

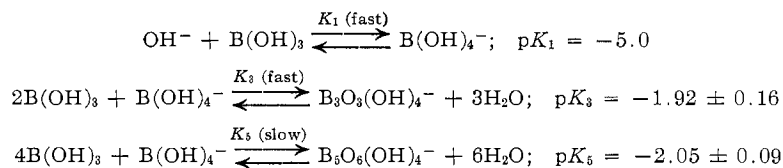
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR THE STUDY OF METALS,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS

Nuclear Magnetic Resonance Study of Borate-Polyborate Equilibria in Aqueous Solution

BY ROBERT K. MOMII AND NORMAN H. NACHTRIEB

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The nuclear magnetic resonance of B^{11} in aqueous solutions of boric acid and alkali meta- and polyborate salts provides information on their polymerization equilibria. Solutions of mononuclear species (H_3BO_3 and MBO_2) yield one-line spectra that show no chemical shift with concentration. Two B^{11} lines are observed in aqueous NaB_5O_8 , whose relative amplitudes (but not resonance frequencies) are concentration dependent. They lead to the equilibria



Solutions of $Na_2B_4O_7$ and $K_2B_4O_7$ give one-line spectra that broaden and shift upfield with concentration; at low concentration their dissociation into $B(OH)_3$ and $B(OH)_4^-$ is complete, and at high concentration several polyborate ion species exist.

Introduction

Numerous approaches have been made to identify the complex equilibria that exist among borate and polyborate ions in aqueous solution,¹ including cryoscopic measurements, conductance studies, pH titrations, infrared and Raman investigations, and more recently temperature-jump² and nuclear magnetic resonance studies. The results are not completely concordant, although it is well recognized that polymeric anions exist both in crystalline salts and in concentrated solutions in which the B_2O_3/M_2O ratio is high. Shapiro, *et al.*,³ observed two B^{11} nmr signals in aqueous sodium pentaborate and suggested that they arise from a polynuclear borate species (possibly tetraborate or pentaborate) and an equilibrium mixture of boric acid and monoborate ion. It is the principal aim of the present study to investigate the B^{11} resonance of this system and of aqueous tetraborates in greater detail, and to compare the equilibrium evidence it provides with that which has been obtained by Ingri⁴ from electrometric titration studies of boric acid.

Hibben⁵ concluded that aqueous solutions of alkali tetraborates are identical in ionic composition with equimolar mixtures of boric acid and the corresponding alkali metaborate, but it is not clear whether the depolymerization of $B_4O_7^{2-}$ is complete. It appears that borate-polyborate equilibria are quite facile² in aqueous solution, and equilibrium among the species is attained in a time which is short compared with mixing times. It follows that there is nothing unique about the distribution of ionic species in solutions prepared from pure crystalline salts, such as $NaBO_2 \cdot 4H_2O$, $Na_2B_4O_7 \cdot$

$10H_2O$, or $NaB_5O_8 \cdot 5H_2O$: the monomer-polymer anion distribution depends upon the B_2O_3/M_2O ratio, and it should be possible to prepare solutions having the same distribution of species from boric acid and sodium hydroxide. Moreover, there is no *a priori* basis for supposing the existence of a particular polyanion in solution merely because of its presence in a crystalline salt, although structure studies of solid borates undeniably provide valuable clues to the probable structures of ions in solution. They constitute, in fact, the only presumptive evidence at present of the possible structures of polyborates in solution. Techniques, such as Raman spectroscopy, that might offer structural evidence have been disappointing. Thus, Laubengayer and Rosenstein⁶ found no support from Raman studies for the association of borate ions in solution.

Nuclear magnetic resonance may often provide additional information on such equilibria, since the theory of time-dependent effects⁷ shows that the properties of a resonance line may be sensitive to the random motions of resonant nuclei among different chemical sites. If the mean time of stay of an atom on each of several different sites is long compared with the inverse of the difference of the Larmor frequencies of its nucleus on these sites, the spectrum will consist of more than one line. On the other hand, if the characteristic exchange time is short compared with the inverse of the difference in the resonant nuclear precession frequencies, a single line with a weighted mean frequency will be observed. For intermediate exchange rates, and in particular when other factors cause a broadening of the individual species' resonance, the composite line shape is more complex. In favorable cases one hopes, by varying the stoichiometric concentration, to alter the dis-

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(3) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *ibid.*, **69**, 1533 (1959).

(4) N. Ingri, *Acta Chem. Scand.*, **16**, 439 (1962).

(5) J. H. Hibben, *Am. J. Sci.*, **35**, A113 (1938).

(6) A. W. Laubengayer and R. D. Rosenstein, Symposium on Complex Ions and Polyelectrolytes, Cornell University, 1951.

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

tribution of chemically distinct sites and to deduce their equilibrium populations from the nmr spectrum. In this study the B^{11} resonance has been measured only in solutions in which the solute has the average composition of a single pure compound, whose concentration is varied.

Experimental Section

B^{11} resonances were observed with a Varian V-4200B wide-line spectrometer operating at about 14 Mcps. Separate single-coil probes with a conventional radiofrequency bridge⁸ were used for the sample and reference solutions. Chemical shifts were measured directly against a concentrated $NaBO_2$ solution at approximately 25° and ultimately referred to a saturated aqueous solution of boric acid, whose B^{11} resonance was found to be independent of concentration. Stock solutions, prepared from analytical reagent grade salts or recrystallized technical grade compounds, were analyzed by volumetric methods and used to prepare other solutions by dilution.

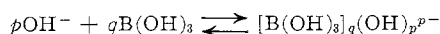
Results and Discussion

In the following discussion we shall refer to the crystalline borates as meta-, tetra-, and pentaborates and to the oxyboron anions in solution as mono-, tri-, and pentaborates, or as monomers, trimers, pentamers, etc. The distinction between meta- and mono- is especially important, since in the crystalline state of alkali 1:1 borates (MBO_2) the boron and oxygen atoms occur in planar six-membered rings ($B_3O_6^{3-}$). These cyclic metaborate anions dissociate completely into monoborate anions ($B(OH)_4^-$) in solution.

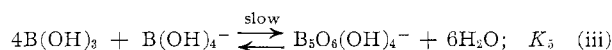
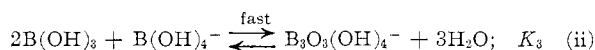
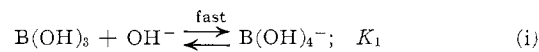
Alkali Metaborates (MBO_2).—In the concentration range 0.090–0.900 M the B^{11} chemical shifts of $NaBO_2$ and KBO_2 relative to a saturated solution of boric acid were found to be independent of concentration and to have the following values: δ_{NaBO_2} $17.4 \pm 0.5 \times 10^{-6}$ and δ_{KBO_2} $15.5 \pm 0.5 \times 10^{-6}$. No line-width change with concentration was observed. These results are consistent with Raman spectra⁹ and cryoscopic¹⁰ evidence that the alkali metaborates are binary electrolytes at all concentrations in aqueous solution, with only one anion configuration (presumably tetrahedral $B(OH)_4^-$).

Alkali Pentaborates (MB_5O_8).—Aqueous sodium pentaborate solutions display two B^{11} signals, as Shapiro, *et al.*,³ have observed. Their relative amplitudes vary with concentration, but to within experimental error the separation of the lines and their widths are independent of concentration (δ 1.1×10^{-6} and 15.0×10^{-6}). It is evident that boron exists in at least two chemically different sites with an exchange rate that is slow compared with the inverse of the difference in their respective nuclear precession frequencies.

Ingri¹¹ assumed that aqueous borate complexes are all of the form $[B(OH)_3]_q(OH)_p^{p-}$, formed by such reactions as



There may be any number of such equilibria as p and q are permitted to assume integral values from 1 to n . We find that our nmr data are best fitted to three such equilibria, for which $p = 1$ and $q = 1, 3,$ and 5 . Ingri obtained equilibrium constants from electrometric titrations of boric acid corresponding to these three equilibria, and it will be the purpose of our analysis to determine how consistent the nmr data are within his values. It will be equally correct and more in accord with our notions of the cyclic structures of the trimer and pentamer in the later discussion if, for $q = 3$ and $q = 5$, we represent their compositions as $B_3O_3(OH)_4^-$ and $B_5O_5(OH)_4^-$ instead of $[B(OH)_3]_3(OH)^-$ and $[B(OH)_3]_5(OH)^-$, respectively



Since there are two lines in the B^{11} spectrum, at least one of these equilibria must be slow. Supported by the temperature-jump studies of Eyring, *et al.*,² we conclude that equilibrium is established more slowly in (iii) than in (ii) or (i). These reactions are written as over-all reactions, of course, and we cannot establish which of the consecutive steps in (iii) is limiting. Presumably, it is one of the steps in the trimer–pentamer equilibrium. We shall assume that $B_5O_5(OH)_4^-$ is the longest-lived species, and that it is responsible for the high-field line at δ 15.0×10^{-6} . The low-field resonance line at δ 1.1×10^{-6} we attribute to a rapid exchange of B^{11} among $B(OH)_3$, $B(OH)_4^-$, and $B_3O_3(OH)_4^-$. Eyring established that (i) has a characteristic relaxation time shorter than the resolving time of their instrument (10 μ sec) and that the rate constant for (ii) is about an order of magnitude greater than for (iii).

The ratio of the amplitudes¹² of the high-field and low-field peaks gives the relative number of B^{11} atoms in $B_5O_5(OH)_4^-$, as compared with the total in $B(OH)_3$, $B(OH)_4^-$, and $B_3O_3(OH)_4^-$. This ratio may be expressed as $R = (1 - \alpha)/\alpha$, where α is the degree of dissociation of $B_5O_5(OH)_4^-$. Table I shows the variation of R and α with the stoichiometric concentration of NaB_5O_8 , from which we find that $R = ac_0$; $a = 0.90 \pm 0.03$ and c_0 is the stoichiometric concentration of sodium pentaborate.

For convenience, we designate the equilibrium concentrations of boron-containing species by the following symbols: $c_1 = [B(OH)_3]$; $c_2 = [B(OH)_4^-]$; $c_3 = [B_3O_3(OH)_4^-]$; $c_5 = [B_5O_5(OH)_4^-]$. From the condition of charge balance (neglecting $[OH^-]$, which is always 10^{-6} M or less), we may write

$$c_0 = c_2 + c_3 + c_5 \quad (1)$$

Moreover, from the condition of mass balance for boron, we have

$$5c_0 = c_1 + c_2 + 3c_3 + 5c_5 \quad (2)$$

(12) Analysis of the line shapes shows that the ratios of the amplitudes of the derivative signals agree within experimental error with the ratios of the areas of the absorption lines.

(8) H. L. Anderson, *Phys. Rev.*, **76**, 1460 (1949).

(9) J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, *J. Am. Chem. Soc.*, **77**, 226 (1955).

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(11) N. Ingri, *Svensk Kem. Tidnsv.*, **75**, 199 (1963).

TABLE I
DEGREE OF DISSOCIATION OF PENTABORATE
IN AQUEOUS $\text{NaB}_5\text{O}_{13}$

c_0, M	R	α
0.115	0.11	0.90
0.153	0.13	0.88
0.191	0.16	0.86
0.229	0.22	0.82
0.268	0.24	0.80
0.306	0.28	0.77
0.344	0.31	0.76
0.382	0.34	0.75

From (i) the metaborate ion concentration is

$$c_2 = K_1[\text{OH}^-]c_1 \quad (3)$$

K_1 is evaluated in the later section on alkali tetraborates. Finally, the equilibrium pentaborate ion concentration is

$$c_5 = (1 - \alpha)c_0 = R\alpha c_0 = Rc_0/(1 + R) = ac_0^2/(1 + ac_0) \quad (4)$$

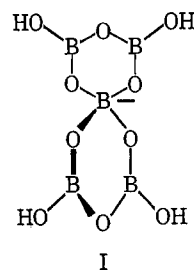
The simultaneous solution of eq 1-4 leads to explicit expressions for the concentration of each boron-containing species and in turn to mass law equations for K_3 and K_5

$$K_3 = \frac{c_3}{c_2c_1^2} = \frac{(1 - 4K_1[\text{OH}^-])(1 - 2K_1[\text{OH}^-])^2(1 + ac_0)^2}{8K_1[\text{OH}^-]c_0^2} \quad (5)$$

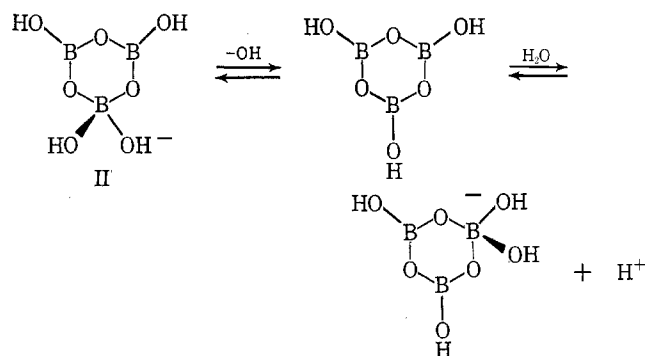
$$K_5 = \frac{c_5}{c_2c_1^4} = \frac{a(1 + ac_0)^4(1 - 2K_1[\text{OH}^-])^5}{32K_1c_0^3[\text{OH}^-]} \quad (6)$$

The evaluation of eq 5 and 6 for seven pentaborate concentrations, with $K_1 = 1.0 \times 10^5$, and with pH values tabulated by Kemp,¹ leads to $\text{p}K_3 = -1.92 \pm 0.16$ and $\text{p}K_5 = -2.05 \pm 0.09$. These are in quite good agreement with Ingri's values in 0.1 M NaClO_4 : $\text{p}K_3 = -1.71 \pm 0.02$; $\text{p}K_5 = -2.23 \pm 0.10$. Figure 1 shows distribution of the four boron-containing species in the aqueous sodium pentaborate as a function of concentration, based upon the nmr data and Kemp's pH values. We cannot exclude the possibility that finite concentrations of other polyborate anions are also present in aqueous alkali pentaborate solutions, even though the nmr data are quite consistent with the assumption that $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, and $\text{B}_5\text{O}_6(\text{OH})_4^-$ are the dominant species in the pH range 6.8-8.0. Ingri drew the same conclusion,⁴ finding no positive evidence for diborate or tetraborate species from emf glass electrode studies.

We may speculate at this point on the reason why only one nmr line is observed for $\text{B}_5\text{O}_6(\text{OH})_4^-$, when its supposed bicyclic structure (I) possesses four boron atoms with trigonal symmetry and one boron atom with tetrahedral symmetry. It may be that an intramolecular rearrangement of the pentamer, occurring on a time scale which is short with respect to its dissociation into the trimer, makes all five boron atoms nmr equivalent. Such rearrangements have been proposed by



Piper and Wilkinson¹³ to account for the nmr equivalence of protons in $(\text{C}_6\text{H}_5)_2\text{Hg}$ and by Cotton, *et al.*,¹⁴ for protons in π -cyclopentadienyliron dicarbonyl σ -cyclopentadiene. We have no certain evidence to support this conjecture, nor indeed to rule out positively the possibility that two B^{11} lines exist for the pentamer, with one hidden under the low-field line. While this possibility exists, we think it unlikely because there is no observable change in the shape of either the upfield or downfield line with concentration as their relative amplitudes vary. If the pentamer has but a single B^{11} resonance, as our evidence indicates, the uncertainty principle sets an upper limit of 7×10^{-4} sec for the lifetime of the discrete states in the supposed valence tautomerism of boron. This is within the lifetime of the pentamer by an order of magnitude, based upon the temperature-jump measurements by Eyring, *et al.*² It is difficult to visualize a mechanism for such a configuration averaging, nevertheless, without postulating the concerted rupture and re-formation of several boron-oxygen linkages in the bicyclic pentamer. No similar difficulty presents itself in understanding the nmr equivalence of B^{11} in the equilibrium among $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, and $\text{B}_3\text{O}_3(\text{OH})_4^-$. The rapid interchange of boron from trigonal to tetrahedral coordination could be readily brought about by the solvent. This is indicated for the cyclic trimer (II) by the exchange



Alkali Tetraborates ($\text{M}_2\text{B}_4\text{O}_7$).—In both sodium and potassium tetraborates the B^{11} spectrum consists of a single line, which broadens and shifts upfield with increasing concentration as shown in Figure 2. The apparent line width increases about 73% from 0.030 to 0.50 M in the case of the more soluble salt, $\text{K}_2\text{B}_4\text{O}_7$, but there is no indication of resolution into components. For both salts the extrapolation of the chemical shift

(13) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(14) M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

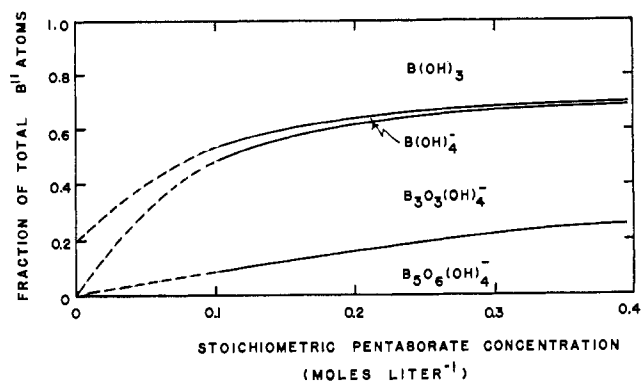
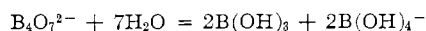


Figure 1.—Distribution of B^{11} atoms among borate species in aqueous sodium pentaborate solutions.

to infinite dilution is to the mean of the chemical shifts of boric acid and monoborate ion. We conclude from this that dissociation into these species is complete at low stoichiometric tetraborate concentrations



This is not a simple equilibrium, however. Fairly rapid exchange of boron atoms must be occurring between at least two distinct sites. That these sites might be only monomeric boric acid and monoborate ion is excluded because the chemical shift is concentration-dependent while the pOH of tetraborate solutions is essentially independent of concentration.¹ That is to say, the $[B(OH)_4^-]/[B(OH)_3]$ ratio is fixed over the whole concentration range by the equilibrium expression $[B(OH)_4^-]/[B(OH)_3] = K_1[OH^-] = \text{constant}$. It has the value of unity at all concentrations, evaluated from the chemical shift at $c = 0$ ($\delta_{Na_2B_4O_7}$, 8.7×10^{-6}) we obtain $K_1 = 1.0 \times 10^5$, in good agreement with Ingri's value,⁴ $K_1 = 1.86 \times 10^5$.

More than one polyborate species must be present at

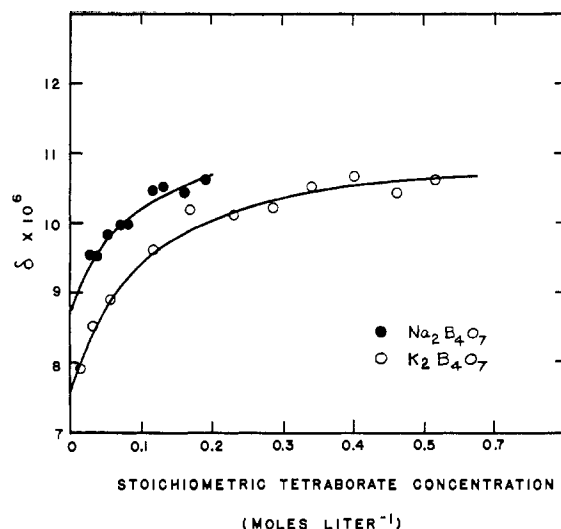


Figure 2.— B^{11} chemical shifts in alkali tetraborate solutions.

all finite tetraborate concentrations, however, because the data of Figure 2 cannot be fitted to equilibria involving boric acid, monoborate ion, and only one polyborate species, such as $B_2O(OH)_5^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, or $B_5O_6(OH)_4^-$. The upfield trend of the chemical shift with increasing concentration makes it appear highly probable that tetramers and/or pentamers may be present. Because there is no resolution of the single B^{11} resonance into its components, however, it is not possible to identify all the polyborate species and to determine their distribution uniquely.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Gaseous Boroxine: Mechanism of Reaction with Boron Trihalides¹

BY M. NADLER AND RICHARD F. PORTER

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Low-pressure reactions of gaseous boroxine ($H_3B_3O_3$) with boron trihalides to produce dihaloborane and boric oxide have been studied by infrared absorption techniques. Kinetic data indicate that the reaction is close to first order in boroxine pressure. The pressure dependence of BF_3 in the $BF_3-H_3B_3O_3$ reaction is close to zero order for BF_3 pressures above 10 mm but tends toward a higher order at lower pressures. Reactions are accelerated in cells coated with $B_2O_3(s)$. Reaction rates increase in the order $BF_3 < BCl_3 < BBr_3$. Spectra of products of the reaction of ^{10}B -labeled compounds show that the boron atoms in $H_3B_3O_3$ appear in HBX_2 and the boron atom in BX_3 appears in $B_2O_3(s)$. A surface mechanism which accounts for the ^{10}B distribution in the products is proposed.

Introduction

Studies of the chemical behavior of boroxine ($H_3B_3O_3$) have shown that the compound is reactive with a

(1) Work supported by the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency.

number of reagents including oxygen, carbon monoxide,² and the boron trihalides.³ The kinetic behavior of gaseous boroxine may be investigated provided its

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(3) R. F. Porter and S. K. Wason, *J. Phys. Chem.*, **69**, 2208 (1965).