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Highly Sensitive Low Temperature Fractionation Method for Separation and Measurement of Boron Hydrides

SIR: A highly sensitive method capable of detecting quantities of the boron hydrides, B_4H_{10} and B_5H_{11}, as small as 0.02 μmole was required for the analysis of the products of a very low conversion kinetic study of the photolysis of diborane (*7*). Various analytical methods have been described in the literature for boron hydrides: infrared absorption (*2, 9, 10*), neutron absorption (*3*), gas chromatography (*5*), low temperature fractionation (*4, 11*), and mass spectroscopy (*1*). Neutron absorption was used to determine total B^{10} content of individual boron hydrides for use in isotopic exchange studies. Gas chromatography was used successfully for B_4H_{10} and B_5H_9, though not for B_5H_{11} because of the latter's instability. Minimum detectable amounts for mixtures were given only for the infrared absorption method, where they were about 0.5 μmole of B_4H_{10} and B_5H_{11}, so that the method was too insensitive for much of our investigation. A method was needed where a minimum detectable amount in the presence of large amounts of B_2H_6 was as low as 5×10^{-4} mole per cent. It is necessary in certain studies with boron hydrides to proceed to very low per cent conversions to avoid complications due to the reactions of the products.

The products were separated in a low temperature LeRoy fractionation column (*8*) and measured in a special gas buret. The principal components in the analytical scheme were the LeRoy column and a double-range gas buret capable of measuring up to 200 μmoles. Its collection arm was sealed, instead of containing the usual greased stopcock, to eliminate solubility of the boron hydrides in the grease under pressure. A measurement error of about 0.2 cm. in the gas buret corresponded to 0.001 μmole, and the smallest amount required by the experimentation was 0.02 μmole. A LeRoy column had previously been applied to the determination of B_4H_{10} and B_5H_9 (*4*) in considerably larger quantities.

The procedure evolved after detailed vapor pressure measurements of the pure components and of mixtures: H_2 from the photolysis was first separated from the boron hydrides at −196° C. The major portion of the B_2H_6 was next removed at −136° C. in a simple trap-to-trap distillation. The boron hydrides were then collected in the LeRoy column at −196° C., and the temperature was slowly raised to −154° C. After the pressure had become constant, the B_2H_6 was removed by trapping at −196° C. until a pressure of about 0.5 micron was achieved. This procedure was repeated for B_4H_{10} and B_5H_{11}, whose separation temperatures were −120° C. and −74° C., respectively. The most critical separation, B_4H_{10} from B_5H_{11} at −120° C., was performed at the very low pressure of about 10 microns to obtain the maximum separation efficiency. After being collected at −196° C. separately, B_4H_{10} and B_5H_{11} were transferred to the gas buret using a Toepler pump and by direct expansion, respectively. About 250 analyses were made, and the amounts of these higher boron hydrides varied from 0.02 to 34 μmoles.

Table I. Analysis of Known Mixtures of B_4H_{10} and B_5H_{11}

Expt. No.	Product	Known mix. (μmoles)	Analyzed mix. (μmoles)	Diff. (μmole)	%
ST2	B_4H_{10}[a]	0.86	0.92	+0.06	+7
ST2	B_5H_{11}[a]	1.32	1.29	−0.04	−3
ST1	B_4H_{10}	5.18	5.16	−0.02	−0.5
ST1	B_5H_{11}	4.46	4.33	−0.13	−3

[a] These products were identified by means of their infrared absorption spectra (*9*).

Several experiments were designed to determine the effectiveness of the separation and possible loss due to internal reactions with the analytical system which contained greased stopcocks. By unusually extensive conditioning (*6, 7*) of the apparatus with B_4H_{10} and B_5H_{11} and by keeping the pressure less than about 10 microns during gas transfers, this loss was minimized. Known mixtures from the separated and purified products of a photolysis of diborane were analyzed (Table I).

Further indirect evidence for the accuracy and precision of the detection of very small amounts of B_4H_{10} can be found in the two plots of B_4H_{10} *vs.* time of photolysis for a diborane pressure of 0.08 cm. These are depicted elsewhere (*6*). The B_4H_{10} varied between 0.02 and 0.15 μmole, and the two curves were straight lines which extrapolated to within 0.02 μmole of the origin.

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W. C. KREYE
R. A. MARCUS

Department of Chemistry
Polytechnic Institute of Brooklyn
Brooklyn 1, N. Y.

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