

Zero Source Contact Mass Spectral Analysis of Isotopically Labeled Tetraboranes

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Abstract: The mass spectra of $^{10}\text{B}_4\text{H}_{10}$, $^{10}\text{B}_4\text{D}_{10}$, specifically labeled $^*\text{B}^{10}\text{B}_3\text{H}_{10}$, and $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$ have been obtained under zero ion source contact conditions using a specially designed mass spectrometer and compared with spectra obtained previously on conventional spectrometers. In the latter case there are significant contributions to the spectra from neutral species formed by pyrolysis of tetraborane in the ion source, which acts as a flow reactor. A parent peak and several new metastable transitions have been observed in the zero source contact spectra. Analysis of an ^{11}B -labeled tetraborane, $^*\text{B}^{10}\text{B}_3\text{H}_{10}$, has shown that the B_1H_x^+ , B_2H_x^+ , and B_3H_x^+ fragment ions are formed in part by nonrandom dissociation processes of the B_4H_x^+ framework. A reinvestigation of the process by which hydrogen atoms are lost leading to the formation of B_4H_x^+ ions does not appear to support the earlier proposed specific fragmentation scheme. The reaction of $^2\text{B}_2\text{D}_6$ with $^7\text{B}_4\text{H}_{10}$ at 45° has been reinvestigated using nmr and gas volumetric techniques. No evidence for specific deuterium labeling is found. Pentaborane was formed.

The mass spectrum of tetraborane-10 has been reported previously by Shapiro, *et al.*,¹ and investigated in some detail by Fehlner and Koski.² On the basis of metastable transitions, appearance potential measurements, and the spectrum of a mixture of partially deuterated tetraboranes,³ the latter investigators² proposed an energetically favored series of unimolecular dissociations to account for B_4H_x^+ ions in the spectrum. Also, they suggested that the B_4H_x^+ ions formed in this fragmentation scheme bore a structural relationship to the parent molecule (*i.e.*, hydrogen atoms are lost from specific positions during dissociation).

Although the process in which B_4H_x^+ ions are formed has been studied, no information concerning the mode of B_1H_x^+ , B_2H_x^+ , and B_3H_x^+ ion formation has been reported. Recently, methods for the preparation of tetraborane-10 labeled specifically with the ^{11}B isotope at the 2 position^{4,5} and with a single deuterium atom in a bridging (μ) position⁶ have been demonstrated. In these cases the degree and position of labeling has been established independently from ^{11}B nmr and infrared spectra. It might be expected that an examination of the mass spectrum of the boron-labeled sample (hereafter designated as $^*\text{B}^{10}\text{B}_3\text{H}_{10}$)⁷ would yield information concerning fragmentation of the tetraborane framework. Also, since $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$ is a specifically labeled sample free of other partially deuterated tetraboranes, an examination of its spectrum should make possible a confirmation of the proposed hydrogen fragmentation scheme of Fehlner and Koski.

(1) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, *Advances in Chemistry Series*, No. 32, American Chemical Society, Washington, D. C., 1961, p 127.

(2) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **85**, 1905 (1963).

(3) J. E. Todd and W. S. Koski, *ibid.*, **81**, 2319 (1959).

(4) The numbering system is that recommended for boron compounds by the preliminary report of the advisory committee on the Nomenclature of Organic Boron Compounds, available through *Chemical Abstracts*.

(5) R. Schaeffer and F. N. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

(6) A. D. Norman and R. Schaeffer, *Inorg. Chem.*, **4**, 1225 (1965).

(7) In this paper the superscripts 10 and *n* refer to boron isotopic contents of 96% ^{10}B -4% ^{11}B and 18.8% ^{10}B -81.2% ^{11}B , respectively.

The previously reported mass spectra of tetraborane were obtained with mass spectrometers having conventional inlet systems and hot (*ca.* 250°) ion sources. Under these conditions isotopic scrambling and/or pyrolysis of samples in the inlet system⁸ or ion source might be expected since tetraborane has been shown to decompose at an appreciable rate below 100°.⁹⁻¹¹ Recently, a means of avoiding this problem has been developed. The major portion of the following investigation of $^{10}\text{B}_4\text{H}_{10}$, $^{10}\text{B}_4\text{D}_{10}$, $^*\text{B}^{10}\text{B}_3\text{H}_{10}$, and $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$ was carried out with a mass spectrometer^{12,13} in which tetraborane was freshly distilled from the solid *via* variable-temperature conduits (total contact time *ca.* 0.5 sec) into a molecular beam. Only those molecular beam molecules that had zero contact with the ion source are considered.

Experimental Section

Preparation of Samples. All operations and manipulations performed in this investigation involved standard high-vacuum techniques described elsewhere.^{14,15}

Calcium fluoroborate (enriched to 96% in the ^{10}B isotope) obtained from the Oak Ridge National Laboratories was converted to $^{10}\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ as described previously.¹⁶ Lithium aluminum hydride and lithium aluminum deuteride (isotopic purity >99.5%) obtained from Metal Hydrides, Inc., and deuterium oxide, obtained

(8) J. F. Ditter, J. R. Spielman, and Robert E. Williams, *Inorg. Chem.*, **5**, 118 (1966).

(9) R. K. Pearson and F. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., 1957, p 15N.

(10) J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

(11) G. Brennan and R. Schaeffer, *ibid.*, **20**, 205 (1961).

(12) E. J. Sinke, G. A. Pressley, Jr., A. B. Baylis, and F. E. Stafford, *J. Chem. Phys.*, **41**, 2207 (1964).

(13) A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **86**, 5358 (1964); *ibid.* (in press).

(14) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(15) R. T. Sanderson, "High Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(16) R. E. Fedler, "A Laboratory Procedure for Boron Trifluoride Generation and Purification for Use in Thermal Neutron Counters," U. S. Atomic Energy Commission; available through Oak Ridge National Laboratories, Box X, Oak Ridge, Tenn.

from the Atomic Energy Commission, were used without further purification.

Isotopically enriched diboranes, $^{10}\text{B}_2\text{H}_6$, $^{10}\text{B}_2\text{D}_6$, and $^{11}\text{B}_2\text{D}_6$, were prepared by the reduction of $^{10}\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and $^{11}\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ with LiAlH_4 and LiAlD_4 , respectively.¹⁷ Normal diborane, $^{11}\text{B}_2\text{H}_6$, was obtained from a laboratory supply. All samples were purified by routine fractional condensation techniques.

Pentaboranes-11 were prepared from the appropriate isotopically enriched diboranes and purified as described previously.^{6,18}

Isotopically enriched tetraboranes, $^{10}\text{B}_4\text{H}_{10}$ and $^{10}\text{B}_4\text{D}_{10}$, were prepared by cleavage of $^{10}\text{B}_5\text{H}_{11}$ and $^{10}\text{B}_5\text{D}_{11}$ with H_2O and D_2O , respectively.¹⁹ A sample of $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$ was prepared as reported earlier.⁶ Infrared analysis of this sample indicated that the deuterium atom was, within the limits of this analytical method, located exclusively in a bridging position. Tetraborane labeled with an ^{11}B atom in the 2 position, $^*\text{B}^{10}\text{B}_3\text{H}_{10}$, was prepared as described by Schaeffer and Tebbe.⁵ Integration of the ^{11}B nmr spectrum of this sample indicated that the ratio of the ^{11}B isotope in the 2(4) position to that in the 1(3) position was 4.50 ± 0.10 to 1.0. Determination of the total ^{11}B percentage in the sample was carried out mass spectrometrically and is described in detail below. Normal tetraborane, $^{11}\text{B}_4\text{H}_{10}$, was obtained from the reaction of tetramethylammonium triborohydride with polyphosphoric acid.²⁰ Final purification of all samples was effected by low-temperature fractional distillation.²¹ Sample purity was determined mass spectrometrically.

Spectroscopic Techniques. "Zero source contact" mass spectra were obtained with a modified Nuclide Analysis Associates Model 12-60 HT Inghram-type mass spectrometer.^{12,13,22,23} Tetraborane was directly distilled from samples maintained at -127.3° (methylcyclohexane "slush") into the spectrometer through the $3/4$ -in. id. stainless-steel baffled crucible (1-mm orifice) used previously.^{12,13} The furnace temperature could be kept as low as 10° and was measured by one Pt-Pt-10% Rh and two Chromel-Alumel thermocouples spot welded to it. Differential pumping was maintained between the furnace (250 l./sec), ion source (20 l./sec), and mass analyzer (20 l./sec) chambers.

A movable beam defining slit ("shutter") located between the crucible orifice and the ion source allowed sampling of only those molecules which constituted a molecular beam originating from the orifice. Using this shutter it was possible to obtain the mass spectrum of species which had undergone no collisions with spectrometer walls or the hot ion source assembly, *i.e.*, zero source contact. Details of the procedure are given elsewhere.^{13,23}

The spectrometer was equipped with a 60° sector, 12-in. radius mass analyzer. Typically, an ionizing voltage of 70 v, an emission current of 1.2 ma, a trap current of $12 \mu\text{a}$, and an accelerating voltage of 4 kv was used. Positive ions of 7250 ev total energy were detected by means of a 50% transmission grid collector and a secondary electron multiplier. Multiplier gains ranged from 5×10^4 to 5×10^5 , and were measured for each peak in the spectrum when necessary. The exit slit from the mass analyzer was routinely opened to 0.012 in.; however, for observation of metastable species or to improve resolution, the slit was adjusted to 0.020 or 0.003 in. as desired.

Several experiments were carried out using a Consolidated Electroynamics Corp. Model 21-620A cycloidal mass analyzer mass spectrometer. With this instrument the sample material is allowed to diffuse into the heated ion source chamber (*ca.* 250°) through a small leak from a 3-l. room-temperature sample volume in the conventional manner. Typically, inlet sample pressures of 50 to 100μ were used.

^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates Model 4300B spectrometer operating at 19.3 Mc/sec equipped with standard Varian variable-temperature probe accessories. Tetraborane samples were routinely examined at -20 to -40° to prevent isotopic scrambling or thermal decomposition.

Infrared spectra were obtained on a Perkin-Elmer Model 137G spectrometer. All spectra were obtained on gaseous samples at 30

to 40 mm pressure using a 5-cm path length cell. The samples were kept frozen on the cell wall until scanning was begun to minimize isotopic scrambling and decomposition.

$^{11}\text{B}_4\text{H}_{10}$ - $^{11}\text{B}_2\text{D}_6$ Exchange Reaction. The conditions for this reaction were chosen to duplicate those used previously.⁸ Normal tetraborane (0.78 mmole) and $^{11}\text{B}_2\text{D}_6$ (2.52 mmoles) in a 500-ml reaction bulb were warmed from -196 to about 0° with a heat gun and then rapidly to $45 \pm 0.3^\circ$ in a constant temperature bath. The exchange period was measured from the time the bulb was immersed in the 45° bath until the reaction was quenched to -196° . The calculated partial pressures of diborane and tetraborane during the reaction were 10.1 and 3.12 cm, respectively. After a 15 min exchange period, the reactants were separated by repeated passage through a -157° trap, trapping diborane at -196° . The material which condensed at -157° was then removed from the vacuum line for low-temperature (-23 to -26°) ^{11}B nmr analysis. After measurement of the spectrum of a standard sample of unexchanged $^{11}\text{B}_4\text{H}_{10}$, the material from the exchange reaction was analyzed. In this way it was assured that change observed in the spectra were real and not due to changes in the spectrometer itself. After the nmr analysis, the partially exchanged material was reintroduced to the reaction flask with the diborane and the exchange procedure was repeated for second and third exchange periods of 20.0 and 40.0 min, respectively. After the final nmr analysis, 2.47 mmoles of diborane were separated from the reaction mixture by repeated passage through a -157° trap. Low-temperature column distillation at -110 to -115° effectively separated the material of lower volatility into tetraborane (0.68 mmole) and pentaborane-11 (0.06 ± 0.01 mmole). Total recovery of boron from the exchange mixture was not accomplished, around 2.0% presumably having been converted to nonvolatile residues in the reaction flask.

Data and Results

Mass Spectra. In the experiments carried out on the zero source contact spectrometer, only those positive ions which were shown to arise from neutrals in the molecular beam, exhibited dependence on inlet valve setting and reaction cell temperature, and whose neutral progenitors could be attributed to material from the sample were considered. Final assignment of peaks on the basis of mass defects and isotope ($^{10}\text{B}/^{11}\text{B}$) ratios was accomplished as a result of the high resolution (*ca.* 1 part in 10^3) of the instrument (Figure 1). Peaks from 4 to 10 *m/e* units beyond the parent peak of every sample were routinely examined and when necessary peaks up to *m/e* 90 were scrutinized.

The polyisotopic mass spectra of $^{10}\text{B}_4\text{H}_{10}$ and $^{10}\text{B}_4\text{D}_{10}$ obtained under zero source contact conditions and the spectrum of $^{10}\text{B}_4\text{H}_{10}$ obtained in the conventional mass spectrometer are documented elsewhere.²⁴ The normal isotopic spectra from the two sources are compared in Figure 2. No peaks of relative intensity greater than 0.05% arising from pentaborane were observed in the spectra of $^{10}\text{B}_4\text{H}_{10}$ and $^{10}\text{B}_4\text{D}_{10}$ under the former conditions; however, in the conventional spectrometer peaks at *m/e* 51-59 of 0.5 to 1.0% relative to the major tetraborane peak were observed.

The complete monoisotopic spectra of $^{10}\text{B}_4\text{H}_{10}$ and $^{10}\text{B}_4\text{D}_{10}$ (Table I) were obtained by stripping an ^{11}B content of 4.0% from the polyisotopic spectra.^{1,25} Owing to small variations in secondary electron multiplier gains for adjacent peaks in the spectra, the H

(24) This information noted as Tables I and III-V is of interest to the specialized reader. When referred to in the text the tables are marked by the superscript 24 and an asterisk. They have been deposited as Document No. 8795 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$2.50 for photoprints or \$1.75 for 35-mm microfilm. Make checks payable to Chief, Photoduplication Service, Library of Congress, Washington, D. C.

(25) (a) V. H. Dibeler, F. L. Mohler, and L. Williamson, *J. Res. Natl. Bur. Std.*, **44**, 489 (1950); (b) V. H. Dibeler, F. L. Mohler, L. Williamson, and R. M. Reese, *ibid.*, **43**, 97 (1949).

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(20) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **3**, 438 (1964).

(21) J. Dobson and R. Schaeffer, to be published.

(22) Nuclide Analysis Associates, State College, Pa.

(23) M. G. Inghram and J. Drowart in "Proceedings of an International Symposium on High Temperature Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

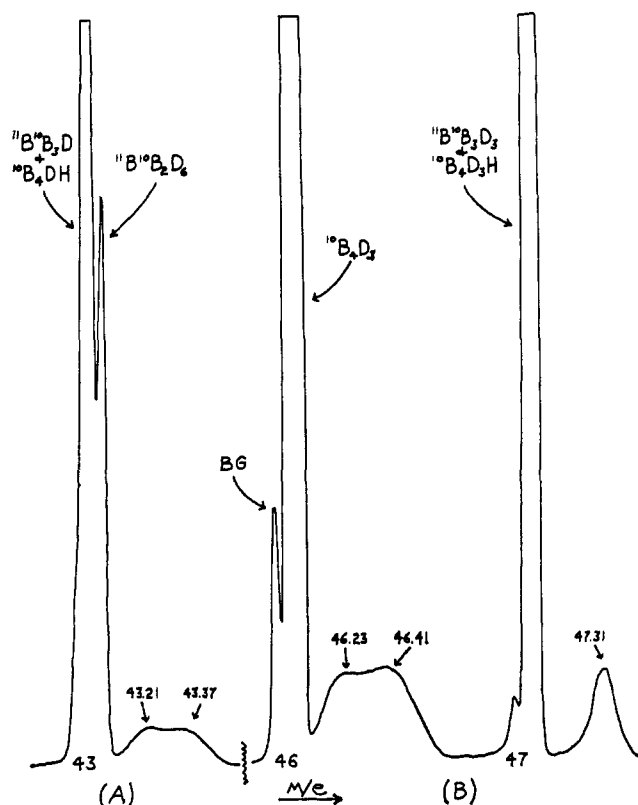


Figure 1. Part of the $^{10}\text{B}_4\text{D}_{10}$ spectrum showing resolution of the high and low mass components of m/e 43, 46, and 47 peaks and metastable transition peaks at an entrance and exit slit openings of 0.005 and 0.012 in. BG refers to the residual (hydrocarbon) background.

content was not easily determined in the $^{10}\text{B}_4\text{D}_{10}$ spectrum; however, it was possible to remove contributions from about 1.5% H without obtaining negative residues.

Table I. Monoisotopic Spectra of $^{10}\text{B}_4\text{H}_{10}$ and $^{10}\text{B}_4\text{D}_{10}$ Taken with Zero Ion Source Contact

$^{10}\text{B}_4\text{H}_{10}$				$^{10}\text{B}_4\text{D}_{10}$			
Ion	Rel intens	Ion	Rel intens	Ion	Rel intens	Ion	Rel intens
B_4H_{10}	0.2	B_3H_3	6.7	B_4D_{10}	<i>a</i>	B_3D_3	6.7
B_4H_9	1.8	B_3H_2	5.5	B_4D_9	1.3	B_3D_2	5.6
B_4H_8	11.1	B_3H_1	1.1	B_4D_8	11.2	B_3D	1.0
B_4H_7	24.9	B_3	0.3	B_4D_7	14.0	B_3	0.4
B_4H_6	100			B_4D_6	100		
B_4H_5	13.5	B_2H_6	~ 0.05	B_4D_5	6.9	B_2D_6	< 0.01
B_4H_4	38.6	B_2H_5	1.5	B_4D_4	26.5	B_2D_5	1.6
B_4H_3	12.0	B_2H_4	0.5	B_4D_3	5.5	B_2D_4	0.6
B_4H_2	9.5	B_2H_3	1.0	B_4D_2	4.9	B_2D_3	1.3
B_4H	5.9	B_2H_2	1.0	B_4D	3.1	B_2D_2	1.5
B_4	2.6	B_2H	0.5	B_4	1.1	B_2D	0.3
		B_2	0.08			B_2	0.07
B_3H_8	~ 0.01						
B_3H_7	0.3	BH_3	0.03	B_3D_7	<i>a</i>	BD_3	0.01
B_3H_6	2.0	BH_2	1.2	B_3D_6	1.6	BD_2	1.6
B_3H_5	12.5	BH	0.2	B_3D_5	12.0	BD	0.5
B_3H_4	4.6	B	1.7	B_3D_4	3.9	B	1.5

^a Peaks too small to be definitely assigned.

Peaks of low intensity were observed at m/e 50 and 51 in the zero source contact spectrum of $^{10}\text{B}_4\text{H}_{10}$. Since contributions from pentaborane peaks in this region were *ca.* 0.01%, the m/e 51 peak in the poly-

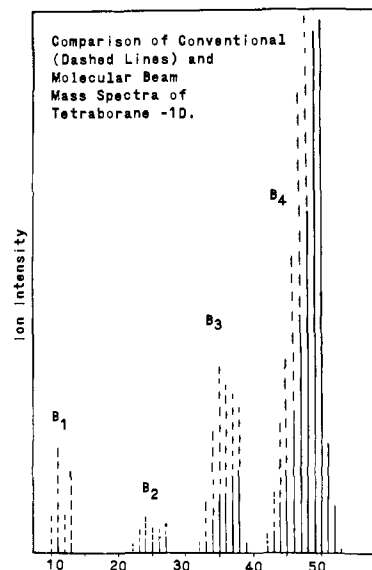


Figure 2. Comparison of the $^{10}\text{B}_4\text{H}_{10}$ mass spectrum taken under zero ion source contact conditions, solid lines (corrected for secondary electron multiplier discrimination), and conventional conditions where the material may be pyrolyzed by contact with the hot ion source (dashed lines). In the latter case B_3H_2 and B_3H_3 ions also were reported (API Research Project No. 44 Mass Spectral Data, Series No. 30; taken with a Consolidated Model 21-103B (180° sector) instrument).

isotopic spectrum was readily assigned to the $^{11}\text{B}^{10}\text{B}_3\text{H}_{10}^+$ ion. The 0.2% contribution to the m/e 50 peak in the monoisotopic spectrum was attributed to the $^{10}\text{B}_4\text{H}_{10}^+$ ion fragment. Within limits of experimental error, the $I(^{10}\text{B}_4\text{H}_{10}^+)/I(^{11}\text{B}^{10}\text{B}_3\text{H}_{10}^+)$ ratio agreed with the expected value of 6.0:1.0.

Peaks arising from doubly charged ion fragments were observed at m/e 23.5, 22.5, and 21.5 for $^{10}\text{B}_4\text{H}_{10}$ and at m/e 25.5, 24.5, 23.5, and 22.5, arising from $^{11}\text{B}^{10}\text{B}_3\text{D}_x^{2+}$ ions, in the $^{10}\text{B}_4\text{D}_{10}$ spectrum. Weak peaks (*ca.* 0.001%) appeared at m/e 21.5 and 20.5 in the latter spectrum; however, positive identification of these peaks was not possible. Attempts were made to observe peaks arising from $^{10}\text{B}_4\text{D}_x^{2+}$ ions at integral m/e values; however, they could not be sufficiently resolved from the large singly charged ion peaks to be assigned or measured.

The metastable peaks newly observed in the zero source contact spectra of $^{10}\text{B}_4\text{H}_{10}$ and $^{10}\text{B}_4\text{D}_{10}$ and the corresponding transitions are shown in Tables II and III. The presence of metastable peaks was verified when the intensity of the peaks relative to peaks at integral m/e values in the spectrum increased with an increased exit slit width. Apparent masses (m^*) were determined by adjusting the exit slit to 0.003 in. for maximum resolution and interpolating between the integral m/e boron hydride peaks (Figure 1B). Apparent mass to charge ratios were determined to ± 0.05 mass unit. The transitions were assigned using the relationship $m^* = m_2^2/m_1$ (where m_1 refers to the initial ion and m_2 to the final ion).²⁶ Metastable peaks of low intensity were observed in the spectrum of $^{10}\text{B}_4\text{D}_{10}$ at $m^* = 47.8$, 49.8, and 51.8; however, since transitions corresponding to these m^* values could not be determined, they are not listed in Table III.

(26) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960.

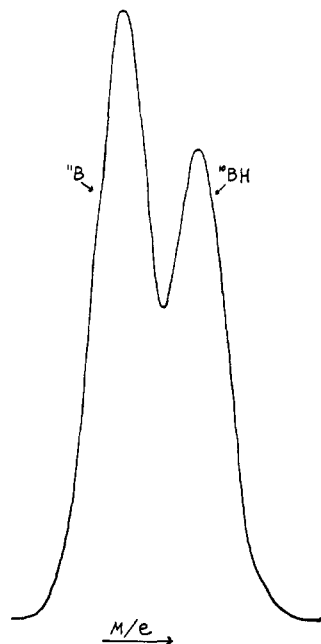


Figure 3. The m/e 11 peak resolved into its high and low mass components (^{10}BH and ^{11}B) at an exit slit opening of 0.003 in.

The zero source contact mass spectrum of $^*\text{B}^{10}\text{B}_3\text{H}_{10}$ (labeled with ^{11}B in the 2 position) is shown in Table IVa.^{24*} The spectra were routinely measured at an exit slit opening of 0.012 in.; however, closing the slit to 0.003 in. and scanning the spectrum slowly allowed the m/e 11 peak to be resolved into its low and high

Table II. Metastable Transitions Observed for $^{10}\text{B}_4\text{H}_{10}^a$

m^* , obsd	Rel intens ^b	Transition
45.09	0.17	$^{10}\text{B}_4\text{H}_9^+ \rightarrow ^{10}\text{B}_4\text{H}_7^+ + \text{H}_2$
43.15	0.23	$^{10}\text{B}_4\text{H}_8^+ \rightarrow ^{10}\text{B}_4\text{H}_6^+ + \text{H}_2 + \text{H}$
42.07	0.48	$^{10}\text{B}_4\text{H}_6^+ \rightarrow ^{10}\text{B}_4\text{H}_4^+ + \text{H}_2$
33.10	0.007	$^{10}\text{B}_3\text{H}_7^+ \rightarrow ^{10}\text{B}_3\text{H}_5^+ + \text{H}_2$
27.9	0.001	$^{10}\text{B}_4\text{H}_9^+ \rightarrow ^{10}\text{B}_3\text{H}_7^+ + \text{BH}_2$

^a A complete list of the metastable transitions observed by us is given in ref 24. ^b Intensities relative to m/e 46 = 100% at an exit slit opening of 0.012 in.; entrance slit 0.005 in.

Table III. Metastable Transitions Observed for $^{10}\text{B}_4\text{H}_{10}^a$

m^*	Rel intens ^b	Transitions
51.27	0.02	$^{11}\text{B}^{10}\text{B}_3\text{D}_9^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3\text{D}_7^+ + \text{D}_2$
49.29	0.18	$^{10}\text{B}_4\text{D}_8\text{H}^+ \rightarrow ^{10}\text{B}_4\text{D}_6\text{H}^+ + \text{D}_2$
47.31	0.07	$^{11}\text{B}^{10}\text{B}_3\text{D}_7^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3\text{D}_5^+ + \text{D}_2$
45.40	0.09	$^{11}\text{B}^{10}\text{B}_3\text{D}_6^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3\text{D}_4^+ + \text{D}_2$
43.37	0.02	$^{11}\text{B}^{10}\text{B}_3\text{D}_5^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3\text{D}_3^+ + \text{D}_2$
41.29	0.009	$^{11}\text{B}^{10}\text{B}_3\text{D}_4^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3\text{D}_2^+ + \text{D}_2$
39.29	0.006	$^{11}\text{B}^{10}\text{B}_3\text{D}_3^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3\text{D}^+ + \text{D}_2$
37.30	0.003	$^{11}\text{B}^{10}\text{B}_3\text{D}_2^+ \rightarrow ^{11}\text{B}^{10}\text{B}_3^+ + \text{D}_2$
35.35	0.004	$^{11}\text{B}^{10}\text{B}_2\text{D}_6^+ \rightarrow ^{11}\text{B}^{10}\text{B}_2\text{D}_4^+ + \text{D}_2$
31.39	0.006	$^{11}\text{B}^{10}\text{B}_2\text{D}_4^+ \rightarrow ^{11}\text{B}^{10}\text{B}_2\text{D}_2^+ + \text{D}_2$

^a A complete list of the metastable transitions observed by us is given in ref 24. ^b Intensities relative to m/e 52 = 100% at an exit slit opening of 0.012 in.

mass components (^{11}B and ^{10}BH) as shown in Figure 3. The m/e 13 peak was resolved well enough to allow an accurate curve subtraction of it into its components. Peak intensities quoted in Table IVa of ions in the B_1 region were measured directly from the 0.003-in. resolved spectrum and normalized to the m/e 10 peak intensity obtained with a 0.012-in. slit opening. In all cases the relative peak intensities from the 0.012-in. spectra were in close agreement with the sum of the intensities of the resolved peaks in the 0.003-in. slit width spectrum.

Determination of the degree of labeling of $^*\text{B}^{10}\text{B}_3\text{H}_{10}$ was accomplished by an analysis of the B_4H_x^+ region of the polyisotopic spectrum, and will be discussed later in the paper. Details, including Table IVb are given in ref 24*.

The boron isotopic composition of ion fragments in the B_3 and B_2 regions of the $^*\text{B}^{10}\text{B}_3\text{H}_{10}$ spectrum was determined by stripping the polyisotopic spectrum using various $^{10}\text{B}_3/^{10}\text{B}_2^{11}\text{B}$, $^{10}\text{B}_3/^{10}\text{B}^{11}\text{B}_2$, $^{10}\text{B}_2/^{11}\text{B}^{10}\text{B}$, and $^{10}\text{B}_2/^{11}\text{B}_2$ ratios until the best possible "fit" to the data could be obtained. In the B_3 region, using $^{10}\text{B}_3/^{10}\text{B}_2^{11}\text{B} = 2.9$, $^{10}\text{B}_3/^{10}\text{B}^{11}\text{B}_2 \approx 49$, and constant $\text{B}_3\text{H}_x/\text{B}_3\text{H}_{x-1}$ ratios, an acceptable fit to the observed data was obtained in which peak residues were less than 5% and of alternating sign. When $^{10}\text{B}_3/^{10}\text{B}_2^{11}\text{B}$ and $^{10}\text{B}_3/^{10}\text{B}^{11}\text{B}_2$ ratios appreciably less than 2.9 and 49.0 were used in the analysis large systematic negative residues above m/e 36 resulted. A similar stripping procedure in the B_2 region resulted in $^{10}\text{B}_2/^{11}\text{B}^{10}\text{B} \approx 3.4$ and $^{10}\text{B}_2/^{11}\text{B}_2 \approx 100$ producing a reasonable fit to the observed spectrum with random residues of less than 5%. It was found that increasing the $^{10}\text{B}_3/^{11}\text{B}^{10}\text{B}$ ratio above 3.4 and/or decreasing $^{10}\text{B}_2/^{11}\text{B}_2$ to much less than 100 caused systematic negative residues above m/e 26.

Accurate determination of the $^{10}\text{B}-^{11}\text{B}$ content in the B_1 region of the $^*\text{B}^{10}\text{B}_3\text{H}_{10}$ spectrum was possible, since the peaks at m/e 11 and 13 could be resolved into their high and low mass components as in Figure 3. The contribution of ^{11}BH to the m/e 12 peak was small and not adequately resolved from the higher mass $^{10}\text{BH}_2$ component; hence, the relative contribution of ^{11}BH was calculated indirectly using the BH^+/B^+ ratio obtained from the monoisotopic spectrum of $^{10}\text{B}_4\text{H}_{10}$. On the basis of the data shown in Table IVa,^{24*} isotope ratios of 6.40 ($^{10}\text{BH}_3/^{11}\text{BH}_3$), 5.20 ($^{10}\text{BH}_2/^{11}\text{BH}_2$), 6.15 ($^{10}\text{BH}/^{11}\text{BH}$), and 6.27 ($^{10}\text{B}/^{11}\text{B}$) were obtained. A marked effect on the $^{10}\text{BH}_x/^{11}\text{BH}_x$ ratio was observed when the ionizing voltage was lowered below 70 ev. For example, the ratio of the ion intensities $I(^{10}\text{BH}_2^+)/I(^{11}\text{BH}_2^+)$ remained nearly constant at 5.20/1.0 to 5.06:1.0 between 70 and 24 ev. Below 24 ev the ratio decreased rapidly and at 23 ev a ratio of 4.69:1.0 resulted. Further lowering of the ionizing voltage to 21 ev caused the ratio to decrease slightly to 4.29:1.0.

The B_4 region of the zero source contact polyisotopic spectrum of $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$ before and after partial scrambling is shown in Table V.^{24*} Infrared analysis of the sample prior to scrambling indicated that no detectable amount of deuterium was present in terminal 2(4) or 1(3) positions. After 21 min in the gas phase at room temperature (sample pressure during scrambling <0.5 atm) the sample was substantially scrambled as evidenced by the decreased intensity of the BD bridge

absorption peak and the appearance of BD terminal absorptions. Within limits of experimental error, no significant difference between the mass spectrum of the unscrambled and scrambled material could be observed. Small peaks of *ca.* 0.10% relative intensity above *m/e* 52 were present in the spectrum of the scrambled sample. These were attributed to pentaborane formed by $\mu\text{-}^{10}\text{B}_4\text{H}_9\text{D}$ decomposition.

$^{10}\text{B}_2\text{D}_6\text{-}^{11}\text{B}_4\text{H}_{10}$ Exchange Reaction. The results of the $^{10}\text{B}_2\text{D}_6\text{-}^{11}\text{B}_4\text{H}_{10}$ exchange reaction are shown in Figure 4 and Table IV. The ^{11}B nmr spectrum (Figure 4A) of $^{11}\text{B}_4\text{H}_{10}$ prior to the first exchange period was free of extraneous peaks which could be attributed to other boron hydrides. After 15 min at 45° , small peaks on the low and high field sides of the tetraborane triplet ($\text{B}_{2(4)}$) and doublet ($\text{B}_{1(3)}$), respectively, were visible (X and Z, Figure 4B). Additional exchange periods of 20 (Figure 4C) and 40 min (Figure 4D) resulted in increased intensity of the impurity peaks along with a noticeable asymmetry of the tetraborane, $^{11}\text{B}_4\text{D}_x\text{H}_{10-x}$ low field triplet. The peaks at $\delta = -6.5$ (X), $+0.03$ (Y), and $+52.3$ (Z) ppm (relative to boron trifluoride diethyl etherate) corresponded in relative area and chemical shifts to basal $\text{B}_{2(3)}$, $\text{B}_{3(4)}$, and apex B_1 borons of deuterated pentaborane-11, respectively. Calculations based on relative peak areas indicated that after 75 min at 45° the mixture was comprised of 89.4 mole % tetraborane and 10.6 mole % pentaborane-11.

Table IV. Percentage Areas of Species from the $^{10}\text{B}_2\text{D}_6\text{-}^{11}\text{B}_4\text{H}_{10}$ Exchange Contributing to the ^{11}B Nmr Spectra

Time, ^a min	$^{10}\text{B}_2\text{D}_6\text{-}$ H_{11-x} (total area)	$^{11}\text{B}_4\text{D}_x\text{H}_{10-x}$				
		$\text{B}_{2(4)}$		$\text{B}_{1(3)}$		
		BH_2	BHD	BD_2	BH	BD
0	0	50.4	0	0	49.6	0
15.0	2.7	46.2	1.1	2.3	46.9	0.8
35.0	4.5	42.0	2.3	3.3	45.4	2.5
75.0	10.6 ^b	35.6	4.2	5.6	37.8	6.2

^a Total exchange time (± 0.1 min) at $45.0 \pm 0.3^\circ$. ^b Measurement of the gas volumes of materials separated from these small samples gave 8.6 mole % B_5X_{11} and 91.4 mole % tetraborane.

Since the center peak of the low field "triplet" increased in intensity relative to the outer peaks and a singlet appeared between the lines of the upfield doublet, it was clear that deuterium exchange had occurred. By subtracting the contribution of triplet and doublet, arising from unexchanged $\text{B}_{2(4)}\text{H}_2$ and $\text{B}_{1(3)}\text{H}$ groups of $^{11}\text{B}_4\text{H}_{10}$, from the spectra in Figure 4B–D it was possible to determine approximately the amount of $\text{B}_{2(4)}\text{HD}$ doublet, $\text{B}_{2(4)}\text{D}_2$ singlet, and $\text{B}_{1(3)}\text{D}$ singlet contributing to the spectrum after each exchange period (see Figure 4D). The results are shown in Table IV.

Conclusions and Discussion

Significant differences exist between the zero source contact and conventional mass spectra of tetraborane. For example, in the conventional spectrum of $^{10}\text{B}_4\text{H}_{10}$ appreciable quantities of B_3H_x^+ ion fragments (*ca.* 0.5–1.0%) are routinely present and peaks at masses below *m/e* 46 are more intense than those in the zero source contact spectrum. It appears clear²⁷ that pyro-

(27) A. B. Baylis, G. A. Pressley, Jr., M. E. Gordon, and F. E. Stafford, *J. Am. Chem. Soc.*, **88**, 929 (1966).

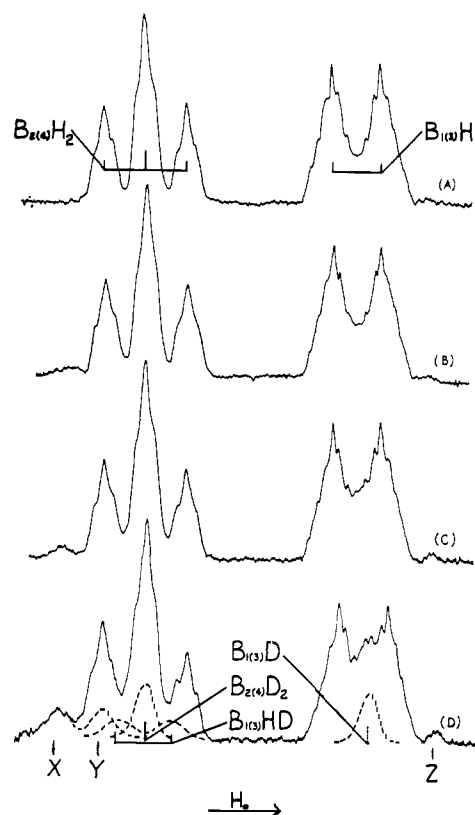


Figure 4. ^{11}B nmr spectra of products (diborane removed) from the $^{10}\text{B}_2\text{D}_6\text{-}^{11}\text{B}_4\text{H}_{10}$ (10.1 and 3.12 cm of Hg, respectively) exchange reaction at 45.0° . Peaks at X, Y, and Z arise from deuterated pentaborane-11 formed during the exchange. The spectra were measured at -23 to -26° . A is the initial spectrum; B, C, and D were taken after 15, 35, and 75 min.

lysis of tetraborane in the ion source of the conventional spectrometer occurs. Formation of pentaboranes, tetraborane-8, and diborane in this way can account for the presence of B_5H_x^+ ion fragments and the high intensity of peaks in the remainder of the spectrum. This explanation is substantiated by pyrolysis studies of tetraborane which show, *e.g.*, that the spectrum obtained with a reactor at *ca.* 250° closely resembles that obtained on a conventional spectrometer.²⁷

The previously unreported metastable transition at $m^* = 27.9$ observed in the zero source contact spectrum of $^{10}\text{B}_4\text{H}_{10}$ (Table II) assignable to the process, $^{10}\text{B}_4\text{H}_9^+ \rightarrow ^{10}\text{B}_3\text{H}_7^+ + ^{10}\text{BH}_2$, is of interest since it indicates one process which must contribute to dissociation of the boron framework of tetraborane ion. However, it should be noted that other transitions involving losses of boron atoms also may occur which result in peaks too weak for detection or at a rate that is slow or fast with respect to 10^6 sec^{-1} , the approximate decomposition rate for observation of metastable species.²⁸

The analysis of the zero source contact mass spectrum of $^{10}\text{B}_3\text{H}_{10}$ also provides interesting information concerning the fragmentation mechanism of the tetraborane framework. If B_3H_x^+ , B_2H_x^+ , and BH_x^+ ions arise only by random fragmentation and/or dissociation processes, the ratios given in the second column of Table V, corresponding to a random system of 88% ^{10}B and 12% ^{11}B ,²⁴ should best fit the observed data.

(28) J. A. Hipple, *Phys. Rev.*, **71**, 594 (1947).

Table V. Comparison of Observed Fragment Ion Intensity Ratios with Those Predicted for Random Fragmentation^a of ¹⁰B¹⁰B₂H₁₀

Species	Ion intensity ratios	
	Random	Obsd
¹⁰ B ₃ / ¹⁰ B ₂ ¹¹ B	2.4	≥ 2.9
¹⁰ B ₃ / ¹⁰ B ¹¹ B ₂	18	≈ 49
¹⁰ B ₂ / ¹⁰ B ¹¹ B	3.7	≤ 3.4
¹⁰ B ₂ / ¹¹ B ₂	54	≈ 100
¹⁰ B/ ¹¹ B	7.3	5.2 to 6.4

^a Cf. Table IVb.^{24*}

It was found, however, that the best fits were obtained using the significantly different stripping ratios shown in the last column.

It appears that B₃H_x⁺, B₂H_x⁺, and BH_x⁺ ions result, in part, from dissociation and/or ionization processes in which the ion fragments are lost in a specific fashion and which bear a structural relationship to the original tetraborane molecules. Therefore, B₃H_x⁺ ions are formed by the loss of a monoboron species from the 2 or 4 positions of tetraborane. Since the two-boron fragments contain considerably more ¹¹B than would be expected if they arose exclusively from B₃H_x⁺ ions, it appears that direct formation of B₂H_x⁺ ions from tetraborane is a significant process; and, since the ¹⁰B/¹¹B ratios of the one-boron fragment ions are consistently lower than 7.3:1.0, preferential loss of BH_x⁺ ions from the 2 or 4 positions of tetraborane must occur. It must be emphasized, however, that at an ionizing voltage of 70 ev contributions to the spectrum from random dissociation processes, dissociations of partially scrambled molecules, and ions resulting from direct cleavage of tetraborane molecules upon electron impact must be considered.

The metastable transitions observed in the zero source contact spectra of ¹⁰B₄H₁₀ and ¹⁰B₄D₁₀ in part substantiate the previously reported² stepwise dissociation process leading to the formation of B₄H_x⁺ ions; however, the data obtained from the specifically labeled sample, μ-¹⁰B₄H₉D, provides no evidence for an energetically favored process involving loss of hydrogen

or deuterium from specific positions in the molecules, since the spectrum of the scrambled material is unchanged (within the limits of experimental error) from that of the labeled material. Earlier work on μ-¹⁰B₄D₉H has shown that the label atom drifts nonpreferentially to all positions of the molecule upon scrambling;²⁹ therefore, it is necessary to conclude that at an ionizing voltage of 70 ev, hydrogen atoms are lost by random processes or that the deuterium and hydrogen atoms of the labeled sample become isotopically scrambled prior to dissociation.

It had been concluded previously² that H and D are lost from specific positions during dissociation of B₄H_x⁺ ions on the basis of a mass spectral analysis of a mixture of partially deuterated tetraboranes assumed to contain a greater-than-statistical concentration of 1,3-dideuteriotetraborane molecules.³ The results of the ¹⁰B₂D₆-¹⁰B₄H₁₀ experiment (Figure 4, Table IV) do not indicate that a preferential exchange process involving only the 1(3) positions of tetraborane exists. Also, as expected from earlier work,⁹⁻¹¹ considerable tetraborane decomposition and deuterated pentaborane-11 formation took place during the exchange. It seems possible that a reinterpretation of the previous ¹⁰B₂D₆-¹⁰B₄H₁₀ exchange data, considering tetraborane decomposition, and B₂D₆ exchange processes with both pentaborane and tetraborane might lead to a simpler explanation for the observed kinetic exchange data.

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(29) A. D. Norman and R. Schaeffer, unpublished work.

Transition Metal Complexes of Triethylenetetramine. III. *cis*-α-Diacidotriethylenetetraminechromium(III) Complexes¹

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Abstract: The synthesis, characterization, properties, and infrared and visible absorption spectra of *cis*-α-[Cr(trien)Cl₂]Z (Z = Cl, ClO₄, NCS, NO₃), *cis*-α-[Cr(trien)(NCS)₂]Z (Z = Cl, NCS, NO₃), *cis*-α-[Cr(trien)(N₃)₂]Br, and α-[Cr(trien)ox]Z (Z = Br, ClO₄, NCS) are described.

Previous papers in this series^{2,3} have described some nickel(II) and copper(II) complexes containing triethylenetetramine ligand (N,N'-bis(2-aminoethyl)-

ethylenediamine, H₂NCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂, abbreviated trien). In the present paper we report the synthesis, characterization, properties, and infrared and visible absorption spectra of some diacido-

(1) This work was partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California.

(2) D. A. House and N. F. Curtis, *J. Chem. Soc.*, 3149 (1963).

(3) N. F. Curtis and D. A. House, *ibid.*, 6194 (1965).