seems to be the most plausible. The $2p_y \rightarrow \pi_-$ transition is the n-π transition assigned to the 2200 Å. region. (It would appear that the experimental results for the 1660 band, polarization and nearness to the NV_1 transition, make it possible to assign the band as n-π; however the allowed intensity is too high. The formally allowed intensity for the n-π transition must, it should be remembered, be quite small.) The $\pi_+ \rightarrow \pi_-$ transition is also the NV_2 transition and on the most general theoretical grounds would not be expected to lie so close to the NV_1 transition. (This closeness is most acutely demonstrated in the spectrum of formamide itself[10] where the absorption around 1600 A. is not even resolved, but shows up as a broadening of the NV_1 band relative to the band in dimethylformamide.) The $\pi_+ \rightarrow$ 3s transition would be at shorter wave lengths than the $2p_y \rightarrow$ 3s transition, so unless there is yet another Rydberg band at longer wave lengths the $2p_y \rightarrow$ 3s assignment is to be preferred.

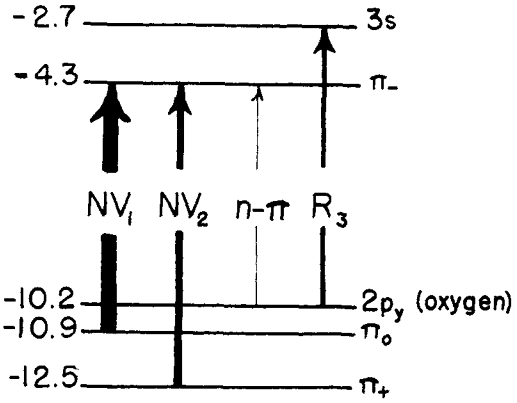

Fig. 7.—Orbital energy diagram for myristamide: (e.v.) intensities are depicted by varying widths of the arrows representing the various transitions.

The picture of the orbital reached in the transition is a linear combination of 3s orbitals, all in phase, with perhaps the greatest amplitude on the oxygen, though the higher Rydberg members gradually become more and more like atomic orbitals. The structure in the 1600 Å. region of formamide,[10] with a spacing of 1600 cm.$^{-1}$, may then be interpreted as vibrational intervals corresponding to a carbonyl stretching motion in the upper state (the ground state stretching frequency is 1740 cm.$^{-1}$).[29]

Examination of Fig. 1 shows that the absorption in the 1660 Å. region is likely to be partly from the *b*-axis component of the NV_1 transition (considered from the strong coupling point of view) and partly from the long wave length part of the band below 1600 Å. Nevertheless the qualitative result

$$D_b > D_a$$

is believed to be a characteristic of the Rydberg member itself. It is found using the trigonometric methods illustrated in the foregoing that this result is consistent with the polarizations expected for all four possibilities considered above, in particular for the possibility which is considered the most likely

$$2p_y \longrightarrow 3s$$

If we adopt this latter process we can, by considering various combinations, represent all the transitions found in this research for myristamide by means of an orbital energy diagram. This is done in Fig. 7. The effective orbital energy of the π_+ orbital is obtained by adopting for the NV_2 absorption a value of 1520 Å. This is estimated by assuming for myristamide an NV_1/NV_2 energy ratio intermediate between the ratio for formamide and dimethylformamide.[10] The zero of energy is taken as the ionization limit for the observed Rydberg series.

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SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, AND CHEMICAL WARFARE LABORATORIES]

Nuclear Magnetic Resonance Study of the B_2D_6–B_5H_9 Exchange Reaction[1]

BY WALTER S. KOSKI, JOYCE J. KAUFMAN AND PAUL C. LAUTERBUR

RECEIVED NOVEMBER 15, 1956

The exchange of deuterium between diborane and pentaborane was investigated by nuclear magnetic resonance. It was found that the exchange proceeded preferentially in the terminal hydrogen positions in pentaborane. The rate of exchange of the apex hydrogen appeared to be within ±10% the same as the exchange rate of the base terminal hydrogen. Under the experimental conditions the bridge hydrogens in pentaborane did not participate in the exchange.

Introduction

Recently we have had occasion to investigate the exchange of deuterium between diborane and pentaborane and we have found that the reaction proceeds through borane, derived from the dissociation of diborane, as an intermediate. By means of a mass spectroscopic study[2] we were able to disentangle the exchange from a complicating reaction due to the pyrolysis of diborane to form pentaborane, and by an infrared study[3] to show that only the five terminal hydrogens participated in the exchange reaction. The bridge hydrogens

[1] This research was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] W. S. Koski, Joyce J. Kaufman, L. Friedman and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

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of pentaborane did not participate in the exchange reaction and neither did the boron atoms under the conditions of the experiments.

The pentaborane molecule has a tetragonal pyramidal arrangement of borons with a hydrogen attached to each boron by a normal boron to hydrogen bond (terminal hydrogens). Four other hydrogens are attached to the base borons by bridge bonds. It was of interest to our program to confirm by an independent technique our previous observations on the difference in the exchangeability of bridge and terminal hydrogens in pentaborane and to determine whether the rate of exchange of the hydrogen attached to the apical boron in pentaborane differed from the exchange rate of a terminal hydrogen attached to the base of the molecule. This report summarizes our study of this exchange using nuclear magnetic resonance as a tool.

Experimental

All of the spectra used in this study were obtained with a Varian Model 4300A high resolution nuclear magnetic resonance spectrometer at a frequency of 40 Mc./sec. and a magnetic field of about 9400 gauss. They were recorded with a Sanborn recorder at a speed of 25 mm./sec. In most cases, the sweep width was 700 milligauss and the sweep rate 70 milligauss/sec. Calibration was made by a water signal modulated at 400 cycles/sec.

The radiofrequency power was kept low enough so that the spectra appeared to be about the same when swept through in either direction. This precaution ensured that saturation effects were largely eliminated.

All of the samples were sealed in Pyrex glass tubes, 5 mm. outside diameter and 3 mm. inside diameter, except for the 55.6% deuterated pentaborane samples which were in tubes 3 mm. outside diameter and 1 mm. inside diameter, because only small quantities were available. The lengths of the samples ranged from 5 to 25 mm. All spectra were taken at room temperature.

Pentaborane of normal isotopic content was prepared by pyrolysis of diborane at 180°. The procedure and purification method has been published previously.[3] The 5% deuterated pentaborane sample was prepared by treating 53.2 cm. of B_2D_6 and 12.55 cm. of B_5H_9 in a 325-cc. bulb at 80° for 2 hours and 50 minutes. The sample, after separation and purification, was sealed in the standard 5 mm. outside diameter tube. The length of this liquid sample was 25 mm. The pentaborane samples containing 26.5 and 55.6% deuterium were prepared in a similar manner except that the reaction times were 11.5 and 48 hours. The latter time actually consisted of two 24-hour contact times with the diborane being replaced with a fresh sample of B_2D_6 at the end of the first 24-hour period. The procedure for separation of the diborane and pentaborane and the purification methods were similar to that previously used.[2] The analysis for total deuterium content was made by decomposing the boron hydride and subjecting the resulting hydrogen-deuterium mixture to a thermal conductivity method.[4] The deuterium content of the B_2D_6 used for deuteration of the pentaborane ranged from 96–98%.

Results and Discussion

The structure of pentaborane has been established by X-ray diffraction of the crystal,[5,6] electron diffraction[7,8] and microwave spectroscopy[9,10] work on the gas. The nuclear magnetic resonance spectra of H and B^{11} in pentaborane have been reported and analyzed by Shoolery[11] and Kelly, Ray and Ogg.[12] The H spectrum of pentaborane of normal isotopic content shown in Figs. 1a and 2a is identical with the ones reported by the earlier observers. Three main sets of peaks are found and are assigned to hydrogen attached to B^{11} atoms. Other smaller peaks, usually unresolved, arise from those hydrogens bonded to B^{10}. Figure 3 shows a step by step reconstruction of the theoretical spectrum, using the experimentally determined relative chemical shifts and spin couplings estimated on the assumption that there are four large peaks from base terminal hydrogens attached to B^{11}, four small peaks from the apex hydrogen attached to B^{11}, and a broad unresolved peak from the bridge hydrogens. The synthesized spectrum in Fig. 3 has the following contributions: (a) four lines arising from the coupling of the four base terminal protons with B^{11}; (b) four equal lines, one-fourth the intensity of those in (a) representing the apex protons attached to B^{11}; (c) seven lines

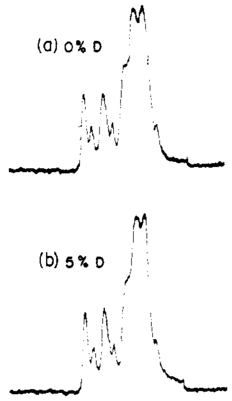

Fig. 1.—High resolution proton magnetic resonance spectra of pentaborane (a) normal isotopic content, (b) 5% deuterium.

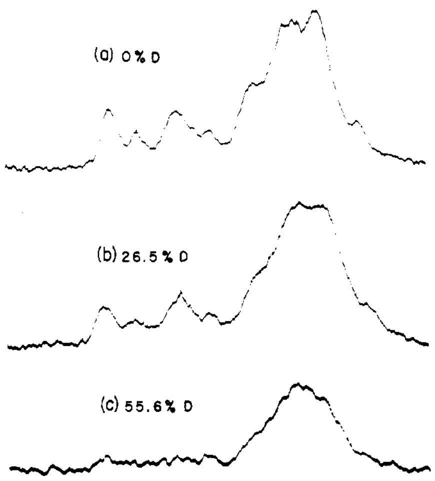

Fig. 2.—High resolution proton magnetic resonance spectra of pentaborane containing (a) normal isotopic abundance, (b) 26.5% deuterium and (c) 55.6% deuterium.

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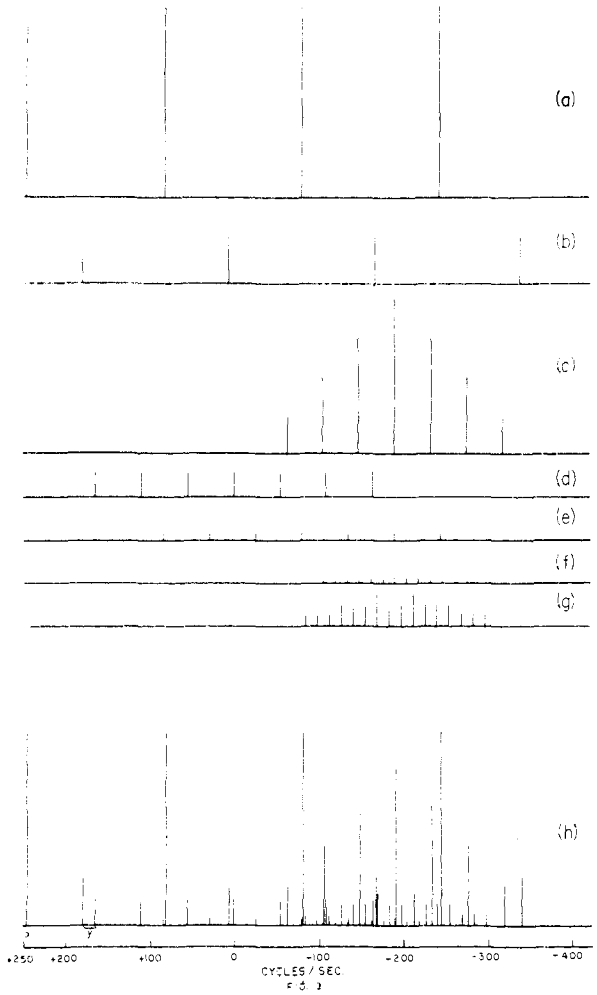

Fig. 3.—Reconstruction of the proton magnetic resonance spectrum in pentaborane for a proton resonance frequency of 40 Mc./sec. The magnetic field increases to the right. The abscissa gives the equivalent frequency shift in cycles relative to water.

from those bridge protons flanked by two B^{11} atoms; (d) seven lines from the base hydrogens bonded to B^{10}; (e) seven more lines, all equal, from apex protons on B^{10}; (f) a set of small lines arising from the fact that 3.5% of the bridge hydrogens are situated between two B^{10} atoms; (g) this contribution arises from bridge protons joining one B^{10} and one B^{11}; (h) the addition of all these contributions results in a spectrum that compares very well with the experimental results when instrumental resolution is taken into account. In assembling Fig. 3, it was assumed that B^{11} has an isotopic abundance of 81.17%, a nuclear magnetic moment of 2.6880, and a spin of 3/2. B^{10} has an abundance of 18.83%, a magnetic moment of 1.8006, and a spin of 3.

The peaks designated as x and y in Fig. 3h were used in this study to follow the progress of deuteration in the base and apex terminal hydrogen positions, respectively. Our first analysis of the n-m-r spectra of partially deuterated pentaborane prepared by exchange was made to obtain a measure of the relative rates of exchange of the terminal and bridge hydrogens in the molecule. It was found that the best place to divide the spectrum in order to separate the two types of hydrogens was between peaks x and y mentioned above, and the rest of the spectrum. A number of spectra of both the undeuterated and deuterated samples were taken and only those which showed no evidence of a field shift or other irregularity were used. Both forward (from low to high field) and backward sweeps were used and the results were calculated separately.

The areas under the peaks were determined by cutting out the entire spectrum, snipping it in two at the minimum after the first two peaks, and weighing for both the forward and backward sweep directions. The ratio of the large area to the smaller one was 7.79 and 7.31 for the forward and backward directions, respectively. The error is estimated as being ±0.03. The corresponding theoretical ratio as obtained from Fig. 3 was 7.02. The experimental ratios obtained with the 26.5% deuterium sample for the forward and backward sweeps were 10.5 ± 0.1 and 10.0 ± 0.1, respectively. We assume in treating these data that the differences between calculated and observed ratios for the undeuterated pentaborane are possibly caused by the arbitrary process of selecting the point at which to cut the spectrum apart, or more likely the discrepancy probably arises because of a difference in the spin-lattice relaxation times of the different types of protons. We have attempted to minimize this effect by keeping the power level low so as to avoid saturation. The patterns obtained for the forward and backward sweeps indicated an absence of such saturation effects. At any rate the point at which the spectrum was cut was quite far away from any bridge hydrogen lines, so we have further assumed that the ratio of the observed to theoretical values will remain constant in going from one sample to the other. Applying this correction, we get the corrected ratio for the 26.5% deuterium sample as 9.47. Applying simple stoichiometric calculations to these ratios, we find that in the 26.5% sample more than 90% of the deuterium has gone into the terminal hydrogen positions and somewhat less than 10% has gone into the bridge positions. In view of the fact that all of the deuterium in the bridge positions can be accounted for by the pyrolysis of diborane,[2] we conclude that to within experimental error none of the bridge positions in pentaborane participate in the exchange reaction under the conditions of our experiments.

Further qualitative evidence for the difference in rates is provided by the 55.6% deuterium sample, the spectrum of which is shown in Fig. 2c. It is clear that only a trace of the terminal hydrogen remains, whereas the bridge hydrogen peak is still strong.

In view of the fact that the n-m-r technique can, at least partially, resolve the apex and base terminal hydrogens, it is possible to make some deductions on the relative rates of exchange in these positions. Examination of Fig. 3 shows that the small peak y is made up of two lines, one from apex protons on B^{11} and a second smaller contribution from base protons on B^{10}. Admittedly this is not a completely satisfactory situation; however, it is the best place in the spectrum to check on progress of deuteration at the apex position.

The procedure chosen was to run somewhat compressed spectra, similar to those shown in Fig. 1. The heights of the two peaks were measured from the base line and the ratio of the second to the first was calculated. Pentaborane samples containing 0, 5 and 26.5% deuterium gave 0.660, 0.675 and 0.681, respectively, as peak ratios. At least five measurements were made for each deuterium content. If we make a rough calculation of the peak height ratio to be expected, taking into account the composite nature of peak y, the differences between the ratios listed above can be accounted for by a 10% difference in the extents of deuteration in the base terminal and apex hydrogen positions. We therefore conclude that as far as terminal hydrogens in pentaborane are concerned the rates of exchange in the base and apex positions are the same to within ±10%.

It should be pointed out that these studies do not permit us to eliminate mechanisms in which only base or apex terminal protons exchange with BD_3 followed by a more rapid intramolecular exchange between base and apex terminal protons. In view of the properties of pentaborane, however, we feel that this is an unlikely situation and a more probable mechanism is the exchange of deuterium between deuterated borane and each of the terminal hydrogen positions independently.

BALTIMORE, MD.
ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Interpretation of Abnormalities in Atom Polarization in Terms of Electric Moment

BY C. C. MEREDITH, L. WESTLAND AND GEORGE F WRIGHT

RECEIVED DECEMBER 14, 1956

Dielectric constant determinations of pelletted solid benzoquinone, naphthoquinone and anthraquinone show that the atom polarizations are not abnormally high. Assignment of the non-electronic polarization chiefly as orientation polarization has been confirmed by demonstration of temperature dependence. The distortion polarization of 4,4'-dinitrobiphenyl has also been shown to be normal, so this substance must have an electric moment of 1 *D*. All of these substances must have non-planar and non-linear structures. The so-called abnormal polarization (57 cc.) of ferric acetylacetonate seems to be partly (21 cc.) atomic and partly due to orientation polarization according to dielectric constant determinations of solids and solutions. Since some of these studies contradict earlier evidence the reliability of the measurements and the interpretation is discussed.

A discrepancy has been observed between the total electrostatic polarization and the electronic polarization in certain substances. This discrepancy has been assigned as atom polarization.[1] Typical compounds to which these molecular deformations are attributed are quinones, *p*-substituted biphenyls and metal acetylacetonates, none of which are presumed to contribute to orientation polarization. These types have been considered in the present study.

The Quinones

The difference, $P_T - P_E = 8\text{–}10$ cc., for a series of 1,4-benzoquinones would indicate moments of 0.6–0.7 *D* but the orthodox expectation that quinones are planar, as well as the temperature-independent constancy of $P_T - P_E$ among these quinones, has brought forth the theory[2] of an atom polarization due to lateral deformation of "balanced carbonyl dipoles." The apparent dipole moment for 2,5-di-*t*-butylbenzoquinone (= 0.81 ± 0.03 *D* in benzene at 25°)[3] seems to be the only, and minor, exception to this generalization.

In view of this conclusion we sought by use of benzoquinone to test our method[4] for determination of atomic plus electronic polarization by use of solid organic compounds pelletted to maximum density. Already we had found reasonable agreement between our capacitance measurements of pelletted mercuric chloride ($P_A = 5$ cc.) and the value calculated from vapor phase dielectric constants ($P_A = 6$ cc.).[5] However our pelletted benzoquinone at 22 ± 2° showed a polarization of 30.1 cc.

This value is slightly lower than the 30.9 cc. determined for the electronic polarization at 5892.6 Å. in benzene solution but is slightly higher than the 28.4 cc. value accepted by many workers[1] and derived from group polarizations (26.8 cc.) plus 1.58 cc. of "exaltation."[6] In any event the derived value deviates from the observed pellet polarization only by the amount expected[7] for normal atom polarization. But this pellet polarization is 7–9 cc. less than the total polarization reported from benzoquinone in solution or in the gaseous state. Therefore the difference cannot be attributed to atom polarization.

In view of this discrepancy we have determined at several temperatures the dielectric constants and specific volumes of a series of solutions of benzoquinone. The precision of these determinations may be judged from Fig. 1 (solutions in benzene) and Fig. 2 (solutions in dioxane) from which the

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