The method reported here utilizes the reaction between sulfur dichloride and *N*-(trimethylsilyl)sulfinylamine and gives a 68% yield of bis(sulfinylamino) sulfide conveniently. The other product, trimethylchlorosilane, was found to be an excellent recrystallization solvent for the amino sulfide. Benzene had been used previously.[5]

$$2Me_3SiNSO + SCl_2 \longrightarrow S(NSO)_2 + 2Me_3SiCl$$

The large, yellow rhombic crystals of the product were sensitive to traces of moisture. They could be conveniently handled in an atmosphere of dry nitrogen. The sample went red on heating and appeared to boil after melting, as previously reported.[2] The infrared spectrum in carbon disulfide contained two major peaks at 1184 and 988 cm^{-1}, attributable to the asymmetric and symmetric stretching vibrations of the sulfinylamino group.[7]

Experimental Section

Sulfur dichloride was purified by distillation in the presence of 10% of phosphorus trichloride,[8] which inhibits disproportionation into sulfur monochloride and chlorine; the distillate was promptly used.

***N*-(Trimethylsilyl)sulfinylamine** was prepared in 88% yield according to the method of Scherer and Horning[9] from tris(trimethylsilyl)amine[10] and thionyl chloride. The fraction boiling at 108°, $n^{25}D$ 1.4254, was used.

Bis(sulfinylamino) Sulfide.—In one experiment, 41.4 g (0.307 mol) of the silylsulfinylamine was placed in a 100-ml two-necked flask, fitted with a reflux condenser, and a 50-ml dropping funnel fitted with a by-pass. The whole apparatus was flushed with and maintained under an atmosphere of dry nitrogen, and 14.5 g (0.145 mol) of sulfur dichloride was slowly added to the sulfinylamine, with stirring. The reaction was exothermic, and fine, yellow crystals were deposited. The mixture was heated under reflux for 48 hr to ensure complete reaction. Long, yellow needles formed on cooling and the liquid was then pumped off, trapped (30.2 g), and redistilled to yield trimethylcholorosilane (26.5 g, 87%), bp 57°, $n^{25}D$ 1.3864.

The yellow crystals were dissolved in 50 ml of hot trimethylchlorosilane, recrystallized, and filtered under a dry nitrogen atmosphere. They were washed with a little cold trimethylchlorosilane and all traces of solvent were pumped off over a period of 3 hr. The crystals melted in sealed tube at 100–101° (lit.[4] mp 100.7°) (14.9 g, 68%). *Anal.* Calcd for $S_3N_2O_2$: S, 61.58; N, 17.93; O, 20.49. Found: S, 61.62; N, 18.11; O, 20.44.

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(7) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed. Engl.*, **1**, 90 (1962).

(8) B. D. Stone and M. L. Nielson, *J. Amer. Chem. Soc.*, **81**, 3580 (1959).

(9) O. J. Scherer and P. Hornig, *Angew. Chem., Int. Ed. Engl.*, **5**, 729 (1966).

(10) W. L. Lehn, *J. Amer. Chem. Soc.*, **86**, 305 (1964).

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Boron-11 Nuclear Magnetic Resonance Study of Polyborate Ions in Solution

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The study of ^{11}B nuclear magnetic resonance is complicated by the fact that boron possesses a nuclear quadrupole moment which causes, in many cases, excessive signal broadening and the resultant overlap of signals which would otherwise appear as distinctly separated resonance lines. Instruments operating at higher magnetic field strengths have slowly become available in recent years and as a result we have seen the unraveling of numerous heretofore unresolved spectra. This is most dramatically illustrated in the areas of boron hydride and carborane chemistry. An extensive review and a very helpful introduction to the nmr of boron compounds is given in a recent book by Eaton and Lipscomb.[2]

The properties of borates, *i.e.*, inorganic boron–oxygen compounds, in aqueous solution have been studied using a variety of techniques.[3] The earliest report of the ^{11}B nmr spectra of borates in solution appears to be that of Shapiro, *et al.*,[4] in which a polyborate ion is postulated to explain a high-field line in aqueous sodium pentaborate.

The existence of polyborates in aqueous solution is inferred from structural studies on crystalline borates. Data obtained from pH titrations, conductance, and cryoscopic studies are best interpreted as involving various polyborate equilibria.[3] The detection of polyborate species by ^{11}B nmr depends on two main factors, the stability of the polyborate ion in solution and the exchange rate of boron atoms between different chemical sites in the molecule. Momii and Nachtrieb[5] studied the borate–polyborate equilibria in aqueous solution using nmr techniques and concluded that three equilibria sufficiently explained the nmr data obtained on sodium pentaborate

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^- \quad K_1 \qquad (1)$$

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \quad K_3 \qquad (2)$$

$$4B(OH)_3 + B(OH)_4^- \rightleftharpoons B_5O_6(OH)_4^- + 6H_2O \quad K_5 \qquad (3)$$

Metaborate and tetraborate solutions gave only one nmr signal and provided little information on polyanion formation.

We have undertaken a study of the ^{11}B nmr spectra of aqueous borate solutions at 80 MHz with the hope that more meaningful data can be obtained at the higher magnetic strength.

Results and Discussion

At 80 MHz the ^{11}B nmr spectra of aqueous borate solutions are seen to be considerably more resolved than previously reported. There was, however, no evidence of polyborate formation in metaborate or boric acid solutions. These species presumably represent the extremes in the $B(OH)_4^-$–$B(OH)_3$ system. A plot of the chemical shift *vs.* the $Na_2O:B_2O_3$ ratio (or $B(OH)_4^-$: total boron) for dilute solutions of boric acid (0:1), sodium pentaborate (1:5), sodium tetraborate (1:2), and sodium metaborate (1:1) shows a linear relationship when the single peaks in the nmr spectra of boric acid and sodium metaborate are used as the extremes and the most intense low-field peak in the pentaborate and tetraborate solutions are used. A solution containing Na_2O and B_2O_3 in a 1:3 ratio gave a single

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(2) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(3) N. P. Nies and G. W. Campbell, "Boron, Metallo-Boron Compounds and Boranes," Wiley-Interscience, New York, N. Y., 1964, Chapter 3.

(4) T. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(5) R. K. Momii and N. H. Nachtreib, *Inorg. Chem.*, **6**, 1189 (1967).

peak in dilute solutions in agreement with the relationship as shown in Figure 1. This linear relationship also holds at high concentrations in which the pentaborate and tetraborate solutions show additional nmr peaks which are attributed to polyborate ion formation.

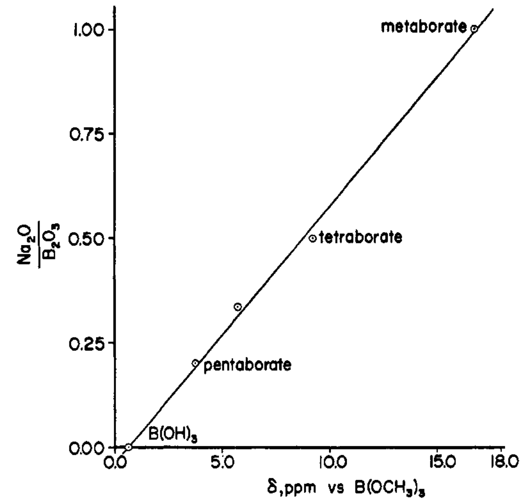

Figure 1.—Chemical shift as a function of the $Na_2O:B_2O_3$ ratio for dilute solutions of sodium borates. The unlabeled point is for a synthetic solution with an $Na_2O:B_2O_3$ ratio of 1:3.

The solid-state structures of the majority of borates contain six-membered ring systems,[6] and it is believed that the most stable polyborate ions in solution are six-membered ring species derived from the depolymerization of the solid borates.

At 80 MHz the ^{11}B nmr spectrum of potassium tetraborate consists of a single relatively sharp absorption at low tetraborate concentrations. As the concentration increases, a new absorption appears as a shoulder at lower field (Figure 2). Continued increase of the concentration produces a third absorption, this time at higher field relative to the original low concentration absorption. This is accompanied by an apparent increase in the ratio of the peak at lowest field to the original single peak. Finally, in a saturated solution, the two low-field peaks merge into a rather broad absorption while the high-field absorption increases in relative intensity. A logical interpretation of the nmr spectrum seems to be that the single peak observed at the low concentrations represents an equilibrium involving $B(OH)_3$ and $B(OH)_4^-$. The first new absorption that appears represents the formation of a polyborate species produced through the interaction of $B(OH)_3$ with $B(OH)_4^-$. Since the B_3O_3 ring system is the most stable polyborate species, its formation can be represented as

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- \qquad (4)$$

The new peak at high field undoubtedly represents a more complex polyborate ion.

Sodium tetraborate displayed a similar behavior with the exception that no high-field absorption could be detected. A saturated solution of sodium tetraborate is only about 0.3 *M* at room temperature and this probably explains the lack of a high-field peak since polyborate formation is a function of concentration and the high-field absorption probably represents the polyanion of least stability.

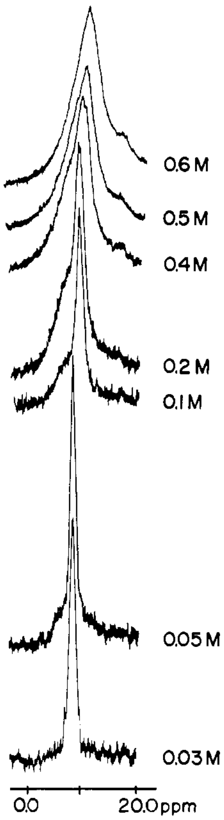

Figure 2.—The ^{11}B nmr spectra of various concentrations of $K_2O \cdot 5B_2O_3 \cdot 8H_2O$ in water at ambient temperature.

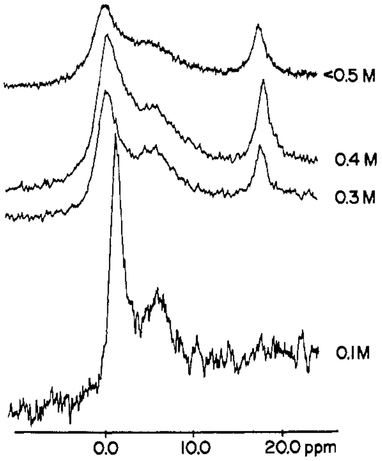

Figure 3.—The ^{11}B nmr spectra of aqueous $Na_2O \cdot 5B_2O_3 \cdot 10H_2O$ solutions.

The 80-MHz spectrum of aqueous sodium pentaborate displays three absorptions at concentrations between saturation and 0.2 *M*. Below approximately 0.2 *M* only the two low-field lines are observed. At the higher concentrations the two low-field absorptions tend to broaden and merge slightly as seen in Figure 3. There is also a slight shift of the low-field absorption to lower field with increased concentration.

As suggested earlier the low-field absorption is believed to represent an equilibrium concentration of $B(OH)_4^-$ and $B(OH)_3$ formed by the reaction

$$B_5O_6(OH)_4^- + 6H_2O \rightleftharpoons 4B(OH)_3 + B(OH)_4^- \qquad (5)$$

The peak at approximately 5 ppm (see Figure 3) is

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[6] V. F. Ross and J. O. Edwards in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., Wiley, New York, N. Y., 1967, pp 155–207.

probably due to the equilibrium condition described by the reaction

$$2B(OH)_3 + B(OH)_4 \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \qquad (6)$$

and represents the polyanion $B_3O_3(OH)_4^-$. The high-field peak then represents the polyanion $B_5O_6(OH)_4^-$.

A solution of potassium pentaborate shows two absorptions at concentrations up to saturation at room temperature. These absorptions correspond to the two low-field absorptions in the sodium pentaborate spectra. If a saturated potassium pentaborate solution is prepared at 30°, a third absorption is observed which corresponds to the high-field absorption in the sodium pentaborate spectrum (Figure 4). Unfortunately, our nmr spectra are not sufficiently resolved to permit quantitative calculations of equilibrium constants, although this should be possible with the aid of Fourier transform techniques. An estimate of the areas under the peaks in the pentaborate spectra (Figure 3) allowed a calculation of the ratio of boron atoms in the high-field peak to those in the low-field peaks, an exercise carried out by Momii and Nachtrieb. Our results were in rather poor agreement with those reported previously.[1] We also found it difficult to obtain an accurate value for the chemical shift at infinite dilution for tetraborate solutions although a reasonable estimate did appear to be $\delta_{Na_2B_4O_7}$ 9.0 ± 0.5, in agreement with the value reported by Momii and Nachtrieb. Assuming the equilibria proposed by Momii and Nachtrieb (eq 1–3) and using the value 10^5 for K_1, we obtained values of pK_3 and pK_5 which were approximately 20 and 50% lower, respectively.

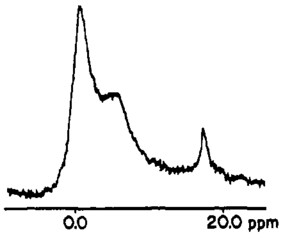

Figure 4.—The ^{11}B nmr spectrum of a saturated $K_2O \cdot 5B_2O_3 \cdot 8H_2O$ solution at 30.0°.

It is interesting to note that the chemical shifts of the high-field absorptions in both the tetraborates and pentaborates have approximately the same values. If one estimates the position of the low-field absorption in tetraborates and compares it with the position of the middle absorptions of the pentaborate spectra, a similar correlation is seen. This suggests that two stable polyborate species occur in both tetraborate and pentaborate solutions and that they are identical. The high-field absorption +18 ppm probably represents $B_5O_6(OH)_4^-$ as suggested by Momii and Nachtrieb while the absorption at approximately 6 ppm could represent the $B_3O_3(OH)_4^-$ species not observed by Momii and Nachtrieb but postulated as one of the species involved in a rapid interchange of boron among three distinct sites. It is hoped that with the aid of Fourier transform spectroscopy we will be able to obtain quantitative equilibrium data in the near future.

Experimental Section

Chemicals.—All of the borates used in this work were special quality products produced by U. S. Borax and Chemical Corp.

Spectrometer.—The 80-MHz ^{11}B nmr spectra were obtained on an instrument designed by Professor F. A. L. Anet, Department of Chemistry, University of California, Los Angeles, Calif.

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Preparation and Characterization of Phosphitochromium(III)

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In a recent study of the reduction of Cr(VI) in excess hypophosphorous acid,[1] we observed that the Cr(III) product was formed as cationic complexes both of P(I) and P(III). Characterization of the 1:1 complex between Cr(III) and hypophosphite has been reported by Espenson and Binau;[2] and although complexes between Cr(III) and phosphite have been reported by Ebert and Podlaha,[3] their work dealt with the solid state and solutions of pH 6 or greater. A more detailed study of the 1:1 complex formed between Cr(III) and P(III) in acidic media was undertaken as a basis for further study of the products of Cr(VI) reductions.

Experimental Section

Reagents and Preparation.—Commercially available chromium(III) perchlorate was recrystallized from dilute $HClO_4$; sodium perchlorate was recrystallized from water. Calcium perchlorate was prepared from calcium carbonate and $HClO_4$ and was recrystallized. Water was redistilled from alkaline permanganate and other reagents were used without further purification. Chromium and phosphite analyses were performed as previously described.[1]

Solutions of monophosphitochromium ion, presumably, phosphitopentaaquochromium(III), $Cr(H_2O)_5(O_3PH_2)^{2+}$, were prepared as follows. A solution *ca.* 0.4 *F* in both chromium perchlorate and phosphorous acid was deoxygenated in a stream of N_2 and was then heated in a stoppered flask to 45° for 6–8 days. The desired complex was separated from the cooled reaction mixture containing Cr^{3+} and P(III)–Cr(III) complexes by cation exchange. Espenson, *et al.*,[2] reported a very low flow rate was required for good separation of their P(I)–Cr(III) complex from by-products. We used, successively, two columns, each with about 50% excess resin capacity, for the separation and flow rates of up to 0.3 ml/min. In the primary separation, species of charge 1+ or less were eluted with 0.3 *F* $HClO_4$, after which 0.5 *F* $Ca(ClO_4)_2$ was used to displace the 2+ and 3+ species. The central 90% of the dark green band preceding the purple Cr^{3+} was collected, placed on a smaller secondary column, and eluted with 0.8 *F* $HClO_4$. Initially, high P(III):Cr(III) ratios and anomalous spectral results led us to suspect small quantities of another, presumably polymeric, P(III)–Cr(III) complex were contaminating the leading edge of the 2+ band; portions of the effluent of the secondary preparation column were diluted and their absorbances were measured with a Beckman DU at 418 and 420 nm. Samples for which $A_{420} \neq A_{418}$ were rejected. In general the central 90% of the 2+ band on the second column was collected. The product was typically 0.15

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[1] J. N. Cooper, *J. Phys. Chem.*, **74**, 955 (1970).

[2] J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5**, 1365 (1966).

[3] M. Ebert and J. Podlaha, *Collect. Czech. Chem. Commun.*, **26**, 753, 1879 (1961).