanism proposed in Scheme II that was based on our observations at 100 torr.

Application to Jovian Atmospheric Chemistry. Photolyses of PH_3–NH_3 mixtures result in the decomposition of PH_3, regardless of the proportion of light absorbed by each gas. This finding confirms Strobel's postulate[21] that the photochemistry of PH_3 and NH_3 will be coupled when mixtures are irradiated but it does not define the mechanism of the coupling. It is clear that the hydrogen atoms, formed by the photolysis of NH_3, hydrocarbons, and PH_3, will react with PH_3 at the low temperatures present in the Jovian atmosphere as predicted by Strobel.[21] The rate constant for this reaction of hydrogen atoms with PH_3 (eq 2), which was measured in the 209–495 K range, has a value of 3.3×10^{-13} cm^3 molecule^{-1} s^{-1}[12] when extrapolated to 150 K. The competing reaction of hydrogen atoms to give molecular hydrogen (eq 5) has a comparable rate constant of 3.6×10^{-13} cm^3 molecule^{-1} s^{-1} at 150 K and a pressure of 1 atm of hydrogen.[13] Since the mixing ratio of PH_3 is 2×10^{-7}[25] and that of H is 10^{-10}–5×10^{-12},[6] the concentration of PH_3 is at least 10^3 times greater than that of H. Consequently the rate of PH_3 loss by reaction with H will always be at least 10^3 times greater than the quenching of the hydrogen atoms by reaction 5. PH_3 will also be destroyed by reaction with H on Saturn. The PH_3 mixing ratio is 2×10^{-6} on Saturn[26] while the concentration of H must be less than that on Jupiter because the solar flux is less. The higher PH_3 mixing ratio on Saturn reflects a lower steady-state concentration of H there as compared to Jupiter.

Strobel also postulated that the NH_2 radical formed by NH_3 photolysis will initiate the decomposition of PH_3 by hydrogen abstraction (eq 9).[21] Reaction 9 proceeds at room temperature and the formation of N_2H_4 (eq 11) is inhibited. It is not clear that reaction 9 will predominate over reaction 11 in the Jovian atmosphere as shown by the values to be substituted in the expressions

$$r_9 = k_9[\mathrm{NH_2}][\mathrm{PH_3}]$$

$$r_{11} = k_{11}[\mathrm{NH_2}]^2$$

Approximate values of k_9 and k_{11} at 150 K are 3×10^{-15}[27] and 3×10^{-11}[24] cm^3 molecule^{-1} s^{-1} and the estimated mixing ratios of PH_3 and NH_2 on Jupiter are 2×10^{-7}[25] and 10^{-12},[6] respectively. The greater mixing ratio of PH_3 is balanced by the greater magnitude of k_{11}. The calculated rate of reaction 9 is about ten times greater than that of reaction 11, suggesting that reaction 9 is a significant process in the Jovian atmosphere. But the uncertainties in the values used to calculate these rates are at least 1–2 orders of magnitude, so this conclusion must be considered as quite tentative. Low-temperature photolysis studies are currently in progress to determine if PH_2NH_2 and N_2H_4 are formed from PH_3–NH_3 mixtures at 150 K.

It can be concluded that the hydrogen atom initiated decomposition of PH_3, P_2H_4, and other phosphorus hydrides will be an important process in the atmosphere of Jupiter. Since P_2H_4 and these higher hydrides are solids at 150 K, it is likely that the haze observed above the Jovian cloud tops (Axel[28] or Danielson[29] dust) may consist mainly of phosphorus hydrides and red phosphorus rather than N_2H_4 as was proposed originally.

Red phosphorus appears to be the end product of PH_3 photolysis. We conclude that this material can be classified as red phosphorus on the basis of its stability in the presence of oxygen, its insolubility in organic solvents,[9] and the absence of a P–H stretching frequency in its infrared spectrum. The photochemical formation of red phosphorus was questioned because the product was yellow.[30] But it has been noted that the red phosphorus ranges in color from yellow to violet so color is not a characteristic property.[9] The UV–vis absorption spectrum of our photoproduct is almost identical with that reported by Noy et al.,[30] indicating the same photoproduct was formed in these two different experiments.

Red phosphorus formation on Jupiter will be inhibited somewhat because P_2H_4, the intermediate in its formation, condenses to a solid at the atmospheric temperatures above cloud tops. We also observed that the presence of NH_3 decreases the rate of conversion of P_2H_4 to P_n by a yet to be determined process. PH_3 photolysis is unaffected by the presence or absence of hydrogen. The hydrogen that is present in abundance in the atmospheres of Jupiter and Saturn does not react with the intermediates involved in the photolysis of PH_3 to P_n.

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Experimental Section

The experimental procedures were outlined previously.[2] A 206.2-nm iodine lamp[31] was used for the photolyses, and the formation of P_2H_4 was monitored by its increase in UV absorption at 235 nm. The correct value for the extinction coefficient of P_2H_4 at 235 nm is 2174 M^{-1} cm^{-1}, base 10 (205 atm^{-1} cm^{-1}, base *e*), and not the value given in ref 2. The extinction coefficients of PH_3 and NH_3 at 206 nm were found to be 23 and 33 atm^{-1} cm^{-1}, base *e*, respectively. These values are comparable to the extinction coefficients reported previously.[16–18] In general, the error limits for the quantum yields were estimated on the basis of a 20% variation in the lamp flux and a 10% error in the determination of the extent of NH_3 photolysis in the actinometer by gas chromatographic analysis of the H_2 formed. Each quantum yield plot comprised at least six data points. A linear plot was constructed by a least-squares analysis. Correlation coefficients for the slope of each plot exceeded 0.92 in most cases. The relative amounts of P_n formed were determined from the optical density at 206 nm after the gases were removed from the photolysis cell.

An improved procedure was developed for the determination of the amount of H_2 formed by PH_3 photolysis. Both ends of the sample loop for the gas chromatograph were evacuated before the gas mixture was transferred to the loop. Also 100 torr of Ar was added to the H_2 before transfer to the sample loop so that there would be a pressure differential and therefore reproducible transfer of an aliquot of the gas mixture each time.

The sampling procedure of Toupance[32] was used to enhance the sensitivity of the gas chromatographic N_2 analysis. The NH_3 and PH_3 remaining after the photolysis was condensed with liquid N_2, and 70 torr of He was added to the cell. The noncondensible gases were then transferred to an evacuated coil (530 cm^3), which was attached to the sample loop of the gas chromatograph. A 2-L reservoir containing 1 atm of He attached to the other end of the coil was opened, and the gases in the coil were compressed into the sample loop. In control experiments it was determined that 90% of the contents of the photolysis cell was transferred to the sample loop of the gas chromatograph by this procedure.

Photolyses were performed at 227 and 157 K by immersing the cell, except for one window, in a chlorobenzene or ether slush bath, respectively. It was not feasible to use the merry-go-round in these studies so the actinometry was done prior to and after a series of low-temperature photolyses. The deviations in the lamp flux in each series of experiments did not exceed 10%.

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Registry No. Phosphorus, 7723-14-0; phosphine, 7803-51-2.

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Intermetallic Charge-Transfer Spectra of Copper(I)–Metal(III) Centers in Doped Crystals of $CsMgCl_3$

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Abstract: When crystals of $CsMgCl_3$ are co-doped with small concentrations of Cu(I) and Cr(III), Mo(III), Ru(III), or Rh(III), charge-compensation stabilized Cu(I)–M(III) dimers are formed in the linear chain lattice. The absorption spectra of the crystals containing the Cu(I)–M(III) impurity centers exhibit intense, strongly polarized bands that cannot be attributed to electronic excitations localized on either Cu(I) or M(III). These bands are assigned to intermetallic charge-transfer (IT) transitions where an electron from Cu(I) is transferred to M(III). In some cases more than one IT transition is observed. The spectral properties of the Cu(I)–M(III) centers are compared to those of the analogous Li(I)–M(III) centers. A relatively simple theoretical treatment is presented that accounts for many of the features in the IT spectra of the Cu(I)–M(III) centers.

It has been demonstrated in a number of spectroscopic studies that crystals of $CsMX_3$ salts such as $CsMgCl_3$ incorporate a wide variety of trivalent ions in low concentrations as substitutional impurities. These host materials adopt the linear chain $CsNiCl_3$ structure in which the MX_6^{4-} octahedra share opposite faces to form infinite linear chains of the stoichiometry, $[MX_3^-]_n$.[1,2] The cesium ions occupy positions between the chains and balance the anionic charge. Trivalent impurities enter the lattice in a manner that preserves the overall charge balance of the $[MX_3^-]_n$ chains.[3–7] As a result the trivalent impurities cluster as pairs in association with a divalent ion vacancy. This produces linear M(III)–vacancy–M(III) centers which are electrostatically equivalent to three divalent ions. The presence of small monovalent ions provides an alternate mode by which trivalent ions can enter the $[MX_3^-]_n$ chains. A trivalent ion and a monovalent ion enter adjacent divalent sites to give a M(I)–M(III) center that is electrostatically equivalent to two divalent ions. The EPR spectra of crystals doped with chromium(III) indicate that M(I)–Cr(III) centers are formed when lithium, sodium, or copper(I) ions are present.[5,7] In the course of the EPR studies it was noted that crystals of $CsMgCl_3$ and $CsCdBr_3$ containing the Cu(I)–Cr(III) centers exhibited an unusual coloration. This observation prompted an investigation of the electronic spectrum of the Cu(I)–Cr(III) system. At low

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