Carborane Formation in Alkyne–Borane Gas-Phase Systems. IV. A Mechanism Study of the Tetraborane(10)–Acetylene Reaction[1]

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Abstract: The reaction of B_4H_{10} with C_2H_2 in the gas phase has been examined with the aid of deuterium-labeling experiments and rate measurements at 40–60° employing the initial-rate method. Reaction orders of one and zero have been determined for B_4H_{10} and C_2H_2, respectively, in the overall reaction. The formation of the carboranes 2-$CH_3C_3B_3H_6$, 2,3-$(CH_3)_2C_3B_3H_5$, and 2,4-$(CH_3)_2C_3B_3H_5$ is first order in B_4H_{10} and shows a negative-order dependence on C_2H_2. Activation energies and entropies of activation have been determined for the formation of the major carborane products, and the effects upon the reaction rate of adding B_2H_6 and increasing the surface area have been studied. A mechanism is proposed in which the initial formation of B_4H_8 is rate determining, followed by successive addition of four C_2H_2 units to B_4H_8 to produce a polymer of composition $[C_2BH_4]_x$ as the major product. These conclusions are discussed in relation to other borane–alkyne reaction systems.

The gas-phase synthesis of carboranes from small boron hydrides and acetylene usually involves extremely complex reactions which yield inhomogenous solids and numerous volatile products.[3] Since these systems obviously offer poor prospects for detailed kinetic investigation, direct information bearing on the mechanisms of such reactions has been essentially limited to deuterium-labeling experiments.[4]

The reaction of B_4H_{10} with C_2H_2 below 70° offered a rare opportunity for a kinetic study of carborane formation in the gas phase. This system is relatively clean, yielding a homogeneous white solid and three major carborane products,[5–7] and has the mechanistically significant feature that two of the carboranes contain odd numbers of carbon atoms, thus requiring carbon–carbon cleavage steps in their formation. These considerations led us to examine in some detail the kinetics of both the overall reaction and the formation of specific carborane products.

Results

General Observations. When B_4H_{10} and C_2H_2 are mixed at 25–70° a smooth reaction occurs over a period of several hours, during which particles of a nonvolatile white solid form continuously in the vapor phase and settle to the lower half of the bulb, leaving the upper half clear. This solid, which from mass balance calculations has the approximate composition $[C_2BH_4]_x$, accounts for ~80% of the boron consumed; its extreme sensitivity to air and moisture has prevented definitive structural characterization, but its infrared spectrum and general properties suggest a polymer containing BH_2 and CH groups.[6]

The major volatile products[5] (exclusive of B_2H_6 and B_5H_9, which are normal decomposition products of B_4H_{10}) are the 2-methyl, 2,3-dimethyl, and 2,4-dimethyl derivatives of 2,3,4-tricarbahexaborane(7), $C_3B_3H_7$ (Figure 1), in respective yields[8] of 3.3, 6.5, and 5.3% based on boron consumed. Minor products, together accounting for less than 2% of the boron consumed, are 4-$CH_3CB_5H_8$, 2,3-$C_2B_4H_8$, and parent 2,3,4-$C_3B_3H_7$. When the initial C_2H_2:B_4H_{10} mole ratio is 10:1 and the reaction is quenched at an early stage, the novel carborane[9] 1,2-$C_2B_3H_7$ is obtained in appreciable yield (~6% based on boron consumed); this compound is not obtained, however, if the reaction is allowed to proceed to completion.[10]

Deuterium-Labeling Studies. The reaction of dideuterioacetylene with B_4H_{10} was investigated at C_2D_2:B_4H_{10} mole ratios of 1:1 and 10:1. In both cases, the major volatile products were identified[4d] as partially deuterated derivatives of 2-methyl-, 2,3-dimethyl-, and 2,4-dimethyltricarbahexaborane(7), in virtually the same yields as the corresponding products of the C_2H_2–B_4H_{10} reaction. Characterization of these products by infrared, nmr, and mass spectroscopy has shown that (1) no detectable H-D scrambling occurs at the nonmethylated cage carbon atoms (*i.e.*, only D is bound at these positions); (2) the methyl groups contain both D and H; (3) all three carborane products consist of both trideuterated and tetradeuterated species; and (4) the relative abundance of tetra- *vs.* trideuterated

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[1] (a) Part III: R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.*, **8**, 55 (1969); (b) presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, and abstracted in part from the Ph.D. dissertation of D. A. F., University of Virginia, 1970.

[2] National Science Foundation Graduate Fellow, 1967–1970.

[3] For recent reviews, see R. E. Williams, *Progr. Boron Chem.*, **2**, 37 (1970); R. Köster and M. A. Grassberger, *Angew. Chem., Int. Ed. Engl.*, 6, 218 (1967).

[4] (a) I. Shapiro, C. D. Good, and R. E. Williams, *J. Amer. Chem. Soc.*, **84**, 3837 (1962); (b) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963); (c) J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, and T. Onak, *Inorg. Chem.*, 7, 216 (1968); (d) D. A. Franz, J. W. Howard, and R. N. Grimes, *J. Amer. Chem. Soc.*, **91**, 4010 (1969).

[5] C. L. Bramlett and R. N. Grimes, *ibid.*, **88**, 4269 (1966).

[6] R. N. Grimes and C. L. Bramlett, *ibid.*, **89**, 2557 (1967).

[7] R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.*, **7**, 1066 (1968).

[8] Yields obtained from reactions having initial C_2H_2:B_4H_{10} mole ratio of 10:1. Relative yields of these carboranes do not vary appreciably with different reactant ratios (see ref 7).

[9] D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970).

[10] This observation initially suggested that $C_2B_3H_7$ might be an intermediate in the formation of $C_3B_3H_7$ derivatives. However, spiking of the B_4H_{10}–C_2H_2 reaction mixture with a measured quantity of $C_2B_3H_7$ produced no change in the yield of the three major tricarbahexaborane products over a 2-hr period (see Experimental Section). Further work on the chemistry of $C_2B_3H_7$ is in progress and will be reported at a later date.

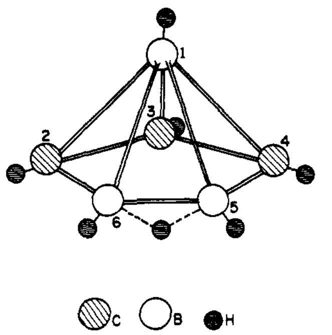

Figure 1. Structure and numbering system for 2,3,4-$C_3B_3H_7$.

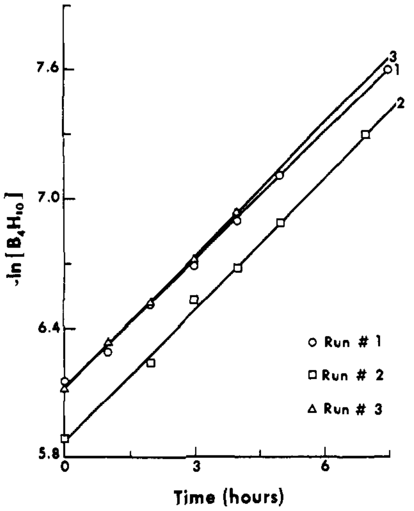

Figure 2. First-order rate plots for B_4H_{10} consumption at 50°, based on data in Table I.

carboranes is three to four times as large in the 10:1 reaction as it is in the 1:1 reaction.

These data show that with the exception of those cage carbon atoms which become methyl substituted, the original C-D bonds of C_2D_2 remain intact in the carborane products. The presence of both tri- and tetradeuterated species indicates that some, but not all, of the D atoms lost by the methyl-substituted cage carbons are retained in the carboranes. The ^{11}B nmr and ir spectra give evidence of partial deuteration at the base boron atoms, but there is no indication of deuterium substitution at the apex positions. The possibility of deuterium exchange between C_2D_2 and the carboranes was eliminated by allowing the latter compounds to stand in a 100-fold excess of C_2D_2 for 10 days at 50°, after which no evidence of exchange was found.

The diborane recovered from the 1:1 reaction contained traces of B_2H_5D (which probably forms *via* exchange of B_2H_6 with the deuteriocarboranes), but no D_2 or HD was detected.

The Kinetics of B_4H_{10} Consumption. The rates of disappearance of B_4H_{10} were measured at 40, 50, 55, and 60° by an infrared technique described in the Experimental Section. The C_2H_2 concentration was maintained effectively constant in each run by employing a large excess of C_2H_2. In different experiments, the initial C_2H_2 concentration was varied over a fourfold range to determine the reaction order with respect to C_2H_2. Expressing the rate of B_4H_{10} disappearance as

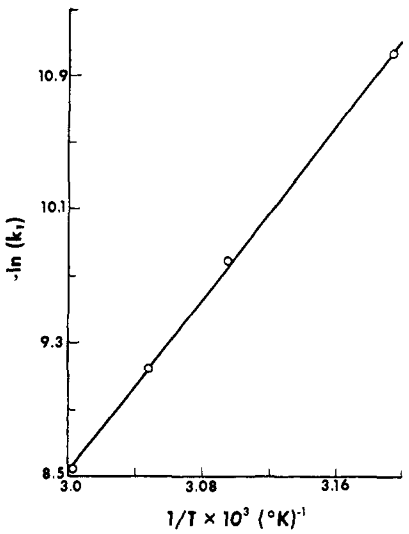

Figure 3. Arrhenius activation energy plot for B_4H_{10} consumption.

$$-R[B_4H_{10}] = -d[B_4H_{10}]/dt = k[B_4H_{10}]^m[C_2H_2]^n \qquad (I)$$

and setting $[C_2H_2]$ constant, eq I may be written as

$$-R[B_4H_{10}] = k'[B_4H_{10}]^m \qquad (II)$$

where $k' = k[C_2H_2]_0{}^n$.

The appropriate integrated forms of eq II were plotted for reaction orders (m) of $^1/_2$, 1, $^3/_2$, and 2. Since the first-order plots of ln $[B_4H_{10}]$ *vs.* time (Figure 2) gave by far the best linear correlation (0.998–1.000) and average deviation (1.4%), it is concluded that the rate is pseudo first order in B_4H_{10}. The rate data and calculated rate constants are summarized in Table I. From the fact that k' at each temperature is independent of the initial C_2H_2 concentration, the reaction order (n) for C_2H_2 is zero and $k' = k$.

An Arrhenius plot (ln k *vs.* $1/T$) using first-order rate constants measured at 40, 50, 55, and 60° (Figure 3) yielded an activation energy (E_a) of 25.8 kcal mol^{-1} and a preexponential factor (A) of 1.83×10^{13} sec^{-1}, calculated from the expression $k = Ae^{-E_a/RT}$.

These results clearly indicate that the first step in the reaction is a first-order fragmentation of the B_4H_{10} molecule. Comparison of the rate constant and activation energy with published values[11-13] from other gas-phase reactions of B_4H_{10} (Table II) strongly suggests that the common initiating step in these reactions is the formation of B_4H_8.

$$B_4H_{10} \longrightarrow B_4H_8 + H_2$$

This process has been postulated[11,12] to be rate determining in the reactions of B_4H_{10} with B_2H_6 and CO, and the existence of B_4H_8 as a reaction intermediate has been well established in studies of the mass spectra of B_4H_{10}[14] and B_4H_8CO.[15]

Further evidence that B_4H_8 formation is rate determining in the B_4H_{10}–C_2H_2 reaction is the observation

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(11) J. A. Du Pont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

(12) G. L. Brennan and R. Schaeffer, *ibid.*, **20**, 205 (1961).

(13) A. C. Bond and M. L. Pinsky, *J. Amer. Chem. Soc.*, **92**, 32 (1970).

(14) A. B. Baylis, G. A. Pressley, M. E. Gordon, and F. E. Stafford, *ibid.*, **88**, 929 (1966).

(15) R. E. Hollins and F. E. Stafford, *Inorg. Chem.*, **9**, 877 (1970).

Table I. Analytical Data and Rate Constants for B_4H_{10} Consumption

Temp, °C	Run	Initial reactants, mmol/216 ml C_2H_2	(ratio)	B_4H_{10}	Time, hr	$[B_4H_{10}]$, $M \times 10^4$	First-order rate constant, sec^{-1}, $k \times 10^5$
40		8.63		0.514	0.0	21.6	
					2.0	21.4	
			(18.5/1)		4.0	18.9	
					6.0	16.9	
					8.5	14.6	1.600
50	1	8.69		0.462	0.0	21.4	
					1.0	18.6	
			(18.8/1)		2.0	14.9	
					3.0	12.4	
					4.0	10.1	
					5.0	8.15	
					7.5	5.00	5.461
50	2	8.63		0.596	0.0	27.6	
					2.0	19.4	
			(14.5/1)		3.0	14.6	
					4.0	12.6	
					5.0	10.2	
					7.0	6.78	5.636
50	3	16.45		0.452	0.0	21.9	
					1.0	17.9	
			(36.4/1)		2.0	14.7	
					3.0	12.1	
					4.0	9.68	
					4.87	8.15	5.644
						Av $k_1^{50°}$	5.581
55		8.68		0.454	0.0	20.3	
					0.75	15.2	
			(19.1/1)		1.58	10.9	
					2.25	8.48	
					3.0	6.51	10.606
60	1	8.63		0.452	0.0	20.9	
					0.5	15.5	
			(19.1/1)		1.0	10.5	
					1.5	7.34	
					2.0	5.22	19.61
60	2	8.64		0.546	0.0	25.3	
					0.5	18.2	
			(15.8/1)		1.0	12.2	
					1.5	8.59	
					2.0	6.08	19.37
60	3	4.40		0.419	0.0	19.4	
					0.5	14.0	
			(10.5/1)		1.0	9.68	
					1.5	6.69	
					2.0	4.85	19.50
60	4	18.0		0.429	0.0	19.86	
					0.5	14.5	
			(42.1/1)		1.0	9.81	
					1.5	6.96	
					2.0	5.00	19.39
						Av $k_1^{60°}$	19.46

Table II. Kinetics Parameters of B_4H_{10} Reactions

B_4H_{10} reaction order	Second reactant Identity	 Order	Rate constant at 50°	E_a, kcal	A, sec^{-1}	Ref
1	C_2H_2	0	5.6×10^{-5} [a]	25.8	1.83×10^{13}	This work
1	B_2H_6	0	3.4×10^{-5} [a,b]	24.3	6.5×10^{13}	11
1	CO	0	3.7×10^{-5} [a,b]	24.6	1.12×10^{14}	12
3/2	. . .		7.14×10^{-4} [c]			This work
3/2	. . .		7.21×10^{-4} [c]	16.2	1.4×10^{8}	13

[a] Units of sec^{-1}. [b] Calculated for 50° from reported equation. [c] Units of $(\text{l./mol})^{1/2}$ sec^{-1}.

that the rate of B_4H_{10} disappearance in the *absence* of C_2H_2 is less than half that obtained in the reaction with C_2H_2 (Figure 4).[16] A reasonable assumption, consistent with a suggestion made several years ago by Parry and Edwards,[17] is that in the absence of a second reactant, B_4H_{10} fragments in two ways, the faster of which involves an equilibrium between B_4H_{10} and B_4H_8.

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(16) Our measurements of B_4H_{10} consumption in the absence of C_2H_2 agree very well with the results of Bond and Pinsky[13] (Table II), who postulated an initial fragmentation of B_4H_{10} to B_3H_7 followed by a lengthy chain mechanism.

(17) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

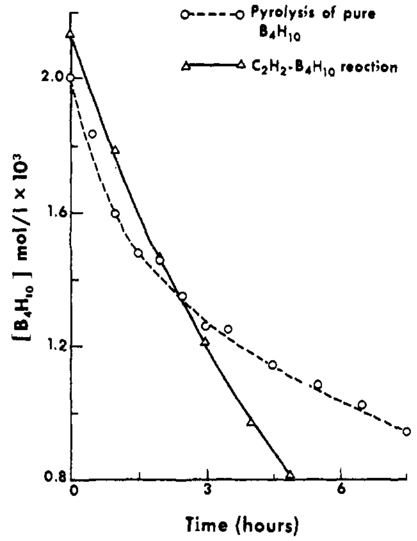


Figure 4. Disappearance of B_4H_{10} at 50° as a function of time in the absence of a second reactant (- - -) and in the presence of excess C_2H_2 (——).

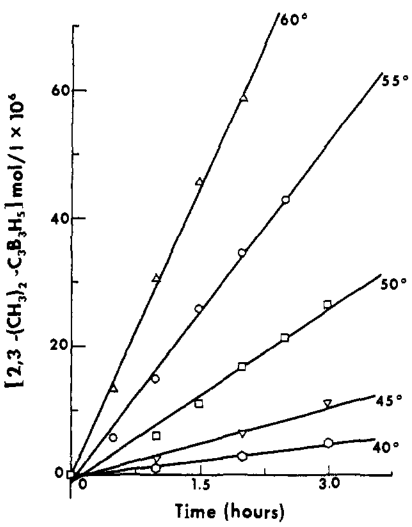


Figure 6. Initial rate plots of formation of $2,3\text{-}(CH_3)_2C_3B_3H_5$ at different temperatures.

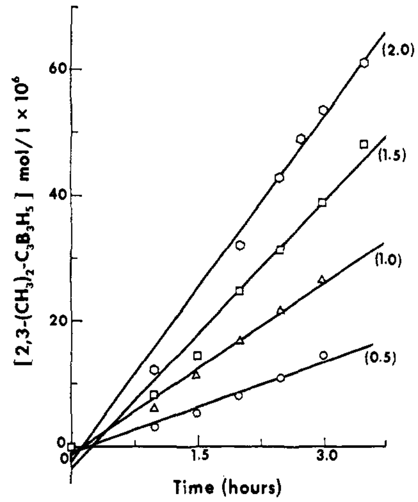


Figure 5. Initial rate plots of the formation of $2,3\text{-}(CH_3)_2C_3B_3H_5$ at 50° at varying initial concentrations of B_4H_{10}. Values of $[B_4H_{10}]_0$ (mmol/520 ml) are given in parentheses.

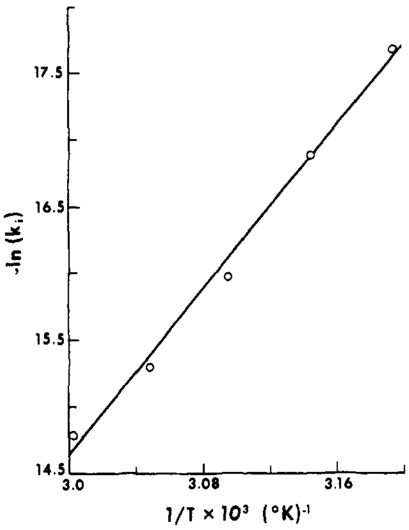
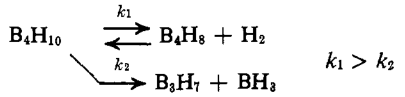


Figure 7. Arrhenius activation energy plot of formation of $2,3\text{-}(CH_3)_2C_3B_3H_5$.



$$B_4H_{10} \begin{array}{l} \overset{k_1}{\rightleftarrows} B_4H_8 + H_2 \\ \xrightarrow{k_2} B_3H_7 + BH_3 \end{array} \qquad k_1 > k_2$$

Thus, in the decomposition of pure B_4H_{10}, the equilibrium of step 1 is quickly established and the overall rate is controlled by the slower step 2; in the presence of C_2H_2, B_2H_6, or CO, rapid reaction with B_4H_8 occurs, so that in effect, the equilibrium is never attained and the overall reaction rate is $k_1[B_4H_{10}]$. In this connection, it seems significant that the total H_2 produced in the B_4H_{10}–C_2H_2 reaction is approximately equimolar with the B_4H_{10} consumed.

The existence of an equilibrium involving B_4H_{10}, B_4H_8, and H_2 has been postulated previously,[17,18] and evidence for it has been observed in the exchange of deuterium between D_2 and B_4H_{10},[19] and in the synthesis of $B_4H_8D_2$ from B_4H_8CO and D_2.[20] However, such an equilibrium is not essential to the mechanistic proposals presented below.

The Kinetics of Formation of Tricarbahexaborane(7) Derivatives. The initial rate method was used to study the rates of formation of the $2\text{-}CH_3$, $2,3\text{-}(CH_3)_2$, and $2,4\text{-}(CH_3)_2$ derivatives of $C_3B_3H_7$ between 40 and 60°. At 50°, two series of rate studies were carried out, in which the initial concentration of B_4H_{10}, and then of C_2H_2, was varied while the other was maintained effectively constant. As an example, the data obtained at constant $[C_2H_2]_0$ for $2,3\text{-}(CH_3)_2C_3B_3H_5$ are plotted in Figure 5. In all runs, C_2H_2 was present in large excess. For each of the three main carborane products, the reaction orders with respect to B_4H_{10} and C_2H_2 at 50° were determined from the expression

$$\frac{d[\text{carborane}(i)]}{dt} = R_i = k_i[B_4H_{10}]^{b_i}[C_2H_2]^{c_i} \qquad \text{(III)}$$

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[18] R. K. Pearson and L. J. Edwards, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., 1957, p 15N.

[19] J. E. Todd and W. S. Koski, *J. Amer. Chem. Soc.*, **81**, 2319 (1959).

[20] A. D. Norman and R. Schaeffer, *ibid.*, **88**, 1143 (1966).

Table III. Analytical Data for Carborane Formation at Constant C_2H_2 Concentration; 50°

C_2H_2/B_4H_{10} ratio, mmol[a]	$[B_4H_{10}]_0$, $M \times 10^3$	Time, hr	$C_3B_3H_7$ derivatives, $M \times 10^6$		
			[2-CH_3-]	[2,3-$(CH_3)_2$-]	[2,4-$(CH_3)_2$-]
20/0.5	0.950	1.0	1.90	3.15	6.38
		1.5	2.70	5.37	8.6
		2.0	2.96	8.18	11.8
		2.5	4.16	10.9	14.0
		3.0	6.06	14.5	17.1
		Initial rate[b]	0.5151	1.340	1.5578
		r[c]	0.977	0.987	0.999
20/1.0	1.923	1.0	3.15	6.13	11.4
		1.5		11.24	20.0
		2.0	6.64	16.9	22.9
		2.5	7.75	21.6	25.6
		3.0	9.56	26.6	29.2
		Initial rate[b]	0.8819	2.5305	2.7127
		r	0.999	0.994	0.981
20/1.5	2.96	1.0	4.53	8.3	15.3
		1.5	7.45	14.4	23.1
		2.0	9.74	24.8	33.6
		2.5	11.4	31.4	40.3
		3.0	15.0	39.1	45.0
		3.5	16.35	48.2	52.6
		Initial rate[b]	1.3253	3.9358	4.2138
		r	0.997	0.990	0.997
20/2.0	4.00	1.0	7.15	12.3	23.2
		1.5	9.46		
		2.0	13.1	32.2	46.1
		2.5	14.75	42.9	54.8
		2.75	18.1	49.3	60.0
		3.0	16.8	53.7	61.3
		3.5	20.4	61.3	70.1
		Initial rate[b]	1.5928	5.0967	5.6237
		r	0.991	0.995	0.995

[a] $[C_2H_2]_0$ = 38.8×10^{-3} M in all cases. [b] Units of $M\ sec^{-1} \times 10^9$. [c] Linear correlation coefficient.

and its logarithmic form

$$\log R_i = \log k_i + b_i \log [B_4H_{10}] + c_i \log [C_2H_2] \quad \text{(IV)}$$

Restriction of the rate measurements to the early stages of the reaction allowed substitution of the initial concentrations of B_4H_{10} and C_2H_2 in eq III and IV. The analytical data are presented in Tables III and IV.

Plots of $\log R_i$ *vs.* $\log [B_4H_{10}]_0$ (type I) and of $\log R_i$ *vs.* $\log [C_2H_2]_0$ (type II) yield slopes of b_i and c_i, respectively, with intercepts of $\log k_i + c_i \log [C_2H_2]_0$ (type I) and $\log k_i + b_i \log [B_4H_{10}]_0$ (type II). The excellent agreement between the rate constants obtained from plots of types I and II for all three carborane products (Table V) lends confidence in the essential validity of the method.

Arrhenius plots of $\ln k_i$ *vs.* $1/T$ were obtained from rate measurements at 40, 45, 55, and 60°, assuming that the reaction orders determined at 50° are valid at the other temperatures. For illustration, the initial-rate plots and Arrhenius plot for 2,3-$(CH_3)_2C_3B_3H_5$ are presented in Figures 6 and 7, respectively. The values of E_a, $\Delta S^{\ddagger}$,[21] and the preexponential factor A for each carborane are given in Table V. The $\Delta S^{\ddagger}$ values must be taken with some reserve, since they are based upon activation energies for the overall reaction; however, the low $\Delta S^{\ddagger}$ for the 2,3-dimethyl derivative is probably significant, as discussed below.

Effect of Surface Area on Reaction Rates. No measurable variation in the rate of carborane formation was detected in experiments in which the surface area in contact with the reactants was doubled by the introduction of Pyrex beads. Rates measured in a bulb filled with glass wool, representing an ~60-fold increase in surface area, were reduced by about one-third; this small effect is probably attributable to slow thermal equilibration of the glass wool in the 50° bath, and has no apparent mechanistic significance.

Effect of Added Diborane. Spiking of the initial reaction mixture with measured quantities of B_2H_6 produced no change in the yields of carborane products over a 2-hr period, as compared with the normal kinetic runs. This result clearly indicates that despite the known reactivity[11] of B_2H_6 toward B_4H_8, such interaction proceeds more slowly than the attack of B_4H_8 on C_2H_2. It also confirms that B_2H_6 does not interact significantly with organoboron intermediates in the carborane-forming processes.

Discussion

The negative reaction order with respect to C_2H_2, observed for all three major carborane products, seems

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(21) Average value calculated from the equations $k_i = (k_bT/h) \cdot e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$ and $E_a = \Delta H^{\ddagger} - (\Delta n^{\ddagger} - 1)RT$, where k_b = Boltzmann's constant, h = Planck's constant, k_i = the rate constant, by assuming that $\Delta n^{\ddagger}$ (number of molecules in the activated complex less the number of molecules in the ground state) is −1 for 2-$CH_3C_3B_3H_6$ and −2 for the two isomers of $(CH_3)_2C_2B_3H_5$.

Table IV. Analytical Data for Carborane Formation at Constant B_4H_{10} Concentration; 50°

C_2H_2/B_4H_{10} ratio, mmol[a]	$[C_2H_2]_0$, $M \times 10^3$	Time, hr	$C_3B_3H_7$ derivatives, $M \times 10^6$		
			$[2\text{-}CH_3\text{-}]$	$[2,3\text{-}(CH_3)_2\text{-}]$	$[2,4\text{-}(CH_3)_2\text{-}]$
14.3/1	27.5	1.0	4.96	8.25	14.6
		1.5	6.28	13.5	20.0
		2.0	8.10	18.7	26.3
		2.5	10.2		29.6
		3.0	10.7	33.3	40.9
		Initial rate[b]	1.0054	3.0653	3.5667
		r[c]	0.988	0.990	0.993
15.7/1	30.2	1.0	4.20	6.57	11.5
		1.5	6.44	13.3	20.1
		2.0	7.33	18.25	25.1
		2.5	11.0	27.7	32.85
		3.0	10.7	29.6	34.2
		Initial rate[b]	1.0478	2.9541	3.3488
		r	0.982	0.986	0.991
17.1/1	32.9	1.0	3.94	7.15	12.9
		1.5	5.87	12.9	20.9
		2.0	8.10	19.0	26.7
		2.5	8.98	23.65	29.5
		Initial rate[b]	1.0322	2.6911	3.4084
		r	0.995	0.994	0.992
30/1	57.7	1.0	2.77	5.11	9.20
		2.0	5.05	15.2	20.0
		3.0	7.37	23.4	27.7
		Initial rate[b]	0.6775	2.2303	2.6083
		r	0.999	0.993	0.998
40/1	78.1	1.0	219	3.94	6.61
		2.0	4.09	10.4	14.9
		3.0	5.75	18.25	20.4
		Initial rate[b]	0.5319	1.7003	1.9303
		r	0.998	0.990	0.997
50/1	96.15	1.0	1.61	2.92	5.91
		2.0	3.15	8.85	11.3
		3.0	4.13	13.4	16.6
		Initial rate[b]	0.3869	1.2814	1.5331
		r	0.994	0.992	0.999

[a] $[B_4H_{10}]_0 = 1.923 \times 10^{-3}\ M$ in all cases. [b] Units of $M\ \text{sec}^{-1} \times 10^9$. [c] Linear correlation coefficient.

Table V. Kinetics Parameters of Tricarbahexaborane Formation

$C_3B_3H_7$ derivative	Reaction orders		50° rate constants, k_i[a]		E_a, kcal	A[b]	$\Delta S^{\ddagger}$, cal deg^{-1}
	B_4H_{10} (b_i)	C_2H_2 (c_i)	Type I	Type II			
$2\text{-}CH_3$	0.808	−0.758	1.18	1.13	22.55	2.15×10^7	−29
$2,3\text{-}(CH_3)_2$	0.937	−0.6305	11.65	11.4	30.65	5.5×10^{13}	−1.8
$2,4\text{-}(CH_3)_2$	0.895	−0.627	10.0	10.3	21.5	3.4×10^7	−30

[a] Units of $(\text{l./mol})^{b+c-1}$ $(\text{sec}^{-1}) \times 10^8$. [b] Units of $(\text{l./mol})^{b+c-1}$ (sec^{-1}).

accountable only in terms of a common intermediate which is a precursor both to the solid polymer and the carboranes *via* competing reactions. Assuming that the formation of B_4H_8 is rate determining for the reaction, as discussed above, the addition of four intact C_2H_2 units to B_4H_8 without substantial gain or loss of hydrogen (as suggested by the overall stoichiometry and the deuterium-tracer results) would yield a product corresponding to the observed $[C_2BH_4]_x$ composition of the solid. Formation of the $C_3B_3H_7$ derivatives is undoubtedly a consequence of slower side reactions involving rearrangements of intermediates. The following scheme incorporates these conclusions and is consistent with all available evidence.

$$B_4H_{10} \xrightarrow[\text{slow}]{k_1} B_4H_8 + H_2 \qquad (1)$$

$$B_4H_8 + C_2H_2 \xrightarrow[\text{fast}]{k_2} C_2B_4H_{10} \ (I_1) \qquad (2)$$

$$I_1 \xrightarrow{k_3} C_2B_3H_7 + BH_3 \qquad (3)$$

$$I_1 + C_2H_2 \xrightarrow[\text{fast}]{k_4} C_4B_4H_{12} \ (I_2) \qquad (4)$$

$$I_2 \xrightarrow{k_5} 2\text{-}CH_3C_3B_3H_6 + BH_3 \qquad (5)$$

$$I_2 + C_2H_2 \xrightarrow[\text{fast}]{k_6} C_6B_4H_{14} \quad (I_3) \qquad (6)$$

$$I_3 \xrightarrow{k_7} \text{2,3- and 2,4-}(CH_3)_2C_3B_3H_5 + CBH_3 \qquad (7)$$

$$I_3 + C_2H_2 \xrightarrow[\text{fast}]{k_8} [C_2BH_4]_x \quad \text{(solid)} \qquad (8)$$

In this sequence, the steps leading to polymer formation (2, 4, 6, and 8) are the dominant processes. Side reactions which generate the minor products (*e.g.*, $C_3B_3H_7$, $CH_3CB_5H_8$, and $C_2B_4H_8$) may involve the BH_3 or CBH_3 fragments shown, but are unimportant in the overall scheme and are omitted for simplicity.

Under the condition that step 1 is rate determining, concentrations of the intermediates I_1, I_2, and I_3 are considered vanishingly small[22] and may be treated by the steady-state approximation $d[I]/dt = 0$. As an illustration, the rate of formation of either $(CH_3)_2$-$C_3B_3H_5$ isomer may be written as rate $= k_7[I_3]$. Application of the steady-state treatment to I_3 with no approximations leads to

$$\frac{d[\text{carborane}]}{dt} = \frac{k[B_4H_{10}]}{k'[C_2H_2] + \frac{k''}{[C_2H_2]} + \frac{k'''}{[C_2H_2]^2} + k''''} \qquad (V)$$

where $k = k_1k_4k_6k_7$, $k' = k_4k_6k_8$, $k'' = k_4k_5k_7 + k_3k_6k_7 + k_3k_5k_8$, $k''' = k_3k_5k_7$, and $k'''' = k_3k_6k_8 + k_4k_5k_8 + k_4k_6k_7$. A similar expression is derivable for 2-$CH_3C_3B_3H_6$. Equation V accounts very well for the observed first-order dependence of carborane formation on B_4H_{10} and the negative, fractional-order dependence on C_2H_2. Since k' involves only the rate constants of polymer propagation, the first term in the denominator is relatively large and tends to produce an order of -1 for C_2H_2. However, the remaining terms in the denominator contribute to a lesser, but significant, extent, leading to an overall C_2H_2 reaction order between 0 and -1, in agreement with experiment.

A reasonable postulate is that addition of C_2H_2 units during the polymer-forming steps constitutes lengthening of a carbon chain appended to B_4H_8; when the propagating units become sufficiently heavy, they settle out of the gas phase as solid particles. Occasionally, a chain undergoes rearrangement leading to an electron-delocalized carborane cage. Rearrangements involving highly ordered transition states, such as ring-forming processes, are consistent with the large negative entropies of activation measured for 2-CH_3C_3-B_3H_6 and 2,4-$(CH_3)_2C_3B_3H_5$. The smaller $\Delta S^{\ddagger}$ and the relatively large E_a for 2,3-$(CH_3)_2C_3B_3H_5$ suggest a more sterically hindered rearrangement; this appears to be related to the fact that in the 2-CH_3- and 2,4-$(CH_3)_2$- derivatives, the carbon atoms form a continuous chain, whereas in 2,3-$(CH_3)_2C_3B_3H_5$ their relationship is isopentane-like.

We shall not speculate at length on the detailed-stereochemistry of the chain-forming process. However, as a working hypothesis we propose that if B_4H_8 contains a vacant orbital, as suggested elsewhere,[11] such an orbital may interact with a filled molecular orbital of C_2H_2 to form the $C_2B_4H_{10}$ (I_1) intermediate. Conceivably, the resulting decrease in electron density on the bound C_2H_2 unit would facilitate addition of a second C_2H_2 molecule to the first, thus leading to propagation of a chain of -CH=CH- units.

Evidence from other borane–alkyne reactions is consistent with the main conclusions reached in this study. For example, the gas-phase reaction[7] of methylacetylene with B_4H_{10} yields a small quantity of 2-C_2H_5-3,4-$(CH_3)_2$-$C_3B_3H_4$ but no other $C_3B_3H_7$ derivatives; the major volatile products are propylene and 2-CH_3-2,3-$C_2B_4H_7$, and only a small amount of solid is formed. Clearly, the methyl group hinders chain formation and thus favors alternative processes. Even more strikingly, dimethylacetylene and B_4H_{10} yield mostly 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$ (which can form *via* simple addition) and no solid product at all.[7]

The fact that $C_3B_3H_7$ derivatives are obtained[7] in low yield from C_2H_2 and B_5H_{11} can be attributed to the formation of some B_4H_8 *via* cleavage of BH_3 from B_5H_{11}. Similarly, the failure to detect $C_3B_3H_7$ derivatives in reactions of C_2H_2 with B_2H_6, B_5H_9, or B_6H_{10} probably derives from the absence of significant concentrations of B_4H_8 in these systems. Finally, it seems relevant to mention the reaction of B_4H_{10} with ethylene in the gas phase.[23] The main product, 2,4-dimethylenetetraborane ($C_2H_4B_4H_8$), contains a CH_2CH_2 bridge joining the two ends of a tetraborane unit, and may form *via* interaction of C_2H_4 with B_4H_8 as has been proposed.[23] The rather startling contrast between this reaction and that involving B_4H_{10} and acetylene probably arises, in part, from the stability of 2,4-dimethylenetetraborane (obtained[23] in 70% yield) toward both internal rearrangement and interaction with the reactants. Thus, incorporation of the saturated dimethylene bridge into a carborane-like cage would require C–H cleavage and seems energetically unlikely under mild conditions. In the C_2H_2–B_4H_{10} reaction, an analogous -CH=CH- bridged species may well form initially, but high reactivity would be expected for the unsaturated linkage in such a molecule. Conceivably, it may be possible to isolate an intermediate of this type from the C_2H_2–B_4H_{10} reaction at low temperatures in a hot–cold reactor.

Experimental Section

All experimental procedures were carried out under high-vacuum conditions using standard vacuum techniques. The vacuum system used for preparative work and quantitative PVT measurements of compounds was constructed of Pyrex glass using greaseless Teflon stopcocks equipped with Viton-A O rings. Gas-phase reactions were run in round-bottom Pyrex reactors fitted with 5-mm Teflon vacuum stopcocks. Following each reaction, nonvolatile solids were cleansed from the bulb using a sequence of acetone, water, 5% HF, water, and acetone rinses. Bulbs were then evacuated and heated externally with an annealing gas flame to ensure removal of any absorbed moisture.

Materials. Diborane (Matheson) and acetylene (Matheson) were purified by repeated fractionation through a $-128°$ trap. Tetraborane was synthesized by the method of Gaines and Schaeffer,[24] in which tetramethylammonium triborohydride, $(CH_3)_4$-NB_3H_8 (Callery Chemical Co.), is allowed to react with polyphosphoric acid at 45° over a period of several hours. The B_4H_{10} was purified by fractionation through -95 and $-128°$ traps; the latter trap retained B_4H_{10} but permitted B_2H_6 to pass through.

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(22) Additional evidence that the concentrations of the intermediates remain very low is given by the fact that the total rate of boron incorporation into final products (measured or estimated for steps 3, 5, 7, and 8) is approximately equal to the rate of disappearance of boron as a reactant (measured for step 1). This requires that B_4H_8, I_1, I_2, and I_3 all are consumed at rates greater than that of step 1.

(23) B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

(24) D. F. Gaines and R. Schaeffer, *Inorg. Chem.*, **2**, 438 (1963).

Dideuterioacetylene was synthesized by dropping D_2O (Strohler Isotopes, 99.4% deuterium content) onto calcium carbide in an evacuated two-neck bulb. Volatile materials were removed to the vacuum line where C_2D_2 was purified by repeated fractionation through a −128° trap.

Reactant purities were verified by infrared spectra of small gas samples.

Chromatography. Except for unreacted acetylene and tetraborane, which were removed by preliminary vacuum-line fractionation, all reaction products were isolated, purified, and measured by gas-phase chromatography on a 9.8 ft × 0.25 in. column (30% Kel F on Chromosorb W) using helium as a carrier gas. Peak areas in square inches were measured by planimeter and converted to millimoles using a previously determined calibration (1 mV in. = $(7.6 \pm 0.3) \times 10^{-4}$ mmol).

Instrumentation. Infrared, mass, and nmr spectra were recorded on Beckman IR-8, Hitachi Perkin-Elmer RMU-6, and Varian HA-100 spectrometers, respectively. All ir spectra were recorded on gas-phase samples using a 31-ml infrared cell fitted with sodium chloride windows.

Computerized Data Treatment. All kinetics data were treated graphically by least-squares analyses of linear plots. Slopes, intercepts, and linear correlation coefficients were calculated by computer (Hewlett-Packard 9100B) using standard library programs (H-P No. 09100-70818). Graphs presented in the figures were originally drawn by the H-P 9125A plotter.

Deuterium-Labeling Experiments. The mass and infrared spectra of deuterated tricarbahexaborane(7) derivatives obtained from C_2D_2–B_4H_{10} reactions have been discussed elsewhere.[4d] The 32.1-MHz ^{11}B nmr spectra of the deuterated 2,3- and 2,4-dimethyl derivatives have been obtained from the neat liquids, and are nearly identical with the spectra of their nondeuterated counterparts. Thus, both spectra display a high-field doublet of area 1.0 (δ +50 ppm relative to $BF_3 \cdot (C_2H_5)_2O$, J = 175 Hz), assigned to the apex B–H; this precludes extensive deuteration at the apex boron atoms. The doublets at lower field (δ +3 ppm) in the spectra of the deuterated samples lack the secondary splitting which is attributed to bridge hydrogen coupling in the nondeuterated species, suggesting that some deuterium is bound to the basal borons either in terminal or bridging positions.

Diborane recovered from the 1:1 reaction (C_2H_2:B_4H_{10}) has a mass spectrum containing a cutoff at *m/e* 28 (pure B_2H_6 has a cutoff at *m/e* 27 under identical conditions). The infrared spectrum exhibits weak bands at 1700 and 1260 cm^{-1} (not present in the ir of pure B_2H_6) which are B–D counterparts of stronger B–H bands at 2600 and 1850 cm^{-1}, respectively, and agrees with a published spectrum of a B_2H_6–B_2H_5D mixture.[25]

Molecular hydrogen removed from the C_2D_2:B_4H_{10} reaction products showed no traces of D_2 or HD in the mass spectrum.

Rate Measurements of B_4H_{10} Consumption. The rates of tetraborane consumption were measured by means of an infrared spectroscopic determination of B_4H_{10} concentration at periodic intervals. This was achieved by monitoring the intensity of the strong, narrow B_4H_{10} absorption at 2140 cm^{-1} assigned to bridge hydrogen stretch. The intensity of this band is quite pressure sensitive within a range of tetraborane concentrations which suitably overlapped that used in normal B_4H_{10}–C_2H_2 reactions. No other volatile species in the reaction system exhibited absorptions between 2100 and 2300 cm^{-1}.

The apparatus consisted of a Pyrex bulb (216 ml) equipped with a 5-mm Teflon vacuum stopcock. Mounted at a 45° angle to the main axis of this bulb was a small gas infrared cell, attached to the bulb *via* a second greaseless vacuum stopcock. The entire assembly could be seated on a specially constructed holder which reproducibly positioned the ir cell in the light path of the spectrometer. An excellent linear correlation between absorbance and $[B_4H_{10}]$ was obtained by admitting measured amounts of B_4H_{10} and measuring per cent transmittance (% T) at 2140 cm^{-1}, manually scanning the band to determine the lowest % T value; 100% T was set to correspond to the evacuated cell. Least-squares treatment of the calibration data produced the following equation, which was used to convert subsequent absorbance readings (A) to millimoles of B_4H_{10}, n (monitoring volume, 247 ml).

$$A = 2.471(n) - 0.015$$

Prior to each kinetics run, the Beckman IR-8 was zeroed and adjusted to eliminate pen drift. After charging the bulb with the desired amount of acetylene, 100% T at 2140 cm^{-1} was set to compensate for any small absorbance or reflectance on the part of acetylene. The bulb was then replaced on the vacuum line and charged with the proper amount of tetraborane. Infrared determination of this initial tetraborane concentration agreed with the known amount (by PVT measurement) within ±2%.

Following each ir reading, all volatile material was condensed back into the reactor portion of the apparatus by immersing the bulb in liquid nitrogen. The ir cell was then closed off to the reaction mixture, thereby preventing contamination of the cell windows. Following a brief immersion in warm tap water to remove the initial frost, the reactor was submerged in a thermostated (±0.2°) water bath and clamped in position. The infrared cell remained above the water and was doubly enclosed in plastic bags to prevent moisture from reaching the salt windows. After an appropriate time had elapsed, the reaction was quenched by immersing the bulb in ice water, the apparatus was dried and equilibrated, the B_4H_{10} concentration was determined, the reactants were recondensed into the bulb, and the reactor was returned to the water bath for another time interval. It was assumed that the very slow reaction at room temperature introduced insignificant error during the 5 min necessary to make each ir reading.

Rate Measurements of Carborane Formation. An initial rate of product formation is normally obtained by curve fitting a plot of product concentration *vs.* time; the slope of the tangent to this curve at the origin represents the initial rate of formation. Such curves were obtained in this study. However, for times of 3.5 hr or less at 50°, product yields were linear with time; obvious curvature was not evident except for reaction times exceeding 5 hr. Therefore, initial rates were measured by determining the slopes of least-squares straight lines through yield *vs.* time points up to 3.5 hr, with the origin included in each case. Each data point was obtained by reacting the proper ratio of B_4H_{10} and C_2H_2 for a fixed time interval, quenching the reaction, and determining the yield chromatographically. A series of such determinations for a given set of reactants provided the data necessary for calculation of the initial rate of formation. Yields of the three major carborane products could be determined simultaneously from the chromatogram of each reaction.

All reactions were carried out in identical 520-ml Pyrex reactor bulbs equipped with 5-mm Teflon vacuum stopcocks. Each bulb was evacuated and charged with the proper amounts of C_2H_2 and B_4H_{10} by condensation at −196°. At 10 sec prior to time zero the reactor was immersed in warm tap water to remove the initial frost, then submerged in a thermostated (±0.2°) water bath. When the proper time interval had elapsed, the bulb was removed and set into a dewar of liquid nitrogen, thereby quenching the reaction. The reactor was then placed on a small vacuum-fractionation train connected to the gas chromatograph, and noncondensables were pumped off at −196°. In order to avoid swamping the chromatographic column with the large quantities of unreacted C_2H_2 and B_4H_{10}, these materials were removed by distillation at −95°. The remaining volatile products were transferred to the injection U tube of the glpc apparatus and separated by chromatography. Occasional checks demonstrated that no tricarbahexaboranes were lost during this fractionation.

Surface Effects. Three experiments were run, each employing 20.0 mmol of C_2H_2 and 1.0 mmol of B_4H_{10} in the same 520-ml Pyrex bulb, for 2.0 hr at 50°. Relative surface areas were 1.0 (normal bulb), 1.9 (400 glass beads of 0.5-mm diameter added), and 63 (5.3 g of 3950 Pyrex glass wool added). Yields of the three $C_3B_3H_7$ derivatives were identical in the first two cases and lower by about one-third in the last.

Diborane Spiking. In three experiments, a 20.0/1.0-mmol ratio of C_2H_2 to B_4H_{10} was employed at 50° in the same 520-ml reactor, but the initial amounts of B_2H_6 present were 0.0, 0.5, and 1.0 mmol, respectively. Yields of the $C_3B_3H_7$ derivatives after 2.0 hr were identical in all cases.

$C_2B_3H_7$ Spiking. A measured amount of $C_2B_3H_7$ (0.50 mmol) was added to an initial 20.0/1.0-mmol ratio of C_2H_2 to B_4H_{10} and the mixture was allowed to react in a 520-ml bulb for 2.0 hr at 50°. Yields of the three $C_3B_3H_7$ derivatives were identical with those obtained in the absence of $C_2B_3H_7$.

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