by the investigation of the reaction of CF_3SiF_2I with water vapor. Mixing of the two vapors was effected in a gas-mixing cell in which one compartment was a gas infrared cell. Infrared spectroscopic monitoring of the system revealed initial formation of CF_3SiF_3 and a compound with a strong absorption at 1180 cm^{-1}, a frequency typical of Si–O–Si stretches in fluorosiloxanes. Although not observable in the infrared spectra, HI is also initially present. Admission of additional water vapor and/or subjection of the reactants to quench-vaporize cycles result in, sequentially, (1) depletion (and finally consumption) of the CF_3SiF_2I, (2) loss of the siloxane, and (3) appearance of the known hydrolytic products of CF_3SiF_3—CF_3H and SiF_4—and formation of CF_2HI.

The presence of HI in the system strongly suggests hydrolytic attack of the silicon–iodine bond to give a silanol, which rapidly condenses to a siloxane

$$CF_3SiF_2I + H_2O \rightarrow HI + CF_3SiF_2OH$$

$$2CF_3SiF_2OH \rightarrow CF_3SiF_2OSiF_2CF_3 + H_2O$$

The identity of the siloxane was verified by its independent synthesis from the reaction of CF_3SiF_2I with HgO (see Experimental Section for details). The siloxane itself is attacked by water vapor—somewhat less rapidly than the starting material—to give CF_3SiF_3 and involatile polymeric materials.

An important related experiment is the determination of the source of difluorocarbene responsible for the formation of CF_2HI (HI is one of the few efficient room-temperature traps for CF_2). The facts that CF_2HI is not observed so long as CF_3SiF_2I remains in the system and that SiF_3I is not observed among the products suggest that CF_3SiF_3 may be the source of the CF_2. In a control experiment, CF_3SiF_3 in the presence of excess HI was exposed to water vapor under conditions similar to those described above for the hydrolysis of CF_3SiF_2I. CF_2HI is indeed formed under these conditions, along with SiF_4. Anhydrous HI alone does not affect CF_3SiF_3.

CF_3SiF_2Cl and CF_3SiF_2Br behave similarly to CF_3SiF_2I on exposure to water vapor. Each suffers hydrolytic attack on the heavier halogen and generates CF_3SiF_3 through the intermediate siloxane $(CF_3SiF_2)_2O$. A secondary reaction of CF_2 with HBr leads to CF_2HBr; however, reaction of CF_2 with HCl at 25° is apparently too slow to suppress effectively the dimerization of the carbene to C_2F_4.

In summary, the hydrolytic reactions suggest the rate of attack of water vapor on Si–X bonds follows the order $I > Br > Cl$, $O > F$. When only Si–F bonds are present—in CF_3SiF_3—the Si–F bond is apparently not directly attacked.[20] Instead, water vapor, perhaps acting through an intermediate acid–base complex, promotes α transfer of fluorine to form SiF_4 (again, perhaps complexed) and CF_2. In the presence of the unusually good halocarbene traps HBr and HI the difluorocarbene can be trapped as CF_2HX.

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Registry No. CF_3SiF_2I, 27668-68-4; CF_3SiF_2Br, 54484-28-5; CF_3SiF_2Cl, 54484-29-6; CF_3SiF_3, 335-06-8; $(CF_3SiF_2)_2O$, 54484-30-9; $SbCl_3$, 10025-91-9; $SbCl_5$, 7647-18-9; HgO, 21908-53-2.

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Kinetics and Mechanism of Carborane Formation

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The kinetics of 1,2-dicarba-*closo*-dodecaborane(12) formation from $B_{10}H_{12}[(CH_3)_2S]_2$ and several acetylenes [$HC{\equiv}CCH_2Br$, $HC{\equiv}CCH_2OC({=}O)CH_3$, $HC{\equiv}C(CH_2)_2CH_3$, $HC{\equiv}C(CH_2)_5CH_3$, $HC{\equiv}C(CH_2)_3Cl$] have been studied. A mechanism is proposed consistent with the data obtained. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ correlate well with the Taft polar substituent constants for the acetylene substituents.

A wide variety of substituted 1,2-dicarba-*closo*-dodecaborane(12) derivatives have been synthesized and characterized.[2-4] The most common method for their preparation is through the use of diligand derivatives of decaborane, $B_{10}H_{12}L_2$ (L = Lewis base), and acetylenes. Alkyl derivatives are generally prepared in low yields, ca. 30–40%, from the corresponding acetylenes while other derivatives from acetate and halogen-containing acetylenes are prepared in higher yields (ca. 80–90%).

Except for some preliminary work carried out by the authors at the Rohm and Haas Redstone Research Laboratories in the middle and late 1960's, very little attention has been given to the kinetics of carborane formation. Our preliminary studies indicated that the reaction was first order in $B_{10}H_{12}L_2$ and

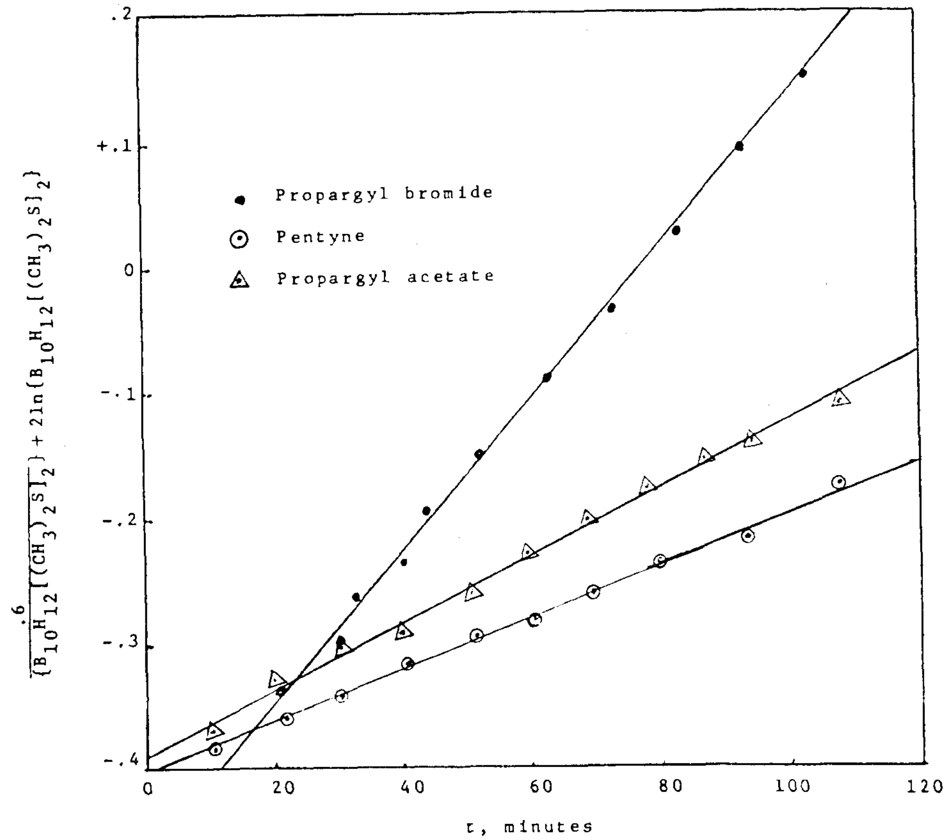

Figure 1. Typical plots to determine k_1K. [Acetylene]$_0$ = 0.30 M, $[B_{10}H_{12}[(CH_3)_2S]_2]_0$ = 0.30 M, and $[(CH_3)_2S]_0$ = 0.00 M; T = 37°.

first order in acetylene.[5] The reaction rate was retarded by the addition of excess L [L = CH_3CN, $(C_2H_5)_2S$]. These data suggested the reaction sequence

$$B_{10}H_{12}L_2 \rightleftarrows B_{10}H_{12}L + L \qquad (1)$$

$$B_{10}H_{12}L + RC{\equiv}CR \rightarrow B_{10}C_2H_{10}R_2 + H_2 + L \qquad (2)$$

An intermediate of the type $B_{10}H_{12}L$ has been suggested by Beachell.[6] Hawthorne has confirmed the importance of the intermediate in a kinetic study of $B_{10}H_{10}{}^{2-}$ preparation from $B_{10}H_{12}L_2$[7] and suggested that the $B_{10}H_{12}L$ intermediate may be involved in carborane formation.[8] Stable $B_{10}H_{12}L$ compounds can be isolated. However, these are not identical with (but are convertible into) the kinetic intermediate.[7]

We wish to report here the results of a study on the mechanism and kinetics of the formation of 1,2-dicarba-*closo*-dodecaboranes from $B_{10}H_{12}L_2$ and a variety of acetylenes.

Results

Bis(dimethyl sulfide)-*nido*-decaborane(12) undergoes a first-order ligand-exchange reaction with diethyl sulfide at a rate (k = 3.21 × 10^{-4} sec^{-1} at 38°) independent of the concentration of free ligand. This suggests that the rate-determining step is dissociation of $B_{10}H_{12}[(CH_3)_2S]_2$ according to

$$[(CH_3)_2S]_2B_{10}H_{12} \rightarrow [(CH_3)_2S]B_{10}H_{12} + (CH_3)_2S$$

Similar dissociations have been shown to be the important step in other ligand-exchange reactions of $B_{10}H_{12}L_2$ compounds.[8] Attempts to measure the equilibrium constant for the $B_{10}H_{12}[(CH_3)_2S]_2$ system were frustrated by the apparent precipitation of a monoligand species (or polymer thereof) in the absence of excess ligand. However our most careful attempts gave a maximum value of ca. 4 × 10^{-3} for K_{diss}.

From our initial runs it was apparent that the reaction rates of bis(dimethyl sulfide)-*nido*-decaborane(12) and acetylenes were slower than the ligand exchange reaction. Therefore the data were analyzed according to the mechanism

$$BL_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} BL + L$$

$$BL + A \xrightarrow{k_1} \text{carborane} + H_2 + (CH_3)_2S$$

where $BL_2 = B_{10}H_{12}[(CH_3)_2S]_2$, $BL = B_{10}H_{12}[(CH_3)_2S]$, and $L = (CH_3)_2S$. Treating BL as a steady-state intermediate, we have

$$[BL] \cong \frac{k_f[BL_2]}{k_r[L] + k_1[A]}$$

so

$$\frac{d[C]}{dt} \cong \frac{-d[BL_2]}{dt} \cong \frac{k_1k_f[BL_2][A]}{k_r[L] + k_1[A]}$$

and if $[BL_2]_0 = [A]_0$, $[BL_2] = [A] = \chi$ and $[L] = [L]_0 + 2([BL_2]_0 - \chi)$; assuming $k_1 < 2k_r$, dividing by k_r, and integrating

$$([L]_0 + 2[BL_2]_0)\left(\frac{1}{[BL_2]} - \frac{1}{[BL_2]_0}\right) + 2\ln\frac{[BL_2]}{[BL_2]_0} = k_1Kt$$

which arranges to

$$\frac{2[BL_2]_0 + [L]_0}{[BL_2]} + 4.606\log[BL_2] = k_1Kt + \frac{2[BL_2]_0 + [L]_0}{[BL_2]_0} + 4.606\log[BL_2]_0$$

Figure 1 shows typical plots from which values of k_1K were obtained.

The reactions of $B_{10}H_{12}[(CH_3)_2S]_2$ with various acetylenes were investigated over a temperature range of 37–60°.

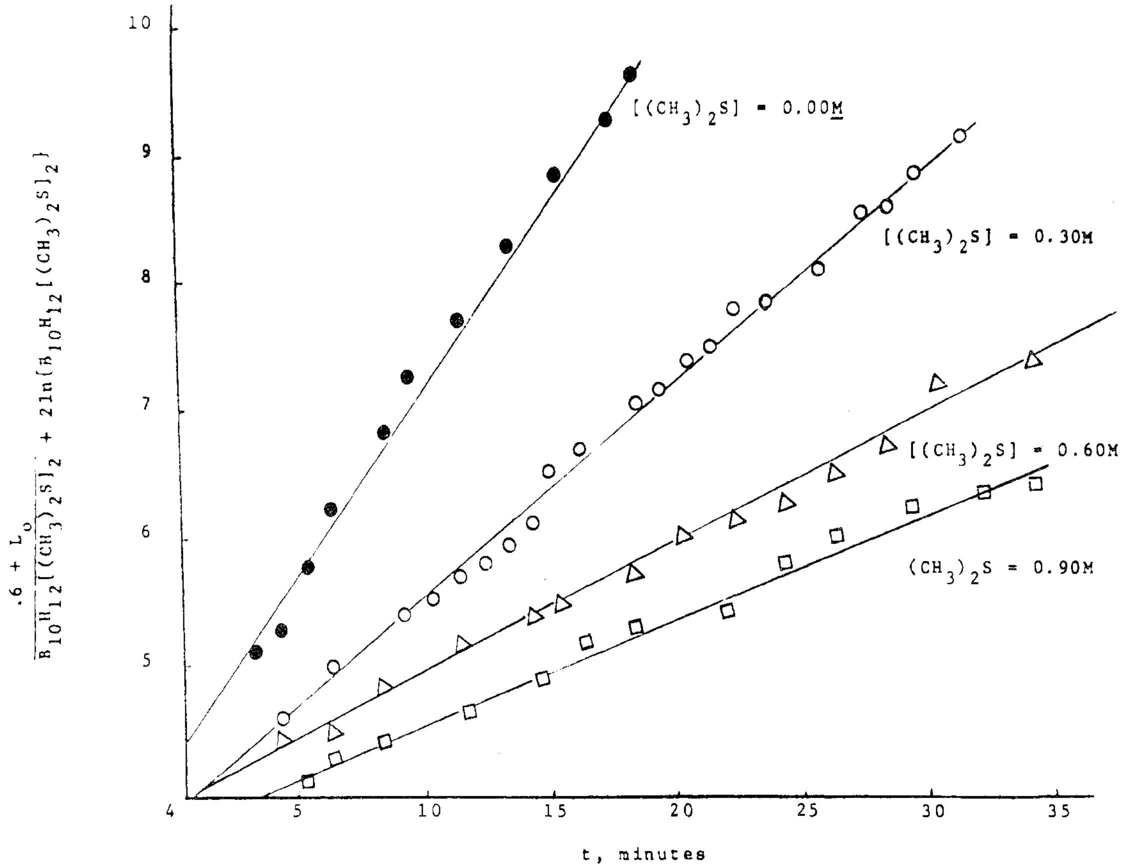

Figure 2. Variation in rate with initial ligand concentration at 56°. [Propargyl bromide]$_0$ = $[B_{10}H_{12}[(CH_3)_2S]_0 = 0.300\ M$.

Reactions were carried out by monitoring the appearance of unbound $(CH_3)_2S$ and the disappearance of bound $(CH_3)_2S$ by proton NMR. In general, the reactions were followed to 75% completion. Acetylenes were chosen to give as large a variation in inductive effects as possible, subject to the limitations imposed on the acetylene by the system (i.e., the acetylene could have no strongly coordinating site, e.g., OH, CN, $R_2C{=}O$, NH_2; no strongly oxidizing group could be used, e.g., NO_2). Acetylenes with functional groups attached directly to the C≡C linkage gave extremely low yields (<10%) and therefore their kinetics were not studied. Products were identified by gas chromatography and percent yield of the 1,2-dicarba-*closo*-dodecaborane(12) was measured. Propargyl bromide, propargyl acetate, and 2-butyne-1,4-diacetate all gave yields of carborane in excess of 80%. 1-Octyne and 1-pentyne gave yields of only 30% although the reactions followed second-order kinetics (Figure 1). Yields of carboranes were *independent of temperature* (over the range of 38–100° for octyne) suggesting that the activation parameters for both carborane formation and the formation of side products are essentially the same. In all cases the reaction mixture remained homogeneous throughout the course of the investigation.

Table I contains the collected rate data. Experimental difficulties associated with the sensitivity of the NMR technique used to follow the reaction and with the solubility of $B_{10}H_{12}[(CH_3)_2S]_2$ precluded the desired wide variation in initial reactant concentration. However, it should be pointed out that initial addition of 0.30 *M* dimethyl sulfide tripled the half-life of the reaction with no variation in the observed value of k_1K. Figure 2 illustrates the variation in rate with different concentrations of $(CH_3)_2S$ for propargyl bromide.

The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for each reaction are also reported in Table I. It should be pointed out that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ reported here are really sums of ΔH or ΔS for the equilibrium (or equilibria) plus $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the slow step. Hence it is not surprising that the values of $\Delta S^\ddagger$ are very different from those expected for a simple bimolecular reaction. A three-step mechanism could also account for the very high $\Delta S^\ddagger$

$$BL_2 \rightleftarrows BL + L$$

$$BL + A \rightleftarrows BLA$$

$$BLA \xrightarrow{\text{slow}} \text{carborane} + L + H_2$$

The net contribution of the two equilibria to $\Delta S^\ddagger$ is small, while the contribution of the dissociative step may vary from near zero to highly positive as the transition state varies from "reactant-like" to "product-like". This three-step mechanism is, of course, kinetically indistinguishable from the two-step mechanism used in this analysis. We have preferred the simpler mechanism in view of the uncertainties of interpreting $\Delta S^\ddagger$ for complex processes in solution.[9] Strict interpretations of $\Delta S^\ddagger$ for such processes are notoriously uncertain. Steric factors do not seem to be especially important since the $\Delta S^\ddagger$ of the disubstituted acetylene does not differ markedly from the $\Delta S^\ddagger$ of propargyl bromide or acetate. It is interesting to note that $\Delta S^\ddagger$ values for the more nucleophilic acetylenes (1-octyne, 1-pentyne, 5-chloro-1-pentyne) are much smaller than those for the less nucleophilic acetylenes.

The values of $\Delta H^\ddagger$ reflect the nucleophilicity of the acetylenes. 1-Octyne, 1-pentyne, and 5-chloro-1-pentyne all have lower activation energies than propargyl bromide or acetate and 2-butyne-1,4-diacetate. In fact $\Delta H^\ddagger$ and $\Delta S^\ddagger$ correlate quite well with the Taft polar substituent constant, σ^*, for monosubstituted acetylenes (Figure 3).

A plot of $\Delta H^\ddagger$ vs. $\Delta S^\ddagger$ for the various acetylenes gives a straight line with an isokinetic temperature of 12°, so that it is not surprising that the variation in rates among the acetylenes is small.

Attempts were made to identify the by-products obtained in the low-yield reactions. While a complete characterization

Table I. Rates of Carborane Formation[a]

Acetylene	$[(CH_3)_2S]_0$, M	T, °C	k_1K, sec^{-1}	ΔH (±0.7), kcal/mol	ΔS (±2.0), eu
Propargyl bromide	0.0	37.0	1.04×10^{-4}	36.1	40
	0.0	48.0	7.68×10^{-4}		
	0.0	56.0	1.68×10^{-3}		
	0.3		1.74×10^{-3}		
	0.6		1.52×10^{-3}		
	0.9		1.46×10^{-3}		
	0.0	58.1	5.76×10^{-3}		
Propargyl acetate	0.0	36.8	4.35×10^{-5}	34.9	34
	0.0	41.1	9.32×10^{-5}		
	0.0	56.5	1.36×10^{-3}		
	0.0	58.8	1.95×10^{-3}		
5-Chloro-1-pentyne	0.0	36.8	1.80×10^{-5}	26.6	6
	0.0	37.9	2.16×10^{-5}		
	0.0	56.0	2.57×10^{-4}		
	0.0	59.4	3.39×10^{-4}		
2-Butyne-1,4-diacetate	0.0	37.6	5.22×10^{-5}	33.4	29
		38.6	5.70×10^{-5}		
		57.6	1.39×10^{-3}		
1-Pentyne	0.0	37.0	3.35×10^{-5}	26.4	6
		50.6	1.90×10^{-4}		
		58.0	5.56×10^{-4}		
1-Octyne	0.0	39.0	2.62×10^{-5}	24.8	0
		39.9	2.98×10^{-5}		
		51.7	1.04×10^{-4}		
		58.7	2.90×10^{-4}		
		59.0	3.39×10^{-4}		

[a] $[B_{10}H_{12}[(CH_3)_2S]_2]_0 = 0.300$ M; $[\text{acetylene}]_0 = 0.300$ M; solvent = chloroform.

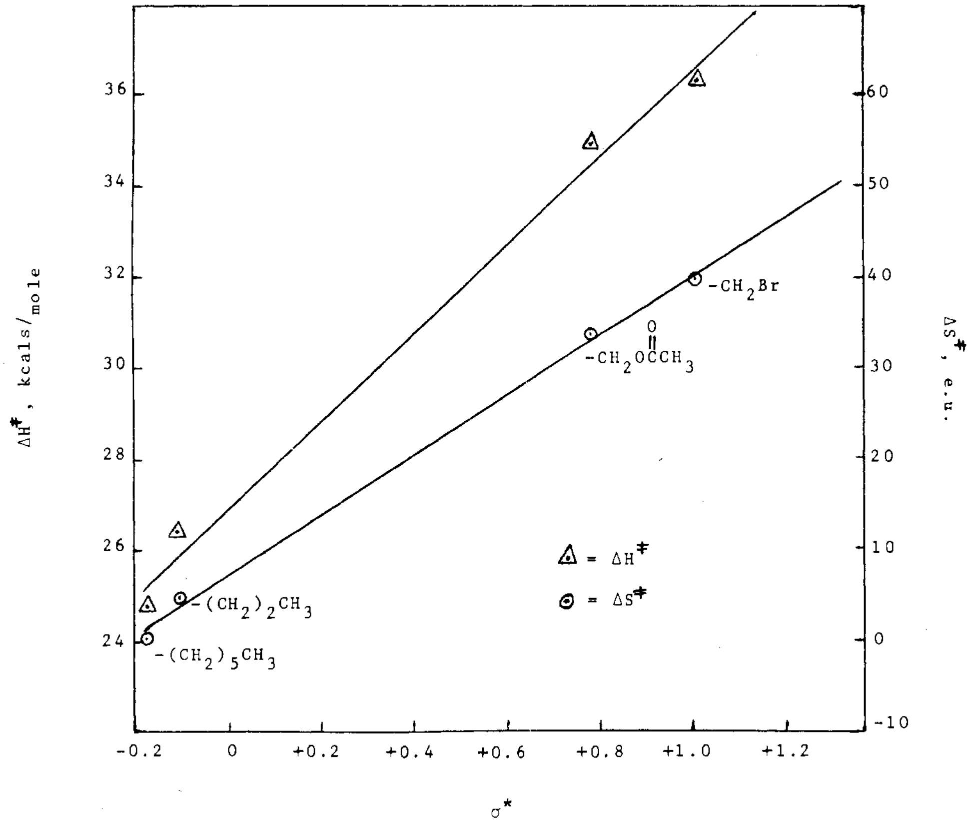

Figure 3. Plot of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ vs. Taft polar substituent constant, σ^*, for acetylenes of the type HC≡CR.

was not accomplished, the by-products are polymeric and they contain both acetylene and ligand units in addition to the boron moiety. In the case of the 1-octyne reaction with $B_{10}H_{10}[(CH_3)_2S]_2$, the by-product had a molecular weight of ~560 and elemental analysis showed approximately three $B_{10}H_{10}$ units, two octyne residues, and two dimethyl sulfide molecules. Oxidative degradation of the residue gave 1-octanoic acid. These data suggest that by-products are formed by hydroboration of the acetylene to destroy the C≡C. If this process is occurring, it is not surprising that lower yields of alkyl-1,2-dicarba-*closo*-dodecaborane(12) derivatives are obtained since it is well-known that electron-rich olefins and acetylenes hydroborate much more readily than do those containing electron-withdrawing groups.[10]

Partially deuterated $B_{10}H_{12}[(CH_3)_2S]_2$ was prepared by the method of Hawthorne[11] and the reaction with 2-butyne-1,4-diacetate studied. The amount of B–D bond breaking was determined by the abundance of deuterium in the effluent gas.

The gas composition as determined by mass spectroscopy was as follows: D_2, 24.5%; HD, 48.4%; H_2, 27.7%. The ratio $(k_1K)_D/(k_1K)_H$ was 1.09, indicative of a secondary isotope effect.

Propargyl acetate containing a terminal C–D bond was treated with $B_{10}H_{12}[(CH_3)_2S]_2$. Deuterium content of the effluent gas was not greater than the natural abundance and a strong carboranyl C–D bond at 2850 cm^{-1} appeared in the infrared spectrum of the product. Therefore, all hydrogen evolved in the synthesis of carboranes from $B_{10}H_{12}L_2$ must originate on $B_{10}H_{12}L_2$.

Discussion

The correlation between $\Delta H^‡$ and the nucleophilicity of the acetylene plus the lack of a primary deuterium isotope effect suggests that the rate-determining process is attack by the acetylene on $B_{10}H_{12}[(CH_3)_2S]$ possibly to form $B_{10}H_{12}[(CH_3)_2S]$·acetylene. $B_{10}H_{12}[(CH_3)_2S]$ is expected to be a highly reactive electrophile because of an unfilled orbital at the 6-boron atom. Details of the steps leading from $B_{10}H_{12}[(CH_3)_2S]$·acetylene to products are not clear, though experiments with terminally deuterated acetylenes rule out all mechanisms which predict loss of the acetylenic proton as hydrogen gas. An attractive sequence for carborane formation would involve loss of the second ligand molecule at the 9-boron, followed or assisted by bonding of the acetylene to the 9-boron. The C_2 residue then sits across the open end of the B_{10} moiety in position to yield the *closo*-carborane cage on loss of H_2 and minor rearrangement of carbon and boron. Other products, such as the hydroboration type suggested above, may arise from initial loss of the second ligand at B-9 to give the same transition state, followed by H–C and B–C bond formation. A positive $\Delta S^‡$, the rather wide range of $\Delta S^‡$, and the temperature-invariant carborane:by-product ratio appear more consistent with a transition state located somewhere within this dissociation–reorganization sequence rather than the preceding BL + A association.

Knoth and Muetterties have reported the preparation of a $B_{10}H_{12}(CH_3)_2S$ compound by distillation of dimethyl sulfide from $B_{10}H_{12}[(CH_3)_2S]_2$. That this compound is not the $B_{10}H_{12}(CH_3)_2S$ intermediate involved in carborane formation was shown by the fact that this monoligand derivative (a) forms carboranes only very slowly and in poor yields when heated with acetylenes and (b) reacts with $(CH_3)_2S$ to form $B_{10}H_{12}[(CH_3)_2S]_2$ only at more elevated temperatures. In fact, the NMR chemical shift of the Knoth and Muetterties compound is such that if this compound were present in the reaction solution it would have been detected. In their study of $B_{10}H_{10}{}^{2-}$ formation, Hawthorne and coworkers reached the same conclusion concerning intermediacy of the Knoth and Muetterties compound.[7]

It is clear that the $B_{10}H_{12}$(ligand) intermediates formed by the reversible dissociation of $B_{10}H_{12}(\text{ligand})_2$ compounds are very reactive species. They react with (a) other ligands to form $B_{10}H_{12}$(ligand 1)(ligand 2), (b) bases to form the $B_{10}H_{10}{}^{2-}$ ion, and (c) acetylenes to form carboranes. It is not yet possible to propose a precise structure for this intermediate; thus many details of its reactions are lacking.

Experimental Section

Materials. Reagent grade chloroform was purified by passage through alumina to remove the ethanol stabilizer.

Reagent grade dimethyl sulfide, diethyl sulfide, 2-butyne-1,4-diacetate, propargyl bromide, and 5-chloro-1-pentyne were redistilled using a 100-cm spinning-band column.

Propargyl Acetate. Propargyl alcohol (33.6 g, 0.6 mol), acetic acid (43.2 g, 0.9 mol), and *p*-toluenesulfonic acid (0.9 g) in 90 ml of methylene chloride were placed in a 300-ml flask equipped with a heating mantle, stirrer, and a short Vigreux column fitted with a condenser and water trap fashioned to return the refluxing solvent. The mixture was refluxed for 22 hr to obtain 10.7 ml of water, then cooled, and transferred to a separatory funnel. The solution was washed with 60 ml of water, 60 ml of saturated sodium bicarbonate, and again with 60 ml of water, then dried with magnesium sulfate, and filtered. The solvent was removed by a crude distillation and the product residue transferred to a smaller flask and carefully distilled to obtain 53.9 g (92%) of propargyl acetate, bp 124°.

$CH_3CO_2CH_2C{\equiv}CD$. To a solution of 5 ml of propargyl acetate in 20 ml of hexane was added 22 ml of 1.5 *M* butyllithium in hexane. After the gassing ceased, 1.5 ml of D_2O was added. The solution was then dried with magnesium sulfate and filtered. After the solvent was removed on a rotary evaporator the remaining solution was carefully distilled to give the deuterated product; ir 2580 cm^{-1}.

$B_{10}H_{12}[(CH_3)_2S]_2$. Twenty grams of sublimed $B_{10}H_{14}$ was dissolved in 125 ml of dimethyl sulfide and the solution refluxed for 3 hr. On cooling, crystals separated and the excess dimethyl sulfide was decanted from the solid. The crystals were then washed four or five times with 200-ml portions of pentane and stored at 0° under pentane. The pentane was removed by filtration followed by evaporation under vacuum immediately prior to each kinetic run; mp 125° (lit.[7] mp 124–126°).

Kinetic Procedure. Kinetic runs were carried out in NMR tubes using the Varian V-6040 variable-temperature controller with Varian HA-60IL NMR. Samples of $B_{10}H_{12}[(CH_3)_2S]_2$ (usually 0.0734 g or 0.300 mol) were weighed into the NMR tubes; chloroform, acetylene, and free ligand were added by a Hamilton microliter syringe. The tubes were sealed with pressure caps, shaken well, and used immediately.

Temperatures were measured using a YSI Model 425C thermistor thermometer with a YSI Model 403 probe at sample depth in an NMR tube. Checks against the Varian ethylene glycol temperature standard and temperature-shift calibration curve were satisfactory (±1°). Checks of the YSI thermometer against an NBS-calibrated mercury-in-glass thermometer were satisfactory within the readability of the YSI instrument (±0.1°). Temperatures were measured before and after each run; occasionally the results differed by more than 0.5° and the run was discarded.

Some runs were carried out in volumetric flasks immersed in a water bath controlled by a Sargent Thermonitor (±0.02°). Samples were withdrawn through a septum by syringe and introduced into NMR tubes, and the integrals were measured immediately.

In the NMR spectrum of $B_{10}H_{12}[(CH_3)_2S]_2$ the methyl protons apppear as a sharp singlet near 1.5 ppm. The methyl protons of free $(CH_3)_2S$ also appear as a sharp singlet at about 20 Hz further upfield. On reaction of $B_{10}H_{12}[(CH_3)_2S]_2$ with acetylenes the $B_{10}H_{12}[(CH_3)_2S]_2$ singlet decreases and the $(CH_3)_2S$ singlet increases correspondingly. The total area under the two peaks remains constant. Thus the concentration of $B_{10}H_{12}[(CH_3)_2S]_2$ in each sample was calculated by

$$[B_{10}H_{12}[(CH_3)_2S]_2] = \frac{A_1}{A_1 + A_2} \times \left[[B_{10}H_{12}[(CH_3)_2S]_2]_0 + \frac{[(CH_3)_2S]_0}{2}\right]$$

where A_1 is the area of the $B_{10}H_{12}[(CH_3)_2S]_2$ peak and A_2 is the area of the $(CH_3)_2S$ peak. In some cases, notably 5-chloro-1-pentyne, resonances of acetylene protons overlapped the $(CH_3)_2S$ protons of the diligand adduct. Appropriate corrections to the expression for diligand adduct concentration were difficult to make and thus it is not surprising that the values of $\Delta H^‡$ and $\Delta S^‡$ do not fall on the lines in Figure 3.

Calculations of k_1K were done by a least-squares procedure using a Hewlett-Packard 2000E computer system. Correlation coefficients greater than 0.99 were obtained for all rate runs. Calculations of $\Delta H^‡$ and $\Delta S^‡$ were done on the same system; correlation coefficients greater than 0.994 were found.

Registry No. $B_{10}H_{12}[(CH_3)_2S]_2$, 28377-92-6; propargyl bromide, 106-96-7; propargyl acetate, 627-09-8; 5-chloro-1-pentyne, 14267-92-6; 2-butyne-1,4-diacetate, 1573-17-7; 1-pentyne, 627-19-0; 1-octyne, 629-05-0.

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Boron-11 Nuclear Magnetic Resonance Study of the 7,9-$B_9C_2H_{12}^-$ Ion and Some Substituted Derivatives

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The 70.6-MHz ^{11}B NMR spectrum of 7,9-$B_9C_2H_{12}^-$ consists of six doublets of relative intensities 2:1:2:2:1:1 reading upfield which are assigned to B(2,5), B(8), B(3,4), B(10,11), B(6), and B(1), respectively. Substituted 7,9-$B_9C_2H_{12}^-$ derivatives obtained by reaction of Lewis bases [e.g., $CH(CN)_2^-$, $OC_2H_5^-$, and $N(C_2H_5)_3$] with *closo*-2,3-$B_9H_9C_2R_2$ (R = H, CH_3) have the base attached at B(10).

Introduction

The application of ^{11}B NMR spectral information to boron hydride research has been in existence for almost as long as the use of proton NMR spectral data in organic chemistry. However, the utilization of ^{11}B NMR data has lagged far behind proton NMR applications. This shortcoming in boron NMR has been due to (a) poor spectral resolution, (b) insufficient understanding of the relationships of ^{11}B chemical shifts to molecular structure, and (c) inadequate understanding of the bonding in boron hydrides, particularly the higher boron hydrides. With the advent of high-field Fourier transform NMR instruments and associated techniques, the resolution problem is rapidly being overcome. It is now of importance to determine the specific assignment of each boron resonance to a particular boron atom in a molecule and to do these studies for a large number of classes of boron hydride molecules. In this manner generalized empirical rules concerning structure–chemical shift relationships will be found. Such rules will greatly enhance the usefulness of ^{11}B NMR measurements.

Recently we and others have carried out structure–chemical shift studies of $B_{10}H_{12}$(ligand)$_2$,[2] B_9H_{13}(ligand),[3] $B_{10}H_{13}^-$,[4] $B_9H_{12}S^-$,[5] and 7,8-$B_9C_2H_{12}^-$.[6-8] In this paper we outline our study of the ^{11}B NMR spectra of 7,9-$B_9C_2H_{12}^-$ and specifically substituted derivatives by which we have elucidated the majority of the boron atom–chemical shift relationships of this carborane anion.

Experimental Section

The ^{11}B NMR spectra were measured on equipment consisting of a pulsed NMR apparatus built in this department operating at 70.6 MHz, a Varian 51.7-kg superconducting magnet, and a 16K Nicolet 1080 series computer. Additional details have been reported elsewhere.[9] The ^{11}B NMR spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

Spin–lattice relaxation measurements were made by the inversion–recovery method[10] at 70.6 MHz using a 40-μsec 180° pulse and a recycle time of 610 msec. Probe temperature was maintained at 26 ± 1° for all T_1 measurements.

One thousand twenty-four scans were accumulated with a sweep width of 5000 Hz at each of 16 τ values in the range of 300–22 msec (inclusive). Spin–lattice relaxation times were determined by a linear least-squares fit of the data to the equation

$$T_1 = \frac{N\Sigma\tau_i^2 - (\Sigma\tau_i)^2}{N(\Sigma L_i\tau_i) - (\Sigma L_i \Sigma\tau_i)}$$

where $L_i = \ln(1 - A_i/A_\infty)$, A_i is the peak amplitude at τ_i, and N is the number of τ's observed [$|A_\tau| \geq |A_\infty - 0.05A_\infty|$ values are omitted in the calculation of T_1]. We feel the accuracy of the T_1 values calculated by this method is better than ±10% and the standard deviation for the least-squares fit is better than ±3% of T_1 for all peaks.

The method of Hawthorne[11] was used to convert 1,7-$B_{10}C_2H_{12}$ and 9,10-Br_2-1,7-$B_{10}C_2H_{10}$ to 7,9-$B_9C_2H_{12}^-$ and 1,6-Br_2-7,9-$B_9C_2H_{10}^-$, respectively. Anal. Calcd for $(CH_3)_4N[B_9C_2H_{10}Br_2]$: C, 19.72; H, 6.06; Br, 43.74. Found: C, 20.00; H, 6.43; Br, 44.04. The synthesis of Cs[3,4-$O_2C_6H_4$-7,9-$(CH_3)_2$-7,9-$B_9C_2H_8$] (where $O_2C_6H_4$ is 1,2-phenylenedioxy) has been reported elsewhere.[12]

$(CH)_4N[C_2H_5OB_9C_2H_{11}]$. To 0.47 g (3.54 mmol) of 2,3-$B_9C_2H_{11}$ was added a solution containing 39.2 g (0.7 mol) of KOH in 40 ml of ethanol. The solution was stirred for 15 min and then CO_2 was bubbled through the solution to precipitate the excess KOH as K_2CO_3. The mixture was filtered and 20 ml of saturated aqueous tetramethylammonium chloride solution was added to the filtrate. The volume of reaction mixture was reduced to approximately 20 ml on a rotary evaporator. The resulting white crystalline product was collected and recrystallized from acetone–water. The quantity of $(CH_3)_4N[C_2H_5OB_9C_2H_{11}]$ obtained was 0.48 g (54% yield). Anal. Calcd for $C_8H_{28}B_9NO$: C, 38.17; H, 11.22. Found: C, 37.56; H, 10.82. This compound decomposes in the solid state at a moderate rate upon exposure to the atmosphere. The compound was stored in an evacuated vial prior to obtaining its elemental analysis.

$(C_2H_5)_3N \cdot B_9H_9C_2(CH_3)_2$. In a 100-ml, three-neck flask equipped with a magnetic stirring bar, gas inlet, and addition funnel was dissolved 2,3-dimethyl-2,3-dicarba-*closo*-undecaborane(11) (0.1 g, 0.62 mmol) in 20 ml of freshly distilled benzene. The triethylamine (0.3 g, 3.0 mmol) was dissolved in 10 ml of freshly distilled benzene in the addition funnel and this solution was added dropwise to the stirred solution in the flask over a 5-min period. The resulting solution was allowed to stir an additional 15 min after completing the addition. The benzene and excess triethylamine were removed at low pressure and the white residue was dried under vacuum. The product was recrystallized from acetonitrile to give 0.07 g (51%, 0.3 mmol) of the adduct. Anal. Calcd for $C_{10}H_{30}B_9N$: C, 45.88; H, 11.56; N, 5.35. Found: C, 45.96; H, 11.44; N, 5.04.

Results and Discussion

The 70.6-MHz ^{11}B NMR spectrum of $(CH_3)_3NH$[7,9-$B_9C_2H_{12}$] is presented in Figure 1. The numbering system of the nido anion is given on the right-hand side of Figure 2. The boron NMR spectrum of the bridge-deuterated derivative was previously described[7] and this indicated that the resonance centered at 22.3 ppm was associated with atoms B(10) and B(11). These atoms are located on the open face of the anion and share a single bridge hydrogen atom. This result was confirmed by observing the ^{11}B NMR spectrum while proton decoupling the bridge hydrogen resonance which yielded two