however, since the observed shortening of the edges shared by tetrahedra is in accord with Pauling's rules for stability of ionic crystals.[10]

Around each Rb^+ ion are eight F^- ions at distances ranging from 2.78 to 3.16 Å. (average 2.95 Å.) in an asymmetrical array. The array approximates very roughly an antiprism with its $\bar{4}$ axis along *b*. A similar grouping occurs around the Cs^+ ion, but six F^- ions are at distances of 2.96 to 3.15 Å. (average 3.07 Å.) and two are at 3.50 and 3.53 Å. Since the interatomic distances from Pauling's crystal radii are r(Rb–F) = 2.95 Å. (eight-coordination) and r(Cs–F) = 3.05 Å. (six-coordination), it is appropriate to designate the coordination numbers of Rb^+ and Cs^+ ions in the two compounds as eight and six, respectively. Thus it appears that, while the sheets of tetrahedra make available about the same configuration of anions to each kind of large cation, the Rb^+ ion attracts more neighbors than the Cs^+ ion, which is to be expected considering their relative anion : cation radius ratios.[3]

Acknowledgment.—We thank G. M. Hebert for preparing the samples and R. E. Thoma for suggesting this problem.

[10] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 561.

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Isotope Effects in Boron Hydrides. X.[1] The Reaction of Diborane with Basic D_2O

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Received May 10, 1965

In earlier papers of this series the kinetic isotope effects of numerous hydride transfer reactions have been reported. In continuing these studies of complex isotope effects, it seemed important to vary the number of deuterium atoms on borohydride ion and also study the reaction of borane (or diborane) with heavy water. In this way one could obtain further insight into the primary inverse isotope effect of 0.70 in the acid hydrolysis of sodium borohydride.[3] Since aquated borane was suggested as a reaction intermediate we surveyed

$$BH_4^- + 4H_2O \longrightarrow 4H_2\uparrow + B(OH)_4^- \qquad (1)$$

$$BD_4^- + 4H_2O \longrightarrow 4HD\uparrow + B(OH)_4^- \qquad (2)$$

the literature for the reaction of diborane and other boranes with aqueous base[4] and then experimentally rediscovered the synthesis of sodium borohydride.[5,6]

Since early data[7] suggested rather unusual isotopic rearrangements, and since it was wished to prepare and study the mixed isotopic species, $NaBH_{4-x}D_x$, gaseous diborane, B_2H_6, in a stream of nitrogen was allowed to react with an aqueous solution of sodium hydroxide and also with sodium deuteroxide, NaOD, in heavy water at 4°.

Diborane was generated by the gradual addition of solid sodium borohydride to methanesulfonic acid.[8] Pure nitrogen swept the diborane through a safety trap, a cold trap at −78°, and then a fritted gas dispersion tube placed under a solution of aqueous sodium hydroxide (0.10 or 1.0 *M*). A sample of the solution was then treated with dilute acid to decompose any boron hydride and the total amount of boron obtained. Another sample was treated with excess iodate and the amount of the hydride determined. In different experiments, it was determined that 83 to 90% of the diborane reacted immediately to produce borate and hydrogen.

$$B_2H_6 + 2OH^- + 6H_2O \longrightarrow 2B(OH)_4^- + 6H_2 \qquad (3)$$

However, 10 to 17% of the diborane produced sodium borohydride.

$$B_2H_6 + 2OH^- + 2H_2O \longrightarrow B(OH)_4^- + BH_4^- + 2H_2 \qquad (4)$$

The current experiments did not seek to maximize the yield of borohydride, but somewhat greater yields were realized if the addition of diborane was slow and the ratio of nitrogen to diborane large.

Diborane was passed into solutions of 0.1 *M* sodium deuterioxide at 4° in heavy water of 99.62% isotopic purity. The excess water was then removed under very high vacuum at 0°. The powdery residues containing sodium borate and sodium deuterioxide were added to borate buffers in *a large excess* of light water. The evolved gases were analyzed for deuterium (as HD) using a mass spectrometer. The results are presented in Table I. Essentially all of the hydridic hydrogens arise from the diborane. It is unlikely that exchange between hydrogen gas (produced by hydrolysis) and diborane contributes significantly to the present reaction.[9,10] Since the total amount of sodium deuterioxide added is known and since the isotopic purity of the heavy water is known, the total amount of any deu-

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[1] Paper VIII: R. E. Davis, C. L. Kibby, and C. G. Swain, *J. Am. Chem. Soc.*, in press; paper IX: *Chem. Commun.* (London), in press.

[2] (a) Alfred P. Sloan Fellow, 1962–1966; (b) N.S.F. Summer Research Participant, 1961.

[3] Paper III: R. E. Davis, E. Bromles, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962). The hydrolysis of borohydride in aqueous solution containing trimethylamine produced trimethylamine borane. Recently Collat [J. A. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, **87**, 1692 (1965)] has obtained evidence for a species as BH_3OH^-, a species first postulated by J. Goubeau and H. Kallfass [*Z. anorg. allgem. Chem.*, **299**, 160 (1959)].

[4] R. C. Ray, *J. Chem. Soc.*, **121**, 1088 (1922); R. C. Ray, *Chem. Ind.* (London), 322 (1946); M. W. Travers and R. C. Ray, *Proc. Roy. Soc.* (London), **A87**, 163 (1912); A. Stock and E. Kuss, *Ber.*, **47**, 810 (1914); A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; A. Stock, W. Sutterlin, and Z. Kurzen, *Z. anorg. allgem Chem.*, **225**, 225 (1935); L. Klemm and W. Klemm, *ibid.*, **225**, 258 (1935).

[5] R. E. Davis and J. A. Gottbrath, *Chem. Ind.* (London), 1961 (1961).

[6] P. F. Winternitz, U. S. Patent 2,532,217 (Nov. 28, 1950); *Chem. Abstr.*, **45**, P2162 (1951). Unfortunately *Chemical Abstracts* has abstracted this patent *only* as to the reaction of LiH with BF_3 and *no* mention is made in this abstract of the reaction of diborane with aqueous potassium hydroxide. Had we known this, we would not have published our earlier paper[5] on "The Nature of Stock's Hypoborate." The "Official Gazette" of the U. S. Patent Office contains *only* the abstract on the lithium hydride reaction [**640**, (4) 1354 (1950)].

[7] W. L. Jolly and R. E. Mesmer, *J. Am. Chem. Soc.*, **83**, 4470 (1961).

[8] H. G. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959).

[9] R. A. Marcus, *J. Chem. Phys.*, **23**, 1107 (1955).

[10] P. C. Maybury and W. S. Koski, *ibid.*, **21**, 742 (1953).

teride present in sample I or II in Table I can be computed to be less than 0.7%. No usual bands were observed in the n.m.r. spectra of these samples.

TABLE I

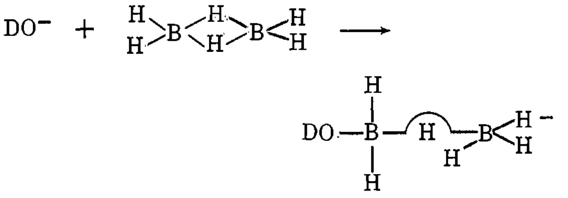
HYDROLYSIS IN H_2O

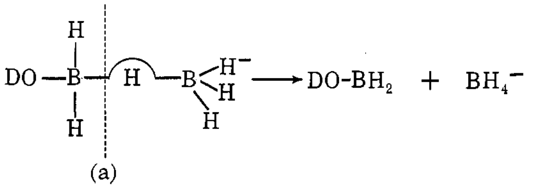
	I[a]	II[b]	III[c]
H_2	98.4	98.6	99.980
HD	1.6	1.4	0.020[d]
D_2	0.00	0.00	0.000

[a] Trials on the material from diborane into basic heavy water, ±0.05%. [b] Trials using another sample prepared at a different flow rate of diborane. [c] Hydrolysis of sodium borohydride in a light water buffer, ±0.0007%. [d] Natural abundance of deuterium.

The infrared spectra of samples I and II in potassium bromide pellets and in Nujol mulls showed only the infrared-active bands of the borohydride. Kenson and Davis[11] have computed infrared spectra to be expected from $BH_xD_{4-x}^-$ ions using the F and G matrix method and the force constants reported by Taylor[12] from the analysis of BH_4^- and BD_4^-. None of the bands of BH_3D^- was seen at 2261 (e), 2200 (a_1), 1697 (a_1), 1168 (e), 1075 (a_1), or 955 (e) cm.$^{-1}$, which are the values computed for this ion.

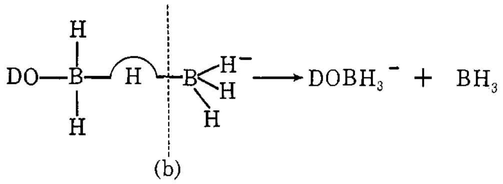
Parry[13] has reviewed numerous reactions and suggested that many occur by nonsymmetrical cleavage of the double bridge bond of diborane and other boron hydrides.[14] This suggestion is supported by the present data in which even the isotopic integrity of the boron hydrogens is maintained. The minor reaction of deuterioxide with diborane producing BH_4^- can be postulated[15] as occurring with rupture of bond (a) about 14% of the time.


(5)


(6)

$$DOBH_2^- \xrightarrow[\text{fast hydrolysis}]{D_2O} D_3BO_3 + 2HD \qquad (7)$$

Heavy water could also function as a nucleophile. If $B_2H_6OD^-$ is an intermediate then cleavage of the (a) boron–hydrogen bond could occur to produce borohydride. If the other bond cleaves to produce BH_3OD^- and BH_3 only total hydrolysis products[3] would result.


(8)

$$BH_3 + DOBH_3^- \xrightarrow[\text{fast hydrolysis}]{D_2O} D_3BO_3 + HD\uparrow \qquad (9)$$

Further experimental work is required to provide further information.

Experimental

Materials.—All materials were analytical reagents. Diborane was generated from sodium borohydride and methanesulfonic acid. Borate analysis was made by electrometric titration in the presence of mannitol. The iodate technique[3] was used for borohydride. The kinetic techniques have been discussed.[3]

Matched infrared cells (0.1 mm.) of IRtran-2 were obtained from the Connecticut Instrument Corp. The spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer. Salt plates were also used to obtain the spectra.

The n.m.r. spectra were recorded using a Varian A-60. Mass spectral analyses were determined using both a Bendix Model 12-1-1 time-of-flight mass spectrometer and a Consolidated-Nier Model 21-201 isotope-ratio mass spectrometer.

Acknowledgments.—The present study was supported by a Frederick Gardner Cottrell grant from the Research Corporation and the Sloan Foundation. The support of J. A. G. by the National Science Foundation is also greatly appreciated.

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(13) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(14) A latter review of the literature is given by W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963, pp. 154–197.

(15) Postulated by analogy from the data of R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

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The Dipole Moments of the Isomers of Dicarbadecaborane, $B_{10}H_{10}C_2H_2$[1]

BY A. W. LAUBENGAYER AND W. R. RYSZ

Received May 10, 1965

The recent synthesis[2] of *p*-dicarbadecaborane has completed the list of the three isomeric forms possible for this remarkable three-dimensional aromatic framework and sets the stage for much interesting research on the physical and chemical characteristics of such icosahedral structures. In order to further substantiate the assignments[3,4] of the structures shown in Figure 1 we have measured the dipole moments of the three isomers.

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(1) Based on part of a thesis submitted by W. R. Rysz to the Graduate School of Cornell University, Feb. 1965, in partial fulfillment of the requirements for the M.S. degree.

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