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SYNTHESIS AND INFRARED ABSORPTION SPECTRUM OF DIBORANE-^{10}B

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ABSTRACT

Essentially pure diborane-^{10}B ($^{10}B_2H_6$) was prepared for the Physics Division. The compound was prepared by the incremental addition of $^{10}BF_3$-etherate to a diethyl ether solution of lithium aluminum hydride. The product was purified by fractional condensation, and its purity was established from its infrared absorption spectrum and mass spectroscopic analysis.

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INTRODUCTION

The ORNL Physics Division requested the synthesis of about 100 ml of the gas, diborane-^{10}B ($^{10}B_2H_6$), to contain boron enriched to 96% in ^{10}B; the compound was needed in fundamental studies. The most convenient method for producing diborane probably is by the reaction of lithium aluminum hydride with boron trifluoride in diethyl ether solution. In studies of the vibrational spectra of diborane and some of its isotopic derivatives, Lord and Nielsen[1] prepared $^{10}B_2H_6$ by making $^{10}BF_3$ from calcium fluoborate-^{10}B ($CaF_2 \cdot {}^{10}BF_3$) forming the BF_3-etherate, and then causing the etherate to react with $LiAlH_4$ in diethyl ether solution.

Shapiro and co-workers[2] studied the chemistry of this preparation in some detail. They found that at least two separate reactions are involved, which can be expressed by the equations

$$LiAlH_4 + BF_3 \rightarrow LiBH_4 + AlF_3 \qquad (1)$$

$$3\ LiBH_4 + BF_3 \rightarrow 2\ B_2H_6 + 3\ LiF \qquad (2)$$

or, in sum,

$$3\ LiAlH_4 + 4\ BF_3 \rightarrow 2\ B_2H_6 + 3\ LiF + 3\ AlF_3 \qquad (3)$$

Their data indicated that, since BF_3 must be present in excess before the active hydrogen in $LiAlH_4$ appears in the form of B_2H_6, the B_2H_6 might be generated as soon as $LiAlH_4$ is added to BF_3. Therefore, they added $LiAlH_4$ to the BF_3-etherate and thereby obtained B_2H_6 immediately. They thus found that Eqs. 1 and 2 occur concurrently. The synthesis described here is a modification of the procedure outlined by Shapiro and associates.

EXPERIMENTAL

Reagents

Lithium Aluminum Hydride Solution. A solution of lithium aluminum hydride, $LiAlH_4$, was prepared by grinding lumps of the 95% pure material (obtained from Metal Hydrides Inc.) in diethyl ether. The clear solution was decanted from the insoluble portion. The concentration of $LiAlH_4$ in the solution was determined by evaporating a weighed 10-ml portion to dryness and weighing the residue.

Boron-10 Trifluoride Etherate. The $^{10}BF_3$-etherate was supplied by the ORNL Chemistry Division; it had been prepared by forming an etherate of $^{10}BF_3$ enriched to 96% in ^{10}B. Boron-10 trifluoride is available through the Atomic Energy Commission as the complex salt $CaF_2 \cdot {}^{10}BF_3$, which is a white powder. In principle, $^{10}BF_3$ is liberated by heating the complex

$$CaF_2 \cdot {}^{10}BF_3 \longrightarrow CaF_2 + {}^{10}BF_3 \qquad (4)$$

Theoretically, 6.45 g of the complex will produce 1 liter of $^{10}BF_3$ at S.T.P. The $^{10}BF_3$-etherate was supplied in 2-to-3 ml break-seal containers, which were fitted with ground-glass female ball joints (Fig. 1).

Apparatus

Figure 1 shows the apparatus used to prepare $^{10}B_2H_6$. It consisted essentially of a 3-neck 100-ml reaction flask connected through a 3-in. vigreux column to a 10-in.-long Dry Ice—acetone condenser and then to a series of traps in which $^{10}B_2H_6$ was collected and purified. The system was provided with ground-glass joints for the attachment of gas-collection flasks, an infrared gas-sampling cell, and vacuum.

Synthesis Procedure

The mole ratio of BF_3 to $LiAlH_4$ required for the synthesis reaction was known to be about 4 to 3. A calculated amount (0.42 g) of $LiAlH_4$ in diethyl ether (35 ml) was placed in the reaction flask. Small portions of $^{10}BF_3$-etherate were added by rupturing the vertical break-seal container with an enclosed nickel bar and then rotating the container. The mixture in the flask was stirred magnetically at room temperature. A vigorous reaction resulted during which a gelatinous precipitate formed. A Dry Ice—acetone mixture was used to cool the reflux head. The cooling, together with the vigreux column, effectively prevented the ether from carrying over into the traps. Dry argon was used to transfer the $^{10}B_2H_6$ from the reaction flask into the series of traps. The first trap, in which the $^{10}B_2H_6$ was collected, was cooled with a carbon disulfide—liquid nitrogen mixture to -111°C; diborane boils at -87°C. After the addition of each portion of the $^{10}BF_3$-etherate, the flushing with dry argon was continued for 5 min.

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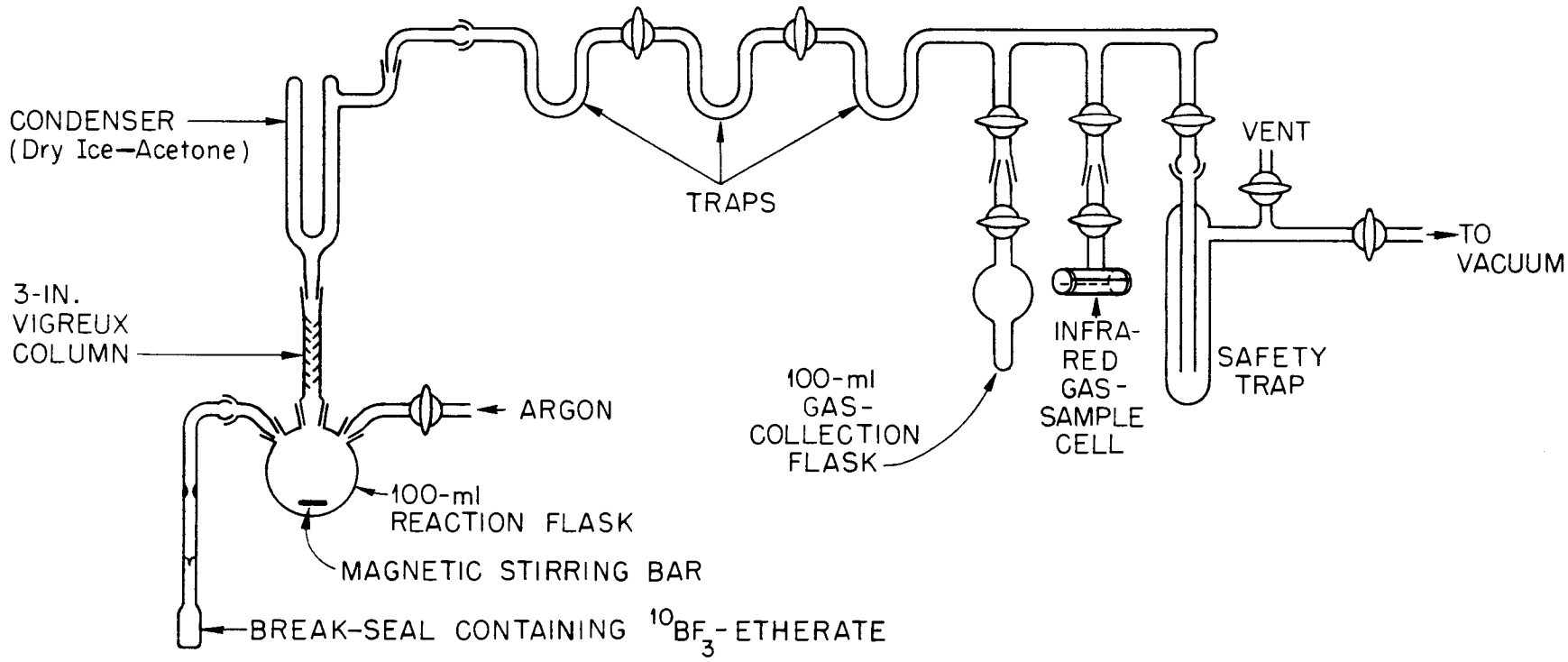

Fig. 1 Apparatus Used to Prepare $^{10}B_2H_6$.

The small amount of ether that passed through the reflux head was separated by fractional condensation of the $^{10}B_2H_6$ through a Dry Ice—acetone trap and into a liquid-nitrogen trap. The $^{10}B_2H_6$ was then transferred to an evacuated, 100-ml, gas-collection flask.

Analysis of the Diborane-^{10}B Product

Samples of the $^{10}B_2H_6$ product were taken from the flask for infrared and mass spectroscopic examination. Figure 2 gives the infrared absorption spectrum of $^{10}B_2H_6$ vapor from 700 to 4000 cm^{-1}. In Table I the observed

Table I. Comparison of Frequencies (cm^{-1}) of the Major Infrared Absorption Bands of $^{10}B_2H_6$ [a]

Observed [b]		Reported [1]	
978	s	977	s
1182	vs	1181	vs
1608	vvs	1606	vvs
1869	m	1869	ms
1887	m	1887	m
		2359	m
2522	vs	2528	vs
2622	vs	2625	vs
3640	m	3641	s
3660	m	3662	s
3670	m	3670	s
3706	m	3712	s

[a] Abbreviations: s, strong; m, medium; v, very.

[b] See Fig. 2.

frequencies of the major bands are compared with those reported by Lord and Nielsen.[1] The frequencies of the major bands of this spectrum are nearly identical with those observed previously.[1] The infrared spectrum, together with the results of mass spectroscopic analysis, showed that the product was essentially pure diborane.

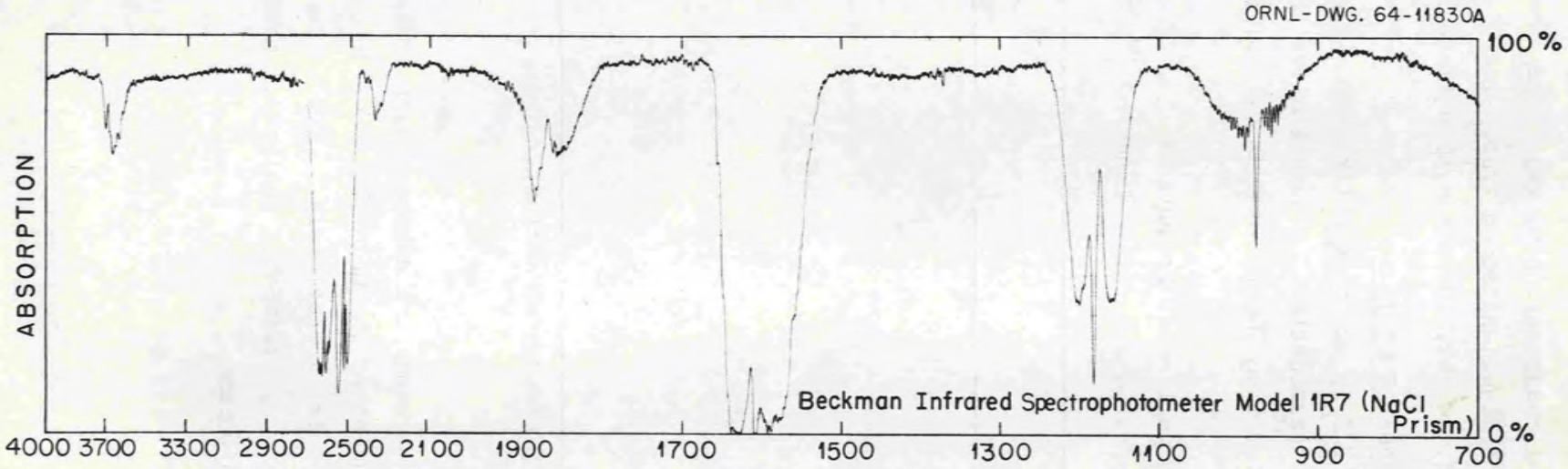

Fig. 2 Spectrum of $^{10}B_2H_6$ from 700 to 4000 cm^{-1} (10-cm vapor).

ACKNOWLEDGEMENT

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[2] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, J. Am. Chem. Soc. 74, 901 (1952).

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