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A Study of the Reaction of Hydroxide Ion with $B_{20}H_{18}^{-2}$

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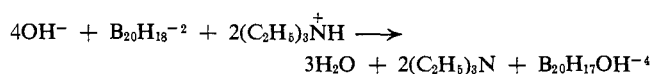
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The reaction of aqueous hydroxide ion with $B_{20}H_{18}^{-2}$ produces $B_{20}H_{17}OH^{-4}$ (isomer i) which subsequently rearranges to a second $B_{20}H_{17}OH^{-4}$ (isomer ii). Both $B_{20}H_{17}OH^{-4}$ ions may be protonated to produce a $B_{20}H_{18}OH^{-3}$ ion. Structures were assigned on the basis of ^{11}B n.m.r. spectra. Oxidation of $B_{20}H_{18}OH^{-3}$ with a variety of oxidants produced $B_{20}H_{17}OH^{-2}$. The kinetics of the reaction of OH^{-} with $B_{20}H_{18}^{-2}$ was of the form rate = $k_1[B_{20}H_{18}^{-2}] + k_2[OH^{-}][B_{20}H_{18}^{-2}]$. A mechanism is proposed for the hydroxide ion reaction.

Introduction

The preparation,^{2,3} structure,^{2,4} and reactions^{2,3,5,6} of the $B_{20}H_{18}^{-2}$ ion have been the subject of considerable research. Among the reactions of $B_{20}H_{18}^{-2}$ is its facile reaction with hydroxide ion in aqueous media to produce the $B_{20}H_{17}OH^{-4}$ ion⁵ which was first formulated² as $B_{10}H_9OH^{-2}$. Three recent, brief accounts^{2,3,5} of that reaction have appeared, and it is the purpose of this paper to extend these discussions further.

Isomeric $B_{20}H_{17}OH^{-4}$ Ions. The reaction of the triethylammonium salt of $B_{20}H_{18}^{-2}$ with aqueous hydroxide ion consumed 4 equiv. of base and liberated 2 equiv. of triethylamine. The $B_{20}H_{17}OH^{-4}$ ion



(isomer i) formed in this reaction was quantitatively rearranged to an isomeric ion (isomer ii) when heated in aqueous solution or when treated with acid followed by the addition of excess base. A large-scale preparative method was devised for isomer ii which involved the slow reaction of $B_{20}H_{18}^{-2}$ with aqueous triethylamine solutions and subsequent rearrangement. Both isomers of $B_{20}H_{17}OH^{-4}$ consumed 1 equiv. of acid when subjected to potentiometric titration. The resulting $B_{20}H_{18}OH^{-3}$ ion was isolated as its cesium, tetramethylammonium, or triethylammonium salt.

Neutralization of the cesium or tetramethylammonium salts with excess base produced isomer ii. Similar treatment of the triethylammonium salt gave isomer i. However, if the triethylammonium salt was heated for 30 min. in ethanol at the boiling point and then neutralized, isomer ii resulted. These results suggest that two isomeric $B_{20}H_{18}OH^{-3}$ ions are in equilibrium and represent intermediates in the rearrangement sequence. One of these $B_{20}H_{18}OH^{-3}$ isomers appears to separate selectively from aqueous solutions as the triethylammonium salt, and the other isomer separates as the cesium or tetramethylammonium salt. The latter isomer is apparently produced when the triethylammonium salt of the former isomer is heated in ethanol solution. The ^{11}B n.m.r. spectra of the cesium (or tetramethylammonium) salt and the isolated triethylammonium salt were virtually identical at 19.3 Mc./sec., and all salts displayed a B-H-B bridge absorption at 1800 cm^{-1} in the infrared. These results are in agreement with those of Chamberland and Muetterties.³

The direct conversion of $B_{20}H_{17}OH^{-4}$ isomer i to the isomer ii under equilibrium conditions proves that isomer ii is the thermodynamically more stable member of the isomer pair. The direct formation of isomer i from $B_{20}H_{18}^{-2}$ is therefore a result of kinetic control of the reaction products. The isomerization reaction observed in this system appears to be analogous to the isomerization reactions observed in the parent $B_{20}H_{18}^{-4}$ system.⁶

During the course of the chemical characterization of the $B_{20}H_{17}OH^{-4}$ and $B_{20}H_{18}OH^{-3}$ ions, $B_{20}H_{18}^{-2}$ was converted to $B_{20}H_{17}OCH_3^{-4}$ by reaction with methoxide ion in anhydrous methanol. These results and the facile oxidation of $B_{20}H_{17}OH^{-4}$ to $B_{20}H_{17}OH^{-2}$ are in agreement with the results of Chamberland and Muetterties.³

The ^{11}B N.m.r. Spectra of $B_{20}H_{17}OH^{-4}$ Isomers. The charge, empirical formula, and chemical behavior of the $B_{20}H_{17}OH^{-4}$ isomers identify them as hydroxy-substituted derivatives of the $B_{20}H_{18}^{-4}$ ions.⁶ It has been shown^{3,6} that the ^{11}B n.m.r. spectra of the $B_{20}H_{18}^{-4}$ ions can be readily interpreted if it is assumed that the resonances for the apical boron atoms of the B_{10} polyhedra occur at low field between -12 and $+6$ p.p.m. and that resonances for the equatorial boron atoms occur at high field near 28 p.p.m. It has also been shown that for equatorially substituted $B_{10}H_9OH^{-2}$ there is a shift to the low-field region for the equatorial atom attached to the hydroxyl group.⁷ The ^{11}B

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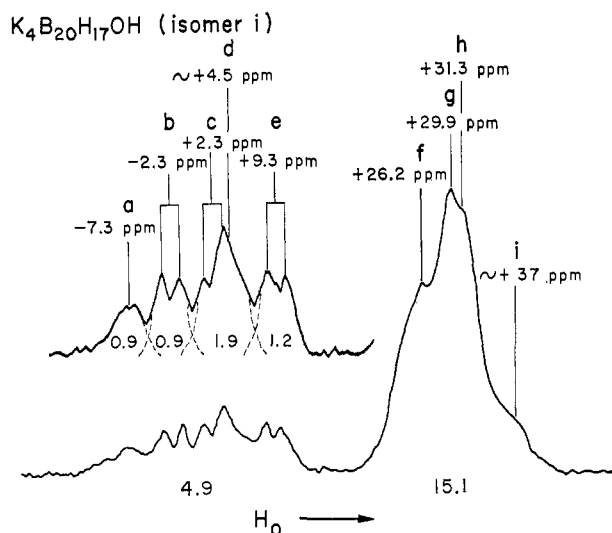


Figure 1. The ^{11}B n.m.r. spectrum of $\text{K}_4\text{B}_{20}\text{H}_{17}\text{OH}$ (isomer i) in H_2O at 64.16 Mc./sec. Chemical shifts were measured at 32.1 Mc./sec. relative to $\text{BF}_3 \cdot \text{OEt}_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

n.m.r. spectra of the $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ isomers are consistent with these two correlations if the range for resonance of the apical boron atoms is increased to cover the interval from -12 to $+10$ p.p.m. The spectra of the $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ ions can be divided into two regions, one at low field of relative intensity 5 and one at high field of relative intensity 15. The low-field resonances were assigned to the four apical boron atoms plus one equatorial boron atom which bears a hydroxyl group. The high-field array was assigned to the remaining equatorial boron atoms.

The 64.16-Mc./sec. ^{11}B n.m.r. spectrum of isomer i is shown in Figure 1. Examination of this spectrum reveals a remarkable similarity at low field to the corresponding region of the spectrum of $\text{B}_{20}\text{H}_{18}^{-4}$, ae isomer.⁶ This region has a total integrated area of 4.9 between -9 and $+10$ p.p.m., and reading from low to high field consists of a singlet a of area 0.9, a doublet b of area 0.9, a superimposed doublet and singlet c and d of area 1.9, and a doublet e of area 1.2. This low-field array of three doublets and two singlets is only compatible with a structure which has an apical-equatorial B-B bond and an equatorial hydroxyl group.⁸ The six possible isomers with these structural features are shown as A-F in Figure 2. Structures C, D, E, and F each contain two groups of four equivalent boron

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(8) The qualitative composition of the low-field group as a function of possible structural features of the $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ isomers can be predicted if it is assumed that (i) apical boron atoms produce resonances which occur at lower field than equatorial boron atoms, as in $\text{B}_{10}\text{H}_{10}^{-2}$ and the $\text{B}_{20}\text{H}_{18}^{-4}$ isomers⁶; (ii) substitution of an OH group for a terminal hydrogen atom shifts the resonance of a boron atom in a B_{10} unit to lower field as in $\text{B}_{10}\text{H}_9\text{OH}^{-2}$ (see also Table I in this paper). The expected low-field groups are: (a) three doublets and one singlet of area 1 for an equatorial-equatorial B-B bond and an apically substituted OH group; (b) four doublets and one singlet of area 1 for an equatorial-equatorial B-B bond and an equatorially substituted OH group; (c) two doublets and two singlets of area 1 for an apical-equatorial B-B bond and an apically substituted OH group; (d) three doublets and two singlets of area 1 for an apical-equatorial B-B bond and an equatorially substituted OH group; (e) one doublet and three singlets of area 1 for an apical-apical B-B bond and an apically substituted OH group; (f) two doublets and three singlets of area 1 for an apical-apical B-B bond and an equatorially substituted OH group.

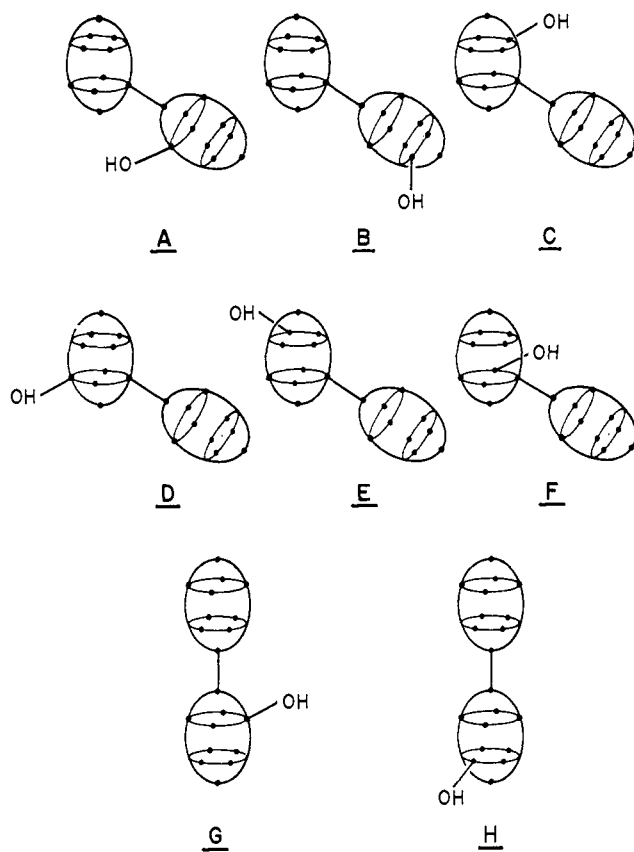


Figure 2. Possible structures for isomers i and ii of $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$. A-F are the possible structures for isomer i based on the ^{11}B n.m.r. G and H are the possible structures for isomer ii based on the ^{11}B n.m.r.

atoms in the apically substituted B_{10} polyhedron. This arrangement occurs in the 32.1-Mc./sec. ^{11}B n.m.r. spectrum of $\text{B}_{20}\text{H}_{18}^{-4}$ a² isomer⁶ in which the two groups of four boron atoms are unresolved and produce a well-defined doublet. If it is assumed that an OH group on one polyhedron has little or no influence on chemical shifts in the other polyhedron, then structures C, D, E, and F would be expected to produce a doublet of area 8 of sufficient intensity to stand out from the high-field array. This assumption is justified by the presence of such a doublet in the spectrum of $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ isomer ii and by the close similarity of the high-field groups in spectra of $\text{B}_{20}\text{H}_{18}^{-2}$ and $\text{B}_{20}\text{H}_{17}\text{OH}^{-2}$ and of $\text{B}_{20}\text{H}_{18}^{-3}$ and $\text{B}_{20}\text{H}_{18}\text{OH}^{-3}$. Since such a doublet is not present in the observed spectrum of isomer i, it is probable that it is not C, D, E, or F. The remaining possibilities are A and B, and of these two A is preferred because of the mode of formation of isomer i from $\text{B}_{20}\text{H}_{18}^{-2}$ (*vide infra*).

The previously published³ spectrum of $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ at 19.3 Mc./sec. shows an overall similarity to that of isomer ii. The 64.16-Mc./sec. ^{11}B n.m.r. spectrum of isomer ii is shown in Figure 3. At low field the spectrum consists of two groups with a total area of 4.8. The low-field singlet a has an area of 1.9, and integration of the group of area 2.9 shows the relative areas of its three component peaks to be 1.43:0.96:0.50. This group is seen to be a singlet b of area 1.0 and two doublets c and d of areas 0.9 and 1.0, respectively, both by successive subtraction of those areas, which must be doublets, and by comparison with the ^{11}B n.m.r.

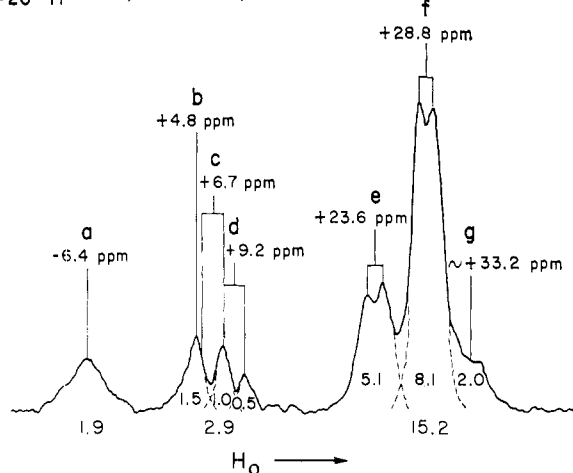
$K_4B_{20}H_{17}OH$ (isomer ii)

Figure 3. The ^{11}B n.m.r. spectrum of $K_4B_{20}H_{17}OH$ (isomer ii) in H_2O at 64.16 Mc./sec. Chemical shifts were measured at 32.1 Mc./sec. relative to $BF_3 \cdot OEt_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

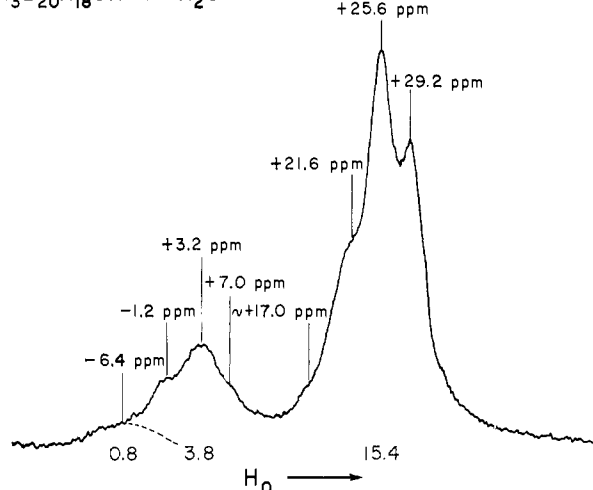
 $K_3B_{20}H_{18}OH$ in H_2O 

Figure 4. The ^{11}B n.m.r. spectrum of $K_3B_{20}H_{18}OH$ in H_2O at 32.1 Mc./sec. Chemical shifts were measured relative to $BF_3 \cdot OEt_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

spectrum at 19.3 Mc./sec. This low-field array, which consists of two doublets and three singlets (two superimposed in a), correlates with a structure containing an apical-apical B-B bond and an equatorial hydroxyl group.⁵ This structure is also supported by the predominant doublet f of area 8 at high field which is presumably due to the two unresolved groups of four boron atoms in the equatorial belts of the apically substituted B_{10} polyhedron as in the $B_{20}H_{18}^{-4}$ a² isomer.⁶ It is impossible to distinguish between the two possible isomers G and H using the n.m.r. data alone. If the proposed mechanism for the rearrangement of the $B_{20}H_{18}^{-4}$ isomers is correct,⁶ then the most probable structure for isomer ii is G.

The ^{11}B N.m.r. of $B_{20}H_{18}OH^{-3}$. The ^{11}B n.m.r. spectrum of $B_{20}H_{18}OH^{-3}$ in water shows similarities to the spectra of both $B_{20}H_{17}OH^{-4}$ isomers and to the

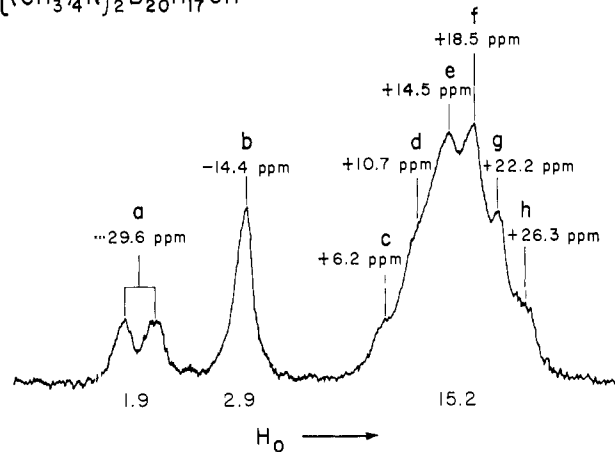
 $\{(CH_3)_4N\}_2B_{20}H_{17}OH$ 

Figure 5. The ^{11}B n.m.r. spectrum of $\{(CH_3)_4N\}_2B_{20}H_{17}OH$ in CH_3CN at 32.1 Mc./sec. Chemical shifts were measured relative to $BF_3 \cdot OEt_2 = 0$. Numbers below the peaks are integrated areas normalized to give a total area of 20.

spectrum⁶ of $B_{20}H_{19}^{-3}$. For example, the 60-Mc./sec. spectrum of $B_{20}H_{18}OH^{-3}$ shows two incompletely resolved groups of relative area 4.9 and 15.1 centered at 3.2 and 25.6 p.p.m., respectively. The low-field group, in turn, shows a partially resolved singlet of area 0.9 at -6.4 p.p.m. The 32.1-Mc./sec. spectrum (Figure 4) has a triplet at high field which is almost identical in shape, intensity, and position with the high-field group in $B_{20}H_{19}^{-3}$. The spectrum of $B_{20}H_{18}OH^{-3}$ published previously³ shows apparent differences in both chemical shift and integration; these could be due to the use of H_3O^+ as the cation.

The infrared spectrum of $B_{20}H_{18}OH^{-3}$ shows a moderately strong absorption at 1800 cm^{-1} which suggests the presence of a B-H-B bridge. The formation of $B_{20}H_{18}OH^{-3}$ from either isomer i or isomer ii suggests that the most likely structural possibilities are based on the ae or a² skeletal configurations.⁶ The model which best meets these requirements is one in which the two B_{10} polyhedra are joined by an apical-equatorial B-H-B bridge with the hydroxyl group attached to one of the polyhedra at an equatorial position.

The ^{11}B N.m.r. Spectrum of $B_{20}H_{17}OH^{-2}$. The ^{11}B n.m.r. spectrum of $B_{20}H_{17}OH^{-2}$ at 32.1 Mc./sec. (Figure 5) shows some similarities to the spectrum of $B_{20}H_{18}^{-2}$ at 32.1 Mc./sec. The doublet a at -29.6 p.p.m. appears in both spectra with an area of 2. The singlet b at -14.4 p.p.m. for $B_{20}H_{17}OH^{-2}$ appears at -15.3 p.p.m. for $B_{20}H_{18}^{-2}$. Most striking is the change of intensity of the singlet b from an area of 2.0 in $B_{20}H_{18}^{-2}$ to 2.9 in $B_{20}H_{17}OH^{-2}$. The appearance of a third singlet of area 1 in b is presumably due to a shift to low field of the resonance associated with the equatorial boron atom to which the hydroxyl group is attached.

The high-field group of $B_{20}H_{17}OH^{-2}$ is similar to, but less well defined than, that of $B_{20}H_{18}^{-2}$; the loss of definition is to be expected because of the lower symmetry of $B_{20}H_{17}OH^{-2}$.

Chemical Shift Due to Replacement of H by OH on Equatorial Boron Atoms. There are now available a number of pairs of polyhedral ions which apparently

differ only in the substitution of a hydroxyl group for an equatorial terminal hydrogen atom. For each of these pairs of ions, either an accurate or a minimum value can be found for the position of the ^{11}B resonance of the B-H which is converted to B-OH, and an accurate value can be obtained for the ^{11}B resonance of the B-OH. The difference in the two values will represent the change in chemical shift brought about by the substitution of OH for H on an equatorial boron atom. The values determined are given in Table I and are seen to be approximately constant.

Table I. ^{11}B Chemical Shift Differences between Equatorial H and OH

System		$-\Delta\delta$, p.p.m.
$\text{B}_{20}\text{H}_{18}^{-2}$	$\text{B}_{20}\text{H}_{17}\text{OH}^{-2}$	>22
$\text{B}_{20}\text{H}_{18}^{-4}(\text{a}^2)$	$\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ (isomer ii)	23 ± 1
$\text{B}_{20}\text{H}_{18}^{-4}(\text{ae})$	$\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ (isomer i)	24 ± 3
$\text{B}_{20}\text{H}_{19}^{-3}$	$\text{B}_{20}\text{H}_{18}\text{OH}^{-3}$	22 ± 5
$\text{B}_{10}\text{H}_{10}^{-2}$	$\text{B}_{10}\text{H}_9\text{OH}^{-2}$	26^a

^a Values from ref. 7.

Kinetics and Mechanism of $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ Formation. Having established the identity of the reaction products obtained in the reaction of $\text{B}_{20}\text{H}_{18}^{-2}$ with hydroxide ion, it was of interest to examine the reaction kinetics. This was accomplished by making use of the 292-m μ absorption maximum of the $\text{B}_{20}\text{H}_{18}^{-2}$ ion. The $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ ion product (isomer i) is virtually transparent at this wave length, and a spectrophotometric method was employed to follow the consumption of $\text{B}_{20}\text{H}_{18}^{-2}$. In all kinetic experiments a large excess of hydroxide ion was employed in water solvent. Data were obtained at 29.90, 40.00, and 50.00 \pm 0.01 $^\circ$. All kinetic runs were carried out at constant ionic strength (0.20) except for a series of runs conducted at 29.90 $^\circ$ at variable ionic strengths determined by the concentration of potassium hydroxide. Figure 6 presents the results of these experiments as a plot of pseudo-first-order rate constant vs. hydroxide concentration. At constant ionic strength the rate law is seen to be

$$-\frac{d[\text{B}_{20}\text{H}_{18}^{-2}]}{dt} = k_1[\text{B}_{20}\text{H}_{18}^{-2}] + k_2[\text{B}_{20}\text{H}_{18}^{-2}][\text{OH}^-]$$

Table II summarizes the averaged rate constant values

Table II. Average Rate Constant Values and Thermodynamic Activation Parameters for the Reaction of $\text{B}_{20}\text{H}_{18}^{-2}$ with OH^-

Temp., $^\circ\text{C}$.	k_1 , sec. $^{-1}$	k_2 , l. sec. $^{-1}$ mole $^{-1}$
29.90	0.7×10^{-4}	0.598×10^{-2}
40.00	2.5×10^{-4}	1.17×10^{-2}
50.00	6.8×10^{-4}	2.56×10^{-2}
	First-order term	Second-order term
E_a , kcal.	21.8 ± 1.2	14.1 ± 2
H^* , kcal.	21.2 ± 1.2	13.5 ± 2
S^* , e.u.	-7.4 ± 3.0	-24.4 ± 5.0
Z_1Z_2 from Brønsted plot	No salt effect	2.2 for μ < 0.02

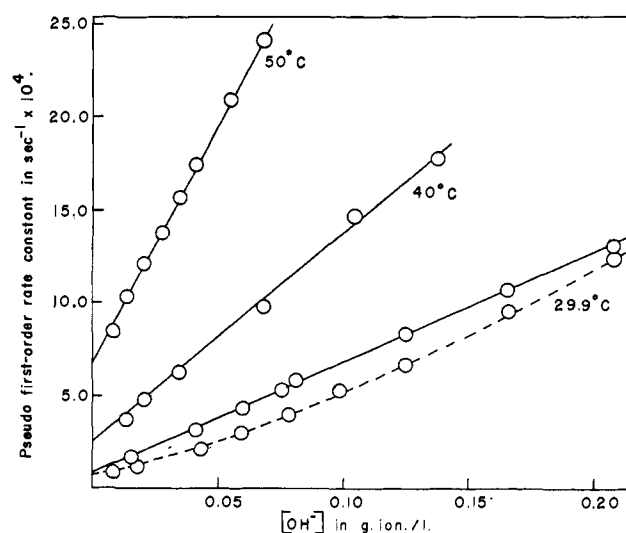
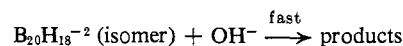
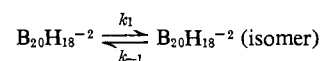


Figure 6. Plot of pseudo-first-order rate constant vs. hydroxide ion concentration for the reaction $\text{B}_{20}\text{H}_{18}^{-2} + 2\text{OH}^- \rightarrow \text{B}_{20}\text{H}_{17}\text{OH}^{-4} + \text{H}_2\text{O}$. Solid line indicates constant ionic strength (0.20). Dashed line indicates variable ionic strength determined by $[\text{KOH}]$.

and the thermodynamic activation parameters. The data obtained at variable ionic strength were correlated with a Brønsted slope⁹ of +2.2 in the case of the second-order term. The first-order term was independent of ionic strength.

Although $\text{B}_{20}\text{H}_{18}^{-2}$ salts may be recrystallized repeatedly from water without significant decomposition, a first-order term appears in the rate law of the hydroxide ion reaction. This observation may be rationalized in terms of (1) a slow, reversible isomerization of $\text{B}_{10}\text{H}_{18}^{-2}$ to an intermediate which is extremely reactive with hydroxide ion, or (2) the slow and reversible complexation of water solvent with $\text{B}_{20}\text{H}_{18}^{-2}$ followed by a rapid proton transfer from adducted water to hydroxide ion. The second possibility appears to require the operation of a reversible B-O bond-breaking process which is thermodynamically unpleasing. We therefore suggest that (1) prevails and that a base labile isomer of $\text{B}_{20}\text{H}_{18}^{-2}$ exists. The product (92%) which arises as a result of the k_1 process and subsequent fast reaction of the labile $\text{B}_{20}\text{H}_{18}^{-2}$ isomer with hydroxide ion was also found to be $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$. The



requisite reactions were conducted at 50 $^\circ$ in the presence of a bicarbonate-carbonate buffer at pH 10. The fact that isomer ii of $\text{B}_{20}\text{H}_{17}\text{OH}^{-4}$ was isolated is of no significance since the isolation procedure employed the initial isolation of a $\text{B}_{20}\text{H}_{18}\text{OH}^{-3}$ salt followed by neutralization with base, and this reaction sequence will convert isomer i to isomer ii.

The $\text{B}_{20}\text{H}_{18}^{-2}$ ion contains two equatorial boron atoms which bear no terminal hydrogen atoms and are at the same time involved in three-centered bonding.⁴ Such a structural arrangement suggests that one of the two unique equatorial boron atoms undergoes nucleo-

(9) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

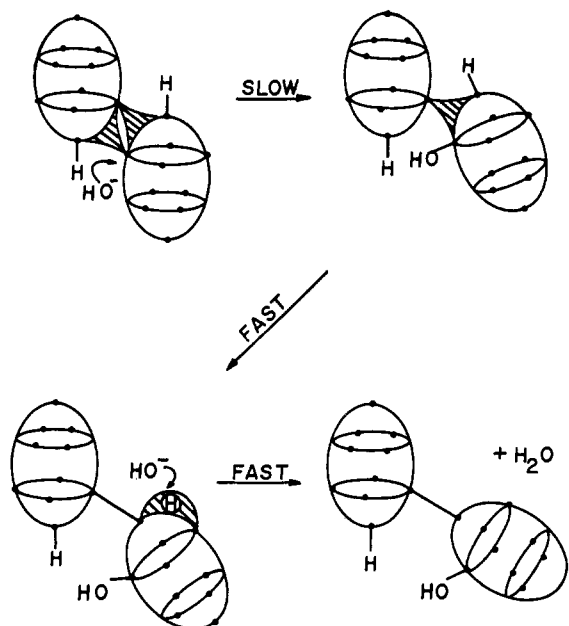


Figure 7. Suggested reaction sequence for the attack of $B_{20}H_{18}^{-2}$ by hydroxide ion.

philic attack by hydroxide ion in the k_2 process. Following this initial attack, a series of molecular rearrangements may occur which lead to the formation of isomer i. One suggested reaction sequence might involve the insertion of a terminal, apical B-H unit into a B-B-B three-center bond to produce a B-H-B bridge and regenerate normal bonding in both B_{10} polyhedra. A more attractive mechanism shown in Figure 7 involves the migration of the three-center edge-bonded B_{10} polyhedron to the apical position of the substituted B_{10} unit with concerted migration of the displaced apical proton to a neighboring edge. The edge-bonded proton would then be removed by a base to produce isomer i. Further speculation regarding this point is unwarranted at this time.

Experimental Section

Spectroscopic Methods. Infrared spectra were obtained as Nujol mulls using a Beckman IR-5 spectrophotometer. Ultraviolet spectra were obtained in aqueous or acetonitrile solutions with a Cary Model 14 spectrophotometer or a Beckman Model DB spectrophotometer.

Molecular Weight Determinations. Molecular weights were determined in aqueous solution at 25° using a Mechrolab vapor pressure osmometer Model 301 A. The osmometer was calibrated using $K_4Fe(CN)_6$ as a standard up to concentrations of 0.30 g.-ion/l. The samples were examined at concentrations between 0.10 and 0.30 g.-ion/l.

Equivalent Weights. The method used for the determination of equivalent weights and pK_a values was the same as that previously reported for the $B_{20}H_{18}^{-4}$ ion.⁶

Analyses for Et_3N^+H . Analyses for Et_3N^+H were carried out as previously reported.⁶

^{11}B N.m.r. Spectra. The ^{11}B N.m.r. spectra reported at 60.0 and 64.16 Mc./sec. were obtained using an experimental n.m.r. spectrometer which employed a

cryogenic magnet.^{10,11} A Varian Associates HR-100 spectrometer was used at 32.1 Mc./sec., and at 19.3 Mc./sec. a Varian Associates HR-60 N.M.R. spectrometer was employed. The n.m.r. spectra were obtained in water, deuterium oxide, or acetonitrile solutions. In all cases chemical shifts were obtained relative to $BF_3 \cdot OEt_2$ as standard.

Preparation of $(Et_3NH)_2B_{10}H_{10}$, $(Et_3NH)_2B_{20}H_{18}$, and $Cs_2B_{20}H_{18}$. The salts $(Et_3NH)_2B_{10}H_{10}$ and $(Et_3NH)_2B_{20}H_{18}$ were prepared using previously described methods.⁶ The salt, $Cs_2B_{20}H_{18}$, was prepared by the reaction of a stoichiometric quantity of CsOH with $(Et_3NH)_2B_{20}H_{18}$ as follows. To a solution of 8.03 g. (18.2 mmoles) of $(Et_3NH)_2B_{20}H_{18}$ in 50 ml. of acetonitrile at 0° was added 53.8 ml. (36.4 mmoles) of a 0.676 N CsOH solution in water. The solvent and free triethylamine were removed at room temperature with a rotary evaporator, and there was obtained 9.16 g. of pale yellow product. After two recrystallizations from 200 ml. of hot water, pale yellow platelets were obtained, which were shown to contain $B_{20}H_{18}^{-2}$ by their ultraviolet spectrum; λ_{max} 292 $m\mu$ (ϵ 9.9×10^3) and λ_{max} 231 $m\mu$ (ϵ 2.1×10^4).

Stoichiometry of the Reaction of $B_{20}H_{18}^{-2}$ with Hydroxide Ions. The stoichiometry of the reaction of $(Et_3NH)_2B_{20}H_{18}$ with hydroxide ion was determined using a modified Kjeldahl apparatus. In a typical determination, 0.2043 g. (0.466 mmole) of $(Et_3NH)_2B_{20}H_{18}$ was added to 25 ml. (2.14 mequiv.) of 0.0857 N potassium hydroxide. Nitrogen was passed through the solution while boiling until it was reduced to half its original volume. The triethylamine released was collected in 20.0 ml. (1.86 mequiv.) of 0.0928 N hydrochloric acid. Titration of the excess potassium hydroxide against standard acid showed that 0.30 mequiv. remained. Titration of the excess hydrochloric acid against standard base showed that 0.92 mequiv. remained. Thus, 0.466 mmole of $(Et_3NH)_2B_{20}H_{18}$ reacted with 1.84 mequiv. of potassium hydroxide and released 2.02 mmoles of triethylamine.

Kinetic Method for Reaction of $B_{20}H_{18}^{-2}$ with Hydroxide Ion. The reaction of $Cs_2B_{20}H_{18}$ with hydroxide ion was followed in aqueous solution by observing the decrease in the intensity of the 292- $m\mu$ absorption of $B_{20}H_{18}^{-2}$. In all kinetic runs the temperature was controlled within ± 0.01 by using a water-filled thermostat operated by a Sargent "Thermonitor" controller. In a typical kinetic run, the reaction was carried out in a 100-ml. volumetric flask containing 25 ml. of 5.9×10^{-4} M solution of $Cs_2B_{20}H_{18}$, sufficient potassium chloride solution to bring the final ionic strength to 0.20, and sufficient deionized, CO_2 -free water to allow free volume for the potassium hydroxide solution to be added. When the flask and contents had reached thermal equilibrium, the reaction was initiated by adding the appropriate volume of a potassium hydroxide solution of known strength. The timer was started, and the volume made up to 100 ml. with water. Samples were withdrawn at known intervals, quenched with an excess of dilute sulfuric acid, and diluted to a known volume. The absorbance of the sample at 292 $m\mu$ was measured using a Beckman DB spectrophotometer. During a typical run, the observed optical density

(10) *Chem. Eng. News*, 42, (No. 23) 55 (1964).

(11) F. A. Nelson and H. E. Weaver, *Science*, 146, 223 (1964).

decreased from 1.9 to 0.08. The observed optical density was corrected for the small absorbance of the reaction products at infinite time. The hydroxide ion concentration was never less than a tenfold excess over the initial $B_{20}H_{18}^{-2}$ concentration. Pseudo-first-order rate constants were obtained from plots of $\ln A_{cor}$ vs. time.

Preparation of $K_4B_{20}H_{17}OH \cdot 3H_2O$ Isomer i. To a solution of 11.5 g. (0.205 mole) of potassium hydroxide in 150 ml. of water at room temperature was added 22 g. (0.05 mole) of solid $(Et_3NH)_2B_{20}H_{18}$. Nitrogen was bubbled through the solution until all the amine had been displaced. The faintly cloudy solution was filtered and ethanol added until the solution became turbid. On cooling to 0° , fine, white needles separated. These were collected by filtration, washed with ethanol, and dried *in vacuo* to give 21.1 g. (91%) of $K_4B_{20}H_{17}OH \cdot 3H_2O$.

The infrared spectrum displayed OH and H_2O at 3520 (s) and 1600 (s) cm^{-1} , B-H at 2420 cm^{-1} (vs), and also unassigned bands at 1167 (m), 1109 (s), 1055 (m), 1005 (s), 901 (vw), 841 (vw), 821 (vw), 746 (w), 725 (w), and 695 (vw) cm^{-1} .

Anal. Calcd. for $K_4B_{20}H_{17}OH \cdot 3H_2O$: B, 46.95; H_2O , 11.72; K/B, 0.200; equiv. wt., 461; mol. wt., 461. Found: B, 46.1; H_2O , 11.15; K/B, 0.198; equiv. wt., 460; mol. wt., 455.

Preparation of $K_4B_{20}H_{17}OH \cdot 3H_2O$ Isomer ii. To a solution of 16.6 ml. (0.12 mole) of triethylamine in 200 ml. of water at 65° was added a solution of 10 g. (23 mmoles) of $(Et_3NH)_2B_{20}H_{18}$ in 70 ml. of acetonitrile. The reaction mixture was stirred at 65° for 3 hr. Excess triethylamine and acetonitrile were removed under reduced pressure using a rotary solvent stripper. A solution of 24 g. (0.245 mole) of potassium acetate in ethanol was added, together with enough ethanol to ensure complete precipitation. There was obtained 9.6 g. (91%) of $K_4B_{20}H_{17}OH \cdot 3H_2O$. The material was recrystallized by dissolving it in a minimum amount of water at room temperature followed by the addition of ethanol, until the solution became turbid, and cooling to 0° .

The infrared spectrum exhibited OH and water bands at 3550 (s) and 1600 (s) cm^{-1} , B-H stretch at 2450 cm^{-1} (vs), and additional bands at 1120 (s), 1004 (s), 755 (w), and 694 (w) cm^{-1} .

Anal. Calcd. for $K_4B_{20}H_{17}OH \cdot 3H_2O$: B, 46.95; H_2O , 11.72; K/B, 0.200; equiv. wt., 461; mol. wt., 461. Found: B, 47.1; H_2O , 12.0; K/B, 0.202; equiv. wt., 461; mol. wt., 441.

Rearrangement of the $B_{20}H_{17}OH^{-4}$ Isomers. A. A solution of 2.00 g. (4.35 mmoles) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i in 10 ml. of water was heated on a steam bath at $90-100^\circ$ for 26 hr. The solution was poured into a large excess of ethanol, cooled to 0° , and filtered. There was obtained 1.90 g. (95%) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii. The infrared spectrum of the product was identical in all respects with that of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii obtained from the reaction of aqueous triethylamine with $(Et_3NH)_2B_{20}H_{18}$, followed by treatment with potassium acetate.

B. More rapid rearrangement could be accomplished in the presence of acids. For example, 0.200 g. (0.435 mmole) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i in 2 ml. of 1.0 N hydrochloric acid at 0° was treated immediately

upon dissolving with an excess of potassium hydroxide at 0° and added to a large excess of ice-cold ethanol to give 0.193 g. (96%) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii.

Preparation of $B_{20}H_{18}OH^{-3}$ Salts. A. $(Me_4N)_3B_{20}H_{18}OH$. To a solution of 0.61 g. (1.32 mmoles) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i or ii in 4 ml. of water at room temperature was added 0.6 ml. (1.8 mequiv.) of 3 N hydrochloric acid. To the resulting solution was added a solution of 3.0 g. (27.4 mmoles) of tetramethylammonium chloride in 5 ml. of water to give a white precipitate which was separated by filtration. After washing with ice-cold water, ethanol, and ether, the compound was dried at room temperature *in vacuo*. There was obtained 0.60 g. (96%) of $(Me_4N)_3B_{20}H_{18}OH$. The compound was recrystallized from warm water to give white needles.

The infrared spectrum contained a B-H stretching band at 2480 cm^{-1} (vs) and a possible B-H-B bridge at 1800 cm^{-1} (m). Other bands appeared at 1620 (w), 1480 (m), 1280 (w), 1145 (m), 995 (m), 948 (s), 794 (w), 723 (m), and 680 (w) cm^{-1} .

The three strongest lines in the X-ray powder pattern using Cu $K\alpha$ radiation with a Ni filter had d values of 5.40, 5.27, and 4.77 Å.

Anal. Calcd. for $(Me_4N)_3B_{20}H_{18}OH$: B, 45.71; equiv. wt., 474. Found: B, 45.6; equiv. wt., 470.

B. $(Et_3NH)_3B_{20}H_{18}OH$. To a solution of 5.10 g. (11.1 mmoles) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i in 10 ml. (30 mequiv.) of 3 N hydrochloric acid was added at room temperature 15 g. (109 mmoles) of triethylammonium chloride dissolved in a minimum amount of water. The product separated slowly as a pale yellow gum which on cooling converted to a white solid. The white solid was separated by filtration and recrystallized by dissolving it in acetonitrile at room temperature, filtering, and adding ethanol to the filtrate until a turbid solution was obtained; on cooling white crystals separated. There was obtained 4.66 g. (75%) of $(Et_3NH)_3B_{20}H_{18}OH$, m.p. $160-162^\circ$.

The infrared spectrum contained a B-H stretching band at 2460 (vs), OH at 3500 (m), and a possible B-H-B bridge at 1800 (m) cm^{-1} . Other unassigned bands appeared at 1310 (w), 993 (w), 986 (m), 909 (m), 889 (w), 833 (m), 794 (m), 687 (m), and 660 (w) cm^{-1} .

Anal. Calcd. for $(Et_3NH)_3B_{20}H_{18}OH$: Et_3N^+H , 54.93; equiv. wt., 558. Found: Et_3N^+H , 54.29; equiv. wt., 561.

Treatment of an aqueous solution of $(Et_3NH)_3B_{20}H_{18}OH$ with a 25% solution of tetramethylammonium chloride precipitated $(Me_4N)_3B_{20}H_{18}OH$ identical in all respects with that obtained in method A.

Treatment of solid $(Et_3NH)_3B_{20}H_{18}OH$, prepared from isomer i, or isomer ii as above, with concentrated aqueous potassium hydroxide followed by precipitation of the product with a large excess of ethanol gave $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i in almost quantitative yield. Attempts to convert $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii to $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i by an analogous route involving $(Me_4N)_3B_{20}H_{18}OH$ or $Cs_3B_{20}H_{18}OH$ or by a rapid reaction sequence in which the intermediate was not isolated gave only $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii.

Heating $(Et_3NH)_3B_{20}H_{18}OH$ in boiling ethanol for 30 min. and cooling gave a white crystalline product with infrared and ^{11}B n.m.r. spectra identical with those ob-

tained from the product in method B. However, immediate treatment with concentrated potassium hydroxide followed by precipitation with a large excess of ethanol gave $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer ii in almost quantitative yield.

Preparation of $(Me_4N)_2B_{20}H_{17}OH$. To a solution of 2.00 g. (4.43 mmoles) of $K_4B_{20}H_{17}OH \cdot 3H_2O$ isomer i in 100 ml. of 0.2 N hydrochloric acid at 0° was added slowly 20 ml. (10.0 mmoles) of 0.5 N ferric chloride solution. The reaction mixture was stirred for 10 hr. after which a saturated solution of tetramethylammonium chloride was added until no further precipitation occurred. The pale yellow $(Me_4N)_2B_{20}H_{17}OH$ was collected and recrystallized from hot water. There was obtained 1.5 g. (85%) of $(Me_4N)_2B_{20}H_{17}OH$. The compound absorbed in the ultraviolet at λ_{max} 300 μ (ϵ 12,000) and λ_{max} 230 μ (ϵ 16,000). The

infrared spectrum contained a B-H stretching band at 2480 cm^{-1} (vs) and an OH stretching band at 3560 cm^{-1} (m). Other bands occurred at 1410 (m), 1290 (m), 1200 (m), 1170 (s), 1090 (s), 1075 (s), 1020 (w), 986 (w), 948 (vs), 909 (w), 889 (m), 875 (s), 855 (w), 826 (s), 811 (m), 775 (s), 738 (s), 692 (s), and 678 (s) cm^{-1} .

Anal. Calcd. for $(Me_4N)_2B_{20}H_{17}OH$: C, 24.09; H, 10.16; N, 7.02; B, 54.26. Found: C, 24.50; H, 10.95; N, 6.27; B, 55.11.

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The Electronic Properties of the 1,2- and 1,7-Dicarbaclododecaborane(12) Groups Bonded at Carbon

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The electronic properties of the 1,2- and 1,7-dicarbaclododecaborane(12) groups bonded at carbon have been examined with the aid of the following data: (1) nitration of the phenyl ring in [1,2-dicarba-1-clovdodecaboranyl(12)]benzene with mixed acid and determination of the ortho, meta, and para isomer ratios; (2) the determination of the pK_a values of *m*- and *p*-[1,2-dicarba-1-clovdodecaboranyl(12)]benzoic acids and anilinium ions; (3) determination of the ^{19}F chemical shifts relative to fluorobenzene of *m*- and *p*-[1,2- and 1,7-dicarba-1-clovdodecaboranyl(12)]fluorobenzenes. The data obtained provide no evidence for ground-state extension of electron delocalization by interaction of the aryl group with the highly delocalized 1,2-dicarba-1-clovdodecaboranyl(12) group, but did provide evidence for ground-state extension of electron delocalization by weak electron donation from the 1,7-dicarba-1-clovdodecaboranyl(12) isomer to the aryl group. The chemical equilibrium data for the 1,2-dicarba-1-clovdodecaboranyl(12) group were correlated with approximately the same Hammett σ constants ($\sigma_m \cong 0.47$, $\sigma_p \cong 0.49$) in both series of equilibria. The ^{19}F data correlated with σ_I constants of $+0.375 \pm 0.010$ and $+0.194 \pm 0.010$ for the 1,2- and 1,7-dicarba-1-clovdodecaboranyl(12) groups, respectively. The σ_R^0 constants $+0.003 \pm 0.005$ and -0.039 ± 0.005 were similarly obtained for the 1,2- and 1,7-dicarba-1-clovdodecaboranyl(12) substituents, respectively.

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Introduction

The reaction of $B_{10}H_{14}$ with ligands such as acetonitrile produces $B_{10}H_{12}(\text{ligand})_2^3$ derivatives which react with substituted acetylenes to produce 1,2-dicarba-1-clovdodecaboranyl(12) (hereafter α -carboranyl)^{4,5} derivatives. The latter compounds possess the geometry of a nearly regular icosahedron with the carbon atoms in neighboring positions.⁶ The α -carboranyl derivatives normally rearrange at 400–450° to 1,7-dicarba-1-clovdodecaboranyl(12) (hereafter, β -carboranyl)^{6,7} derivatives which differ from their α isomers in that the carbon atoms in the icosahedron are separated from each other by a pair of boron atoms.⁸ The organic chemistry of the α - and β -carboranyl systems has been investigated⁹ and evidence has accumulated which

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(5) In previous literature the 1,2 and 1,7 isomers were referred to as *o*- and *m*-carborane, respectively. These isomers will be referred to as the α and β isomers, respectively, in this paper to avoid confusion with the standard nomenclature for phenyl derivatives.

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