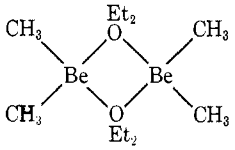
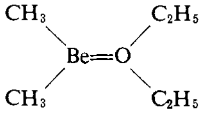
increase relative to the signal at τ 11.32 as the concentration is *reduced.* This excludes the possibility that the τ 11.43 signal represents dimers of the type



(the *methyl*-bridged dimers being already excluded as they would show resonance at *lower* field).

We therefore suggest that the overall reaction is $(CH_3)_2Be \cdot OEt_2 + OEt_2 = (CH_3)_2Be \cdot 2OEt_2$, with the reactant and product having methyl proton chemical shifts of τ 11.16 and 11.43, respectively. The τ 11.32 signal represents an intermediate species which could *possibly* be the ether-bridged dimer discussed above, but which we suggest is



The Be–O system is isoelectronic with C–C and B–N and it is therefore not unreasonable to speculate on the possibility of π bonding in this case. Be–N π bonding has been previously demonstrated[23,34] and we have been informed of X-ray studies that indicate Be–O π bonding[35] analogous to published work indicating Mg–O π bonding.[36] We therefore suggest that at lower temperatures the Be–O bond is strengthened by π bonding, causing an upfield methyl proton chemical shift. This should hinder rotation about the Be–O bond, which could be tested by using an unsymmetrical ether as the solvent, thus rendering the magnetic nonequivalence of the methyl groups bound to the beryllium.

Acknowledgment. We are indebted to the National Science Foundation for support of this work under Grant No. GP-8595.

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Reactions of the 2,4-$C_2B_5H_7$ Carborane System[1]

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Abstract: The 2,4-dilithio, 2-methyl, 2,4-dimethyl, 2-bromo, and 2-trimethylsilyl derivatives of 2,4-$C_2B_5H_7$ have been prepared, but the 2-monolithio derivative is unstable with respect to polymerization in ether–hexane solvent. Electrophilic bromination of 2,4-$C_2B_5H_7$ yields the 5-bromo derivative. The parent carborane is stable in 1 *M* aqueous HCl, but is easily degraded to boric acid in ethanolic KOH. The dilithio salt of the C,C′-dicarboxylic acid is completely degraded by aqueous HCl.

Studies of the derivative chemistry of the polyhedral carboranes[2] in the $C_2B_{n-2}H_n$ series (n = 5–12) have centered almost exclusively upon cage systems having eight or more boron atoms. In this paper we describe some reactions of 2,4-dicarba-*closo*-heptaborane(7) (Figure 1), a stable and relatively accessible[3] carborane which seems ideally suited for research on the smaller polyhedra. Our initial work has been concerned with three types of reactions which are characteristic[2] of the well-studied icosahedral $C_2B_{10}H_{12}$ systems: metalation at carbon and synthesis of C-substituted organo derivatives, halogenation, and degradation by strong bases.

Results and Discussion

Lithiation and Synthesis of C-Substituted Derivatives. The reaction of $C_2B_5H_7$ with n-butyllithium is markedly sluggish in comparison with the lithiation of 1,2-$C_2B_{10}H_{12}$,[4–6] particularly in nonpolar solvents. No reaction is observed in n-pentane or n-hexane when both reactant concentrations are below 1 *M*, but at higher concentrations the white dilithiocarborane slowly precipitates.

$$HCB_5H_5CH + 2C_4H_9Li \longrightarrow LiCB_5H_5CLi + 2C_4H_{10}$$

Typically, 23% of the original carborane was recovered from a solution of 2.5 *M* C_4H_9Li and 1.0 *M* $C_2B_5H_7$ in hexane after 20 hr at room temperature.

A considerable increase in reaction rate and yield of the dilithio derivative is obtained in a 2:1 diethyl ether–hexane solvent, compared to the pure hexane system. In ether–hexane the reaction pro-

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(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969, Abstract No. 74; taken in part from the Ph.D. dissertation of R. R. O., University of Virginia, 1970.

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ceeds to completion in 20 hr at room temperature, even at low (<1 *M*) reactant concentrations (attempts to carry out the lithiation in pure ether produced an intractable gum). The comparatively low reactivity of $C_2B_5H_7$ toward proton abstraction by *n*-butyllithium may reflect a lower positive charge on the carbon atoms than is the case in the $C_2B_{10}H_{12}$ isomers (LCAO MO calculations[7] have given ground state framework charges of −0.171 for each carbon in 2,4-$C_2B_5H_7$ and +0.294 for the carbons in 1,2-$C_2B_{10}H_{12}$).

The dilithio derivative reacts easily with methyl iodide in ether, forming the C,C′-dimethylcarborane in over 70% yield.

$$Li_2C_2B_5H_5 + 2CH_3I \longrightarrow (CH_3)_2C_2B_5H_5 + 2LiI$$

The preparation of the C-monolithio derivative was expected to be straightforward, but this proved not to be the case. The reaction of $C_2B_5H_7$ with an equimolar (or slightly larger) quantity of C_4H_9Li in ether–hexane, and subsequent treatment with CH_3I in ether, produced $CH_3C_2B_5H_6$ and $(CH_3)_2C_2B_5H_5$ in yields of only 3 and 8%, respectively. However, the C-monomethyl derivative was obtained in 60% yield from the dilithiocarborane by successive treatments with an equimolar quantity of CH_3I and excess HCl. The C-trimethylsilyl derivative was prepared by an analogous route.

$$LiCB_5H_5CLi \xrightarrow[-LiI]{CH_3I} LiCB_5H_5CCH_3 \xrightarrow[-LiCl]{HCl} HCB_5H_5CCH_3$$

$$LiCB_5H_5CLi \xrightarrow[-LiCl]{Si(CH_3)_3Cl} LiCB_5H_5CSi(CH_3)_3 \xrightarrow[-LiCl]{HCl} HCB_5H_5CSi(CH_3)_3$$

The unexpected difficulty encountered in preparing the monolithio derivative suggested possible disproportionation to the dilithio derivative and the parent carborane, as has been reported[8] for C-lithio derivatives of 1,2-$C_2B_{10}H_{12}$. This possibility was ruled out, however, when it was found that direct reaction of $Li_2C_2B_5H_5$ and HCl in equimolar amounts in ether produced $C_2B_5H_7$ in 11% yield, H_2, and no other volatile products. Treatment of the remaining material with excess CH_3I yielded no detectable monomethyl- or dimethylcarboranes. In another experiment, the reaction of $Li_2C_2B_5H_5$ with *excess* HCl produced $C_2B_5H_7$ (15% yield) and H_2. The nonvolatile solid which remained was characterized from spectroscopic evidence as a carborane polymer containing $C_2B_5H_x$ cage units. These results indicate that the monolithio derivative is highly unstable with respect to polymerization under the conditions of this study. Polymer formation may proceed by elimination of lithium hydride as shown (reaction of the lithium hydride with HCl would account for the observed formation of H_2).

$$LiCB_5H_5CH + LiCB_5H_5CH \xrightarrow[-LiH]{}$$

$$LiCB_5H_5C\text{–}CB_5H_5CH \xrightarrow{n\,LiCB_5H_5CH} Li\text{—}[CB_5H_5C]_{n+2}\text{—}H + n\,LiH$$

As the data given earlier demonstrate, polymerization is hindered or prevented when excess *n*-butyllithium is present; under such conditions, formation of the dilithio derivative is strongly favored.

Attempted Preparation of the Dicarboxylic Acid. The C,C′-dicarboxylic acid derivatives of 1,2- and 1,7-$C_2B_{10}H_{12}$ are easily obtained by carbonation of the respective dilithio carboranes and subsequent acidification of the acid salts.[4–6,9] In this work, $Li_2C_2B_5H_5$ reacted smoothly with excess CO_2 to yield a white solid assumed to be the dilithium salt of the diacid, $(LiOOC)_2C_2B_5H_5$. Addition of excess aqueous HCl to this product caused rapid evolution of H_2 in a volume corresponding to 84% of that calculated for complete cage degradation.

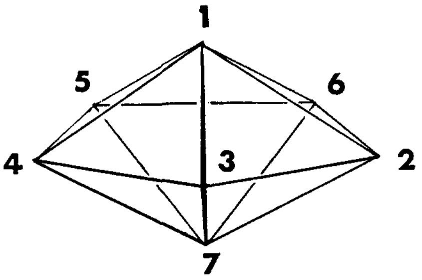

Figure 1. Numbering system for 2,4-$C_2B_5H_7$. The carbon atoms occupy positions 2 and 4.

In a control experiment, parent $C_2B_5H_7$ did not react with 1 *M* aqueous HCl at 50°.

Bromination. The reaction of bromine with $C_2B_5H_7$ in the presence of aluminum powder yielded only one detectable carborane product, characterized as the 5-bromo derivative. Electrophilic halogenation at the equivalent B(5) and B(6) positions is consistent with the calculated ground-state charge distribution[7] for 2,4-$C_2B_5H_7$, in which these boron atoms are assigned the highest negative charge (−0.179) in the cage.

The C-bromo derivative was obtained by treatment of $Li_2C_2B_5H_5$ with HCl and subsequent reaction with Br_2. Owing to polymerization of $LiC_2B_5H_6$ as described above, the yield of 2-$BrC_2B_5H_6$ was only 4%.

Degradation in Basic Solution. The well-known conversion of 1,2- and 1,7-$C_2B_{10}H_{12}$ to open-cage 1,2- and 1,7-$C_2B_9H_{12}^-$ anions[10,11] by Lewis bases suggested that $C_2B_5H_7$ might undergo an analogous degradation to $C_2B_4H_7^-$ *via* removal of an apex B–H group by ethoxide attack. Again, however, the small carborane behaved differently from the icosahedral systems. Since preliminary experiments showed that $C_2B_5H_7$ is completely degraded by excess ethanolic KOH at room temperature, the evolved H_2 was measured as a function of temperature during slow warming of the reaction mixture from −31° to +50°. At −31° very little reaction was observed, but as the temperature was gradually increased, H_2 was evolved in continuous (not stepwise) fashion. After a final period of 20 hr at 50°, the total accumulated H_2 was 5.85 mmol/mmol of carborane reactant. Subsequent glpc analysis of the mixture revealed no other volatile products. Isolation of the remaining solids and treatment of these with anhydrous HCl gave water, triethoxyborane, and boric acid.

The positive charge predicted[7] for B(1) and B(7) (+0.334) and for B(3) (+0.031) in 2,4-$C_2B_5H_7$ suggests high susceptibility to base attack at these positions [particularly the sterically more accessible B(1) and

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B(7)], which may account for the ease of base degradation. Studies of the behavior of B-alkyl derivatives such as 1,7-$(CH_3)_2C_2B_5H_5$[12] toward basic reagents should provide an interesting test of this proposition.

Experimental Section

All operations were carried out in a high-vacuum system using standard techniques. Glpc separations were conducted on 9.5 ft × 0.25 in. columns of Apiezon-L or tricresyl phosphate, both 30% by weight on Chromosorb-W; products were collected in traps at $-196°$. The chromatography of products from solution reactions usually entailed a loss of 10–15% of the carboranes present, owing to the large quantities of solvents which hindered complete recovery. Yields reported herein are not corrected for this effect and represent actual quantities of pure products obtained.

The solvents were reagent grade and were used without further purification except for *n*-pentane, which was washed with concentrated H_2SO_4 and acidic $KMnO_4$ solution and distilled from $LiAlH_4$ prior to use. *n*-Butyllithium in hexane (Alfa), CP grade aluminum powder (Baker), bromine (Baker), and methyl iodide (Baker) were used as received.

The 2,4-dicarba-*closo*-heptaborane(7) was supplied in part by a gift from the Aerojet-General Corp., Los Angeles, Calif. Small quantities of this carborane were also prepared by pyrolysis of 2,3-dicarba-*nido* hexaborane(8) as described in the literature.[13]

The instruments used in this work included a Beckman IR-8 grating infrared spectrophotometer, a Hitachi Perkin-Elmer RMU-6E mass spectrometer, a Hitachi Perkin-Elmer R-20 nmr spectrometer (for proton resonance), and a Varian HA-100 nmr spectrometer (for 32.1-MHz ^{11}B resonance). Gas infrared spectra were obtained in Pyrex cells of 3.5 and 7.0 ml fitted with NaCl windows.

2,4-Dimethyl-2,4-dicarba-*closo*-heptaborane(7). The parent carborane (1.05 mmol) was stirred with 2.35 mmol of *n*-butyllithium in a solvent consisting of 1 ml of hexane and 2 ml of diethyl ether. Precipitation of the white $Li_2C_2B_5H_5$ was noticeable after 20 min at room temperature. The reaction was continued for 20 hr. Since the dilithiocarborane was found to be somewhat soluble in ether–hexane, the solvent was evaporated and replaced with pure pentane. The solid was filtered, washed with two 3-ml portions of pentane in the vacuum line, dried, and suspended in 3 ml of diethyl ether, and 2.35 mmol of methyl iodide was added. After stirring the mixture for 20 hr the volatile materials were separated by glpc. The products obtained were 2,4-$(CH_3)_2C_2B_5H_5$ (0.76 mmol) and 2-$CH_3C_2B_5H_6$ (0.04 mmol, identified from its ir spectrum and glpc retention time). The mass spectrum of 2,4-$(CH_3)_2C_2B_5H_5$ contains a sharp cutoff at *m/e* 114, corresponding to the $^{12}C_4{}^{11}B_5{}^1H_{11}{}^+$ parent ion. The 32.1-MHz ^{11}B nmr spectrum of the neat liquid contains a doublet of area 2 at δ -5.4 ppm relative to external $(C_2H_5)_2O \cdot BF_3$ (J = 165 Hz), assigned to B(5)–H and B(6)–H; a doublet of area 2 at δ $+18.0$ (J = 177 Hz), assigned to B(1)–H and B(7)–H; and a doublet of area 1 at δ -7.6 (J = 175 Hz), assigned to B(3)–H. These data are slightly different from an earlier spectrum[14] obtained at 12.8 MHz. The proton nmr spectrum is identical with that reported earlier,[14] within probable experimental error. The ir spectrum contains absorptions at 3020 (m), 2990 (m), 2950 (vs), 2890 (s), 2600 (vs), 1450 (s, b), 1310 (m), 1200 (s), 1070 (w), 960 (s), 900 (m), 855 (m), 790 (s), and 735 (s) cm^{-1}. The vapor pressure is 60 mm at 22° and 1.5 mm at $-40°$.

2-Methyl-2,4-dicarba-*closo*-heptaborane(7). A suspension of $Li_2C_2B_5H_5$ (1.0 mmol) in 4 ml of diethyl ether was prepared as described above. Exactly 1.0 mmol of methyl iodide was added and the mixture was stirred for 20 hr, following which 2.0 mmol of HCl was added and the mixture was stirred for an additional 2 hr. Chromatography of the reaction mixture yielded 2-$CH_3C_2B_5H_6$[15] (0.60 mmol), 2,4-$(CH_3)_2C_2B_5H_5$ (0.06 mmol), and 2,4-$C_2B_5H_7$ (0.04 mmol), all identified from their infrared spectra and glpc retention times. The vapor pressure of the 2-methyl derivative is 110 mm at 22° and 3 mm at $-40°$. The ^{11}B nmr spectrum (32.1 MHz, neat liquid) exhibits a doublet of area 2 at δ $+18.8$ ppm relative to external $(C_2H_5)_2O \cdot BF_3$ (J = 179 Hz), assigned to B(1)–H and B(7)–H; a broad doublet of area 2 at δ -5.4 (J = 170 Hz), assigned to B(5)–H and B(6)–H; and a doublet of area 1 af δ -8.2 (J = 179 Hz), assigned to B(3)–H.

2-Trimethylsilyl-2,4-dicarba-*closo*-heptaborane(7). A mixture of 1.5 mmol of $Li_2C_2B_5H_5$ in 1.5 ml of pentane was prepared and 1.47 mmol of trimethylsilyl chloride (Matheson Coleman and Bell) was added. After 3 hr of reaction time, 1.62 mmol of anhydrous HCl was added and the mixture was stirred for 16 hr. Chromatographic separation of the products yielded 0.068 mmol of 2-$(CH_3)_3SiC_2B_5H_6$ together with unreacted $Si(CH_3)_3Cl$ and 0.11 mmol of $C_2B_5H_7$. The mass spectrum of 2-$(CH_3)_3SiC_2B_5H_6$ contains a cutoff peak at *m/e* 160 corresponding to the $^{30}Si^{12}C_5{}^{11}B_5{}^1H_{15}{}^+$ parent ion, and a fragmentation pattern which is consistent with the presence of one Si and five B atoms. The ir spectrum contains bands at 2960 (s), 2900 (m), 2600 (vs), 1410 (w), 1330 (w, b), 1255 (vs), 1200 (s), 1150 (m, b), 1100 (w), 1030 (m), 905 (w, b), 830 (vs), 760 (m), and 690 (w) cm^{-1}. This compound is identical with the major product of the pyrolysis[16] of 2-trimethylsilyl-2,3-dicarba-*nido*-hexaborane(8), $(CH_3)_3SiC_2B_4H_7$.

Polymerization of 2-Lithio-2,4-dicarba-*closo*-heptaborane(7). A 1.0-mmol quantity of anhydrous HCl was added to 1.0 mmol of $Li_2C_2B_5H_5$ suspended in 3.0 ml of diethyl ether. After stirring for 3 hr at room temperature, during which 0.13 mmol of H_2 was collected, the only volatile product detected on glpc analysis was $C_2B_5H_7$ (0.11 mmol). The solid remaining was again suspended in diethyl ether and 2.09 mmol of methyl iodide was added. Following a 23-hr reaction period, chromatography yielded no detectable mono- or dimethylcarborane products.

Similar treatment of 1.42 mmol of $Li_2C_2B_5H_5$ with 3.02 mmol of HCl for 20 hr produced 1.13 mmol of H_2. An additional 1 mmol of HCl was added, which produced 0.61 mmol of H_2. The addition of 2.0 more mmol of HCl to the system, followed by stirring for 20 hr, yielded another 0.66 mmol of H_2, but at this point the presence of excess HCl was evident from vapor pressure measurements in the reactor. Separation of the volatile materials by glpc gave 0.22 mmol of $C_2B_5H_7$. The solid products were extracted with ether, which dissolved a portion of the material. The ether-insoluble solid gave a negative boron flame test, but evaporation of the ether solution yielded a brown solid which gave a positive boron flame test. The ir spectrum of this latter material, taken as a thin film between NaCl plates, contains a strong, sharp B–H stretching band at 2600 cm^{-1}, but is otherwise uninformative. The mass spectrum at 300° contains a series of peak groupings, each displaying a characteristic boron isotope spread, which are strongly suggestive of a high-molecular-weight material consisting of $C_2B_5H_x$ cage units. Significant intensities are present up to *m/e* 400, the limit of the spectrum. Intense peak groupings having cutoffs at *m/e* 85 and 169 are assigned to $C_2B_5H_6{}^+$ and $H_6B_5C_2{-}C_2B_5H_5{}^+$ fragments. The fact that no H_2 was evolved during the treatment of $C_2B_5H_7$ with C_4H_9Li is additional evidence that the polymerization occurred without significant cage degradation.

Attempted Synthesis of the 2,4-Dicarboxylic Acid. A suspension of 1.55 mmol of $Li_2C_2B_5H_5$ in 2.5 ml of diethyl ether was saturated with CO_2 gas and stirred for 24 hr. Addition of 4 ml of 3 *M* aqueous HCl to the mixture at 0° gave H_2 measured as 6.5 mmol.

5-Bromo-2,4-dicarba-*closo*-heptaborane(7). To a mixture of 1.0 mmol of aluminum powder, 3.0 mmol of bromine, and 4 ml of carbon disulfide was added 1.0 mmol of $C_2B_5H_7$ at $-10°$. When the reaction subsided, the mixture was allowed to warm to room temperature and was stirred for 20 hr. Separation of the volatile materials by glpc yielded only one significant product, 5-$BrC_2B_5H_6$ (0.38 mmol). The ir spectrum contains absorptions at 2635 (vs), 1220 (vs), 1105 (vs), 1050 (m), 870 (m), 840 (mw), 800 (mw), and 720 (s) cm^{-1}. The mass spectrum contains a sharp cutoff at *m/e* 166, corresponding to the $^{81}Br^{12}C_2{}^{11}B_5{}^1H_6{}^+$ parent ion. The ^{11}B nmr spectrum in CS_2 solution exhibits a doublet of area 2 at δ $+20.7$ ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (J = 184 Hz), assigned to B(1)–H and B(7)–H; a doublet of area 1 at δ -5.0 (J = 180 Hz), assigned to B(3)–H; a broad doublet of area 1 centered at δ -2.2 ($J \sim 185$ Hz), assigned to B(6)–H; and a singlet at δ -5.7, largely hidden by neighboring bands, which is assigned to B(5)–Br. The fact that the doublets arising from B(1,7) and B(3) in the parent compound are not collapsed in this spectrum confirms that the bromine substitution is at B(5).

2-Bromo-2,4-dicarba-*closo*-heptaborane(7). A suspension of 1.0 mmol of $Li_2C_2B_5H_5$ in 4 ml of diethyl ether was allowed to react with 1.0 mmol of anhydrous HCl for 3 hr. After adding 1.0 mmol of Br_2 and stirring for 20 hr, an additional 1.0 mmol of HCl was

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added. Separation of the volatile products by glpc gave 0.03 mmol of 2-$BrC_2B_5H_6$ and 0.17 mmol of $C_2B_5H_7$. The mass spectrum of the 2-bromo derivative contains an intense parent grouping, with a sharp cutoff at *m/e* 166 corresponding to the $^{81}Br^{12}C_2{}^{11}B_5{}^1H_6{}^+$ ion. An almost equally intense grouping with a cutoff at *m/e* 85 indicates substantial cleavage of the C–Br bond in the spectrometer (in contrast, the mass spectrum of 5-$BrC_2B_5H_6$ shows very little evidence of fragmentation other than hydrogen abstraction). The ir spectrum has absorptions at 2620 (vs), 1195 (s), 1080 (s), 1030 (s), 890 (m), 835 (m), 810 (s), 780 (sh), and 710 (s) cm^{-1}.

The ^{11}B nmr spectrum (CS_2 solution) confirms the bromine substitution at C(2), since none of the doublets arising from B–H coupling in the spectrum[17, 18] of 2,4-$C_2B_5H_7$ is collapsed, and B(5)–H and B(6)–H are rendered nonequivalent. Partially overlapped doublets, each of area 1, are centered at δ −9.0 ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (J = 186 Hz), δ −8.0 ($J \sim$ 160 Hz), and δ −3.2 ($J \sim$ 160 Hz). Comparison with the spectrum[17, 18] of unsubstituted 2,4-$C_2B_5H_7$ suggests that these resonances arise from B(3)–H, B(5)–H, and B(6)–H, respectively, although these assignments are equivocal at present. A doublet of area 2, centered at δ +17.5 (J = 186 Hz), is uniquely assigned to the equivalent B(1)–H and B(7)–H bonds.

Degradation of 2,4-Dicarba-*closo*-heptaborane(7) by Alcoholic Base. A mixture of 1.0 mmol of $C_2B_5H_7$ and 3.0 mmol of potassium hydroxide in absolute ethanol was stirred at −31° for 6 hr, during which 0.1 mmol of H_2 was evolved. The temperature was raised to −23° and then to −16°, at which the rate of H_2 evolution was appreciable. The mixture was stirred at −16° for 75 hr, which gave an additional 1.26 mmol of H_2. Subsequent reaction periods of 70 hr at 0°, 60 hr at 25°, and 20 hr at 50° liberated 3.71, 0.72, and 0.16 mmol of H_2, respectively. After removal of all solvent, which contained no detectable volatile products as shown by glpc analysis, the remaining solid material was suspended in pentane and treated with 6.8 mmol of anhydrous HCl. Glpc analysis of all volatile materials gave 2.9 mmol of HCl, 2.0 mmol of H_2O, and 0.78 mmol of triethoxyborane, which was identified from its ir, proton nmr, and mass spectra. Ir analysis of the remaining solid indicated only boric acid.

Acknowledgments. We thank Dr. R. E. Williams of the Aerojet-General Corporation for a generous gift of a mixture of the lower caboranes. This work was supported by the Office of Naval Research.

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Competitive Electron Transfer. Activity-Defined Formation Constants of Cerium(III) Nitrate Complexes Based on Reaction with the Nitrate Free Radical[1]

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Abstract: The rate constant (k_{II}) for the bimolecular electron-transfer process, $Ce^{III} + NO_3 \rightarrow Ce^{IV}NO_3{}^-$, was measured by a kinetic flash photolysis method at 25 ± 1° in aqueous solutions with stoichiometric concentrations of nitric acid ([$HONO_2$]) ranging from about 10^{-3} to 15 M. The observed k_{II}'s were correlated against the activity of undissociated $HONO_2$ (a_u) to keep all changes in solvent composition on the same definable basis. The functional behavior suggested by this correlation was interpreted by a theoretical-chemical model which presumes the participation of different Ce^{III} complexes, each of which competes in consuming NO_3 at a fixed specific rate (k_i) and whose relative concentrations are controlled by the $HONO_2$ environment. It is shown that no fewer than four formation constants (K_0, K_1, K_2, and K_3) interrelating five different Ce^{III} species (C_0, C_1, C_2, C_3, and C_4) are required to fit the data for nitrate solutions where $[H^+] \geq 1.0$ M, and that each formation constant (K_i) is described by an equilibrium of the simple stoichiometric form $C_i + a_u = C_{i+1}$. It is significant that this experimental approach defines a set of thermodynamic K_i's which are constant over the entire a_u range, eliminating their usual dependence upon ionic strength and making it possible to evaluate formation constants in concentration ranges hitherto inaccessible by other methods. Evidence is given to show that the "bare" hydrated Ce^{III} species is not possible in this solvent system and that C_0 possesses at least one nitrate ligand. Arguments are given to explain the trends and relative sizes of the k_i's and to explain why they are so far from the diffusion-controlled limit. It remains to be shown whether this new method of estimating formation constants based upon a spontaneous *competitive electron transfer* among structurally different metal complexes and a free radical can be extended to other systems.

In an earlier communication[3] we proved that the NO_3 free radical can be generated efficiently at room temperature by the photolysis of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, dissolved in aqueous $HONO_2$ solution. Without information about the exact structures of the Ce^{IV} and Ce^{III} complexes involved, the primary photochemical process was represented by a generalized notation as

$$Ce^{IV}NO_3{}^- + h\nu \longrightarrow Ce^{III} + NO_3 \qquad (I)$$

to suggest that the radical is released to the solution following an intramolecular electron transfer in the excited Ce^{IV} complex. Contrary to opinion expressed elsewhere[4] that the NO_3 in this system arises from the

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[1] This work was made possible by the U. S. Atomic Energy Commission (Contract No. AT-(40-1)-2825) and the National Science Foundation (Grant No. GP-2671). R. W. G. is indebted for personal support to the U. S. Steel Foundation and for a Public Health Service Fellowship (No. F1-GM-28, 402) from the National Institute of General Medical Sciences. We are grateful to R. C. Gross for conducting some preliminary experiments, to Dr. R. E. Rummel for drawing Figure 1, and to Dr. L. J. Schaad for assistance in computer programming. T. W. M. also wishes to thank Drs. G. R. Choppin, H. M. Neumann, and B. A. Soldano for their contributions to the success of this research.

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