

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF PENNSYLVANIA]

The Alkali Metal Phosphides. I. Reaction of Alkali Metals and White Phosphorus in Liquid Ammonia^{1,2}

BY E. CHARLES EVERS

Alkali metal phosphides which may be represented empirically as Li_3P , Na_2P and K_3P_2 have been prepared by reacting the elements in liquid ammonia solution; these substances probably are dimeric. The potassium compound may be reduced further by lithium or sodium forming what appear to be mixed phosphides. These compounds are somewhat soluble in liquid ammonia giving stable, yellow-orange solutions which conduct the electric current. Normal phosphides are not formed under these reaction conditions.

Introduction

Although the literature contains numerous accounts of experiments describing the preparation of alkali metal phosphides, the products obtained usually were not well defined and varied considerably with experimental conditions.³

Hackspill and Bossuet^{3a} have prepared the compounds M_2P_3 when M is an alkali metal, by treating the elements directly and subjecting the resulting products to the action of vacuum at high temperatures. This procedure, obviously, excludes all possibilities of identifying substances containing a higher proportion of metal which might possibly be stable at lower temperatures.⁴ Legoux⁵ has prepared the same substances by thermally decomposing metal derivatives of phosphine, thus confirming the existence of the high temperature stable forms reported by Hackspill and Bossuet. When heated, the compounds MPH_2 decompose successively evolving phosphine, then hydrogen and, finally, free metal as the temperature is raised, leaving the compounds M_2P_3 as non-volatile residue.⁶

Hugot⁷ has described the preparation of KP_3 and NaP_2 by using an excess of red phosphorus with the metals in liquid ammonia, and $\text{Na}_2\text{H}_3\text{P}_2$ by treating an excess of sodium with red phosphorus in the same solvent. On the other hand, Brauer and Zintl⁸ report that red phosphorus and lithium react incompletely in liquid ammonia; no definite product was isolated. However, it has been brought to my attention by Dr. C. A. Kraus that studies in his Laboratory made by H. M. Smith have clearly indicated that sodium and white phosphorus combine readily in liquid ammonia, yielding a compound which may be represented empirically

as Na_2P .⁹ In view of the somewhat uncertain status of the alkali metal phosphides it has seemed worthwhile to undertake a fairly detailed investigation covering their preparation and properties.

The present report is the first in a series dealing with the chemistry of the alkali metal phosphides and, specifically, it is concerned with the reaction between white phosphorus and the metals in liquid ammonia. This medium was chosen because it affords a convenient means for treating of the elements in a homogeneous state under controlled conditions. Several well defined phosphides, hitherto unreported, have been prepared in liquid ammonia and it is noteworthy that, all other conditions being the same, the combining capacity of the phosphorus varies with the nature of the particular metal involved. Sodium and lithium form compounds which may be represented empirically as Na_2P and Li_2P , respectively. Potassium, on the other hand, forms K_3P_2 ; this compound may be reduced further by sodium or lithium yielding what appears to be the mixed phosphides K_2NaP_2 or K_3LiP_2 , respectively. Normal phosphides are not formed under the conditions employed in these preparations.

Experimental

Procedure.—Reactions were carried out in liquid ammonia at its boiling point with rigid exclusion of atmospheric air and moisture employing conventional apparatus.¹⁰

In carrying out a reaction, weighed amounts of sodium and potassium metal (40–150 mg.) sealed in capillary tubes¹⁰ were broken into the reaction vessel; lithium was cut and weighed under oil just before use. The metal was dissolved in approximately 50 ml. of anhydrous liquid ammonia¹⁰ and a solution of phosphorus in toluene of known titer (10–20 mg. per ml.) was added slowly from a micro buret attached to the reaction vessel by means of a ground-glass joint. As the reaction proceeded, the blue color of the ammonia solution first acquired a greenish cast, then a deep yellow-green color and, finally, there was a distinct color change to yellow, tinged with orange. Sometimes there was a yellow-orange precipitate present depending upon the amount of metal employed. This definite color change was the criterion employed to establish the combining capacity of phosphorus with the alkali metal under study; the titration was stopped and the empirical formula of the resulting phosphide was calculated from the weight of metal and the volume of phosphorus solution which was used.

The addition of phosphorus solution beyond the endpoint produced deep red-colored solutions, indicating further reaction to form higher phosphides; but no further color change was noted.

2. Analysis.—The toluene stock solution was made up by weight and its titer was checked by analyzing for phosphorus. This was done by treating aliquots with bromine water containing nitric acid. The mixture was heated to boiling to expel free bromine and toluene; then the phosphorus was determined by the standard procedure of converting it to magnesium ammonium phosphate and igniting to the pyrophosphate. In general the titer computed by weighing out the constituents checked the analysis by 0.5%. A somewhat similar method was employed in analyzing for phosphorus in the alkali metal phosphides. Here 25 ml. of bromine water was first admitted to the dried material in the reaction flask (*in vacuo*), the resulting solution was digested for a short time on a steam-bath and then 25 cc. of

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Detroit, Michigan, April, 1950.

(2) This paper is based on work supported by the Office of Naval Research under Contract N8onr-74200.

(3) (a) A fairly complete bibliography of early work is given by L. Hackspill and R. Bossuet, *Compt. rend.*, **154**, 209 (1912). (b) Gmelin, "Handbuch der anorganische Chemie," System Numbers 20, 21, 22, 24, 25. (c) E. Tomkinson and G. Barker, *Chem. News*, **121**, 104, 177 (1920).

(4) Direct union of the elements in various media is said to yield normal phosphides, a conclusion deduced principally from the observation that phosphine is evolved when such products are treated with water. But the production of phosphine is not sufficient evidence in itself to establish the formula of the parent phosphide since phosphides prepared in other ways, as those described in the present research, also yield phosphine on hydrolysis. Refs. 3a, 3c; A. C. Vournasos, *Z. anorg. allgem. Chem.*, **81**, 364 (1913).

(5) C. Legoux, *Bull. soc. chim. (France)*, [5] **7**, 546 (1940); *Compt. rend.*, **207**, 634 (1938); **209**, 47 (1939); *Ann. chim.*, **17**, 100 (1942).

(6) A. Joannis reports that normal phosphides are formed on pyrolysis of NaPH_2 and KPH_2 ; *Compt. rend.*, **119**, 557 (1894); *Ann. chim. phys.*, [1] **7**, 101 (1906). It is also reported that normal phosphides are formed on passing phosphine over the heated metals; W. Schober and F. Spanutius, *This Journal*, **16**, 229 (1894). Here again the formation of normal phosphides was inferred because the products liberated phosphine on treatment with water.

(7) C. Hugot, *Compt. rend.*, **121**, 207 (1895).

(8) G. Brauer and E. Zintl, *Z. physik. Chem.*, **37B**, 323 (1937). These investigators also prepared Li_3P and Na_3P by treating the elements in stoichiometric amounts, basing their findings on the apparent homogeneity of the products and the fact that the powder X-ray diagrams were similar to other normal compounds of the fifth group elements, e.g., NaBi . In the case of potassium, however, only a higher phosphide was formed.

(9) H. M. Smith, M.S. Thesis, Clark University, (1922). This result has been fully confirmed in the present investigation.

(10) C. A. Kraus and E. S. Carney, *This Journal*, **56**, 765 (1934).

concentrated nitric acid was added (*in vacuo*). After approximately 1 hour of digestion, air was admitted to the vessel and the solution was poured into a beaker; all the parts of the vessel were carefully washed and the washings added to the main body of solution. The phosphorus was then determined as outlined above.

3. Reaction of Lithium and Phosphorus.—Lithium and phosphorus react readily in liquid ammonia to form a fairly soluble compound having the empirical formula Li_2P . The results of several experiments are presented in Table I.

TABLE I
REACTION OF LITHIUM AND PHOSPHORUS IN LIQUID AMMONIA

Li, g.	Ml. P soln.	Concn. P soln., m. at./ml.	Milliatoms		Atom ratio Li/P
			Li	P	
0.0160	5.055	0.2406	2.32	1.216	1.90
.0107	2.716	.2879	1.54	0.7817	1.97
.0195	4.945	.2879	2.81	1.414	1.97

4. Reaction of Sodium and Phosphorus.—Sodium reacts with phosphorus to form a compound represented empirically as Na_2P . The reaction with sodium must be carried out more carefully than with lithium because the red polyphosphide, which appears when the drops of phosphorus solution strike the surface of the solution of metal in liquid ammonia, is somewhat less soluble and requires more time to react back with the free metal. The results of several experiments are recorded in Table II.

TABLE II
REACTION OF SODIUM AND PHOSPHORUS IN LIQUID AMMONIA

React. no.	Na, g.	Ml. P soln.	Concn. P soln., m. at./ml.	Milliatoms		Atom ratio Na/P
				Na	P	
7	0.1386	6.489	0.4658	6.036	3.023	1.994
8	.0466	2.217	.4658	2.026	1.038	1.952
10	.0442	2.054	.4658	1.922	0.9568	2.008
13	.0834	7.058	.2571	3.635	1.815	2.003
15	.0325	2.772	.2571	1.413	0.7127	1.983
16	.0622	5.260	.2571	2.704	1.352	1.999
21	.0539	2.311	.5110	2.311	1.181	1.986

The possibility suggests itself that solvent might enter into the reaction, but there is nothing to indicate that such is the case. Gas is not evolved in this reaction (or in the other reactions here described) and the combining ratio of sodium to phosphorus does not depend upon the concentration of metal or upon the length of time spent in completing a titration. It might be pointed out that the reaction between phosphorus and ammonia proceeds exceedingly slowly even at room temperature¹¹; this should exclude the possibility that a direct combination of phosphorus with the solvent takes place during the preparation of the alkali phosphides.

The products from reactions (8) and (15) of Table II were analyzed for phosphorus with the following results: Reaction (8): g. $\text{Mg}_2\text{P}_2\text{O}_7$, 0.1143; milliatoms P, 1.027; atom ratio Na/P, 1.973. Reaction (15): 0.0795; 0.714; 1.979, respectively. These results serve to establish the validity of the analytical method and to check the accuracy of the titration.

The phosphides are obtained as yellow-orange powders on evaporating the solvent and contain ammonia of crystallization which is tightly bound and cannot be removed by suction at room temperature. In the case of the sodium compound, it has been established that the solvate contains one molecule of ammonia per unit of Na_2P ,¹² the most probable formulation being $\text{Na}_2\text{P}_2 \cdot 2\text{NH}_3$. As will be shown in the next communication of this series, the solvate decomposes on heating *in vacuo*, evolving hydrogen and ammonia. The solvent content of the other solid metal phosphides has not been determined.

(11) A. Stock and O. Johansen, *Ber.*, **41**, 1593 (1908); E. C. Franklin and C. A. Kraus, *THIS JOURNAL*, **20**, 820 (1898).

(12) S. Roggenburg, Jr., unpublished observations, this Laboratory.

5. Reaction of Potassium and Phosphorus.—Unlike sodium and lithium, potassium reacts with phosphorus to form K_3P_2 , as may be seen from the data in Table III. The resulting phosphide is even less soluble than the Li and Na salts, and the color at the end-point is slightly more orange than it is with the other two metals. As with sodium and lithium, a red polyphosphide is formed once the end-point is passed.

TABLE III
REACTION OF POTASSIUM AND PHOSPHORUS IN LIQUID AMMONIA

K, g.	Ml. P soln.	Concn. P soln., m. at./ml.	Milliatoms		Atom ratio K/P
			K	P	
0.0552	1.799	0.5110	1.412	0.9139	1.545
.0297	1.669	.3001	0.7596	.5009	1.516
.0535	3.759	.2406	1.371	.9004	1.516
.0437	2.632	.2879	1.118	.7578	1.475
.1520	4.830	.5360	3.887	2.605	1.492

6. Reduction of K_3P_2 .—When sodium is added to a solution of K_3P_2 the blue color of the metal solution does not become evident immediately, suggesting that the metal is reacting with the potassium compound. Since it proved difficult to establish the end-point of the reaction by adding just the right amount of metal to bring about the blue color of free metal in solution, an alternative procedure was employed, as follows: a weighed amount of potassium was dissolved in liquid ammonia and titrated to the yellow end-point with phosphorus solution, forming the compound K_3P_2 . A weighed amount of lithium or sodium was then added to the reaction tube in an amount sufficient to bring about the blue color due to the presence of free metal. The resulting solution was titrated with additional phosphorus solution to the characteristic yellow end-point, and the total metal to phosphorus ratio was calculated. The results of two such experiments are given in Table IV.

TABLE IV
REACTION OF K_3P_2 WITH SODIUM AND LITHIUM IN LIQUID AMMONIA

Milliatoms K	Milliatoms P	Atom ratio K/P	Milliatoms added		Atom ratio total metal/P
			Li or Na	P	
1.624	1.105	1.468	1.15 Li	0.3987	1.85
0.8721	0.6945	1.467	0.748 Na	.2842	1.844

From the above data it is evident that the compound K_3P_2 is reduced by lithium or sodium forming compounds with the empirical formula M_2P , suggesting that they are constitutionally similar to the sodium or lithium phosphides. It seems highly unlikely that these products are mixtures. They are completely soluble in liquid ammonia, and the precipitates obtained on evaporating the ammonia appear uniform.

Discussion

In liquid ammonia, the amphoteric elements of groups IV through VII of the periodic table ordinarily react with strongly electropositive elements, such as sodium, to form first a normal salt of the type M_2A^n , where A is the amphoteric element. The solubility of such substances, as for example, Na_2S or Na_4Pb , is low; but they react quite readily with additional atoms of the amphoteric constituent to form highly colored, soluble compounds of the polytype, which are stable in solution and behave as true electrolytes.¹³

Of the fifth group elements, antimony,¹⁴ ar-

(13) C. A. Kraus, *Trans. Electrochem. Soc.*, **45**, 175 (1924).

(14) E. Peck, *THIS JOURNAL*, **40**, 335 (1918); C. Hugot, *Compt. rend.*, **126**, 1719 (1898); **127**, 553 (1898); P. Lebeau, *Bull. soc. chim. (France)*, **27**, 256 (1902); E. Zintl, A. Harder and B. Danth, *Z. Elektrochem.*, **40**, 588 (1934).

senic,¹⁵ and bismuth^{15,16} have been investigated in some detail and all three elements behave in the expected fashion forming normal salts that react with an excess of the electronegative element to yield colored solutions of polyanionic substances. But phosphorus does not react with the alkali metals under these conditions to form normal salts; instead, polytype salts are formed immediately.

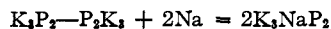
On the basis of evidence presented above, the empirical formulas for those phosphides prepared in liquid ammonia, which contain the highest ratio of metal to phosphorus, may be written as Li_2P , Na_2P and K_3P_2 . It seems obvious, purely on the basis of valence theory, that these substances must be at least dimeric, *i.e.*, Li_4P_2 , Na_4P_2 and K_6P_4 . Since all three phosphides are soluble in liquid ammonia (estimated as 0.1 to 0.3 g./100 cc.) these abnormal combining ratios cannot be attributed to lattice requirements of the solid phase. This indicates that the P-P bond in this type of compound possesses a considerable degree of stability in liquid ammonia solution and is not reduced by the "solvated" electron.¹⁷

Additional support of the dimeric formulas is given by the fact that the potassium compound may be reduced by sodium or lithium to form a phosphide having a total metal to phosphorus ratio of two to one. Likely the reduction takes place through the rupture of a P-P bond, according to the equation

(15) E. Zintl, J. Coubeau and W. Dullenkopf, *Z. physik. Chem.*, **154A**, 1 (1931); Brauer and Zintl, *ibid.*, **537**, 323 (1937); C. Hugot, *Compt. rend.*, **129**, 603 (1899).

(16) C. A. Kraus and H. F. Kurtz, *THIS JOURNAL*, **47**, 43 (1925); G. W. Watt and T. E. Moore, *ibid.*, **70**, 1197 (1948).

(17) However, it will be shown in the next paper that phosphorus in the compound Na_4P_2 may be completely reduced to the trivalent state in the presence of ammonium bromide.



But the existence of hexapotassium tetraphosphide, stable in the presence of excess potassium metal in liquid ammonia, is difficult to rationalize. We have here, it seems, examples where the size of the metal ion determines the extent of the reduction in liquid ammonia, and this must be related in some manner to the structure of the resulting compounds. The sodium compound is highly ionized and conducts the electric current with facility¹⁸ and appears to dissociate into sodium ions and P_2^{-4} ions.

If the potassium compound were likewise completely ionic (it does conduct the electric current in solution) it would be difficult to account for the inability of potassium to effect as complete a reduction as sodium, since steric factors should then be largely inoperative. This suggests that at least part of the potassium in the compound may be bonded covalently; otherwise it would seem that the condition of the electron (the reducing agent) in liquid ammonia would have to be greatly influenced by the nature of the metal ion, which is contrary to experiment.

None of the chemical properties of the sodium compound, which have been investigated, are in contradiction with the dimeric formula; in fact, certain of the reactions of this substance tend to support this formulation, as will be made evident in the next paper of this series. Until evidence is presented to the contrary, it is proposed to use the dimeric formulas to represent these substances, namely, tetrasodium diphosphide, tetralithium diphosphide and hexapotassium tetraphosphide.

(18) J. M. Finn, Jr., unpublished observations. Experiments on the electrolysis of the sodium salt are now in progress.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Low-frequency Dielectric Properties of Some Symmetrical Mixed Triglycerides in the Solid State^{1a,1b}

BY ROBERT W. CROWE² AND CHARLES P. SMYTH

The dielectric properties at frequencies from 0.5 to 50 kilocycles have been investigated for a number of symmetrical mixed triglycerides in the solid state and correlated with existing X-ray diffraction and thermal data. The dielectric properties of the various solid forms of these compounds have also been compared with those of the recently investigated simple triglycerides. It was found that the dielectric properties and dispersion characteristics of the α -forms of 2-palmitoyldistearin, 2-oleoyldipalmitin and 2-oleoyldistearin were quite similar to those of tripalmitin and tristearin, for which it had been suggested that the dipole orientation was that of molecular segments rather than of the entire molecule, a process which could easily account for the observed distribution of relaxation rates. Although α -forms were found for 2-stearoyldipalmitin and 2-lauroyldistearin, they were not of sufficient stability to be isolated in the pure state. In all cases, only the α -form showed any indication of molecular freedom. The sharpness of the freezing point of the unusually stable α -form of 2-palmitoyldistearin indicated that, at least in this compound, the α -form was crystalline and not vitreous as had been reported. Like the simple triglycerides, the thermodynamically stable forms of these substances (usually β) showed slight variation of melting point with thermal history.

The dielectric properties of the 1-mono-, 1,3-di- and simple triglycerides of palmitic and stearic

(1) (a) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted. (b) This paper represents a part of the work submitted by Mr. R. W. Crowe to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Procter and Gamble Fellow in Chemistry, 1949-1951.

acids have recently been investigated in this Laboratory.³ In these investigations, emphasis has been placed upon polymorphic behavior in the solid state, its dependence upon the previous history of the samples and on the presence or absence of molecular orientational freedom in the various crystalline phases. Like the simple tri-

(3) R. W. Crowe and C. P. Smyth, *THIS JOURNAL*, **72**, 4427 (1950); *ibid.*, **72**, 5281 (1950).