system was maintained under high vacuum. The off-gases were trapped at liquid-nitrogen temperature which allowed the hydrogen to be continuously removed. The contents of the trap were separated by fractional condensation,[12] through traps at 0, −80, and −196°. The 0° trap contained 0.0675 g (0.6 mmol) of unreacted $C_2B_7H_{13}$, and the −196° trap contained 0.5 mmol of B_2H_6, both identified by infrared spectra. The −80° (Dry Ice, 2-propanol) trap contained 1.7689 g of a semisolid, white material. A 0.5-ml portion of *n*-pentane was added to liquefy the −80° fraction and the resulting solution was then passed through a vpc[13] in 0.5-ml increments. Four major fractions were collected in traps maintained at −80°. The products were identified by infrared and nmr spectra.[2,3,6–9]

Derivative and reaction chemistry is currently under study on the 1,7-$C_2B_6H_8$ and the 1,7-$C_2B_7H_9$ systems.

Acknowledgment.—This research was supported in part by the Office of Naval Research.

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[12] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[13] Aerograph Model A350-B, equipped with a 0.25 × 10 ft Apiezon L on Chromosorb P column operating at 135° with flow rate 60 cc of helium/min.

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The Alcoholysis of Carbon Monoxide Borane

BY LEO J. MALONE

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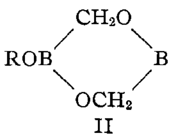
We have recently reported that the reaction of H_3BCO and water yields not only $B(OH)_3$, CO, and H_2 but also hydroxymethylboronic acid.[1] We now report that analogous reactions occur between H_3BCO and alcohols

$$H_3BCO + 3ROH \longrightarrow B(OR)_3 + CO + 3H_2 \qquad (1)$$

$$H_3BCO + 2ROH \longrightarrow \underset{\text{I}}{(RO)_2BCH_2OH} + H_2 \longrightarrow$$



II (2)

Although reaction 1 accounts for most of the products at 0°, reaction 2 occurs exclusively at −78°. This is consistent with the suggestion that reaction 1 occurs as a result of the initial dissociation of H_3BCO and subsequent solvolysis of the diborane formed.[1] At −78° dissociation of H_3BCO would be negligible and thus account for the absence of reaction 1 at low temperatures.

The hydroxymethylboronic esters (I) could not be isolated as such but eliminate alcohol to form the dimeric cyclic esters (II). A similar cyclic boronic acid anhydride has been reported previously.[2] In the present work concrete evidence for ring structure II was provided by the rapid hydrolysis of the cyclic esters in moist air to yield the dimeric hydroxymethylboronic acid anhydride.[1] This facile hydrolysis is inconsistent with the other possible dimeric structure involving a four-membered B–O ring.[3]

We also prepared an ester (II) in high yield by reaction of HCl with ethanolic solutions of $K^+H_3BC(O)OC_2H_5^-$ at 0°.

Experimental Section

Standard vacuum procedures and ₸ apparatus were used throughout.

Materials.—The H_3BCO used was generated as needed by the action of 85% phosphoric acid on an appropriate amount of potassium boranocarbonate.[1,4] The $K^+H_3BC(O)OC_2H_5^-$ (potassium O-ethylboranocarbonate) was prepared in a manner similar to that for $(K^+)_2H_3BCO_2^{2-}$. It was found in this study that the initial product in the reaction of H_3BCO and ethanolic KOH at −78° is $K^+H_3BC(O)OC_2H_5^-$. If the ethanolic KOH solution containing this compound is warmed, the $K^+H_3BC(O)OC_2H_5^-$ reacts with the hydroxide to precipitate $(K^+)_2H_3BCO_2^{2-}$. If, however, an equal amount of diethyl ether cooled to −78° is added to the cold solution of $K^+H_3BC(O)OC_2H_5^-$, the compound precipitates and can be isolated by filtration and washed with a cold 1:1 ether–alcohol mixture. The yield is about 75% based on the initial amount of diborane[5] used. *Anal.* Calcd for $K^+H_3BC(O)OC_2H_5^-$: C, 28.5; H, 6.34; K, 31.1. Found: C, 27.6; H, 6.11; K, 31.8. The equivalent weight was determined by titration of an aqueous solution with standard HCl: calcd, 125.9; found, 121.6.

The Reaction of Gaseous H_3BCO and Alcohol.—The procedures for the reactions of H_3BCO and methyl, ethyl, and isopropyl alcohols were similar to that described for the reaction of gaseous H_3BCO and water.[1] When 2.15 mmol of H_3BCO and 10 ml of absolute ethanol were allowed to react at −78° for 10 days, 1.80 mmol of hydrogen had evolved but no carbon monoxide. When the reaction mixture was allowed to warm slowly to room temperature an additional 0.90-mmol quantity of hydrogen and carbon monoxide evolved. When the ethanol solution remaining was allowed to pass through a trap at −23° the dimeric ethyl ester[6] (II) (mp 1°) condensed in this trap. From the total amount of noncondensable gas evolved, it was determined that reaction 2 accounted for about 92% of the products under these conditions. *Anal.* Calcd for $(C_2H_5OBCH_2O)_2$: C, 41.8; H, 8.16; B, 12.6. Found: C, 40.5; H, 8.27; B, 12.5. The molecular weight was determined cyroscopically in benzene: calcd for the dimer, 171.6; found, 173.1. This reaction was also carried out so that the H_3BCO and ethanol were allowed to warm rapidly to 0° and stand at this temperature for 2 days. In this case the yield of the ester was 20%.

The reactions of H_3BCO and methyl and isopropyl alcohols were carried out by allowing the reactants to stand at −78° for 1 day and then to warm slowly to room temperature over a 1-day period. Under these conditions the methyl ester was formed in 50% yield (reaction 2). The solid dimeric methyl ester was separated by distillation of the methanol solution through a −23° trap. *Anal.* Calcd for $(CH_3OBCH_2O)_2$: C, 33.4; H, 6.95; B, 15.0. Found: C, 34.4; H, 6.70; B, 14.6. Molecular weight: calcd for the dimer, 143.6; found, 141.0. Under the same conditions the isopropyl ester was prepared in 95% yield. This ester (mp 6°) was separated from the isopropyl alcohol by distillation through a trap at 0°. *Anal.* Calcd for $(C_3H_7OBCH_2O)_2$: C, 48.1; H, 9.02. Found: C, 47.5; H, 9.03. Molecular weight: calcd for the dimer, 199.8; found, 195.0.

Reaction of HCl and Ethanolic $K^+H_3BC(O)OC_2H_5^-$.—In a

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[1] L. J. Malone and M. R. Manley, *Inorg. Chem.*, **6**, 2260 (1967).

[2] D. S. Matteson and G. D. Schaumberg, *J. Org. Chem.*, **31**, 726 (1966).

[3] R. T. Hawkins, W. J. Lennarz, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3053 (1960).

[4] L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).

[5] G. F. Freegard and L. H. Lang, *Chem. Ind.* (London), **11**, 471 (1965).

[6] 1,4-Diethoxy-1,4-diboro-2,5-dioxacyclohexane.

typical experiment, a 126-mg (1.00-mmol) quantity of $K^+H_3BC(O)OC_2H_5^-$ was dissolved in 20 ml of absolute ethanol in a 50-ml round-bottomed flask. The flask was attached to the vacuum line, evacuated, and cooled to −196°. A 1.10-mmol quantity of HCl was condensed into the flask and the apparatus was allowed to warm to room temperature. A 1.23-mmol mixture of hydrogen and carbon monoxide was measured by a Toepler pump system indicating the ethyl ester was formed in 95% yield. Distillation of the volatile components through a −23° trap led to the separation of the dimeric ethyl ester (II).

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Ammonia Proton Relaxation Studies for Solutions of $Ni(NH_3)_6(ClO_4)_2$ in Liquid Ammonia

BY W. L. RICE AND B. B. WAYLAND

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Nickel(II) hexaammine in liquid ammonia has recently been investigated by both N^{14} and H^1 nuclear magnetic resonance.[1-3] Analysis of the proton line broadening has previously been reported to yield a pseudo-first-order rate constant for ammonia exchange of $k = (1.9 \pm 0.1) \times 10^5$ sec^{-1} at 298°K and a proton coupling constant of $|A/h| = (3 \pm 1) \times 10^6$ sec^{-1}.[2] Nitrogen-14 line broadening[1] and proton contact shift studies[3] for this system gave values of $k = (1.0 \pm 0.1) \times 10^5$ sec^{-1} at 298°K and $A/h = (-1.5 \pm 0.1) \times 10^6$ sec^{-1}, respectively. In an attempt to resolve these inconsistencies, the temperature dependence of the proton nmr line width for solutions of $Ni(NH_3)_6^{2+}$ in liquid ammonia has been redetermined and extended to higher temperatures.

Experimental Section

Preparation of Complexes.—The hydrated perchlorate complex $Ni(H_2O)_6(ClO_4)_2$ was dehydrated by stirring in contact with 2,2-dimethoxypropane for approximately 3 hr. Anhydrous ammonia (Matheson) was then bubbled through the solution and the resulting precipitate was filtered and dried under vacuum. Representative analysis: Calcd for $Ni(NH_3)_6(ClO_4)_2$: H, 5.05; N, 27.25; Ni, 16.31. Found: H, 5.17; N, 27.27; Ni, 16.05.

Solutions.—Solutions of the nickel(II) ammine complex in liquid ammonia were prepared by weighing into a thick-walled nmr tube the dried amine complex along with NH_4ClO_4 used to prevent amide precipitation. The nmr tube was placed on the vacuum system, and ammonia was quantitatively distilled into the nmr tube using a standard technique.

Apparatus.—The nmr spectra were determined on a Varian A-60-A spectrometer. The thick-wall nmr tubes were obtained from Ace Glass Co. and NMR Specialties Inc. The thick-walled nmr tubes were altered for temperature studies from 50 to 90°. The major problem of solution boiling was overcome by sealing the tubes as close as possible to the ammonia solution allowing sufficient volume to accommodate the expansion of the solution when heated.

Results and Discussion

The temperature dependence of the proton line widths has been analyzed using the equations developed by Swift and Connick[4] from solution of the Bloch equations including chemical exchange. The general line width relationship is

$$\frac{1}{T_{2p}} = \frac{P_m}{\tau_m}\left[\frac{\left(\frac{1}{T_{2m}}\right)^2 + \frac{1}{T_{2m}\tau_m} + \Delta\omega_m^2}{\left(\frac{1}{T_{2m}} + \frac{1}{\tau_m}\right)^2 + \Delta\omega_m^2}\right]$$

where P_m is the fraction of ligand complexed, τ_m is the mean lifetime of ligand in the first coordination sphere, $\Delta\omega$ is the contact shift in radians per second, $1/T_{2m}$ is the transverse relaxation rate for the nucleus in the coordinated ligand, and $1/T_{2p}$ is the observed transverse nuclear relaxation rate. In the low-temperature region ($10^3/T = 3.8$–4.1°K^{-1}), where $\Delta\omega_m^2 \gg (1/T_{2m})^2$, $(1/\tau_m)$, the limiting relationship $T_{2p} = \tau_m/P_m$ is obtained. At temperatures above $10^3/T = 3.7$°K^{-1} two or more relaxation mechanisms contribute to the observed relaxation times. The contributing mechanisms have been resolved by curve fitting and are given by the limiting straight lines in Figure 1. The experimental data points and the theoretical curve calculated from the general line width relationship appear in Figure 1.

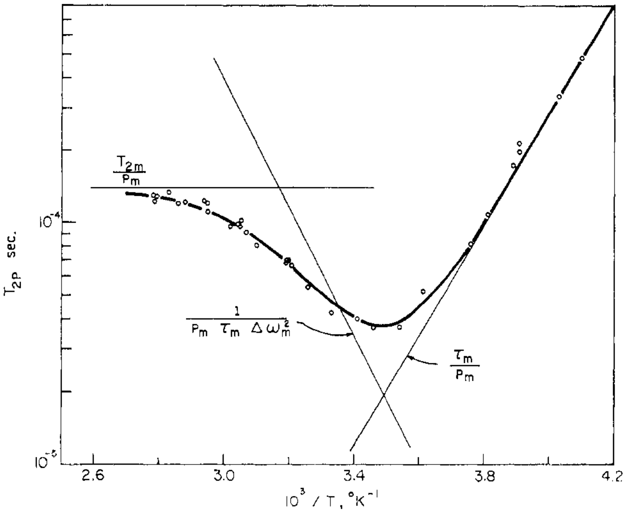

Figure 1.—Plot of proton T_{2p} *vs.* $10^3/T$ for solutions of $Ni(NH_3)_6^{2+}$ in liquid ammonia. The data points represent three independent concentrations normalized to $P_m = 1$. The solutions contain NH_4ClO_4 in order to inhibit amide formation. $T_{2p} = 1/\pi\Delta\nu$ where $\Delta\nu$ (sec^{-1}) is the full line width at half-height: O, data points; —, calculated curve.

The curve-fitting process results in a rate constant

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[4] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).