Preparation of Europium and Ytterbium Phosphides in Liquid Ammonia

By L. L. PYTLEWSKI* and J. K. HOWELL†
(*Chemistry Department, Drexel Institute of Technology, Philadelphia, Pennsylvania* 19104)

RECENT work has shown that some rare-earth compounds with non-metals possess semiconducting properties.[1] Europium and ytterbium dissolve in liquid ammonia to form solutions having the characteristic deep blue colour of metals in ammonia.[2] Calcium phosphides can be readily prepared by the thermal decomposition of $Ca(PH_2)_2$,[3] which results from the reaction of calcium dissolved in liquid ammonia and phosphine. The question was whether europium and ytterbium phosphides could be prepared in a similar manner.

Phosphine gas reacts smoothly with the europium and ytterbium solutions in liquid ammonia at $-78°$ to form a coloured precipitate with the evolution of hydrogen. Completion of the reaction is shown by a colour change from deep blue to orange-brown (in the case of ytterbium) or from blue to dark green (in the case of europium). The dark green (europium) or orange (ytterbium) crystalline precipitate is stable under an atmosphere of ammonia and has the probable composition of $M(PH_2)_2,5NH_3$, where M = Eu or Yb. When subjected to reduced pressure at room temperature, both precipitates rapidly change colour. The orange ytterbium compound changes in *ca.* 10 sec. to a brick-red substance, and after 2 min. to a metallic grey substance. The europium compound changes from dark green to yellow in *ca.* 10 sec., and then to a black substance after 30 min. By venting the vacuum system to the atmosphere, ammonia was detected during the first colour change and phosphine during the second colour change in both cases. Evidence shows that the following two reactions take place:

$$M(PH_2)_2,5NH_3 \rightarrow M(PH_2)_2 + 5NH_3$$
(first colour change)

$$2M(PH_2)_2 \rightarrow 2MP + 2PH_3 + H_2$$
(second colour change)

The higher stability of the Eu^{2+} state, compared to the Yb^{2+} state, is demonstrated by the extra time required for the europium compound to undergo the second reaction under the same conditions.

A sample of ytterbium phosphide, YbP, was heated (2 hr.) in an evacuated system, starting at room temperature and ending at 800°. No reaction appeared to take place since (i) no physical change in the substance was observed, (ii) no appreciable change in the manometer attached to the system took place, and (iii) there was no evidence of distilled phosphorus. An analysis of this material gave the Yb content as $84{\cdot}6 \pm 0{\cdot}8\%$. For purposes of comparison, the metal content of YbP was calculated to be 84·9%. Europium phosphide, EuP, when subjected to the same conditions, gave similar analyses.

When the heating period is prolonged, however, a decomposition reaction definitely takes place. In one experiment, a sample of ytterbium phosphide was gradually heated to 800° in an evacuated system. After *ca.* 3 hr., at 550°, phosphorus began to distill and condense as a yellow–bronze ring in a cooler portion of the reaction tube. After 16 hr. at 820°, the sample was a very dark grey. A metal analysis of this material gave $89{\cdot}6 \pm 0{\cdot}5\%$ Yb, while the percentage of Yb calculated for Yb_3P_2 is 89·4%. Evidently, the following reaction takes place:

$$3MP \rightarrow M_3P_2 + P \quad (M = Eu \text{ or } Yb).$$

Again, europium gave similar results.

Further characterization of both the low-temperature europium and ytterbium dihydrogen phosphides and the higher temperature phosphides (MP and M_3P_2, M = Eu or Yb), as well as the white thermal decomposition products is in progress. All these phosphides are easily hydrolyzable and, upon standing in air, form the oxides and phosphine gas.

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