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THE REACTION OF ELEMENTAL PHOSPHORUS WITH HF SOLUTIONS*

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SUMMARY

Red phosphorus reacted with HF at 200° under autogenous pressure to form PF_3 and H_2. The conversion to PF_3 increased markedly when an alkali or alkaline earth metal fluoride was present in the reaction. When equivalent amounts of phosphorus and alkali or alkaline earth fluorides were used in an excess of HF under similar conditions, corresponding hexafluorophosphate salts were obtained, along with PF_3 and H_2. The conversion to the hexafluorophosphate salts increased as the size of the cations increased, reaching about 90% for KPF_6 in the alkali metals and about 32% of $Ba(PF_6)_2$ in the alkaline earths.

INTRODUCTION

It is generally known that some non-metals such as chlorine[1] or phosphorus[2] disproportionate in aqueous solution to form compounds of higher and lower oxidation state than that of the initial elements, *i.e.*,

$$Cl_2 + 2OH^- \rightarrow Cl^- + OCl^- + H_2O,$$

$$P_4 + 3OH^- + 3H_2O \xrightarrow{\text{boil}} PH_3 + 3H_2PO_2^-$$

The extent of the disproportionation frequently depends on the basicity of the medium. Phosphorus[2], furthermore, behaves as a metal in the reaction with water at elevated temperature to liberate hydrogen:

$$P_4 + 16H_2O\ (g) \xrightarrow{\text{above } 280^\circ} 10H_2 + 4H_3PO_4$$

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The similarity between water and hydrogen fluoride in their properties prompted us to investigate the possibility of parallel behaviors of such elements using hydrogen fluoride as a solvent. This article describes the study of reactions of phosphorus in hydrogen fluoride and in "basic" hydrogen fluoride solutions containing alkali and alkaline earth fluorides.

EXPERIMENTAL

A 300 ml Monel-lined pressure vessel, equipped with a pressure gauge, was charged with 8.63 g (0.278 mole) of red phosphorus and either less than, or an equivalent amount of a fluoride salt. The vessel was then attached to an all-metal vacuum line, and approximately 38 to 140 g of HF was transferred into it under vacuum. The reactor was then placed in a shaking device and heated to 200°–220° for 3–15 h. When the reaction was completed, as observed from the constant reading on the pressure gauge, the vessel was cooled to room temperature and the pressure of the system (which varied from 10 to 70 atm) was noted. A small sample of gaseous products was collected in a Monel cylinder at room temperature for a detection of PF_3 and/or PF_5 by infrared spectrometry[3], and for a determination of the ratio of H_2, PF_3, and/or PF_5 by mass spectrometry. The remaining gases in the reactor were then trapped successively in Monel cylinders at Dry-Ice temperature (HF), liquid nitrogen temperature (PF_3), and allowed to escape from the system (H_2). The amount of PF_3 collected agreed fairly well with the value calculated from the mass spectral data. The vessel was further evacuated to remove most of the HF from the solid residue, which consisted mainly of the hexafluorophosphate salt, the unreacted fluoride and phosphorus.

The existence of hexafluorophosphate salts of lithium[4,5], sodium[4,6–11], potassium[4,6,7,12], calcium[11,13,14], and barium[4,11,13,14] has already been established. Of these, KPF_6 has the highest thermal and hydrolytic stability, and its solubility in water is such as to render facile recrystallization from hot water. Consequently, salts obtained in this investigation were converted to KPF_6 for characterization according to the procedure which follows.

Solid residues from all but KF reactions were extracted with a basic (KOH) solution containing 16.12 g (0.278 mole) of KF, while that from the KF reaction was extracted with hot water. After filtration to remove unreacted phosphorus, a portion of the filtrate was treated with a nitron reagent[4] to give a precipitate similar to that obtained by the reaction of a known aqueous KPF_6 solution with nitron. The yield of hexafluorophosphate in the solid residue was calculated from the amount of nitron precipitate obtained from this treatment. The remaining portion of the filtrate was evaporated to dryness to give a white solid which was shown by infrared spectrometry to contain hexafluorophosphate salt[15]. The solid was further purified by recrystallization from water to yield KPF_6. Potassium in the compound was determined gravimetrically by precipitation as a potassium tetraphenylborate[16], while the hexafluorophosphate was determined as a nitron salt. Calcd. for KPF_6: K, 21.3; PF_6, 78.7. Found: K, 21.2; PF_6, 78.6.

In the CaF_2 reaction, the recrystallized product also showed the same x-ray powder pattern as KPF_6.

RESULTS AND DISCUSSION

The products which might conceivably be obtained from the reaction of phosphorus with hydrogen fluoride include H_2, PH_3, PF_3, and PF_5, or PF_6^- salts when metal fluorides are present. Thermodynamic considerations, using standard-state data, indicate that the reaction to form PF_3 and H_2 is favored. One might also expect that the lattice energy of the PF_6^- salt would favor its production as opposed to that of free PF_5.

When red phosphorus was heated with HF at 200°, the products were indeed PF_3 and H_2 (Table 1). The presence of a small amount of metal fluoride considerably increased the yield. Presumably, the salt provides a nucleophilic fluoride anion which attacks the phosphorus atom, as does the hydroxyl ion in the basic hydrolysis of phosphorus[17] in aqueous system. Muetterties and Castle[18] obtained only a 5% conversion to PF_3 when red phosphorus was heated with HF at 500°. In this case, the reaction temperature was well above the critical temperature* of HF, and the reaction probably took place in the vapor phase where F^- is unlikely to exist.

When equivalent amounts of alkali and alkaline earth fluorides reacted with phosphorus in HF under similar conditions, the PF_6^- salts were formed along with PF_3 and H_2. The results are given in Tables 2 and 3. It seemed likely that PF_3

TABLE 1

FORMATION OF PF_3[a]

HF, g	Conditions	% Conversion to PF_3
64.5	200°, 15 h	27
53.0	210°, 11 h	27
39.0	210°, 11 h	23
43.0	210°, 6.25 h 1 g KF	34.5
63.9	200°, 15 h 7.25 g LiF	41 and 8.15 g $LiPF_6$
66.3	200°, 15 h 10.85 g CaF_2	28.6 and 0.945 g $Ca(PF_6)_2$

[a] Red phosphorus, 8.63 g, was used in all experiments.

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* Reported to be 188° by Spalthoff[19] and 230° by Bond[20].

TABLE 2

FORMATION OF ALKALI METAL HEXAFLUOROPHOSPHATES[a]

HF, g	Conditions	Metal Fluorides, g	% Conversion to PF_3	% Conversion to MPF_6
43.4	210°, 11 h	7.25 (LiF)	2.1	36.6
63.9	200°, 15 h	7.25 (LiF)	41.1	19.2
46.6	220°, 7 h	11.70 (NaF)	18.0	29.0
38.8	210°, 11 h	11.70 (NaF)	21.1	37.4
100.0	205°, 3.5 h	16.10 (KF)		45.8
140.0	200°, 7 h	16.50 (KF)	3.5	70.0
67.9	220°, 7 h	16.10 (KF)	9.6	71.3
50.4	210°, 11 h	16.10 (KF)	9.4	93.0

[a] Red phosphorus, 8.63 g, was used in all experiments.

TABLE 3

FORMATION OF ALKALINE EARTH METAL HEXAFLUOROPHOSPHATES[a]

HF, g	Conditions	Metals Fluorides, g	% Conversion to PF_3	% Conversion to $M\ (PF_6)_2$
66.3	200°, 15 h	10.85 (CaF_2)	28.6	2.0
59.9	210°, 11 h	24.4 (BaF_2)	19.7	32.2

[a] Red phosphorus, 8.63 g, was used in all experiments.

was formed first. Some of it then disproportionated in the presence of fluorides to elemental phosphorus and hexafluorophosphate salts:

$$P_4 + 12HF \rightarrow 6H_2 + 4PF_3$$

$$5PF_3 + 3MF \xrightarrow{HF} \tfrac{1}{2}P_4 + 3MPF_6$$

$$10PF_3 + 3MeF_2 \xrightarrow{HF} P_4 + 3Me(PF_6)_2$$

where M = Li, Na and K; Me = Ca and Ba.

The disproportionation of PF_3 has previously been observed by Muetterties, *et al.*[21], who obtained KPF_6 and elemental phosphorus by passing PF_3 over KF heated to 150°. They detected no reaction, however, when NaF was used under similar conditions, or even in a pressure vessel at 250° for 5 h. The fact that we obtained hexafluorophosphate salts in the reactions involving alkali and alkaline earth fluorides points strongly to the important function of HF as an ionizing solvent in our investigation.

TABLE 4

CORRELATION OF THE CONVERSION OF PF_6- SALTS WITH LATTICE ENERGY AND SOLUBILITY

Cations	Ionic Radii (Å) (a)	Lattice Energy of Fluoride Salts kcal. mole^{-1} (b)	Solubility of Fluoride Salts in HF, in g/100 g HF	(c)	% Conversion to PF_6 Salts
Li^+	0.60	240.1	10.3	(12.2°)	19.2
Na^+	0.95	215.0	30.1	(11.0°)	37.4
K^+	1.33	190.4	36.6	(8.0°)	90.0
Ca^{++}	0.99	617.2	0.817	(12.2°)	2.0
Ba^{++}	1.35	547.1	5.60	(12.2°)	32.2

(a) L. PAULING, *The Nature of the Chemical Bond,* Cornell University Press, 2nd Ed., Ithaca, New York, 1960, p. 514.
(b) J. SHERMAN, *Chem. Rev., 11* (1932) 93.
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The yield of PF_6^- salts increases as the size of the cations increase from Li^+ to K^+ in the Group IA elements, and from Ca^{2+} to Ba^{2+} in the Group IIA elements. This presumably is due to the lattice energy (see Table 4). Metal fluorides with small cations of high charge density such as Li^+, or more so Ca^{2+}, possess a high lattice energy and will have a slight tendency to form the hexafluorophosphate salts (ionic radii of F^- and PF_6^- are, respectively, 1.36 and 2.69Å[22]).

Additionally, the yield of PF_6^- salts seems to correspond fairly well with the solubility of the fluoride salts in liquid HF (see Table 4) as well as with its "basicity" in HF. These properties are of course related to the size–charge ratio or basicity and would provide alternative explanations.

The total conversion of P_4 to PF compounds can also be correlated with the size–charge ratio of the cations. Thus, it appears that when the fluorides of large low-charged cations are used more PF_3 is formed, but it is likely that much of it will be converted to PF_6^- salts.

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