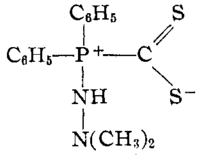
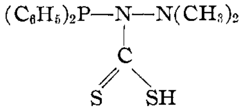
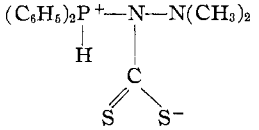
step in the formation of VII by the reaction of carbon disulfide with 2,2-dimethylhydrazinodiphenylphosphine is to form the 1:1 adduct



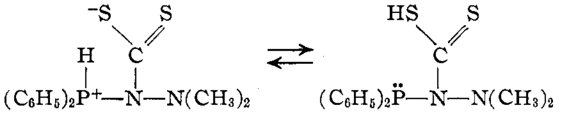
which accounts for the initial red color. The fading of the red color, the disappearance of the NH band in the regions of 1600 or 3400 cm.$^{-1}$ in the infrared spectrum of the white product, the absence of the P–H absorption (*ca.* 2300 cm.$^{-1}$) as well as the appearance of a weak absorption in the S–H region indicate that rearrangement has occurred and give support to the postulated structure



It would, of course, be expected that there would be a tendency for the proton to transfer from the SH group to one of the more basic centers in the molecule, probably the phosphorus, thus giving



This is supported by the presence of a sharp absorption band at 1100 cm.$^{-1}$ in the infrared. All the tetracoördinate phosphorus compounds in this series including the phosphonium salts, phosphine oxides, and phosphine sulfides exhibit this band. The absence of the standard P–H absorption at about 2300 cm.$^{-1}$ argues against this structure; however, the formal charge on the phosphorus may, of course, have greatly shifted this band. The proton magnetic resonance spectrum shows that the molecule contains phenyl and methyl protons in a 10:6 ratio. There is in addition a pair of proton peaks which may be variously interpreted. It is quite reasonable to speculate concerning equilibria involving shifting the proton among the various basic centers on the molecule giving structures which may be partially stabilized by weak hydrogen bonding. One attractive possibility[12] which is in accordance with the present information is



There are, however, other possibilities.

The red color obtained when additional carbon disulfide is added to VII may involve the addition of a second molecule of carbon disulfide to VII (probably through the phosphorus atom) or it may involve only the shifting of the equilibrium back toward the original red species.

Acknowledgments.—Infrared spectra were obtained with the aid of Mr. Leo Pijanowski and Mr. Howard Latz of the University of Florida. Elemental analyses were performed by Mr. Wade Renn of the University of Florida, and Galbraith Microanalytical Laboratories, Knoxville, Tennessee. The assistance afforded by a grant from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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[12] This suggestion by one of the referees is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNSYLVANIA

A Study of the Thermal Decomposition of Calcium Dihydrogen Phosphide[1]

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The thermal decomposition of $Ca(PH_2)_2$, prepared in liquid ammonia, is described for various conditions. Evidence primarily from chemical analysis and X-ray powder diffraction demonstrates that at 600 to 700° the decomposition yields as residue a brick-red crystalline phosphide of formula CaP and that beginning at about 800° the CaP loses phosphorus and is converted to black-violet crystalline Ca_3P_2. The latter compound in turn can be converted to CaP by heating with excess phosphorus at 700°.

Introduction

In connection with a study of the hydrolysis of commercially available "calcium phosphide," we decided to investigate the thermal decomposition of $Ca(PH_2)_2$ as a method of obtaining pure calcium phosphide. Legoux,[2] many years ago, prepared $Ca(PH_2)_2$ in liquid ammonia and reported that gradual heating of the ammoniates to temperatures in the vicinity of 100° produced the over-all decomposition reaction

$$Ca(PH_2)_2{\cdot}xNH_3 \longrightarrow (Ca + P) + PH_3 + {}^1/_2H_2 + xNH_3 \quad (1)$$

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[1] This work was supported in part by Naval Ordnance Laboratory Contract No. N60921s-3346.

[2] C. Legoux, *Ann. chim.*, **17**, 100 (1942); see also W. O. Haas, M.S. Thesis, University of Chicago, 1941.

According to Legoux, his brownish product "(Ca + P)" contained no uncombined calcium or phosphorus and could be heated to 600° with no observable change. He gave no further chemical nor physical characterization of this material but suggested that it might be a mixture of Ca_3P_2 and "CaP_5."

In the present work, the decomposition has been examined under varied conditions and the temperature range has been extended to 1000°.

Discussion

Samples of $Ca(PH_2)_2 \cdot 5NH_3$ were prepared by methods already described.[2] Experiments carried out initially confirmed the results of Legoux in that decomposition by a gradual elevation of the temperature (1 hr. or more at 45 to 100° followed by a similar period at 300°) produced amounts of PH_3 and H_2 which corresponded closely to eq. 1. However, we found that if the sample were heated directly (in a matter of 10 min.) to 300° or above and then held at that temperature for 1 hr. or so, the yield of PH_3 was decreased and that of H_2 increased. Since we were not able in any case to detect a deposit of phosphorus on the walls of the system, we conclude that the increased quantity of H_2 did not result from the thermal decomposition of PH_3 gas. The yields of gaseous products in each experiment were consistent with two simultaneous decompositions

$$Ca(PH_2)_2 \longrightarrow (Ca + P) + PH_3 + {}^1/_2H_2 \qquad (2a)$$

$$Ca(PH_2)_2 \longrightarrow (Ca + 2P) + 2H_2 \qquad (2b)$$

In one experiment, for example, the decomposition of 5.48 mmoles of $Ca(PH_2)_2$ produced 3.05 mmoles of PH_3 and 6.44 mg.-atoms of H_2. For comparison, decomposition of 55.7% of the $Ca(PH_2)_2$ according to eq. 2a and 44.3% according to eq. 2b would have resulted in 3.05 mmoles of PH_3 and 6.39 mg.-atoms of H_2.

The solid residue from the decomposition of $Ca(PH_2)_2$ was generally orange-yellow in color at 300° and dark brown or black at 500°. Upon heating at 600° the residue gradually evolved phosphorus vapor and turned brick-red. The X-ray powder diffraction pattern of a sample of the red product which had been heated for 4 hr. at 600° is given in Table I. Chemical analysis[3] of this material gave a P/Ca ratio of 1.00, indicating the formula CaP.[4]

When the decomposition temperature was carried only to 500°, then the X-ray diffraction pattern of the residue exhibited just two or three weak broad lines corresponding to the most intense lines in the pattern of CaP. From this it is inferred that the 500° material contained only a small percentage of crystalline CaP.

At temperatures above 600° the brick-red CaP began to darken and in the region 800 to 1000° substantial vaporization of phosphorus occurred, leaving a black-violet residue. The formula Ca_3P_2 for this material was supported by chemical analysis, which gave a P/Ca ratio of 0.67. The X-ray diffraction pattern is given in Table I.

Table I

X-Ray Powder Diffraction Patterns of Calcium Phosphides

Residue from 4 hr. at 600°; formula CaP		Residue from 3 hr. at 1000°; formula Ca_3P_2	
d-Spacing	Rel. intensity	*d*-Spacing	Rel. intensity
4.06 ± 0.06	3	3.84 ± 0.05	9
3.26	5	3.20	100
3.02	3	2.84 ± 0.02	17
2.88 ± 0.02	100	2.72	2
2.67	3	2.51	4
2.37	1	2.30	52
2.10 ± 0.01	20	2.21	47
1.98	28	2.06	6
1.77	4	2.02 ± 0.01	3
1.63	12	1.89	2
1.44	3	1.84	5
1.32	5	1.81	12
1.26	4	1.71	11
1.24	4	1.59	11
		1.40	5

Residues obtained from experiments involving intermediate heating treatments gave P/Ca ratios lying between 1.00 and 0.67 and correspondingly their X-ray diffraction patterns were superpositions of the patterns of CaP and Ca_3P_2. In one experiment, a residue whose pattern indicated roughly an equimolar mixture of CaP and Ca_3P_2 was shaken with bromoform (density 2.89 g./ml.). The fraction of the material which floated showed an increase in the CaP content while the more dense material was enriched in Ca_3P_2.

Several attempts were made to obtain single crystal X-ray data on the two calcium phosphides but the efforts in general were unsuccessful. The lack of success probably is attributable to our inability to grow sufficiently large single crystals. The photographs which were obtained suggested tetragonal symmetry for both phosphides.

That Ca_3P_2 can be converted back to CaP was demonstrated by heating a sample of Ca_3P_2 with an excess of red phosphorus for 2 hr. at 700°. The resulting X-ray pattern was identical with that listed for CaP in Table I.

In this investigation of the preparation of calcium phosphide, we examined the products of a number of other reactions. We found, for example, that when CaO reacted with excess red phosphorus at 800°, CaP was formed. Reaction of red phosphorus with CaC_2 at 800°, with CaH_2 at 950°, and with Ca metal at 950° produced in each instance a mixture of CaP and Ca_3P_2.

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(3) The calcium content of the residue was known from the weight of calcium metal used to prepare the $Ca(PH_2)_2$. Phosphorus analyses involved prolonged oxidation treatment to the phosphate, which then was determined by either the "molybdenum blue" colorimetric method or the phosphomolybdate precipitation method.

(4) The diffraction pattern reported here for CaP appears to be the same as that listed in the ASTM X-Ray Powder Data File, Card 3-0682, but attributed, incorrectly we believe, to Ca_3P_2.