

Ammoniated Phosphonitrilic Amides, Imides, and Nitrides. I. The Equilibrium $4\text{NH}_3(\text{g}) + 2\text{P}(\text{r}) = 2\text{PN}_2\text{H}(\text{s}) + 5\text{H}_2(\text{g})$

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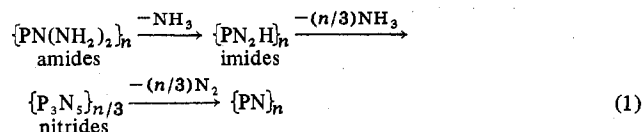
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A novel synthesis of phospham from ammonia and red phosphorus, $4\text{NH}_3(\text{g}) + 2\text{P}(\text{r}) = 2\text{PN}_2\text{H}(\text{s}) + 5\text{H}_2(\text{g})$, was studied over the temperature range 416–555 °C. For the reaction, $\Delta S^\circ = 16.9 \pm 11.3$ eu and $\Delta H^\circ = 9.6 \pm 8.4$ kcal mol⁻¹, and for the formation of phospham at 759 K, $S^\circ = 35.7 \pm 5.7$ eu and $\Delta H_f^\circ = -20.7 \pm 4.2$ kcal mol⁻¹. From thermodynamic considerations and results of initial tests, it appears that phosphonitrilic amides may be prepared at high ammonia pressures by the reaction $n\text{NH}_3(\text{g}) + \{\text{PN}_2\text{H}\}_n(\text{s}) = \{\text{PN}(\text{NH}_2)_2\}_n(\text{s})$.

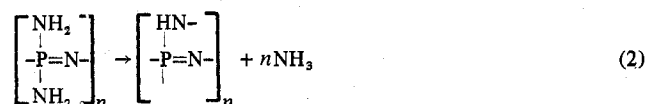
Introduction

Phosphonitrilic amides, imides, and nitrides form a series of solid compounds which are physically and chemically difficult to characterize.¹ All of these compounds are polymeric and their physical and chemical properties vary with variation in the degree of their polymerization.²⁻⁴ These three classes of compounds are closely related through the thermal condensation polymerization processes⁵⁻⁹



Of these materials, the crystalline, water-soluble cyclic hexaamide ($n = 3$) and octaamide ($n = 4$) are the most amenable to investigation¹⁰ and have been prepared and investigated as potential ultra-high-analysis fertilizer sources.¹¹ However, the commercial production of these materials for fertilizer application has generally been considered economically infeasible because of the high cost of the PCl_5 starting material and the involved chemical manipulations required to separate the amides from the by-product NH_4Cl .¹² Higher membered polymeric amides also may exist, but they have not been characterized.⁴

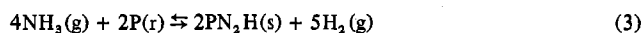
The infusible, highly insoluble phosphonitrilic imides and nitrides show only limited potential as possible fertilizer ingredients.¹² The phosphonitrilic imides are of particular interest, however, because, as seen from eq 1, they are reaction intermediates between the amides and the highly stable nitrides. The amides decompose thermally into the corresponding polymeric imides and ammonia in the reaction



The imide products exist as three-dimensional network polymers. Evidence^{12,13} indicates that the ring systems of the cyclic amides are retained in the resulting polymeric imides so that there should be many distinct imide structures exhibiting various degrees of cross-linking and ring sizes. Because of their chemical stability, their amorphous nature, and their common empirical formula, characterization of the individual imides is difficult. Their infrared spectra show broad, rather nondistinctive bands, the interpretation of which makes structural determinations highly subjective.^{14,15} The individuality of these imides only recently has been recognized, and they are generally lumped together under the common name "phospham" and the empirical formula PN_2H .

During the course of an investigation of the reactions of elemental phosphorus with nitrogen and ammonia, a novel

synthesis of phospham from red phosphorus and ammonia was discovered, i.e.



This reaction, which proceeds to equilibrium, was studied over the temperature range 416–555 °C.

Experimental Section

Materials. The red phosphorus was obtained from Atomic Chemicals Co. (Carle Place, N.Y. 11514), and was reported to be 99.999% pure. It was amorphous to x-rays and was generally in the form of hard, dark red, vitreous lumps. Anhydrous ammonia (Matheson Gas Products, Inc., 99.99% pure) and hydrogen (Air Products and Chemicals, Inc., 99.9% pure) were shown by gas chromatography to be of very high purity and no further purification was attempted.

The gaseous reactants and products were characterized by use of a Lorenc Model 15A gas chromatograph with a thermal conductivity detector and a 1/4-in. × 10-ft stainless steel column packed with 50- to 80-mesh Porapak Q (Waters Associates, Inc.) porous polymer beads. Further characterization was obtained with a Perkin-Elmer Model 521 grating infrared spectrophotometer. The solid reaction products were pressed into KBr wafers for the infrared examinations.

Procedure. Weighed amounts of red phosphorus were placed in fused quartz ampules the volumes of which were about 25 cm³. The amount of unsublimed red phosphorus always exceeded the stoichiometric requirement for eq 3 at the run temperature.¹⁶ Each ampule was evacuated, and measured amounts of ammonia were condensed into the ampule by cooling it with liquid nitrogen. The ampules were sealed, placed in a capped stainless steel tube, and heated in an electric furnace for a predetermined time at the run temperature which was held constant within ± 4 °C.

For runs at temperatures above 500 °C, 24–100 h usually was allowed for attainment of equilibrium, even though inspection of the ampules indicated that the reaction probably was complete within 2–3 h. At temperatures between 500 and 400 °C, 50–870 h was considered sufficient. In one run at 328 °C, equilibrium apparently was not attained in 1200 h, although some reaction had occurred; and no further runs were made at temperatures below 400 °C. Although there was considerable scatter of the equilibrium data, there was no correlation between the calculated equilibrium constants and the length of the runs.

After heating, the ampules were cooled rapidly to room temperature by quenching with water. Along with product, inspection of the ampules showed the presence of clear white phosphorus that had condensed from the vapor phase; the amount of white phosphorus depended upon the sublimation pressure of red phosphorus and hence upon the temperature of the run.

The ampules were placed in a stainless steel tee that was connected to the vacuum system through a metal ball joint. The entire volume of the tee and vacuum system had been determined previously by expansion of measured amounts of ammonia or helium. The ampules were broken with a magnetic iron ball, the unreacted ammonia was condensed in a liquid nitrogen trap, and the pressure of noncondensable gas then was measured to within 0.1 mm with a mercury manometer and corrected for the effect of the liquid nitrogen trap. Gas chromatographic analysis of the noncondensable gas showed it to be only hydrogen, except that traces of nitrogen were observed in the gas from

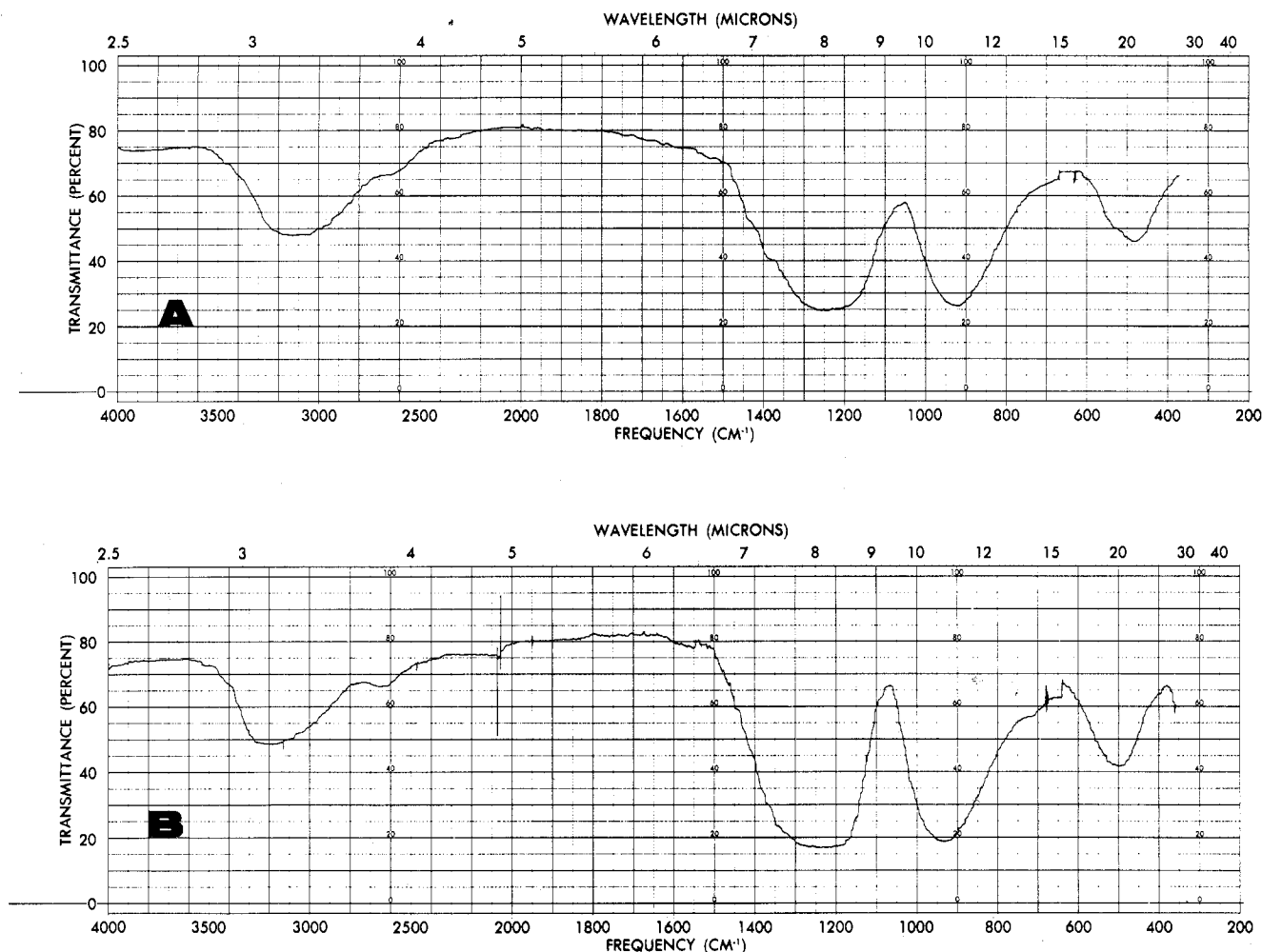


Figure 1. Infrared spectra of phospham prepared from (A) PCl_5 and NH_3 and (B) red phosphorus and NH_3 .

several runs. After the noncondensable gas pressure was measured, this gas was pumped from the system. The liquid nitrogen trap was then removed, the system was allowed to warm to room temperature, and the pressure of the unreacted ammonia then was measured. Gas chromatographic analysis of the condensable gas showed only ammonia, except for several cases in which traces of elemental nitrogen were also detected.

The compositions of both the condensable and noncondensable gases were those predicted by eq 3, and there was no indication of the formation of phosphine which would have been detected chromatographically. The trace amounts of nitrogen in the gas from some runs probably came from the small amounts of air that entered the needle point of the gas syringe during the transfer of the sample from the bulb to the chromatograph. It was concluded that there was no appreciable dissociation of ammonia during these runs, in agreement with the thermal stability of ammonia in the absence of a suitable catalyst.

After determination of the gaseous components, the entire system was evacuated and filled to slightly above atmospheric pressure with helium; and the stainless steel tee was removed and filled immediately with carbon disulfide to dissolve the unreacted white phosphorus. The solids in the tee, which included broken glass in addition to red phosphorus and phospham, were removed and washed several times with carbon disulfide and dried overnight at room temperature. The entire contents of the tee were analyzed for nitrogen by the Kjeldahl procedure.

Product Characterization. Relatively pure phospham was prepared in runs made with a deficiency of red phosphorus so that all unreacted phosphorus was in the vapor phase. The snow white product lumps formed under these conditions were amorphous to x-rays and had the compositions shown in Table I. The absence of a product film on the glass surface of the ampules showed that the reaction was between solid red phosphorus and ammonia and not between phosphorus vapor and ammonia (see Results). The formation of solid phospham under

Table I. Composition of Ammonia-Red Phosphorus Reaction Products

Temp, °C	NH_3 pressure, atm	Compn, %	
		N	P
531	23.3	45.9	51.4
500	36.0	45.6	56.3
500	37.4	42.2	59.1
600	17.1	45.0	52.2
507	21.5	42.1	50.4
		46.69 ^a	51.62 ^a

^a Calculated for PN_2H .

these conditions shows that the reaction between red phosphorus and ammonia was at least as rapid as the sublimation of red phosphorus under the run conditions. The fact that the phospham did not decompose does not indicate that phosphorus vapor was involved in the equilibrium. In the absence of solid red phosphorus, the only mode of decomposition of phospham is reaction 4, which Moureu and



Rocquet⁷ showed to be very slow.

Infrared spectra of phosphams prepared from PCl_5 and NH_3 ⁶ and from red phosphorus and NH_3 are shown in Figure 1. These spectra are practically identical with that reported by Steger.¹⁴

Reversibility. The reversibility of the reaction of eq 3 was demonstrated by the reaction of hydrogen with a mixture of phospham and red phosphorus (runs 8 and 13, Table III). The ammonia that was formed was identified by both gas chromatography and infrared spectroscopy; no phosphine was detected. When mixtures of phospham and red phosphorus were heated in the absence of hydrogen, only trace amounts of ammonia were formed.

Table II. Reaction of Red Phosphorus with Ammonia

Run no.	Ampule vol, cm ³	Charge, mmol		Temp, °C	Time, h	Products, mmol				
		Red P	NH ₃			NH ₃		N in solid	H ₂	
						Found	Consumed		Found	Calcd ^a
9	24.27	21.999	8.235	455	128	4.364	3.871	3.717	4.177	4.850
14	24.85	41.217	8.320	463	72	5.737	2.583	2.437	2.871	3.229
18	24.11	14.598	1.957	481	72	1.262	0.695	0.662	0.772	0.869
19	24.32	9.733	2.649	481	72	1.594	1.055	1.039	1.247	1.319
20	23.95	11.911	4.129	481	72	2.129	2.000	1.903	2.176	2.500
25	23.62	44.724	4.203	515	86	2.002	2.201	2.046	2.333	2.751
27	24.75	47.058	4.192	536	73	2.036	2.156	1.934	2.363	2.695
28	25.60	49.891	2.205	555	24	1.039	1.166	1.059	1.235	1.458

^a Calculated from NH₃ consumed, as determined by pressure measurements.

Results

At temperatures above 500 °C equilibrium was established quite rapidly, within several hours, whereas at temperatures below about 410 °C more than 1 month was required. The product was in the form of lumps of approximately the same shape as the initial lumps of red phosphorus and was reddish brown to grayish white, depending upon the excess amount of red phosphorus. There was no indication of a film of product on the walls of the ampules, and it was concluded that the reaction was between solid red phosphorus and ammonia rather than between phosphorus vapor and ammonia. This result is in agreement with those of other investigators who found that phosphorus vapor does not react with ammonia below red heat.^{17,18}

Results of typical runs are shown in Table II. The agreement between the amount of NH₃ that reacted and the amount of nitrogen that appeared in the solid product is good, considering that the ammonia was determined by pressure measurement and the nitrogen by chemical analysis of the solids. The slight discrepancy of nitrogen, usually about 6% low, in the solid probably can be attributed to loss of material during the washing with carbon disulfide. The measured amounts of hydrogen were about 12% less than predicted by eq 3. Measurement of hydrogen in a vacuum system is difficult because of its tendency to adsorb on the solid products and glass walls of the system and to adsorb in stopcock grease. These effects probably account for the low amounts of hydrogen found, since the possibility that hydrogen was lost by formation of phosphine was not supported by either infrared or gas chromatographic examination.

Since there were discrepancies between the measured and predicted amounts of nitrogen in the product and the amounts of hydrogen liberated, the equilibrium data were evaluated in terms of the ammonia that reacted as determined by pressure measurements and the calculated amounts of hydrogen that were predicted from eq 3. The equilibrium pressures at the reaction temperatures were calculated from the volumes of the ampules and the ideal gas law.

The equilibrium data for reaction 3 are shown in Table III. The equilibrium constants, K_P , were calculated from the equation

$$K_P = P_{H_2}^5 / P_{NH_3}^4 \quad (5)$$

where P_{H_2} and P_{NH_3} are the equilibrium partial pressures (in atmospheres) of hydrogen and ammonia, respectively. In view of the considerable scatter of the equilibrium constants, attempts were also made to treat the data in terms of ideal solid solution behavior; i.e., the equilibrium constants calculated by eq 5 were multiplied by the mole fraction ratio $X_{PN_2H}^2 / X_{P(t)}^2$. However, this procedure resulted in equilibrium constants which varied by several orders of magnitude. Also, the fact that pure phospham could be prepared with a deficiency of red phosphorus (Product Characterization section) suggests

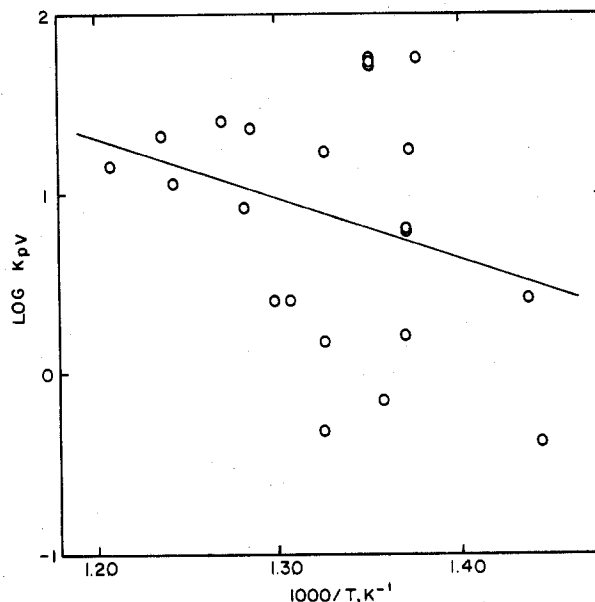


Figure 2. Equilibrium constants for the reaction $4NH_3(g) + 2P(t)_V \rightleftharpoons 2PN_2H(s) + 5H_2(g)$.

that the solid phases act independently of each other and that solid solution behavior should not occur.

The equilibrium constants were corrected to correspond to the equilibrium with respect to red phosphorus, form V, the accepted reference state for phosphorus below 700 K.¹⁹ The correction was made by the equation

$$\log K_{P,V} = \log K_P + [2T(S^\circ - S^\circ_V) + 2(\Delta H^\circ_V - \Delta H^\circ)] / 2.303RT \quad (6)$$

where S°_V , S° , ΔH°_V , and ΔH° are the absolute entropies and heats of formation of red phosphorus, form V, and of the microcrystalline and crystalline forms of red phosphorus^{16,20,21} that were stable at the temperatures of the runs—form II at 416–467 °C and form IV at 481–555 °C.¹⁶

The data were evaluated in terms of the van't Hoff relation

$$\log K_{P,V} = (-\Delta H_r^\circ / 2.303RT) + (\Delta S_r^\circ / 2.303R) \quad (7)$$

where ΔH_r° and ΔS_r° are the enthalpy and entropy of reaction. A plot of the data in terms of eq 7 is shown in Figure 2. Least-squares analysis of these results gives $\Delta H_r^\circ = 9.6 \pm 8.4$ kcal mol⁻¹ and $\Delta S_r^\circ = 16.9 \pm 11.3$ eu. The heat of formation, $\Delta H_f^\circ_{759}$, and absolute entropy, S°_{759} , of PN₂H(s) at the median of the experimental absolute temperature range, 759 K, were calculated from the thermodynamic parameters for hydrogen, ammonia, and form V red phosphorus:¹⁹ $\Delta H_f^\circ_{759} = -20.7 \pm 4.2$ kcal mol⁻¹; $S^\circ_{759} = 35.7 \pm 5.7$ eu. These values should be taken as the average molar values per

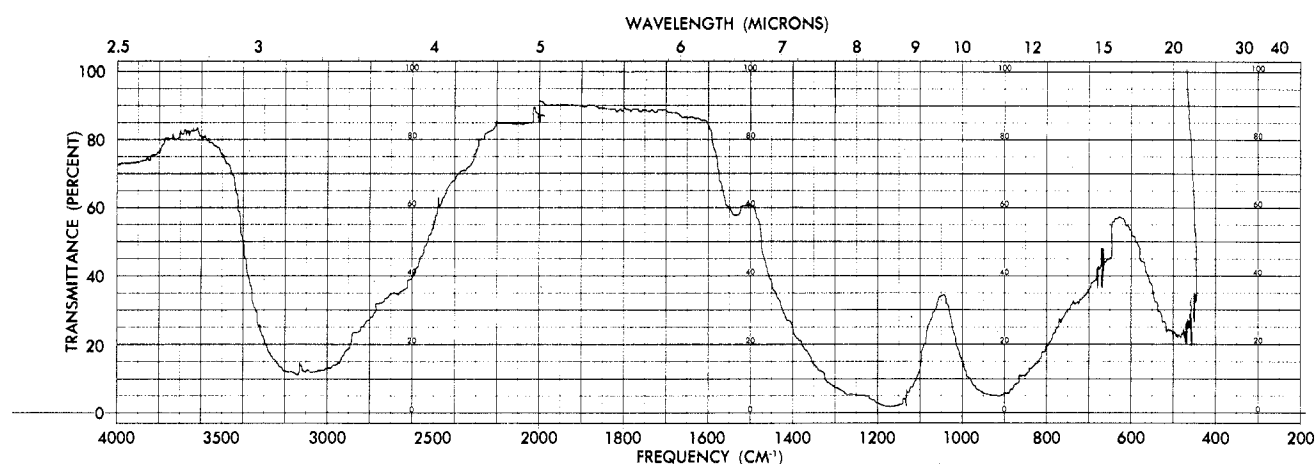


Figure 3. Infrared spectrum of the product of reaction of phospham with ammonia at 440 °C.

Table III. Equilibrium Data for the Reaction $4\text{NH}_3(\text{g}) + 2\text{P}(\text{r}) = 2\text{PN}_2\text{H}(\text{s}) + 5\text{H}_2(\text{g})$

Run no.	Temp, °C	Time, h	Pressure, atm		log K_P	log $K_{P,V}$
			H_2	NH_3		
1	416.0	864	6.01	4.78	1.177	1.086
2	416.0	864	3.96	6.32	-0.212	-0.303
3 ^a	416.0	864	5.01	5.52	0.533	0.511
4 ^a	416.0	864	6.30	4.34	1.446	1.424
5 ^a	416.0	864	5.51	3.78	1.398	1.376
6	418.5	648	6.94	13.18	-0.274	-0.361
7	422.0	312	4.86	5.36	0.518	0.435
8 ^b	453.2	264	3.24	1.54	1.803	1.760
9	455.0	128	11.89	10.74	1.292	1.251
10	456.5	240	6.04	5.76	0.864	0.825
11	456.5	240	4.42	5.52	0.259	0.220
12	456.5	240	5.90	5.58	0.866	0.827
13 ^{b,c}	459.2	112	2.64	0.89	2.306	2.270
14	463.0	72	7.85	13.94	-0.103	-0.134
15	467.0	240	7.30	4.33	1.770	1.744
16	467.0	240	7.68	4.62	1.768	1.742
17	467.0	240	7.70	4.52	1.807	1.781
18	481.2	72	2.23	3.24	-0.302	-0.315
19	481.2	72	3.36	4.05	0.198	0.185
20	481.2	72	6.46	5.50	1.090	1.077
21	491.2	96	3.77	4.11	0.426	0.414
22	496.5	50	10.21	14.28	0.426	0.414
23	505.2	144	6.71	4.86	1.387	1.376
24	507.2	47	6.64	6.19	0.944	0.933
25	515.2	86	7.53	5.48	1.429	1.418
26	531.5	91	12.84	13.07	1.078	1.068
27	535.7	73	7.23	5.46	1.346	1.337
28	555.0	24	3.87	2.76	1.177	1.168

^a Heated at 500 °C for 24 h; temperature then reduced to 416 °C for 864 h. ^b Initial reagents H_2 , PN_2H , and red P. ^c Time was considered insufficient for attainment of equilibrium.

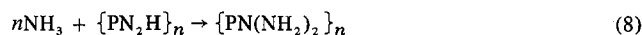
PN_2H unit within the amorphous solid, since the nature and distribution of the imide polymers formed from red phosphorus and ammonia have not been determined.

Discussion

The calculated value of the entropy, S°_{759} , appears to be reasonable for solid amorphous polymers of this type.²² The low exothermic value for the heat of formation of phospham suggests that phospham may react with ammonia under high pressure to form phosphonitrilic amides as in the reverse of eq 2. Recent Russian differential thermal analysis data²³ show that the thermal decomposition of phosphonitrilic hexaamide, eq 2, is endothermic, so that from the value for the heat of formation of PN_2H determined in this study and the known heat of formation of ammonia, it may be calculated that $\Delta H_f^\circ(\{\text{PN}(\text{NH}_2)_2\}_3) < -100 \text{ kcal mol}^{-1}$, and the formation of phosphonitrilic hexaamide from phospham and ammonia is energetically favorable. The driving force for the thermal

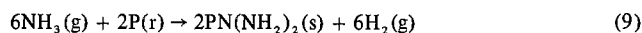
decomposition of phosphonitrilic hexaamide, eq 2, must therefore arise from the entropy increase associated with the change from the crystalline amide to the amorphous phospham.

Results of exploratory tests support the possibility that phosphonitrilic amides may be synthesized from phospham and ammonia. An infrared spectrum of phospham that was heated under 9 atm of ammonia at 440 °C for 14 days is shown in Figure 3. The small band at 1545 cm^{-1} corresponds to $-\text{NH}_2$ bending vibrations²³ and indicates that phospham had reacted with ammonia partially to form phosphonitrilic amides according to the reaction



The partially ammoniated product undoubtedly exists as a three-dimensional network polymer. Much higher pressures of ammonia probably are required to drive eq 8 far to the right.

Addition of eq 3 and 8 gives the overall reaction



This combination of reactions thus may be the basis of a practicable route to phosphonitrilic amides from elemental phosphorus and ammonia.

Although the phosphams prepared during this study were made from red phosphorus and ammonia, there is no apparent reason that the reaction could not be effected between liquid phosphorus and ammonia under such conditions where liquid white phosphorus is converted rapidly to red phosphorus, say, at temperatures of about 500 °C and pressures above 20 atm. Study of the reaction of eq 8 is being continued.²⁴

Registry No. PN_2H , 33849-97-7; NH_3 , 7664-41-7; P, 7723-14-0; $\{\text{PN}(\text{NH}_2)_2\}_3$, 13597-92-7.

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- (22) The entropy of PN_2H may be estimated to be $S_{759} = 36.5$ eu from the expression $s = \frac{3}{2}R \ln A + C$, where s is the entropy contribution of each atomic species in the solid and A is the atomic weight; the constant C is first evaluated with polymeric amorphous red phosphorus¹⁶ as the reference solid: W. M. Latimer, *J. Am. Chem. Soc.*, **43**, 818 (1921).
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- (24) Experimental results confirm the equilibrium of eq 8. This equilibrium is easily established from the amide side of the reaction. However, the reaction of ammonia with phospham generally proceeds only to a slight extent and ceases long before equilibrium is established. Recent results indicate that small quantities of ammonium chloride may be an effective catalyst for promoting reaction 8. These results will be discussed in a subsequent publication.

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Microwave Spectrum, Structure, and Dipole Moment of 1,6-Dicarbanonaborane(9)

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The microwave spectra of six isotopic species of 1,6- $\text{C}_2\text{B}_7\text{H}_9$ have been assigned. This compound is the largest carborane whose structure has been determined by microwave rotational spectroscopy. The bond distances are $\text{B}_8\text{-B}_9 = 1.712$ Å, $\text{B}_5\text{-B}_9 = 1.995$ Å, $\text{B}_3\text{-B}_4 = 1.976$ Å, $\text{B}_7\text{-B}_9 = 1.784$ Å, and $\text{B}_2\text{-B}_3 = 1.805$ Å. The most interesting results of this study are correlations of the B-B bond lengths with the simple inductive rule. A molecular dipole moment of 2.14 ± 0.17 D was determined from the Stark effect.

Introduction

The molecular structures of small carboranes, 2,4- $\text{C}_2\text{B}_5\text{H}_7$,^{1,2} 1,2- $\text{C}_2\text{B}_4\text{H}_6$,³ CB_5H_9 ,⁴ 2-Cl-1,6- $\text{C}_2\text{B}_4\text{H}_6$,⁵ 2,3,4,5- $\text{C}_4\text{B}_2\text{H}_6$,⁶ CB_5H_7 ,⁷ have been determined in this laboratory by microwave rotational spectroscopy, whereas the molecular structures of large carboranes have been determined by x-ray diffraction. Recently we have extended our efforts of structural determinations to a few intermediate carboranes. These carboranes are interesting because both the microwave and x-ray methods which are equally applicable can be compared. These findings are useful to correlate structural parameters between small and large carboranes.

During our studies of intermediate carboranes, two compounds appeared to have rotational spectra amenable to microwave analysis. One of these compounds, 1,6-dicarbaoctaborane(8), 1,6- $\text{C}_2\text{B}_6\text{H}_8$, is reported elsewhere.⁸ Our results of the structural determination of 1,6-dicarbanonaborane(9), 1,6- $\text{C}_2\text{B}_7\text{H}_9$, are reported here. To the best of our knowledge, this is the largest molecule where structure has been determined by microwave rotational spectroscopy.

The synthesis and reaction of 1,6- $\text{C}_2\text{B}_7\text{H}_9$ were recently reviewed by Dunks and Hawthorne.⁹ Early proton and boron NMR measurements on 1,6- $\text{C}_2\text{B}_7\text{H}_9$ ¹⁰ have shown that it has three types of borons—a five-coordinated apical boron, four six-coordinated equatorial borons bonded to one carbon each, and two six-coordinated borons each bonded to two carbons. The x-ray diffraction study of the C,C-dimethyl derivative¹¹ of this compound has been completed. Since there are two molecules per unit cell and no molecular symmetry imposed by the space group, two independent determinations of all bond distances and angles were obtained. Comparison of these two independent determinations indicates that the equivalent bond length differs by as much as 0.07 Å. These deviations are substantially larger than the typical errors for structural parameters.

Our investigation of the rotational spectra of six isotopic species in the gas phase has permitted an accurate structural determination with standard deviations an order of magnitude better than the x-ray work. Furthermore the molecule is slightly distorted in the solid state. Though the gross agreement between the microwave and x-ray results is within the reported standard deviations of the x-ray work, disagreement exists in the relative magnitudes of the bond lengths $\text{B}_2\text{-B}_3$ and $\text{B}_4\text{-B}_5$.

Experimental Section

The sample of 1,6- $\text{C}_2\text{B}_7\text{H}_9$ used in this work was kindly provided by Professor M. F. Hawthorne at the University of California at Los Angeles. The identity of the sample was confirmed by boron-11 NMR. Though a colorless solid at room temperature, it remained vaporized in the gold-plated Stark cell even when cooled to dry ice temperatures. On the other hand, the sample did condense in an ordinary cooled copper Stark cell.

The spectra were measured between 8 and 40 GHz with a 100-kHz Stark-modulated microwave spectrometer. For the less abundant isotopes, double-resonance experiments aided greatly in the successful assignments. Since these experiments depend upon the existence of an energy level common to two transitions of a particular isotope, the technique was found to be a powerful tool for selecting the transitions belonging to the same isotopic species. Standard microwave search techniques were subsequently employed to assign additional transitions. This double-resonance technique has been previously described.¹²

Spectra

The molecule 1,6- $\text{C}_2\text{B}_7\text{H}_9$ is an oblate top with presumably C_{2v} symmetry. Boron has two naturally occurring isotopes. Boron-11, with spin $\frac{3}{2}$, is 81% abundant, and boron-10, with spin 3, is 19% abundant. Assuming C_{2v} symmetry, the six most abundant isotopic species differing in the number and location of ^{10}B atoms incorporated in the molecule will be in the ratio of 1:1:0.5:0.25:0.25:0.25, where the normal species is included. The observed spectrum was extremely dense and intense. However the a-type transitions $J(K, J) \leftarrow J-1(K, J-1)$ where $K = 0$ or 1 were very strong and were readily assigned