[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE AND VARIAN ASSOCIATES]

Nuclear Magnetic Resonance Spectra of Boranes

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Proton and B^{11} nuclear magnetic resonance spectra of B_5H_{11} are presented. The B^{11} spectrum contains sufficient detail to permit an assignment of the peaks to the three types of boron atoms in the molecule. The proton spectrum is complex but by use of the "spin saturation" technique of Bloom and Shoolery,[3] four groups of hydrogens can be observed and related to the molecular structure. Improved spectra have been obtained of both B_5H_9 and $B_{10}H_{14}$ and are correlated with their molecular structures.

Nuclear magnetic resonance provides a unique tool for studying boron hydrides and their derivatives since in many cases a simple, direct correlation can be made between the magnetic resonance spectrum and the molecular structure of the hydride. Unstable pentaborane, B_5H_{11}, had not previously been studied despite its apparent importance in the interconversion reactions of the boranes. The spectra of both pentaborane-9 and decaborane were redetermined in connection with another problem and the greater detail observed permits some further discussion of the relation of their magnetic resonance spectra to their molecular structures.

Experimental

Pentaborane-11 was prepared by the decomposition of diborane and purified from pentaborane-9 by multiple use of the fractional condensation technique in a vacuum apparatus of conventional design. Pentaborane-9 is sufficiently volatile at −80° to pass slowly through a trap cooled by Dry Ice, whereas pentaborane-11 is substantially retained at that temperature. Approximately 20 mg. of B_5H_{11} having a zero vapor tension of 53.5 mm. was condensed into a 5-mm. Pyrex tube; sufficient dry, sulfur-free carbon disulfide was added to fill the tube to about 25 mm. depth and the tube sealed from the system under vacuum. Sample tubes containing about 20% B_5H_9 and $B_{10}H_{14}$ dissolved in carbon disulfide were prepared in a similar fashion. Samples were stored at −80° when not actually being used for spectral observations.

Both proton and B^{11} nuclear magnetic resonance spectra were obtained using a Varian Associates model No. V-4300 B high resolution spectrometer. The B^{11} spectra were obtained at 12.3 Mc./sec. in the usual manner. Proton spectra were obtained both in the usual manner at 30 Mc./sec. and also using a double tuned circuit resonant at both 30.0013 and 9.6257 Mc./sec. The effect of the latter method is to interrupt the spin orientations of the B^{11} nuclei frequently enough so that the H^1 nuclei see only an average value and the multiplet structure collapses.[3]

Results

Spectra of pentaborane-11 under the three conditions described above are shown in Fig. 1. Zero points were chosen for the B^{11} and proton spectra to correspond to the lowest field peak of the appropriate pentaborane-9 spectrum. It is at once apparent from the curves that the proton spectrum is found at approximately the same field in both pentaboranes but the B^{11} spectrum of pentaborane-11 occurs at substantially lower fields than that of pentaborane-9. The spectra given in Fig. 1a span about 540 cycles, the scale being given in parts per million.

The B_5H_{11} molecule contains four hydrogens in terminal BH_2 groups, three single bridge hydrogens, two hydrogens attached only to the type II boron atoms, a single hydrogen attached to the type I boron and a unique hydrogen mostly bonded to the type I boron but sufficiently close to the type III borons so that it must be considered as weakly bonded to them as well.[4] The proton spectrum in Fig. 1a is not sufficiently well resolved to permit complete interpretation. At least two multiplets are present. The weaker of the two is nearly obscured by the stronger, but the component at weakest field can be seen as a shoulder at 0. In addition, the bridge protons give rise to the characteristic broad peak centered somewhere between +8 and +16.[5] Figure 1b shows the proton spectrum collapsed by B^{11} spin saturation. Comparison with Fig. 1a identifies the peak at +11 as arising from the bridge protons and gives a semiquantitative guide since it should be of intensity corresponding to three protons. The largest peak at the left (low field) side is twice the magnitude of the bridge peak and thus accounts for six more hydrogens. The remaining smaller peaks falling above and below the peak associated with the bridge hydrogens must then arise from single protons superimposed on the tails of the bridge peak. The six hydrogens which contribute to the largest peak must clearly be the four terminal hydrogens in BH_2 groups and the two hydrogens attached to the type II borons. No wholly reliable method exists for deciding which of the two single proton peaks is the unique proton and which is wholly owned by the type I boron. However, since in other boron hydrides the protons in the bridge always give peaks at higher fields than other hydrogens, it seems most reasonable to assign the peak at +12.5 to the unique hydrogen. This assignment agrees with the intuitive feeling that the unique proton, being partially bonded to three borons, should be somewhat more shielded than "normal" bridge protons whereas the wholly owned proton should yield a peak at lower field than the bridge peak.

The B_5H_{11} molecule contains three types of boron atoms. A single type I boron is bonded to a wholly owned hydrogen and also to the unique hydrogen. The doublet occurring at the extreme

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[3] (a) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955); (b) J. N. Shoolery, *Disc. Faraday Soc.*, **19**, 215 (1955).

[4] For a compilation of the structures of the boron hydrides, see the paper by William N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954). The numbering system used by Lipscomb for the pentaboranes has been adopted here, but the numbering for decaborane is that used by J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950). The theory of nuclear magnetic resonance is well described by J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955), and the reader is referred to that paper for a description of factors necessary in the interpretation of the spectra that follow.

[5] R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954).

right of the B^{11} spectrum is sufficiently weak so that it must be assigned to a single boron atom split by coupling to a single hydrogen. Apparently the coupling to the unique hydrogen is too weak to cause further splitting, a phenomenon common to "bridge" hydrogens.[3b,5] The two type II borons are each connected to a single hydrogen, exclusive of the bridge hydrogens, and would be expected to show a doublet of approximately twice the intensity of that owing to the type I boron. The type III boron, being bonded to two hydrogen atoms exclusive of the bridge hydrogens, would be expected to give rise to a triplet with components of relative intensity 1:2:1. The four peaks at the left of the spectrum in Fig. 1c can be accounted for only by assuming that an accidental overlap occurs between one component of the doublet and one of the weaker components of the triplet. If the triplet is centered to the left of the doublet, the relative intensities from left to right will be expected to be approximately 1:2:3:2; whereas if the triplet is on the higher field side to the right, the relative intensities from left to right will be approximately 2:3:2:1. The latter set of intensities qualitatively fits the appearance of the curves better than the former. Approximate integration of the area under the curves leads more nearly to a 1:3:3:1 ratio which could best be interpreted as two overlapping triplets arising from two different sets of BH_2 groups. This interpretation is not acceptable since not only does it not fit with the previously determined structure of pentaborane-11, but it also would require eight identical hydrogens and could not be reconciled with the proton spectrum discussed above. Arguments in addition to the visual appearance of the curve can be given in support of the supposition that the triplet is indeed at the high field side of the doublet. Considerable care must be used in an attempt to relate chemical shift to electron density for atoms other than hydrogen. However, for both of the pentaboranes and for decaborane the peaks occurring at the highest fields in the NMR spectra can be unambiguously associated with the boron atoms calculated to be most negative by Eberhardt, Crawford and Lipscomb.[6] Their treatment also leads to the association of greater negative charge with the type III borons than with those of type II which in turn suggests that the triplet should be to the high field side of the doublet. It would appear that this assignment for borons of types II and III is to be preferred but can by no means be regarded as absolute.

Figure 2 shows the magnetic resonance spectra of decaborane under the various conditions described above. As mentioned by Shoolery,[3b] slight tuning of the subsidiary field at 9.6257 Mc./sec. allows one to bring out more clearly resonances of certain protons. All spectra in Fig. 2 have previously been published, but the greater detail produced in the present study permits more detailed description than was previously possible.

The two isolated peaks at highest field in the B^{11} spectrum of $B_{10}H_{14}$ have been demonstrated to belong to the two B-2 borons.[4,7] As explained by Shoolery,[3b] the apparent triplet at the low field side of the spectrum can be interpreted only in terms of accidental overlap of two doublets since interpretation as a single triplet resulting from BH_2 groups in the molecule would require more protons

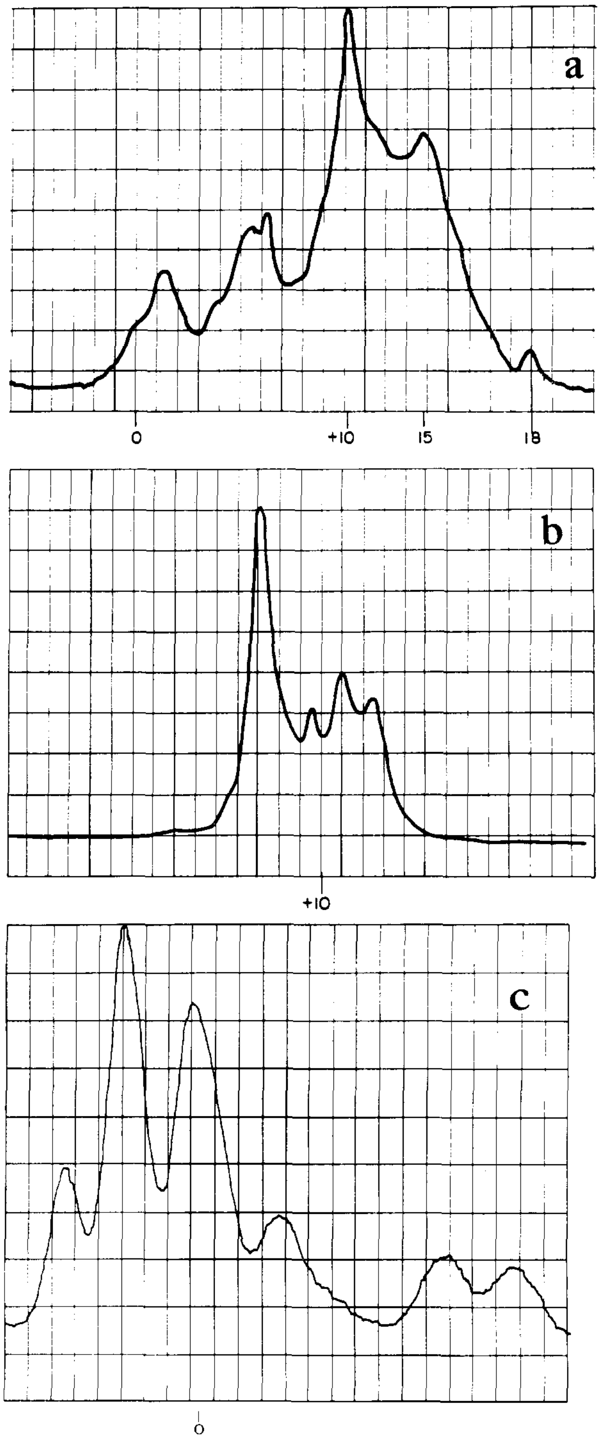

Fig. 1.—(a) H′ magnetic resonance spectrum of B_5H_{11}. (b) H′ magnetic resonance spectrum of B_5H_{11} with B^{11} excited at 9.6257 Mc./sec. (c) B^{11} magnetic resonance spectrum of B_5H_{11}.

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(6) W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(7) R. Schaeffer, J. N. Shoolery and R. Jones, presented at the American Chemical Society Meeting in Atlantic City, N. J., September 19, 1956.

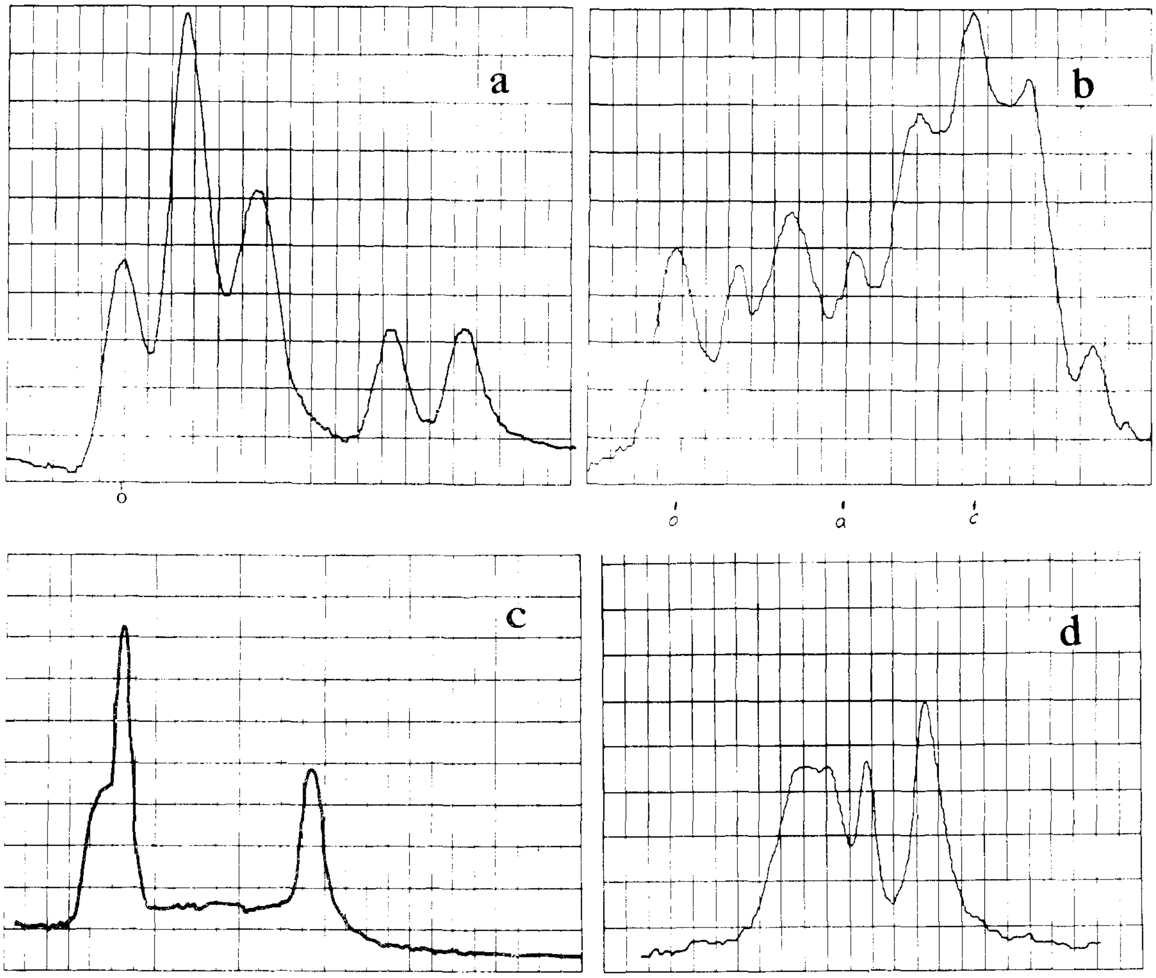

Fig. 2.—(a) B^{11} magnetic resonance spectrum of $B_{10}H_{14}$. (b) H′ magnetic resonance spectrum of $B_{10}H_{14}$. (c) H′ magnetic resonance spectrum of $B_{10}H_{14}$ with B^{11} excited at 9.6257 Mc./sec. (d) H′ magnetic resonance spectrum of $B_{10}H_{14}$ with B^{11} excited at 9.6257 Mc./sec. tuned to center peak.

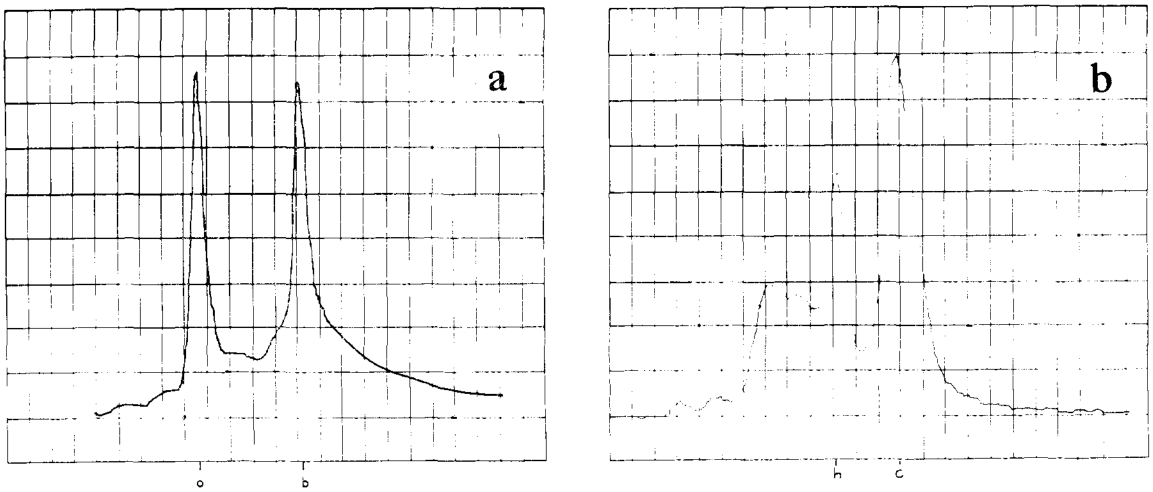

Fig. 3.—H′ magnetic resonance spectrum of B_5H_9 with B^{11} excited at 9.6257 Mc./sec. tuned to: (a) outer peak; (b) center peak.

than are present. The improved spectra show that the two doublets are of equal intensity and of twice the intensity of the peaks assigned to B-2. One doublet must arise from the four equivalent B-1 and B-4 atoms and an argument similar to that used above for pentaborane-11 suggests that this set lies at the left at lowest field since these borons are calculated by Eberhardt, *et al.*, to be the most positive set. The center doublet must then be attributed to coincidence of the peaks owing to B-3 and B-5. It should be again noted that the assignment of the two doublets is not completely certain but is to be preferred on the basis of present knowledge.

The proton spectrum of $B_{10}H_{14}$ shown in Fig. 2b is not sufficiently well resolved to permit new interpretation. Note, however, that there is a slight suggestion of a shoulder at the low field side of the large quartet whose lowest member has been chosen as an arbitrary zero for decaborane derivatives. This suggestion is beautifully confirmed in the boron spin saturated spectrum shown in Fig. 2c. Furthermore, the high field peak in this spectrum arises from the collapse of the poorly split bridge protons and provides a standard of intensity since there are just four protons of this type. Two of the remaining ten protons fall into the space between the two peaks of Fig. 2c as shown in Fig. 2d taken with slightly different tuning of the boron saturating frequency. Furthermore, peak b of Fig. 2d has been shown by a study of halogen-substituted decaboranes to arise from the protons bonded to B-2 borons.[7] The remaining eight hydrogens in the molecule occur as sets of two, two and four and must together make up the partially resolved peak at the left of Fig. 2c. It is at once apparent that better resolution if it could be obtained would lead to peaks of relative intensity two and six. The set of four equivalent protons wholly bonded to the four B-1, B-4 boron atoms must then contribute to the high field component of the pair. No unambiguous way exists at present to decide which of the remaining two sets of two protons joins with the fourfold set to lead to the sixfold peak in Fig. 2c. However, it is more satisfying to assume that the protons attached to B-3 borons will more nearly resemble the fourfold set than will those attached to B-5 borons since the former are bonded to borons more similar in their bonding environment to B-1 and B-4 atoms than are the latter.

Figure 3 shows the B^{11} saturated proton spectrum of pentaborane-9. The possibility of "tuning" in the center peak by slight variation of the saturating field has been previously mentioned but not supported by spectra.[3b] The center peak by reason of its relative intensity must arise from the single proton attached to the apex boron atom of the B_5H_9 molecule.

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Gas Phase Reactions Activated by Nuclear Processes

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It is known from previous work that I^{128} and Cl^{38} activated by radiative neutron capture are able to replace hydrogen in organic compounds by unique processes. The work of the present paper shows that: (1) Br^{80} can undergo similar reactions, following either radiative neutron capture or isomeric transition; (2) all three halogen species can replace hydrocarbon radicals as well as hydrogen atoms; (3) several modes of replacement are possible for reaction of a single type of halogen with a single type of target molecule—at least nine different organic iodides being formed by reaction of I^{128} with *n*-butane; (4) the nature of the compound in which the halogen is contained prior to neutron capture has little or no effect on the reactivity of the activated atom, but the nature of the parent compound seems to affect this reactivity when activation is by isomeric transition; (5) tritium produced by the $He^3(n,p)H^3$ process in gaseous hydrocarbons enters organic combination by a process which is apparently similar to the halogen reactions noted. It is suggested that these reactions are of the ion-molecule type. The demonstration that such reactions occur in the gas phase makes it probable that they contribute to organic yields in the more extensively studied condensed phases, where it is impossible to distinguish them experimentally from radical combination reactions. The application of gas phase chromatography to the analysis of mixtures of tracer amounts of radioactive materials is illustrated in this paper.

Introduction

^{128}I[1,2] and ^{38}Cl[3] freshly produced by the $I^{127}(n,\gamma)I^{128}$ and $Cl^{38}(n,\gamma)Cl^{38}$ processes are able to form organic halides by reacting with gaseous hydrocarbon molecules by displacement processes (*e.g.*, $I + CH_4 \rightarrow CH_3I + H$). This is of particular interest because photochemically or thermally produced halogen atoms which react with hydrocarbons do so by abstraction of hydrogen[4] to form the hydrogen halide and a free radical (*e.g.*, $Cl + CH_4 \rightarrow CH_3 + HCl$), with organic halide formation occurring by reaction of the radical with a halogen molecule ($CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$). The activation energy for hydrogen abstraction reactions by iodine atoms is so high that photoiodination of hydrocarbons cannot take place.

Speculation that this unique displacement type of reaction requires positive halogen ions rather than neutral atoms is strengthened by the observation[2] that a few mole per cent. of additives of ionization potential lower than that of I^+ greatly reduces the yield of the reaction of I^{128} with methane. No similar reactions, of which we are aware, have

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(1) J. F. Hornig, G. Levey and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

(2) G. Levey and J. E. Willard, *ibid.*, **25**, 904 (1956).

(3) (a) J. C. W. Chien and J. E. Willard, This Journal, **75**, 6160 (1953); (b) J. B. Evans, J. E. Quinlan and J. E. Willard, Paper 68 presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the September, 1956, Atlantic City Meeting.

(4) (a) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941; (b) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.