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Thermodynamic Properties of $B_{10}H_{10}{}^{2-}$(aq) and $B_{12}H_{12}{}^{2-}$(aq)

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The oxidation of $B_{10}H_{10}{}^{2-}$ to boric acid by permanganate in dilute aqueous solution has been studied calorimetrically, and the resulting standard enthalpy of formation of the aqueous polyhedral ion at 25° is $+22 \pm 5$ kcal mol^{-1}. This result and several semiempirical schemes are used with existing thermochemical data on other boron hydrides to estimate the standard enthalpy of formation of $B_{12}H_{12}{}^{2-}$ as $+11 \pm 10$ kcal mol^{-1}. The conventional standard entropies of these ions at 25° are estimated as 60 ± 4 and 62 ± 4 cal deg^{-1} mol^{-1} for $B_{10}H_{10}{}^{2-}$(aq) and $B_{12}H_{12}{}^{2-}$(aq), respectively; the standard free energies of formation $\Delta G_f{}^\circ{}_{298}$ are then 65 ± 5 and 63 ± 10 kcal mol^{-1}. The data are used to show the apparent stability of these polyhedral borane anions is kinetic rather than thermodynamic.

Compared to most boranes, the polyhedral ions $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ exhibit unusual thermal and hydrolytic stabilities. Though there is chemical evidence that the hydrolytic stability is kinetic in origin, as the polyhedral ions can be hydrolyzed at elevated temperatures or in the presence of platinum black,[1] no thermodynamic data have so far been obtained for these species. With the discovery[2] that $B_{10}H_{10}{}^{2-}$ in aqueous solution is rapidly and quantitatively oxidized to borate by permanganate, a calorimetric study of this ion became feasible and has now been accomplished, as described below. The oxidation of $B_{12}H_{12}{}^{2-}$ is too slow for calorimetry, but we have estimated its enthalpy of formation by using the data for $B_{10}H_{10}{}^{2-}$ and various other boron hydrides.

The entropies of the polyhedral ions would be accessible through conventional third-law methods, but no experimental investigations are known to us, so we have again made theoretical estimates. Although these are in some respects rather crude and although the uncertainties in the enthalpies of formation are about 5 kcal mol^{-1} for $B_{10}H_{10}{}^{2-}$ and even larger for $B_{12}H_{12}{}^{2-}$, the resulting free energies of formation permit useful thermodynamic discussion of the reactions of the ions. It is confirmed that kinetic factors account for the apparent stability.

Experimental Section

Materials and Apparatus.—$K_2B_{10}H_{10}$ was prepared from the corresponding triethylammonium salt by titration with 2 equiv of KOH, twice recrystallized from 25% aqueous alcohol, and dried over P_2O_5. The triethylammonium salt had been prepared from decaborane and triethylamine in toluene,[3] recrystallized first from water and then from 25% aqueous alcohol. The water used for the solutions was first distilled and then passed through a deionizer, which also removed carbon dioxide. This same water and analytical reagent grade toluene and bromobenzene were used to calibrate the calorimeter. The $KMnO_4$ was analytical reagent grade.

The calorimeter consisted of a dewar flask with a tight-fitting Teflon cover in which holes had been drilled to accommodate a Beckmann thermometer, a Teflon stirring rod, a 7-mm glass tube, and two electric leads. Screwed to the cover from below were four Teflon posts extending to within 5 cm of the bottom of the calorimeter and attached at their lower end to a circular Teflon disk. The disk had a hole in the middle for the stirring rod. The heating element consisted of a nichrome wire sealed in Teflon and wound about the lower half of the four vertical posts. The bottom half of the glass tube was blown into a thin-walled bulb about 10 ml in volume. Attached to the stirring rod right below the disk was a 3-cm Teflon paddle. To improve insulation, the entire assembly was enclosed during each run in a cardboard box loosely filled with cotton. All parts not made of glass were protected from the corrosive permanganate solution by Teflon. As a source of constant direct current for the heat capacity measurements, a Harrison Laboratories (Harrison, N. J.) power supply, Model 855B, was used. The constancy of the current was monitored with the aid of a Varian strip-chart recorder adjusted to detect fluctuations in excess of 0.5 mA. For precise time-interval measurements a Heuer stopwatch was used.

Measurements.—The calorimeter heat capacity and the effective resistance are needed for use in the equation

$$C_p = \frac{i^2Rt}{\Delta T}$$

where i is the current, R is the resistance, t is the heating time, and ΔT the temperature rise. To determine these quantities 400 ml of water, toluene, and bromobenzene were each heated for 5 or 10 min with a constant current of 500 ± 0.5 mA and the accompanying temperature rise was recorded. These calibration measurements were also made at irregular intervals between regular runs to see if the resistance of our wire had undergone any change. Moreover, the dial settings on the power supply unit remained undisturbed in the course of our regular runs from what they were during the calibration run. In a typical run, 395 ml of the $KMnO_4$ solution was poured into the dewar flask and 5 ml of the $K_2B_{10}H_{10}$ solution was pipetted into the glass bulb and washed down with 1–2 ml of water. The calorimeter was then sealed and the stirrer turned on. With the stirrer on, temperature readings were made at 10-min intervals and thermal equilibrium was assumed when the rate of temperature change declined to below 0.001° min^{-1}. To mix the reagents and initiate the reaction, the bulb was pressed against the bottom of the dewar flask and crushed. Thereupon, temperature readings were made at 1-min intervals during the period of rapid change and then continued for about 1 hr at 10-min intervals. As soon as thermal equilibrium was again indicated, a 0.5-A current was sent through the heating coils for precisely 10 min and temperature readings were made at intervals similar to those used during and after the reaction. Throughout this time a constant stirring speed was maintained. Before each run the calorimeter vessel was filled for 1 hr with 2 *M* $NaHSO_3$ to remove all traces of the MnO_2 deposit and then washed thoroughly with distilled water and dried.

In all runs the total volume of the reaction mixture was kept

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(1) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964); B. L. Chamberland and E. L. Muetterties, *ibid.*, **3**, 1450 (1964).

(2) A. Kaczmarczyk, G. B. Kolski, and W. P. Townsend, *J. Am. Chem. Soc.*, **87**, 1413 (1965).

(3) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **81**, 5519 (1959).

at 400 ± 2 ml, to ensure the same degree of immersion for the heating coils and the same empty space above the solution. No attempt was made to set the initial temperature any closer than within 1° of 25°. In the course of the work five different permanganate solutions were used, all made up so that 395 ml would contain at least a 25% excess over the amount required for complete oxidation of the $B_{10}H_{10}^{2-}$ contained in 5 ml of its solution. The data reported in this paper were obtained on six different freshly prepared decaborate solutions ranging in concentration from 0.05134 to 0.1039 *M*. More concentrated solutions were found impractical since the combined temperature rise from the reaction and the subsequent heating would exceed the operating range of a Beckmann thermometer. The heat capacities were determined experimentally after each run.

Enthalpies

Experimental Results for $B_{10}H_{10}^{2-}$.—The calorimetric data for the reaction[2]

$$B_{10}H_{10}^{2-}(aq) + 14MnO_4^-(aq) + 18H_2O(l) = 10B(OH)_4^-(aq) + 14MnO_2(s) + 6OH^-(aq) \quad (1)$$

summarized in Table I lead to an average value of −2258.3 ± 5.1 kcal for the enthalpy change of reaction 1. The standard deviation of the measurements is about three times the minimum error expected from uncertainties in temperature, weight, and volume. From the above figure, the standard enthalpy of formation of $B_{10}H_{10}^{2-}(aq)$ is found to be +22.3 ± 5.1 kcal mol^{-1}. The following standard enthalpies of formation, all in kcal mol^{-1}, were used in our calculations: $H_2O(l)$, −68.32;[4] $B(OH)_4^-(aq)$, −321.3;[5,6] $MnO_2(s)$, −124.4;[4,7,8] $MnO_4^-(aq)$, −129.9;[8] $OH^-(aq)$, −54.96.[4] No significant amount of Mn^{2+} is formed[2] under the experimental conditions used for the calorimetric measurements. Moreover, the conditions of low concentration (0.013 *M*) and high pH (11–12) prevailing after the completion of the reaction make it safe to presume that the borate is almost entirely in the monomeric form.[9] Except for two values that are questionable,[7] the many enthalpies listed in the literature for $MnO_2(s)$ are all within 1 kcal of the value given in the NBS circular.[4] The NBS value is also in good agreement with that found by Shomate,[7] who was the only investigator to work with a heterogeneous solid–water system; all other values were obtained in a bomb calorimeter on dehydrated solids. Although X-ray powder patterns indicated that our material was not pyrolusite, the most common form of MnO_2, enthalpies reported for pyrolusite are not significantly different from those reported for other forms, and it is therefore believed that −124.4 kcal mole^{-1} is a good approximation to the true heat of formation of our material, which very much resembled that used by Shomate. No attempt was made to correct the standard heat of formation of $B_{10}H_{10}^{2-}$ for departures from ideality, since the ionic strength of our dilute solutions was too low to make such corrections significant in comparison with the standard deviation in the experimental value.

Table I

Experimental Enthalpy Changes

$B_{10}H_{10}^{2-}$, mmol	MnO_4^-, mmol	ΔT, °C	C_p, cal deg^{-1}	$-\Delta H_{reactn}$,[a] kcal mol^{-1}
0.5197	9.70	2.705	436.9	2263.7
0.5197	9.70	2.672	438.0	2251.9
0.5197	11.80	2.637	446.5	2265.9
0.5093	11.80	2.552	450.8	2258.8
0.5093	11.80	2.507	457.1	2250.0
0.4991	7.25	2.503	449.8	2255.7
0.4991	7.25	2.475	456.7	2265.0
0.4194	7.25	2.139	443.1	2260.1
0.4194	7.25	2.121	444.8	2249.6
0.4194	8.98	2.062	458.5	2254.3
0.4194	8.98	2.116	449.0	2265.3
0.4194	8.98	2.117	448.1	2262.2
0.4194	8.98	2.093	451.5	2253.5
0.2970	8.61	1.503	444.8	2250.8
0.2970	8.61	1.498	449.8	2268.8
0.2970	8.61	1.495	448.1	2255.7
0.2970	8.61	1.501	447.3	2260.5
0.2567	11.80	1.253	462.5	2257.7

[a] Average ΔH_{298} = 2258.3 ± 5.1 kcal mole^{-1}.

Estimates for $B_{12}H_{12}^{2-}$.—Though the slow oxidation rate prevented us from determining the heat of formation of $B_{12}H_{12}^{2-}$ experimentally, a reasonable estimate of its value was made from the expected difference between the total bonding energies of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. There are at least two simple ways of approaching this problem. Both make use of the atomization scheme

$$\begin{tikzcd}
 & B_{10}H_{10}^{2-}(aq) \arrow[dl, "\Delta H_1"'] & {}+ H_2(g) \arrow[dd, "\Delta H_2"] & {}+ 2B(s) \arrow[dd, "\Delta H_3"] \arrow[r, "\Delta H_0"] & B_{12}H_{12}^{2-}(aq) \\
B_{10}H_{10}^{2-}(g) \arrow[d, "\Delta H_4"] & & & & \\
(2e^- + 10B + 10H) & & {}+ 2H & {}+ 2B(g) \arrow[r, "\Delta H_5"] & B_{12}H_{12}^{2-}(g) \arrow[uu, "\Delta H_6"']
\end{tikzcd}$$

In this scheme only two enthalpies are known accurately from experimental data: the heat of sublimation of boron ΔH_3 = 135.22 kcal mol^{-1} at 298°K[6] and the dissociation energy of hydrogen ΔH_2 = 104.2 kcal mol^{-1} at 298°K.[4] In view of the similarities in shape and size of the two polyhedra, it is reasonable to assume about the same hydration energy (±2 kcal) for the two ions so that $\Delta H_1 + \Delta H_6 \approx 0$. This leaves us with ΔH_4 and ΔH_5, the atomization energies of the two ions. The absolute values of these quantities are more difficult to estimate[10] than the difference between the two. One way of estimating the difference is to follow the approach of Prosen[11] and divide the total energy into contributions from the four types of "bonds," canceling out bonds common to both polyhedra. This approach is very satisfactory for many boron hydrides.[12,13] The bonding electrons in $B_{12}H_{12}^{2-}$ can be distributed among 12 B–H bonds, 3 B–B bonds, and 10

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[4] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950.

[5] W. D. Good and M. Manson, *J. Phys. Chem.*, **70**, 97 (1966); E. J. Prosen, W. M. Johnson, and F. Y. Pergiel, *J. Res. Natl. Bur. Std.*, **62**, 43 (1959).

[6] W. H. Evans, E. J. Prosen, and D. D. Wagman, "Thermodynamic and Transport Properties of Gases, Liquids, and Solids," American Society of Mechanical Engineers, McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 226.

[7] H. Shomate, *J. Am. Chem. Soc.*, **65**, 785 (1943).

[8] L. Hepler and T. A. Zoldan, *Chem. Rev.*, in press; see also Z Z. Hugus and W. M. Latimer, *J. Electrochem. Soc.*, **98**, 296 (1951).

[9] N. Ingri, *Svensk Kem. Tidskr.*, **75**, (4), 199 (1963).

[10] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

[11] E. J. Prosen, 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, March–April 1955; S. H. Bauer, *J. Am. Chem. Soc.*, **80**, 294 (1958).

[12] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).

[13] S. R. Gunn and J. H. Kindsvater, *ibid.*, **70**, 1114 (1966).

B–B–B bonds, with all three-center orbitals alike[10,14] and not too different in their overlap population from those in $B_{10}H_{14}$.[10] In the antiprismatic $B_{10}H_{10}^{2-}$ the electrons are distributed among 10 B–H bonds, 3 B–B, bonds, and 8 B–B–B bonds, but the latter eight cannot be treated as all alike. The simplest bonding scheme uses pentaborane-9 as a model for the bonding between the apical boron and its four neighbors.[14] Though the calculated overlap populations yield slightly different bonding orders for the pentaborane three-center orbital and the apical one in $B_{10}H_{10}^{2-}$, the difference is only half as great as that between the latter and three-center orbitals in $B_{12}H_{12}^{2-}$ or decaborane.[10] The bond orders of the remaining six three-center orbitals in $B_{10}H_{10}^{2-}$ are not significantly different from those in $B_{12}H_{12}^{2-}$. Thus the net effect of the conversion of the $B_{10}H_{10}^{2-}$ to $B_{12}H_{12}^{2-}$ is the creation of two new B–H bonds, 91.16 kcal each,[12] two new decaborane-type three-center boron bonds, 97.78 kcal each,[12] and the conversion of two pentaborane-type, 93.75 kcal,[12] into two decaborane-type three-center bonds. The resulting energy change, $\Delta H_4 + \Delta H_5 \simeq -385.9$ kcal, combined with ΔH_2 and ΔH_3, yields an enthalpy change $\Delta H_0 \simeq -11.3$ kcal.

It is possible to get an independent estimate for the atomization energy difference from the theoretically calculated total electronic or binding energies of the polyhedral species. Hoffmann and Lipscomb[10] have shown that for a number of boranes their total electronic energy ratios and binding energy ratios are in excellent agreement with the corresponding experimental atomization energy ratios (*cf.* Table VI of ref 10). Decaborane is here adopted as a reference compound, since its molar atomization energy is accurately known[12] to be 2078.7 kcal and since the molecule resembles the two polyhedral ions in size and in number of electrons. The theoretical electronic energies[10] of decaborane, the decaborate ion, and the dodecaborate ion are −681.5, −636.1, and −759.5 eV, respectively. It is therefore estimated

$$\Delta H_4 + \Delta H_5 \simeq 2078.7(636.1 - 759.5)/681.5 \simeq -376.4 \text{ kcal mol}^{-1}$$

An alternative ratio method can be based on the calculated bonding energies[10] for the "neutral cores" of the polyhedral ions and leads to a value of −402.2 kcal mol^{-1} for $\Delta H_4 + \Delta H_5$. In view of the fact that this last method implies exact equality of the corresponding electron affinities of the two ions and presumes that the sum of the two electron affinities is small in comparison with the total binding energy, the agreement with the other methods is quite satisfactory. If the three estimates described above are given equal weight, we obtain an average value of $\Delta H_0 = -14 \pm 9$ kcal mol^{-1}, which leads to a standard enthalpy of formation $\Delta H_f° = +8 \pm 10$ kcal mol^{-1} for the dodecaborate ion. However, the first semiempirical estimate should have a weight at least equal to the average of the other two estimates, based on theoretically calculated data, and in view of what has been said above the second and the third estimates should not be weighed evenly either. It has therefore been assumed to be more reasonable to weigh the three estimates in the ratio of 3:2:1 which leads to a value of $\Delta H_f° = +11 \pm 10$ kcal mol^{-1} for $B_{12}H_{12}^{2-}$(aq). This is the figure which shall be used in subsequent calculations.

Entropies and Free Energies

The standard entropies of gaseous $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ were calculated from the usual statistical thermodynamic recipes. The only appreciable uncertainty is in the vibrational contribution. The ir and Raman data[15] do not provide a complete assignment of normal frequencies for $B_{12}H_{12}^{2-}$, and there seems to be even less definite information about $B_{10}H_{10}^{2-}$. However, the entropy of $B_{10}H_{14}$(g) at 378°K has been accurately determined by Furukawa and Park.[16] The vibrational entropy of the latter substance should offer a trustworthy upper limit to that of $B_{10}H_{10}^{2-}$, for the ion has fewer hydrogen atoms to begin with and also can be expected to have a somewhat higher average skeletal vibration frequency because the cage is closed. The general considerations of Keller and Johnston[17] on the distribution of frequencies in $B_{10}H_{14}$ are undoubtedly sound, for they yield a vibrational entropy of 24.5 cal deg^{-1} mol^{-1} at 378°K as compared to the figure of 24.1 cal deg^{-1} mol^{-1} required to fit the experimental entropy.[16] At 298°K, the vibrational entropy of $B_{10}H_{14}$ with the Keller–Johnston assignment is 13.7 cal deg^{-1} mol^{-1}, and with this figure as a guide vibrational entropies are estimated at 12.5 ± 1.5 and 15.5 ± 1.5 cal deg^{-1} mol^{-1} for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, respectively, at this temperature. The moments of inertia of the gaseous ions were calculated from the dimensions given by Lipscomb and co-workers.[18] The symmetry numbers are 8 for $B_{10}H_{10}^{2-}$ (symmetry D_{4d}) and 60 for $B_{12}H_{12}^{2-}$ (symmetry I_h). The resulting rotational entropies are included in Table II.

TABLE II

ESTIMATES OF STANDARD ENTROPIES OF POLYHEDRAL BORANE ANIONS AT 298°K (CAL DEG^{-1} MOL^{-1})

	$B_{10}H_{10}^{2-}$	$B_{12}H_{12}^{2-}$
Gaseous ion		
Translation	40.21	40.75
Rotation	26.73	23.57
Vibration	12.5 ± 1.5	15.5 ± 1.5
Total $S°$(g)	79.5 ± 1.5	79.8 ± 1.5
Hydration[a]	−20 ± 3	−18 ± 3
Aqueous ion, $S°$(aq)	60 ± 4	62 ± 4

[a] From eq 2.

Entropies of hydration for polyatomic ions are often[19] somewhat more negative than would be predicted from the familiar formulas of Powell and Latimer[20] or of

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[14] E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179 (1962).

[15] E. L. Muetterties, R. E. Merrifield, H. C. Miller, W. H. Knoth, Jr., and J. R. Downing, *J. Am. Chem. Soc.*, **84**, 2506 (1962).

[16] G. T. Furukawa and R. P. Park, *J. Res. Natl. Bur. Std.*, **55**, 255 (1955).

[17] W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).

[18] J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960); R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962).

[19] K. B. Yatsimirskii, *Zh. Fiz. Khim.*, **31**, 2121 (1957); *cf. Chem. Abstr.*, **52**, 13,398 (1958).

Laidler[21] for monatomic ions. This is doubtless because such formulas tend to overestimate the orientational freedom of the polyatomic species in aqueous solution. We may, however, examine the data for several other more or less globular polyatomic anions in order to estimate effective radii r_e in the Powell–Latimer formula

$$\Delta S°(\text{hyd}) = S°(\text{aq}) - S°(\text{g}) = +11 - 270\,|Z|\,r_e^{-2} \quad (2)$$

where the standard entropies (all at 298°K) are in cal $\text{deg}^{-1}\ \text{mol}^{-1}$, Z is the ionic charge, and r_e is in Å. In Table III, the entropies and resulting effective radii for several tetrahedral and octahedral anions are displayed together with the distances b from central to peripheral atoms. The excess of r_e over b is greatest for BH_4^- but is quite similar for all the divalent ions shown. From these examples it is concluded that a value of 1.5 ± 0.2 Å for ($r_e - b$) will safely serve for the polyhedral boranes. As the average distance from cage center to hydrogens is 2.7 Å in $B_{10}H_{10}^{2-}$ and 2.8 Å in $B_{12}H_{12}^{2-}$, these figures may now be used in eq 2 to obtain the hydration entropies shown in Table II, leading to final standard entropies at 298°K of 60 ± 4 for $B_{10}H_{10}^{2-}$(aq) and 62 ± 4 cal $\text{deg}^{-1}\ \text{mol}^{-1}$ for $B_{12}H_{12}^{2-}$(aq).

TABLE III

ENTROPIES OF HYDRATION AND EFFECTIVE POWELL–LATIMER RADII FOR SEVERAL GLOBULAR ANIONS[a]

	BH_4^-	BF_4^-	ClO_4^-	SO_4^{2-}	CrO_4^{2-}	SiF_6^{2-}
$S°$(aq)	26.3[b]	40	43.2	4.1	9.2	30.3[c]
$S°$(g)	45.2[d]	63.4[e]	63.1[f]	62.9[f]	64.7[f]	74.5[g]
$-\Delta S°$(hyd)	18.9	24	19.9	58.8	55.5	44.2
Effective radius, r_e Å	3.00	2.78	2.95	2.78	2.87	3.14
Bond length, Å	1.26	1.43	1.48	1.49	1.60	1.72[h]
Difference	1.74	1.35	1.47	1.29	1.27	1.42

[a] Entropy values in cal $\text{deg}^{-1}\ \text{mol}^{-1}$, except where noted, are from ref 4 in the text. [b] S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.*, **77**, 6197 (1955). [c] C. C. Stephenson, C. A. Wulff, and O. R. Lundell, *J. Chem. Phys.*, **40**, 967 (1964). [d] A. P. Altshuller, *J. Am. Chem. Soc.*, **77**, 6187 (1955). [e] A. P. Altshuller, *ibid.*, **77**, 5455 (1955). [f] A. P. Altshuller, *J. Chem. Phys.*, **24**, 642 (1956). [g] Calculated with frequencies given in ref *c* above and bond length given in ref *h*. [h] "Table of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, Burlington House, London, 1958.

The standard free energies of formation may now be calculated. For the reaction

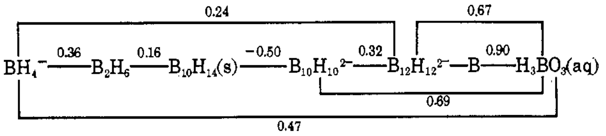
$$10B(s) + 6H_2(g) = 2H^+(aq) + B_{10}H_{10}^{2-}(aq) \quad (3)$$

it is found that $\Delta S°_{298} = -143 \pm 4$ cal $\text{deg}^{-1}\ \text{mol}^{-1}$, which, when combined with the enthalpy of formation, +22.3 kcal $\text{deg}^{-1}\ \text{mol}^{-1}$, leads to $\Delta G_f°_{298} = +65 \pm 5$ kcal mol^{-1} for $B_{10}H_{10}^{2-}$(aq). Similarly, it is found that $\Delta G_f°_{298} = +63 \pm 10$ kcal mole^{-1} for $B_{12}H_{12}^{2-}$(aq).

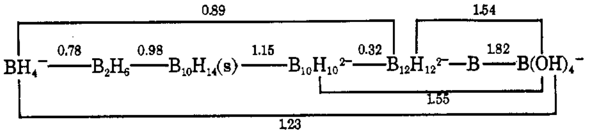
Discussion

With the aid of thermodynamic data in the literature[4,6,22] half-cell emf diagrams relating the polyhedral ions to a number of representative boranes and to boric acid can be constructed

acid solutions ($E_A°$)



basic solutions ($E_B°$)



The diagrams reveal that even the "more stable" boranes are thermodynamically unstable, in the presence of water, with respect to boric acid and elemental hydrogen. Thus kinetic factors are responsible for the great apparent differenes in reactivity with water. This is equally true in acid or basic medium, although of course the hydrolysis reaction is invariably acid catalyzed. For convenience, the standard free energy changes at 298°K for the acid hydrolysis

$$B_nH_m^{a-} + 3nH_2O + aH^+ = nH_3BO_3 + \left(\frac{3n + m + a}{2}\right)H_2(g) \quad (4)$$

are given here (all in kcal): $\Delta G°_{298} = -86.5$ for BH_4^-(aq); −140 for B_2H_6(g); −643 for $B_{10}H_{14}$(s); −666 for $B_{10}H_{10}^{2-}$(aq); and −785 for $B_{12}H_{12}^{2-}$(aq).

The polyhedral boranes can be synthesized with remarkable ease[23,24] from simpler hydrides such as BH_4^-, B_2H_6, $B_3H_8^-$, and others in various nonaqueous media. For the reaction

$$aBH_4^-(aq) + \left(\frac{n - a}{2}\right)B_2H_6(g) = B_nH_m^{a-}(aq) + \left(\frac{3n - m + a}{2}\right)H_2(g) \quad (5)$$

our data yield $\Delta G°_{298} = -67$ and −89 kcal for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, respectively. These figures are large enough to ensure favorable equilibrium for the synthesis in nonaqueous solvents also. The icosahedral ion is favored thermodynamically, for we have

$$B_{10}H_{10}^{2-}(aq) + B_2H_6(g) = B_{12}H_{12}^{2-}(aq) + 2H_2(g) \quad (6)$$

$$\Delta G°_{298} = -22 \pm 10 \text{ kcal};\ K \approx 10^{16\pm7}$$

This figure is in accord with the observations that, with one exception,[23] reactions of the type of eq 5 above produce $B_{12}H_{12}^{2-}$ in preference to $B_{10}H_{10}^{2-}$ and that under similar reaction conditions the decaborate ion itself can be converted to the dodecaborate ion.[24]

The conversion of decaborane to the polyhedral ions has also been reported.[24,25] For the reaction

$$B_{10}H_{14}(s) + 2BH_4^-(aq) = B_{12}H_{12}^{2-}(aq) + 5H_2(g) \quad (7)$$

it is found that $\Delta G°_{298} = -32$ kcal.

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(20) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

(21) K. J. Laidler, *Can. J. Chem.*, **34**, 1107 (1956).

(22) R. M. Adams, Ed., "Boron, Metallo-Boron Compounds, and Boranes," Interscience Publishers, Inc., New York, N. Y., 1964, pp 378, 379; for solid decaborane at 298°K $\Delta G_f° = 41.4$ kcal mol^{-1} was calculated from the entropy given in ref 16 and the enthalpy listed in ref 13.

(23) I. A. Ellis, D. F. Gaines, and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3885 (1963).

(24) H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1456 (1964).

(25) R. M. Adams, A. R. Siedle, and J. Grant, *ibid.*, **3**, 461 (1964); N. N. Greenwood and J. H. Morris, *Proc. Chem. Soc.*, 338 (1963).

The direct closure of decaborane is promoted by bases, such as amines[3] and sulfides[1] in nonaqueous media

$$B_{10}H_{14} + 2L = (LH)_2B_{10}H_{10}(s) + H_2(g) \qquad (8)$$

The standard free energy change for such cage closure depends on the nature of the base and the solvent used. From the free energy data for decaborane and the decahydrodecaborate ion we can derive a general expression for the free energy change accompanying cage closure

$$\Delta G^\circ_{298} = 24 - 1.36(2\text{p}K_\text{a} + \text{p}K_\text{sp}) \qquad (9)$$

where $\text{p}K_\text{a}$ takes into account the base strength of the closing agent and $\text{p}K_\text{sp}$ is the solubility product of the resulting salt in a given solvent. It would appear that, were it not for interference from side reactions such as hydrolysis, any moderate to strong base could be used to close the decaborane cage in water and in a wide range of polar organic solvents. For example, even though $[(C_2H_5)_3NH]_2B_{10}H_{10}$ is quite soluble in water ($\text{p}K_\text{sp} \approx 0$), triethylamine ($\text{p}K_\text{a} = 10.8$) should be capable of closing the cage in water. Use of weakly polar or nonpolar solvents, such as toluene and benzene, in which salts of the polyhedral ion are only sparingly soluble, provides extra advantage by making the $\text{p}K_\text{sp}$ very large.

Even though none of the reactions described by eq 5–8 can be carried out in water, the calculated free energy decrease is in each case large enough to assure that the processes would be favorable in any medium; in other words, free energy changes involving solubilities or changes of solvent will not be large enough to vitiate qualitative conclusions based on our calculations. It may also be remarked that our qualitative conclusions could be changed only by very large alterations in the accepted thermodynamic properties of the substances taking part in reaction 1. For example, the most recent and reliable figure for the enthalpy of formation of the permanganate ion[8] differs from the NBS value[4] by 6 kcal mol^{-1}, which corresponds to a difference of no less than 84 kcal mol^{-1} in the enthalpy of formation of $B_{10}H_{10}^{2-}$(aq), but the resulting shift of about 0.09 V in the related oxidation potentials would not alter the order of stability of the boron hydrides involved.

Finally, it is interesting to estimate the hydration enthalpy of the decahydrodecaborate ion. With the aid of the semiempirical bond-energy additive scheme used earlier,[11–13] the enthalpy change for the reaction

$$10B(s) + 10H(g) + 2e^-(g) = B_{10}H_{10}^{2-}(g) \qquad (10)$$

is found to be −1924 kcal, while the theoretical[10] electronic energy referred to decaborane gives (−2078.7)(636.1/681.5) = −1940 kcal. Using our experimental value for the enthalpy of formation of $B_{10}H_{10}^{2-}$(aq), we then obtain

$$2H^+(g) + B_{10}H_{10}^{2-}(g) = 2H^+(aq) + B_{10}H_{10}^{2-}(aq); \quad \Delta H \cong -660 \pm 10 \text{ kcal} \qquad (11)$$

so that the single-ion enthalpy of hydration on the usual basis[26] is about −140 kcal mol^{-1} for the decahydrodecaborate ion. In the Born equation, which should be useful for such a large ion, this corresponds to an effective ion radius of about 4.5 Å, in pleasant accord with the figure we used earlier in estimating the ionic entropy.

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(26) See, for example, C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. 1, Oxford University Press, London, 1965, pp 160–162.

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The Synthesis and Reactions of 1,2-(2'-Substituted 1',3',2'-Dithiabora)-*o*-carboranes[1]

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1,2-Bis(mercapto)-*o*-carborane reacts with a variety of boranes including diborane and alkyl-, aryl-, chloro-, and aminoboranes to produce 1,2-(2'-substituted 1',3',2'-dithiabora)-*o*-carboranes. Reaction with trichloroborane in a 1:1 mole ratio gives a good yield of 1,2-(2'-chloro-1',3',2'-dithiabora)-*o*-carborane, some reactions of which are reported. Reaction of 1,2-bis(mercapto)-*o*-carborane with trichloroborane in a 2:1 mole ratio gives what appears to be a novel ring system in which boron is tetracoordinated by sulfur.

Introduction

The derivative chemistry of dicarbaclovododecaborane(12) has recently been extended to include mercapto derivatives of both the *ortho* and *meta* isomers.[2] The divalent sulfur atoms are bonded to the carbon atoms of the carborane nucleus. The lability of the

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(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; (b) taken in part from the M.S. Thesis of H. D. Smith, Jr., St. Louis University, 1966.

(2) H. D. Smith, Jr., C. O. Obenland, and S. Papetti, *Inorg. Chem.*, **5**, 1013 (1966).