collinearity of the nonbonding lobes of the C–H axial bond and of the phosphorus lone pair as well as the increased distance from phosphorus to the methylene carbon (2.2 A in VIII and IX *vs.* 2.6 A in II and III as revealed by Dreiding models). The presence of oxygen substitution on the phosphorus atom appears to be necessary for large four-bond phosphorus–proton coupling since coupling can be drastically reduced by transposing oxygen and carbon substituents, without significantly changing the geometry of the system in VIII and X and IX and XI.

The five-bond HCOCCH couplings in I and VII are unexpectedly large for saturated systems. In I the coupling was found by spin decoupling to be specifically between the apical proton and the three axial methylene protons, assigned in previous work.[19] Coupling between the two apical protons in VII was similarly verified. The ratio of the five-bond couplings in I and VII is approximately 2:3, inconsistent with the advent of a new coupling mechanism in VII as was proposed for its phosphorus analogs VIII and IX but consistent with possible equal through-bond contributions *via* two paths in I and three in VII. In both cases the C–H groups involved in coupling are parallel and opposed, but collinear only in VII. The COCC dihedral angle is zero in VII and 60° in I, making it unlikely that this has any great bearing on the mechanism of coupling. A similar opposed and approximately parallel orientation of C–H bonds has been noted in many four-bond couplings in saturated systems[6] and five-bond couplings in some norbornenes having sp^2-hybridized carbon atoms.[23]

Sheppard has observed[24] that five-bond coupling in certain unsaturated systems follows a "straight zigzag" path and suggests a stereospecific σ-bond contribution to coupling. Similar specific coupling has been found in a number of aromatic aldehydes.[25] The coupling systems in I and VII differ from these in that rotation of 180 and 120° about the central bond has taken place. If one mechanism is responsible for all the five-bond couplings cited, it must be independent of the geometry of the central bond. The relative signs of these long-range couplings are being investigated.

Acknowledgments. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors are also grateful to the National Science Foundation for support of this work in the form of a grant to J. G. V. (GP-2328) and a fellowship to K. J. C. E. J. B. thanks the National Aeronautics and Space Administration for a fellowship.

---

(23) R. W. King and P. E. Butler, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 84Q.

(24) N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).

(25) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963).

Isotopically Labeled Tetraborane(10) and Pentaborane(11)[1]

Arlan D. Norman and Riley Schaeffer

Contribution No. 1326 from the Department of Chemistry, Indiana University, Bloomington, Indiana. Received June 23, 1965

Abstract: Reactions of tetraborane(8) carbonyl provide convenient routes to two new isotopically labeled boron hydrides. Reaction of tetraborane(8) carbonyl and deuterium yields a dideuterium-labeled tetraborane(10), μ,1-dideuteriotetraborane(10). Also, B_4H_8CO (enriched in either the ^{10}B or ^{11}B isotope) and B_2H_6 (enriched in the other isotope) react to form pentaborane(11) labeled in basal (2–5) positions. Mass, infrared, and ^{11}B nuclear magnetic resonance spectral evidence establish the position and degree of labeling of these compounds. The ^{11}B nmr spectra also support the previously suggested structures for B_4H_8CO and $B_4H_8PF_3$.

Relatively few reactions have been found which can be used for the preparation of specifically isotopically labeled tetraborane(10)'s. Evidence for tetraborane labeled with an ^{11}B atom in the 2-position[2,3] and with a single deuterium atom in a bridging (μ) position has been reported.[4] Also, kinetic evidence has been cited for the formation of 1,3-dideuteriotetraborane from exchange reactions between tetraborane and deuterated diborane.[5,6] No example of a specifically labeled pentaborane(11) has yet been reported. Recently, we have found that by substituting deuterium or isotopically enriched diborane for hydrogen or normal diborane in the reaction of the latter two with tetraborane(8) carbonyl,[7] a new specifically labeled dideuteriotetraborane(10) and a basal boron labeled pentaborane(11) can be prepared.

Experimental Section

Spectroscopic Techniques. The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates Model 4300B spectrometer operating at 19.3 Mc/sec equipped with standard

---

(1) Studies of Boranes. XXI. For paper XX of this series, see J. Dobson and R. Schaeffer, in press.

(2) 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*.

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

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

(5) J. E. Todd and W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).

(6) T. P. Fehlner and W. S. Koski, *ibid.*, **85**, 1905 (1963).

(7) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).

Varian variable temperature probe accessories. Chemical shift values were determined by the external standard technique relative to boron trichloride and were converted to the boron trifluoride diethyl etherate scale by addition of 47.3 ppm. Mass spectra were obtained on a Consolidated Electrodynamics Corporation Model 21-620A cycloidal mass analyzer mass spectrometer. Infrared spectra were measured with a Perkin-Elmer Model 137G spectrometer on gaseous samples. The samples were frozen at −196° on the cell wall until scanning was begun to prevent decomposition and isotopic scrambling.

Preparation of Starting Materials. All operations and manipulations performed in this investigation involved standard high vacuum techniques described elsewhere.[8,9]

Hydrogen, carbon monoxide (Matheson Co.), and deuterium (Liquid Carbonic, Inc.) were purified prior to use by passage through a −196° glass-wool packed trap. Commercial phosphorous trifluoride was purified by repeated fractionation through a −157° trap until its vapor tension at −112° was 370 mm. Lithium aluminum hydride, lithium aluminum deuteride (Metal Hydrides, Inc.), and calcium fluoroborate (enriched to 96% ^{10}B by the Oak Ridge National Laboratories) were used without further purification. Calcium fluoroborate was converted to $^{10}BF_3 \cdot O(C_2H_5)_2$ by the procedure of Fedler.[10]

Isotopically labeled diboranes, $^{10}B_2H_6$ and $^{n}B_2D_6$, were prepared by the reduction of $^{10}BF_3 \cdot O(C_2H_5)_2$ and $^{n}BF_3 \cdot O(C_2H_5)_2$ with $LiAlH_4$ and $LiAlD_4$, respectively.[11,12] Normal diborane, $^{n}B_2H_6$, was obtained from a laboratory supply. Diboranes were converted to the appropriate isotopically enriched pentaborane(11) samples in a hot–cold reactor using previously described conditions.[4,13]

Tetraborane(8) carbonyl samples, $^{n}B_4H_8CO$, $^{10}B_4H_8CO$, and $^{n}B_4D_8CO$, were prepared from the reaction of $^{n}B_5H_{11}$, $^{10}B_5H_{11}$, and $^{n}B_5D_{11}$, respectively, with 15–20 atm of CO in a 350-ml stainless steel bomb.[7] A sample of $^{n}B_4H_8PF_3$ was prepared from $^{n}B_4H_8CO$ as described previously.[14] Purification of boranes was carried out by routine fractional condensation and temperature-gradient fractional sublimation.[15] From the column, pure pentaborane(11) was collected between −95 and −98°, pure tetraborane(8) carbonyl between −102 and −104°, and $^{n}B_4D_8CO$ and $^{n}B_4H_8PF_3$ between −105 and −107°.

Preparation of $^{n}B_4H_8D_2$. In a typical reaction 1.42 mmoles of $^{n}B_4H_8CO$ was allowed to react at room temperature with 2 atm of D_2 in a 500-ml flask (equipped with a Delmar–Urry O-ring stopcock) for a period of 18 min. At the end of this time the reaction was quenched in liquid nitrogen and the noncondensable gases were pumped from the flask. The condensable material was crudely separated by repeated passage into a −135° trap and $^{n}B_4H_8D_2$ was separated from this condensate using the temperature-gradient apparatus. The $^{n}B_4H_8D_2$ fraction was considered pure when its vapor tension at −45° was 38 mm and when no extraneous peaks were present in its ^{11}B nmr spectrum. Based on the amount of $^{n}B_4H_8CO$ initially present, the yield was approximately 17%.

Preparation of $^{n}B_4D_8H_2$. A sample of $^{n}B_4D_8H_2$ was prepared from suitable compounds in a similar fashion to that described above and differing principally in that three successive 10-min reactions with intermittent product removal were carried out to minimize isotopic scrambling during the preparation. The ^{11}B nmr spectrum showed that less isotopic scrambling occurred using this procedure than with one longer reaction period. The product was purified on the temperature-gradient column.

Preparation of $^{n}B^{10}B_4H_{11}$ and $^{10}B^{n}B_4H_{11}$. The specifically labeled pentaboranes(11) were prepared from the respective carbonyls and diboranes using essentially the conditions of Spielman and Burg. The reactants were allowed to warm to room temperature for two 7-min reaction periods; at the end of each period the reaction was quenched at −196° and noncondensable gases were removed and measured. Initial separation of the reaction mixture was effected by fractional condensation; final separation of the labeled pentaborane(11) from unreacted tetraborane carbonyl and pentaborane(9) was achieved on the temperature-gradient column.

Thermal Scrambling of Labeled Samples. To study isotopic scrambling of $^{n}B_4H_8D_2$ and $^{n}B^{10}B_4H_{11}$, samples were warmed to room temperature for measured periods of time and quenched in liquid nitrogen; then the ^{11}B nmr spectra were reexamined at low temperature (generally between −30 and −40°). Owing to the small volumes of the nmr tubes liquid phases were present during the periods that the samples were at room temperature, and no detailed kinetic studies were attempted.

Results and Discussion

The peaks of highest *m/e* observed in the mass spectra of the tetraboranes obtained from the $^{n}B_4H_8$-CO–D_2 and $^{n}B_4D_8CO$–H_2 reactions occur at *m/e* 54 and *m/e* 60, respectively. This indicates that dilabeled products, $^{n}B_4H_8D_2$ and $^{n}B_4D_8H_2$, are formed and that only traces, if any, of more highly labeled species are present.

The infrared spectra of $^{n}B_4H_8D_2$ and $^{n}B_4D_8H_2$ provide information concerning the position of their labeling. Four scans of the significant region of the spectrum of $^{n}B_4H_8D_2$ (2250 to 1530 cm^{-1}) are shown in Figure 1. In the first scan (I) taken immediately after warming the sample to the spectrometer cell temperature, absorptions at 2150, 1945, and 1605 cm^{-1} assignable to BH bridge, BD terminal, and BD bridge (μ) stretching frequencies are observed.[16] During scans II and III the 1605-cm^{-1} (BD bridge) peak decreases in intensity as the BD terminal peaks grow, and after 1.3 hr (IV) the spectrum does not appear to change further. At the end of this time it is difficult to distinguish between the BD terminal peaks as only a broad absorption centering at 1900 cm^{-1} occurs. After the fourth scanning, the sample was repurified and the infrared spectrum reexamined. No peaks under observation during the scrambling experiment changed in relative intensity upon purification, and therefore none were due to decomposition products. The infrared spectra conclusively show that initially deuterium is specifically located in both bridging (μ) and terminal positions; however, it does not unambiguously indicate which terminal position is labeled or whether scrambling occurs in a specific direction or by several processes.

The ^{11}B nmr spectra of $^{n}B_4H_8D_2$ and $^{n}B_4D_8H_2$ are shown in Figure 2. Spectra of $^{n}B_4H_{10}$ and $^{n}B_4D_{10}$ (2D and 2F) are also shown for comparison purposes. The spectrum of $^{n}B_4H_8D_2$ prior to scrambling (2A) consists of a low-field triplet (δ +7.2 ppm, J = 126 cps) and a high-field resonance centered at δ 42.2 ppm which has the general features of an overlapped singlet and doublet. After warming the sample to room temperature for 5 min, the high-field resonance shows some doublet character (2B). An additional 25-min scrambling period results in a spectrum (2C) which has the appearance of that obtained for normal tetraborane (2D). The spectrum of $^{n}B_4D_8H_2$ (2E) consists

---

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

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

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

(11) In this paper the superscript *n* refers to boron of normal isotopic distribution, 81.2% ^{11}B and 18.8% ^{10}B.

(12) I. Shapiro, H. G. Weiss, M. Schmick, S. Skolnich, and G. B. L. Smith, *J. Am. Chem. Soc.*, **74**, 901 (1952).

(13) M. S. Klein, B. C. Harrison, and I. J. Solomon, *ibid.*, 80, 4149 (1958).

(14) R. Schaeffer, Aeronautical Research Laboratory Technical Report, 60–334, Dec 1960.

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

(16) The assignment of peaks in these spectra are based on those made by A. Dahl, Ph.D. Thesis, University of Michigan, 1963, for $^{n}B_4H_{10}$ and $^{n}B_4D_{10}$. In these cases BH bridge (μ), BD·BD_2 terminal (combination band), BD_2 terminal, and BD bridge (μ) occurred at 2150, 1946, 1826, and 1583 cm^{-1}, respectively.

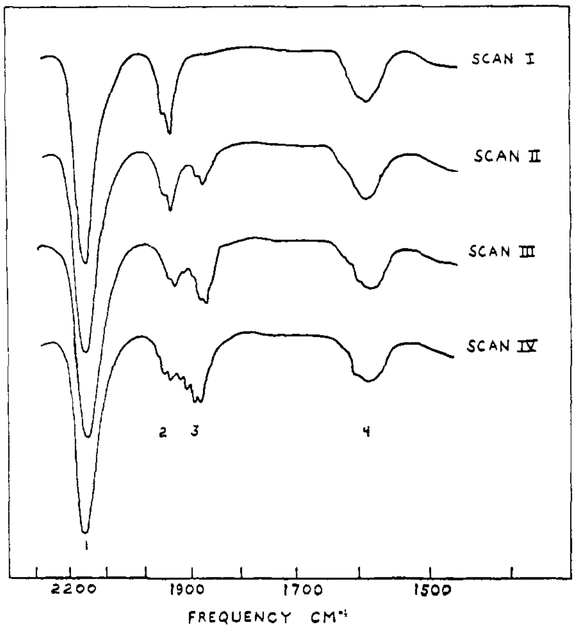


Figure 1. Infrared spectra of μ,1-$^{n}B_4H_8D_2$: scan I, 0 to 3.5 min; scan II, 13.5 to 17.0 min; scan III, 39.0 to 42.5 min; scan IV, 73.0 to 76.5 min. Bands numbered 1, 2(3), and 4 correspond to BH bridge, BD terminal, and BD bridge absorptions, respectively.

of a low-field singlet (δ +6.5 ppm) free of fine structure and a high-field slightly asymmetric signal (δ +41.2 ppm) appearing qualitatively as an overlapped doublet and singlet. Although fine structure is exhibited, it is insufficiently resolved to be measured.

The ^{11}B nmr spectra of $^{n}B_4H_8D_2$ and $^{n}B_4D_8H_2$ show that (within the limits of our analytical method) no molecules are formed in the labeling processes which have the label atoms terminally bonded to the 2 or 4 boron atom, since the low-field resonances appear identical with those of $^{n}B_4H_{10}$ and $^{n}B_4D_{10}$. The collapse of the high-field doublet observed for $^{n}B_4H_{10}$ to a single resonance in $^{n}B_4H_8D_2$, which upon scrambling again gives rise to a doublet, and the presence of a similar broad asymmetric high-field resonance for $^{n}B_4D_8H_2$ provide evidence that the one terminal label atom is attached to a boron atom in the 1- or 3-position. A detailed analysis of the high-field resonances of these labeled tetraboranes is difficult owing to the complex coupling situation which has been shown to exist in the nmr spectrum of tetraborane[17] and is beyond the scope of this discussion.

On the basis of mass, infrared, and ^{11}B nmr spectral data, it is concluded that $^{n}B_4H_8D_2$ and $^{n}B_4D_8H_2$ are dilabeled in bridging (μ) and terminal (1) positions. However, the possibility that small quantities (<5.0%) of 1,3-dideuterio- and/or μ,μ'-dideuteriotetraborane are also formed cannot be overlooked, since the contribution of these species to the infrared and ^{11}B nmr spectra would be small and difficult to observe. In view of the rapid scrambling that occurs at room temperature, it appears unlikely that at higher temperatures a specifically labeled product could be obtained by exchange between B_2D_6 and tetraborane.[5,6]

Labeled Pentaborane(11). In order to obtain the greatest simplicity of interpretation, the reaction between $^{n}B_2H_6$ and $^{10}B_4H_8CO$ was studied rather than the inverse system. The ^{11}B nmr spectrum at −55° of the $^{n}B^{10}B_4H_{11}$ obtained from this reaction is shown in Figure 3. The spectrum consists of an overlapped low-field triplet (δ −2.9 ppm, J = 150 cps) and doublet (δ +2.3 ppm, J = 190 cps) of equal area and a small high-field doublet (δ +53.5 ppm, J = 170 cps). The

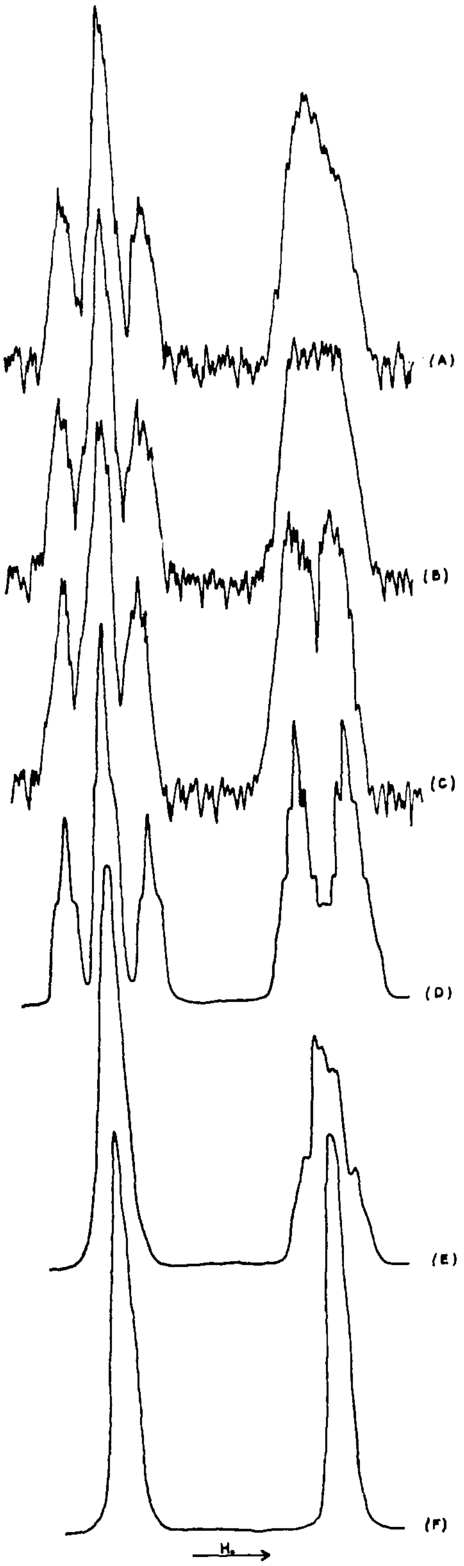


Figure 2. The ^{11}B nmr spectra of μ,1-$^{n}B_4H_8D_2$ (A, B, and C), $^{n}B_4H_{10}$ (D), μ,1-$^{n}B_4D_8H_2$ (E), and $^{n}B_4D_{10}$ (F).

---

(17) R. C. Hopkins, J. D. Baldeschwieler, R. Schaeffer, F. N. Tebbe, and A. D. Norman, *J. Chem. Phys.*, **43**, 975 (1965).

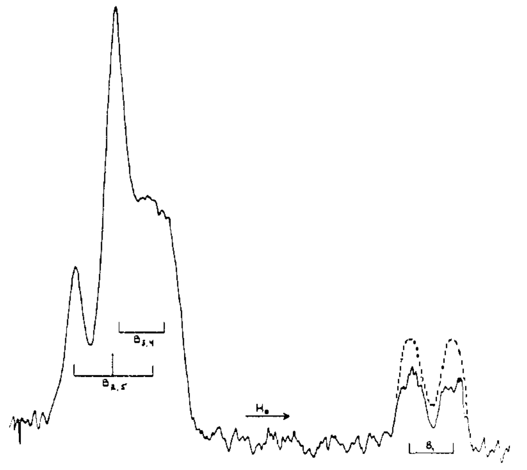


Figure 3. The ^{11}B nmr spectrum of basal boron labeled $^{n}B^{10}B_4H_{11}$. The doublet shown by the dotted line represents the relative area after scrambling.

area of the low-field signal is nearly six times that of the high-field doublet prior to scrambling; however, warming the sample to room temperature results in a relative area increase of the high-field doublet (Table I; Figure 3, dotted line). After 10 min the area ratio approaches a constant value of 4:1, whereas the low-field triplet–doublet ratio remains constant throughout the scrambling period. The ^{11}B nmr spectrum of unlabeled $^{n}B_5H_{11}$ consists of an overlapping low-field triplet–doublet and a high-field doublet of relative areas 2:2:1 attributed to boron atoms in basal 2(5), basal 3(4), and apical (1) positions, respectively.[18]

Table I. $^{n}B^{10}B_4H_{11}$ Scrambling Experiment

Time, min[a]	% ^{11}B in basal positions	% ^{11}B in apex positions	Area ratio
0	85.7	14.3	5.99
3.0	84.5	15.5	5.43
6.0	81.5	18.5	4.42
10.0	80.4	19.6	4.08

[a] Time at room temperature measured from the time the product was isolated from the reaction mixture.

It is clear from relative intensities recorded above that $^{n}B^{10}B_4H_{11}$ is enriched with the ^{11}B isotope in the basal positions prior to scrambling. Since the low-field signal remains qualitatively unchanged during scrambling and identical with that of normal B_5H_{11}, we conclude that the ^{11}B isotope is equally distributed over both basal, 2(5), and 3(4) positions. The rapid attainment of a statistical distribution of ^{11}B in all five positions of the molecule implies that a facile mechanism must exist for boron atom interchange between the apex and basal positions. We resist idle speculation about detailed mechanisms.

^{11}B Nmr Spectra of $^{n}B_4H_8CO$ and $^{n}B_4H_8PF_3$. On the basis of ^{11}B nmr spectra taken at 12.4 Mc/sec, Spielman and Burg have suggested that tautomeric forms might be necessary to describe the structure of $^{n}B_4H_8CO$.[7] During our investigation, it appeared of interest to reexamine[14] the ^{11}B nmr spectra of $^{n}B_4H_8CO$ at 19.3 Mc/sec and to examine the spectrum of another $^{n}B_4H_8$ adduct, $^{n}B_4H_8PF_3$, in an attempt to learn more of the structure of these molecules.

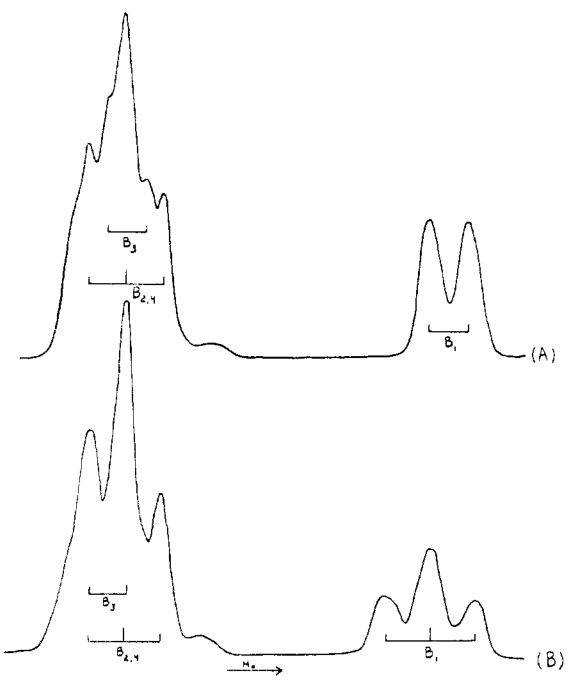
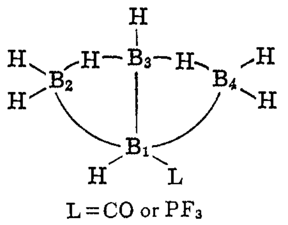


Figure 4. The ^{11}B nmr spectra of $^{n}B_4H_8CO$ (A) and $^{n}B_4H_8PF_3$ (B), measured at −10°.

The 19.3-Mc/sec, ^{11}B nmr spectra (Figure 4, Table II) measured at −24° consist of low-field and high-field resonances of relative area 3 and 1, respectively. The low-field resonance of both compounds appears as an overlapping triplet (area = 2) and doublet (area = 1); however, the high-field doublet of $^{n}B_4H_8CO$ (Figure 4A) becomes a triplet when the CO is replaced by PF_3 in $^{n}B_4H_8PF_3$ (Figure 4B). The small base line peak on the upfield side of the low signal in both spectra is attributed to a trace of B_5H_9 which could not be removed by repeated fractionation. These spectral data strongly suggest that a static model, shown below, may be used to describe the structures of these molecules. The low-field triplet may be assigned to the 2 and 4 borons and the low-field doublet to the 3 boron. Since the upfield signal changes from a doublet to a triplet when CO is replaced by PF_3, due to equivalence of J_{BH} and J_{BP} in this case, it must be assigned to the 1 boron.



The ability to form labeled molecules from the reactions of B_4H_8CO with deuterium or diborane is also

---

[18] R. E. Williams, S. G. Gibbons, and I. Shapiro, *J. Chem. Phys.*, 30, 320 (1959).

consistent with the above structure and suggests a mechanism for its reaction with hydrogen and diborane. Dissociation of B_4H_8CO to B_4H_8 retaining a vacant orbital 2112 structure[19] could be the initial step in the reaction. Interaction of the vacant orbital with hydrogen, followed by minor electronic and molecular rearrangement, would result in tetraborane(10). Substitution of deuterium for hydrogen in this reaction might be expected to yield the bridge (μ), terminal (1) labeled molecule, μ,1-dideuteriotetraborane(10). Similarly, in the reaction with diborane, initial bond formation between B_4H_8 and B_2H_6 might occur with formation of a boron hydrogen bridge bond at B_1. Simultaneous or subsequent dissociation of the diborane followed by electronic and molecular rearrangement of the intermediate species would give rise to the final B_5H_{11}. The fact that $^{n}B^{10}B_4H_{11}$ did not have the ^{11}B isotope located specifically in either basal position, as might be inferred from this mechanism, may indicate that a rapid basal boron equilibration process exists for pentaborane(11), that an intermediate with four equivalent borons is formed, or that the intermediate species formed prior to pentaborane(11) can rearrange to the observed $^{n}B^{10}B_4H_{11}$ by two different mechanisms. Further study will be necessary to attempt to distinguish between these choices.

Table II. ^{11}B Spectral Data for B_4H_8CO and $B_4H_8PF_3$

		BH	BH (BHP)	BH_2
B_4H_8CO	δ, ppm	+2.1	+58.7	+1.5
	J, cps	119	131	127
$B_4H_8PF_3$	δ, ppm	−0.7	+58.7	+3.9
	J cps	122	149	123

Acknowledgment. This work was in part supported by the National Science Foundation. Appreciation for a National Aeronautics Space Administration Traineeship for A. N. is gratefully expressed.

---

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

Kinetics of the Decomposition of BH_3PF_3 and Related Compounds. A Revised Estimate of the Dissociation Energy of Diborane[1]

Anton B. Burg and Yuan-Chin Fu

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received November 4, 1965

Abstract: Very sensitive infrared procedures were used to show that the compounds BH_3PF_3, $BH_3\cdot CF_3PF_2$, and $BH_3\cdot(CF_3)_2PF$ all decompose to B_2H_6 and free phosphine ligand by the same mechanism as found earlier for BH_3CO, namely, the dissociation of BH_3L to BH_3 and free ligand L, followed by action of BH_3 to displace L from BH_3L. The same rate law applies also to the far more complicated case of $B_4H_8PF_3$. Extrapolation of early-stage rate data for BH_3PF_3 to zero time gave first-order rate constants for the initial dissociation at three temperatures. These results, taken with the over-all equilibria, led to $D(BH_3\text{–}BH_3) = 35.0$ kcal, consistent with but more precise than earlier estimates. The only systematic error here would arise from the reasonable assumption that $\Delta H = 0$ for activation of the reverse of the initial dissociation.

The thorough analysis by Garabedian and Benson,[2] of all data on the rates of decomposition of BH_3CO to CO and B_2H_6,[3,4] confirmed the mechanism proposed by Burg[3] and led to a considerably higher value for $D(BH_3\text{–}BH_3)$ than had been estimated by Bauer.[5] Others have proposed still higher values.[6,7] However, all such estimates have been based upon assumptions sufficiently uncertain to allow fairly wide disagreement. A new approach to the problem was needed.

The compound BH_3PF_3 was reported as decomposing by a rate law at least roughly similar to that of BH_3CO.[8] The present work abundantly confirms this mechanism, showing that BH_3PF_3 can be used for an independent development of data relating to $D(BH_3\text{–}BH_3)$. The great advantage here is the high sensitivity of the infrared method of observing the process; fortunately, the very intense P–F stretching peaks shown by PF_3

---

[1] It is a pleasure to acknowledge support of this research by the Office of Naval Research through Contract No. Nonr-228(13). Reproduction in whole or in part is permitted for any purpose of the United States Government. The infrared instrumentation was made available with the aid of Grants G-14669 and GP-199 from the National Science Foundation.

(2) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964).

(3) A. B. Burg, *ibid.*, **74**, 3482 (1952).

(4) Y. C. Fu and G. R. Hill, *ibid.*, **84**, 353 (1962).

(5) S. W. Bauer, *ibid.*, **78**, 5775 (1956).

(6) T. P. Fehlner and W. S. Koski, *ibid.*, **87**, 409 (1965).

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

(8) R. W. Parry and T. C. Bissot, *J. Am. Chem. Soc.*, **78**, 1524 (1956).