1168. *The Preparation and Ammonolysis of Potassium Phosphinide and Potassium Dimethylphosphinide*

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Potassium reacts with phosphine and dimethylphosphine in liquid ammonia to form potassium phosphinide KPH_2 and potassium dimethylphosphinide $KPMe_2$. Both are soluble in liquid ammonia from which they may be recovered unchanged, on removal of the ammonia, as white solids, thermally stable at room temperature and pyrophoric in air. Potassium phosphinide does not ammonolyse in liquid ammonia at temperatures up to $-33°$ but ammonolysis occurs with potassium dimethylphosphinide in liquid ammonia at temperatures above $-63°$, hydrogen being evolved.

It was originally reported that the phosphinide ion PH_2^- could be made by the reduction of phosphine with alkali metals in liquid ammonia.[1] Subsequent work showed that each phosphinide ion was associated with four molecules of ammonia when the alkali metal used in this reaction was lithium,[2] and it was found that this ammonia could not be removed without simultaneous decomposition of the phosphinide ion.[3] That alkali-metal phosphinides are capable of separate existence was shown by the work of Albers and Schuber [4] who prepared the sodium salts in organic solvents.

On methylation of phosphine, removal of a proton to form the methyl-phosphinide ion, became more difficult with increasing methylation.[5] This was as predicted from the observed increase in electron-donor bonding power with methylation.[6]

It has been suggested that in dimethylphosphine the hydrogen atom is hydridic rather than protonic with the result that the dimethylphosphinide ion PMe_2^- probably does not exist.[7]

The present work is devoted to the preparation of potassium phosphinide and potassium dimethylphosphinide. No difficulty was encountered in the preparation of potassium phosphinide and reduction of phosphine with a solution of potassium in liquid ammonia

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[1] A. Joannis, *Compt. rend.*, 1894, **119**, 557.

[2] C. Legoux, *Compt. rend.*, 1938, **207**, 634.

[3] C. Legoux, *Bull. Soc. Chim. france*, 1940, **7**, 545.

[4] H. Albers and W. Schuber, *Ber.*, 1943, **76*B***, 23.

[5] F. Pass, E. Steininger, and H. Schindlbauer, *Monatsh.*, 1959, **90**, 792.

[6] H. C. Brown, E. A. Fletcher, E. Lawton, and S. Sujishi, Abs. of Paper presented to 121st National Meeting of the Amer. Chem. Soc., 1951, p. 9N.

[7] R. I. Wagner and A. B. Burg, *J. Amer. Chem. Soc.*, 1953, **75**, 3869.

gave the desired product as a white, pyrophoric solid, thermally stable at room temperature, after removal of the ammonia. The reaction occurring is shown below and was complete in 10 minutes, stoicheiometric amounts of hydrogen being evolved.

$$K + PH_3 \longrightarrow KPH_2 + \tfrac{1}{2}H_2$$

This solid contained practically no nitrogen as shown by elemental analysis. Hydrolysis with dilute hydrochloric acid occurred according to

$$KPH_2 + HCl(H_2O) \longrightarrow KCl + PH_3$$

at room temperature, but potassium phosphinide was not ammonolysed in liquid ammonia, in which it forms a pale yellow solution, even during several days at −33° no colour change taking place in the solution nor any more hydrogen being evolved. The solid left on removal of the ammonia again contained very little nitrogen.

The preparation of potassium dimethylphosphinide followed a similar course but great care was necessary to prevent ammonolysis.

At −78°, the reduction took about 10 days to complete and followed the equation,

$$K + HPMe_2 \longrightarrow KPMe_2 + \tfrac{1}{2}H_2$$

the colour of the solution changing from blue to golden yellow. This great reduction in reaction rate is a consequence of the relative insolubility of dimethylphosphine in liquid ammonia [7] and also the increased base strength of dimethylphosphine when compared with phosphine. As a result of this extended reaction period great care had to be taken to prevent amide-ion formation. Removal of the ammonia was carried out at −78° and the final product was a white, extremely pyrophoric solid, which analysis showed to contain very little nitrogen. The nitrogen content could be accounted for on the assumption that the solid was contaminated with about 1% of potassium amide, formed simultaneously with the potassium dimethylphosphinide during the extended reaction period.

Solid potassium dimethylphosphinide is thermally stable at room temperature but in liquid ammonia solution rapidly ammonolyses above −63°, the solution becoming darker in colour. Hydrogen is evolved during this ammonolysis but non-stoicheiometric amounts were recovered, even after prolonged reaction at −33°. The solid product left after removal of the ammonia contained up to 9% of nitrogen.

EXPERIMENTAL

Volatile materials were handled in a conventional vacuum system, and reactions were carried out in sealed Pyrex glass vessels. The nitrogen contents of the solid products were determined by conversion into gaseous nitrogen and measurement in a nitrometer. Reactants were prepared by standard techniques and the ammonia was dried over sodium before being distilled into the reaction vessels. In all reactions the molar ratio of phosphine to potassium was greater than 1 : 1 to prevent reduction beyond the stage required.

Typical experiments were as follows.

Preparation and Properties of Potassium Phosphinide.—Phosphine (1·26 mmole) and excess of ammonia were mixed and potassium (1·12 mmole) added at −78°. The blue solution was left until pale yellow in colour, hydrogen (0·53 mmole) being formed. After removal of this hydrogen the vessel was resealed and warmed to −33° for several days but no more hydrogen was evolved. Removal of the ammonia left a white solid, thermally stable at room temperature, which was hydrolysed with dilute hydrochloric acid to give phosphine (1·03 mmole) as the only volatile product. No ammonia could be detected in the residual solution. Microanalysis of a second sample of the solid gave a nitrogen content of 0·5%.

Preparation and Properties of Potassium Dimethylphosphinide.—Dimethylphosphine (0·96 mmole) and excess of ammonia were mixed and potassium (0·86 mmole) added at −78°. The blue solution was maintained at −78° until the colour changed through green to golden yellow (about 10 days), hydrogen (0·43 mmole) being formed. The vessel was maintained at −78° while the ammonia was removed; microanalysis of the white solid residue showed the nitrogen content to be 0·3%. This solid was thermally stable at room temperature. In a second experiment dimethylphosphine (1·14 mmole) and potassium (1·03 mmole) reacted at −78°, hydrogen (0·53 mmole) being formed. On warming to −33° more hydrogen was produced from the ammonia solution (0·66 mmole in 36 hr., then 0·18 mmole in the subsequent 10 days). On removal of the ammonia a thermally stable, white solid was left, of nitrogen content of 8·8%.

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