Stoicheiometric Evidence for the Dihydrate of Diborane

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Summary The dihydrate of diborane has been prepared by the reaction of diborane with water at −130°.

IT is well known that diborane forms adducts with various Lewis bases, including ammonia.[1] However, no adduct with water has previously been isolated because of the relatively high reactivity of water as a protonic acid; even at −80° diborane undergoes hydrolysis with hydrogen evolution.[2] By the following technique, we have achieved hydrate formation without hydrolysis. Diborane and water were co-condensed as an intimate solid mixture at −196° by allowing their vapours to effuse separately but simultaneously into a glass vessel cooled in liquid nitrogen. The mixture was warmed to the highest temperature at which hydrogen evolution was negligible, *i.e.*, −130°; at this temperature diborane has sufficient vapour pressure (50 mm) to facilitate reaction with the water.

In experiments in which an excess of water was used, the reaction mixture was held at −130° for various time intervals, and then any unchanged diborane was pumped out and measured. With a reaction time of 15 min, 14% of the diborane was recovered; with a reaction time of 110 min, only 2% of the diborane was recovered. The fact that continued pumping for 1 h yielded only a trace of diborane is evidence that the unrecovered diborane had reacted with the water.

When an excess of diborane was used, the unchanged diborane was removed at −130° by pumping after a 2 h reaction time. In several experiments, the observed mole ratio of water to consumed diborane ranged from 1·9—2·3, thus indicating the empirical formula $B_2H_6,2H_2O$ for the reaction product. The results of similar studies of the reactions of diborane with methanol and ethanol indicate that alcoholates of the composition $B_2H_6,2ROH$ are formed. When the dihydrate was treated with an excess of trimethylamine at −130° and then warmed to room temperature, hydrogen, trimethylamine borane, and an uncharacterized residue were formed.

The above data give no information regarding the structure of the dihydrate and dialcoholates of diborane. We hope that, in the case of the dihydrate, low temperature i.r. spectrometry and *X*-ray photoelectron spectroscopy can be used to distinguish between the two likely structures, *viz.* $BH_2(OH_2)_2{}^+BH_4{}^-$ and H_2OBH_3.

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[1] M. F. Hawthorne, in "The Chemistry of Boron and Its Compounds," ed. E. L. Muetterties, Wiley, New York, 1967, ch. 5, pp. 250—252.

[2] H. G. Weiss and I. Shapiro, *J. Amer. Chem. Soc.*, 1953, 75, 1221; W. L. Jolly and T. Schmitt, *ibid.*, 1966, 88, 4282.