Separation of $(CH_3)_2NBH_2$ from $B_2H_6\cdot[(CH_3)_2N]_4B_2$.—The 1:1 adduct (1.30 mmoles) prepared in the above manner was washed several times with fresh portions of 2-methylbutane. Precautions were taken to keep the temperature of the system at or below −78°. The white solids which remained on the filter frit decomposed into a white volatile solid and a viscous nonvolatile liquid on warming to −23°. The solid was sublimed away from the liquid at room temperature and was identified as $(CH_3)_2NBH_2$ (1.11 mmoles) by its vapor-phase infrared spectrum. Thus the $(CH_3)_2NBH_2:B_2H_6\cdot[(CH_3)_2N]_4B_2$ rato is 0.86:1. In a second experiment 2.27 mmoles of $(CH_3)_2NBH_2$ was isolated from the decomposition of 1.95 mmoles of the 1:1 adduct giving a $(CH_3)_2NBH_2:B_2H_6\cdot[(CH_3)_2N]_4B_2$ ratio of 1.17:1.

Attempted Isolation of Stable, Monomeric, B–B Bonded Species.—In an attempt to prepare a stable trimethylamine derivative of the fragment remaining after the 1:1 adduct had lost 1 mole of $(CH_3)_2NBH_2$, an excess of the Lewis base was added to the adduct and the mixture was allowed to stand at −23°. From this mixture only a trace of a substance which might be a monomeric B–B bonded species was detected. Most of the fragment formed a nonvolatile liquid which slowly converted to a yellow glass.

Since hydride–dimethylamino exchange occurred in the reaction of B_2H_6 and $[(CH_3)_2N]_4B_2$, an attempt was made to synthesize NaB_3H_8 by allowing a large excess of $NaBH_5$ and B_2H_6 to react with a dilute tetrahydrofuran solution of $[(CH_3)_2N]_4B_2$. No chemical evidence for the presence of $[B_3H_8]^-$ was found in this reaction mixture.

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The Hydrolysis of Carbon Monoxide Borane

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In a recent study of the aqueous chemistry of potassium boranocarbonate ($K_2H_3BCO_2$) the following observations were reported: (a) rapid acidification of $K_2H_3BCO_2$ solutions produces H_3BCO in good yields;[1] (b) titration data indicate that the H_3BCO thus formed is produced *via* the boranobicarbonate ion and boranocarbonic acid[1]

$$H_3BCO_2^{2-} \overset{H^+}{\rightleftharpoons} H_3BCOOH^- \overset{H^+}{\rightleftharpoons} H_3BC(OH)_2 \rightleftharpoons H_3BCO + H_2O$$

and (c) little H_3BCO can be isolated by slow acidification under dilute conditions at room temperature; however, up to 1.5 moles of hydrogen is produced per mole of $K_2H_3BCO_2$ hydrolyzed. Formaldehyde is also formed when slow acidification is carried out exposed to the air.[2]

These points suggest that when H_3BCO is generated slowly in aqueous solution it reacts with water to form products that differ from those expected from the previously reported reaction of H_3BCO and water[3]

$$H_3BCO + 3H_2O \xrightarrow{100°} B(OH)_3 + 3H_2 + CO \qquad (1)$$

The purpose of this work is to elucidate the reactions that occur between H_3BCO and water.

Experimental Section

Standard vacuum procedures and ₸ apparatus were used throughout.

Materials.—Diborane[4] and potassium boranocarbonate[1] were prepared by previously published procedures. In the preparation of potassium boranocarbonate the carbon monoxide was passed through an aqueous sodium hydroxide solution to remove any carbon dioxide present and then three −78° traps to remove water. The carbon monoxide borane used in these experiments was generated as needed by the action of 85% phosphoric acid on an appropriate amount of the boranocarbonate.[1]

The Reaction of Gaseous H_3BCO and Water.—A 20-ml quantity of water in a 100-ml round-bottomed flask equipped with a vacuum adapter was evacuated. The flask and contents were then cooled to −196° and 1.00 mmole of H_3BCO was condensed into the flask. The stopcock on the adapter was closed and the system was kept at 0° for 2 days. After that time the contents volatile at room temperature were passed through a trap at −78° and two at −196°. The noncondensable gases were measured by a Toepler pump system. An infrared spectrum of these gases showed the presence of carbon monoxide. The traps cooled to −196° were found to contain a small amount of unreacted H_3BCO which was identified by its infrared spectrum. Vapor-phase chromatography of the water trapped at −78° confirmed that no other reaction products volatile at room temperature were formed.

The residue left in the reaction flask was found to be a mixture of boric acid and hydroxymethylboronic acid anhydride. The boronic acid anhydride could be sublimed under vacuum at 100° to a cold finger maintained at 0°. The anhydride was identified by its melting point of 146–149° (lit.[5] 147–148°) and analysis. *Anal.* Calcd for $(BO_2CH_3)_n$: B, 18.68; C, 20.70; H, 5.15. Found: B, 18.48; C, 20.75; H, 4.99. Molecular weight measurements indicated that the anhydride was dimeric in ketone solutions. *Anal.* Calcd for the dimer: 115.8. Found: 108 (acetone), 120 (methyl ethyl ketone). These values were obtained by vapor-phase osmometry. The anhydride hydrolyzes to the monomer hydroxymethylboronic acid $[(HO)_2BCH_2OH]$ in aqueous solution as shown by its molecular weight in water which was determined cryoscopically. *Anal.* Calcd: 57.8. Found: 57.0. The equivalent weight of the anhydride in water was also determined by titration in the presence of mannitol. *Anal.* Calcd: 57.8. Found: 57.8.

Similar procedures were employed when the reaction was run at 50°. The reaction of H_3BCO with water at 0° was run at higher initial pressures of H_3BCO in sealed Pyrex tubes equipped with break tips.

The Reaction of $K_2H_3BCO_2$ Solutions and Dilute HCl.—In a typical experiment 136 mg (1.00 mmole) of $K_2H_3BCO_2$ was dissolved in 20 ml of water in a 100-ml round-bottomed flask. A 4.0-ml quantity of 0.50 *N* HCl was then frozen into a rimless 13 × 100 ml test tube. The test tube was placed upright in the flask containing the boranocarbonate solution and the flask was then attached to an adapter equipped with a vacuum stopcock. The system was evacuated while the contents of the test tube were still frozen. The stopcock on the adapter was closed and the apparatus was removed from the vacuum line and allowed to equilibrate to 0°. The apparatus was then tipped slightly to allow a few drops of HCl solution to run out of the test tube and

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mix with the $K_2H_3BCO_2$ solution. This was repeated until the two solutions were completely mixed. The components volatile at room temperature were then fractionated as described in the reaction of gaseous H_3BCO and water. In addition to hydrogen small amounts of carbon monoxide and H_3BCO were identified as products. No other products were formed that were volatile at room temperature. The residue left after removal of solvent was found to be a mixture of potassium chloride, hydroxymethylboronic acid anhydride, and boric acid. The boronic acid anhydride and boric acid were separated from the potassium chloride by extraction with acetone. The yield of the hydroxymethylboronic acid was determined by carbon analysis of the mixture remaining after removal of the acetone.

Results and Discussion

The reaction of H_3BCO and water was examined from two approaches: (a) by reaction of gaseous H_3BCO and water and (b) by generation of aqueous H_3BCO from potassium boranocarbonate solutions. Both were carried out at 0 and 50°. The results of the experiments described below represent the average of several runs under the conditions noted. In all cases the amount of noncondensable gas evolved was reproducible to ±0.1 mmole per mmole of H_3BCO that hydrolyzes. For simplicity, the total species that hydrolyzes will be referred to as H_3BCO. However, as will be discussed later, various possible equilibria in the H_3BCO–H_2O[1] system raise questions as to the actual species that react to give the products observed.

(a) The Reaction of Gaseous H_3BCO and Water.—A 1.00-mmole quantity of H_3BCO gave as hydrolysis products a 3.22-mmole mixture of hydrogen and carbon monoxide per mmole of H_3BCO hydrolyzed after 2 days at 0°. An average of about 0.04 mmole of H_3BCO was recovered unreacted after this time. Removal of the solvent water left a mixture of hydroxymethylboronic acid anhydride and boric acid.

The production of hydroxymethylboronic acid by this hydrolysis may be represented by

$$H_3BCO + 2H_2O \longrightarrow (HO)_2BCH_2OH + H_2 \qquad (2)$$

The presence of a significant amount of carbon monoxide in the noncondensable gases formed, however, indicates that reaction 1 previously described is also important. From the total amount of noncondensable gas evolved, it is found that reaction 1 accounts for approximately 75% of the products and reaction 2 accounts for approximately 25% under these reaction conditions. The yield of $(HO)_2BCH_2OH$ is consistent with this proportion of the two reactions. Carbon analysis of the boric acid–boronic acid anhydride mixture formed showed that about 22% of the hydrolyzed H_3BCO had been converted to the boronic acid.

In the reaction described above the initial pressure of H_3BCO was 0.16 atm assuming no solution or reaction. When the pressure was raised to 0.46 and 0.77 atm, the per cent yield of noncondensable gas was unchanged.

At 50° a 1.00-mmole quantity of H_3BCO is completely hydrolyzed after 1 day. The amount of gas evolved and carbon analysis of the solid residue left after removal of solvent are consistent with about 83% reaction 1 and 17% reaction 2.

(b) The Acid Hydrolysis of $K_2H_3BCO_2$ Solutions.—When a 1.00-mmole sample of $K_2H_3BCO_2$ was allowed to react slowly with 2 equiv of dilute HCl, an average of about 0.07 mmole of H_3BCO was isolated. A 1.20-mmole mixture of hydrogen and carbon monoxide evolved per mmole of H_3BCO hydrolyzed. The amount of noncondensable gas evolved and the yield of $(HO)_2BCH_2OH$ indicate that this reaction occurs in the proportions of 6% reaction 1 and 94% reaction 2. The formaldehyde originally detected in this reaction was found to result from the air oxidation of aqueous hydroxymethylboronic acid solutions and was thus not a primary reaction product.

When this reaction was carried out at 50°, reaction 1 became somewhat more important. The stoichiometry of the reaction was 10% reaction 1 and 90% reaction 2.

Since acid hydrolysis of $H_3BCO_2^{2-}$ solutions and direct reaction of H_3BCO with water produce hydroxymethylboronic acid, it is probable that a common precursor to this compound is involved. In these solutions, however, several species probably exist in concentrations as determined by various equilibria. Any or all of these could react directly to form the products observed. For example, the $H_3BCO_2^{2-}$ and H_3BCOOH^- ions are expected to be present in these solutions. However, these ions are known to be stable in aqueous solution[1,2] relative to the time elapsed for the experiments involving the acidification of $H_3BCO_2^{2-}$ solutions. Thus some other species is most likely the main precursor to the boronic acid. Although no experimental evidence confirms the presence of dissolved but loosely hydrated H_3BCO, it is thought to be present in significant amounts by analogy to carbon dioxide.[1] If so, the data of these experiments do not exclude the possibility of its direct reaction to form the boronic acid. The most attractive possibility consistent with the data is the boranocarbonic acid species. In the case of the reaction of gaseous H_3BCO and water, the $H_3BC(OH)_2$ would be formed by hydration of dissolved H_3BCO. In view of other chemical similarities between H_3BCO and CO_2,[1,6] one might predict that this process of hydration would occur slowly with an unfavorable equilibrium as is known to be the case for the hydration of dissolved CO_2.[7,8] Thus, if formation of $H_3BC(OH)_2$ from gaseous H_3BCO is slow, dissociation of the H_3BCO[3] and subsequent hydrolysis of the borane moiety could account for the importance of reaction 1 in this case. On the other hand, $H_3BC(OH)_2$ would be produced directly by protonation of the $H_3BCO_2^{2-}$ ion and thus account for the almost exclusive formation of the boronic acid under the conditions described. Kinetic data under conditions of controlled pH could help to establish the nature of the reacting species in these reactions.

In any case, the precursor to the boronic acid apparently undergoes loss of hydrogen and, in effect, two hydride shifts from boron to carbon. A single hydride

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shift has been noted previously with certain borane adducts.[9] It has also been postulated that organoboranes form the unstable intermediate R_3BCO in certain solvents containing water followed by shifts of two R groups from boron to carbon.[10,11] It is possible that the mechanism of this shift is similar to that involved in our work.

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Complexes of Sulfinamides

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We have recently initiated a study of the chemistry of alkanesulfinamides, $RS(O)NR_2$, which as might be expected show a number of properties similar to those of corresponding sulfoxides.[1-4] The ligand of primary interest in this work is N,N-dimethylmethanesulfinamide (DMMS), although the nickel(II) perchlorate complexes of N-methylmethanesulfinamide (NMMS) and methanesulfinamide (MS) are also included.

Sulfinamides might also be considered as similar to carboxylic acid amides in that coordination to a metal ion could occur through oxygen or nitrogen. Infrared spectra of the free ligands and the complexes were studied in order to determine the site of coordination which was found to be oxygen for all complexes reported in this paper. The general characterization of the complexes was obtained by a combination of elemental analysis, spectral studies, conductivity studies, and studies of magnetic susceptibilities.

Experimental Section

Reagents and Solvents.—The sulfinamides were prepared by the aminolysis of methanesulfinyl chloride which had been prepared by the chlorination of methyl disulfide in glacial acetic acid.[5] The preparation of DMMS, $CH_3S(O)N(CH_3)_2$, was accomplished by dropwise addition of methanesulfinyl chloride to dimethylamine in ether at −10 to −20°.[6] After removal of the ammonium salts and ether the product was obtained as a colorless liquid by vacuum distillation (bp 38° (2.0 mm)). The compound NMMS, $CH_3S(O)NHCH_3$, was prepared in the same manner by combining a 2:1 mole ratio of monomethylamine and methanesulfinyl chloride. The pure product was obtained as a colorless liquid by vacuum distillation from a small amount of anhydrous $CoCl_2$ (bp 63° (0.15 mm)). Both of these sulfinamides were very hygroscopic. The compound MS, $CH_3S(O)NH_2$, was prepared by dropwise addition of methanesulfinyl chloride in ether to an excess of ammonia in ether at −78°. After refluxing for 10 hr the ammonium salts and the solid product were separated from the ether. The product was extracted from the ammonium salts with methyl ethyl ketone and recrystallized from chloroform (mp 70–73°). This sulfinamide is not hygroscopic. The analytical data are found in Table I.

Fisher reagent grade nitromethane was used without further purification. Pure dry acetonitrile was obtained by distilling Fisher reagent grade materials from phosphorus pentoxide. Eastman 2,2-dimethoxypropane was used without purification.

Hydrated metal perchlorates were obtained from G. F. Smith Chemical Co. Hydrated nickel(II) tetrafluoroborate was obtained from Alfa Inorganics, Inc.

Preparation of the Complexes.—All of the complexes were prepared by the same method. The hydrated metal perchlorate or tetrafluoroborate (0.002 mole) was dehydrated by stirring with 10 ml of N,N-dimethoxypropane and 4 ml of methanol for 1.5–2 hr. The volume of solvent was reduced by half before adding >0.014 mole of DMMS, NMMS, or MS. The ligand MS was added as solute in chloroform. After stirring for 10 min ether was added to complete the precipitation of the complexes which were then filtered, washed with anhydrous ether, and dried under vacuum for 30 min. The DMMS complexes of Mn(II), Co(II), Ni(II), and Zn(II) were only slightly hygroscopic while $[Ni(NMMS)_6](ClO_4)_2$ and the Cu(II) complexes were sufficiently hygroscopic to cause difficulty in weighing. The iron complex $[Fe(DMMS)_6](ClO_4)_2$, which is not very hygroscopic, changed from a pale yellow-brown to brown while standing several weeks in a desiccator. The other compounds showed no changes. The four-coordinate Cu(II) complex was obtained by heating the six-coordinate complex under vacuum at 60° for 20 hr. The analytical data and yields are recorded in Table I.

TABLE I

ANALYSIS AND YIELDS OF SULFINAMIDE COMPLEXES

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	Yield, %
$CH_3S(O)N(CH_3)_2$	33.63	34.40	8.47	8.69	13.08	13.29	...
$CH_3S(O)NHCH_3$	25.80	26.36	7.60	7.64	15.05	14.83	...
$CH_3S(O)NH_2$	15.19	15.20	6.38	5.14	17.72	17.80	...
$[Mn(DMMS)_6](ClO_4)_2$	24.11	24.16	6.03	6.15	9.37	9.33	89
$[Fe(DMMS)_6](ClO_4)_2$	24.08	24.05	6.02	6.29	9.36	9.23	76
$[Co(DMMS)_6](ClO_4)_2$	24.00	23.90	6.00	6.08	9.33	9.20	94
$[Ni(DMMS)_6](ClO_4)_2$	24.00	23.93	6.00	6.21	9.33	9.04	98
$[Ni(DMMS)_6](BF_4)_2$	24.71	24.35	6.22	6.39	9.60	8.89	95
$[Ni(NMMS)_6](ClO_4)_2$	17.65	17.36	5.19	4.99	10.29	10.34	95
$[Ni(MS)_6](ClO_4)_2$	9.84	10.04	4.10	4.30	11.48	11.22	90
$[Cu(DMMS)_6](ClO_4)_2$	23.89	23.69	5.97	6.25	9.29	9.05	81
$[Cu(DMMS)_4](ClO_4)_2$	20.89	20.58	5.22	5.28	8.12	8.49	...
$[Zn(DMMS)_6](ClO_4)_2$	23.82	23.70	5.96	6.08	9.27	9.40	95

Physical Measurements.—Infrared spectra of the ligands and the complexes were obtained using a Perkin-Elmer Model 21 spectrophotometer. Near-infrared and visible spectra of complexes in solution and in Nujol mulls were obtained using a Beckman DK-2 spectrophotometer. The solution spectra were measured in 1.0- and 5.0-cm quartz cells using the ligand proper as a solvent with the same solvent as a reference. The mull spectra were obtained using smears on filter paper. Magnetic susceptibilities were measured using the Faraday method with a Spectromagnetic Industries power source and magnet. The measurements were made at 22° using $Hg[Co(CNS)_4]$ as a calibration standard. The electrolytic conductance measurements were made at 27° in nitromethane and acetonitrile using an Industrial Instruments, Inc., conductivity bridge and a calibrated cell.

Analysis.—The carbon and hydrogen analyses were obtained using a Coleman carbon–hydrogen analyzer. The nitrogen analyses were obtained using a Coleman nitrogen analyzer.

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