occurs at 719 Å (17.24 eV). If this is ascribed to the ΔH_0 for the reaction $B_2Cl_4 + h\nu \rightarrow B_2Cl_2^+ + 2Cl + e$, the usual summation of heats of formation results in $\Delta H_f{}^\circ{}_0(B_2Cl_2^+) = 9.7$ eV (223 kcal mol^{-1}). Estimating values for the first and second B–Cl bond dissociation energies in B_2Cl_4 results in $I(B_2Cl_2) = 9.0$ eV, an entirely reasonable value. If the neutral dissociation products were molecular chlorine rather than chlorine atoms, the ionization energy of B_2Cl_2 would be increased by about 2.5 eV. This would result in the improbable case of the ionization energy of the B_2Cl_2 radical being about 1.2 eV greater than that of the parent molecule.

Finally, the BCl^+ ion exhibits a definite onset at 904 Å (13.71 eV). There is some evidence of weak autoionization immediately in the region of threshold and at shorter wavelengths. The threshold value evidently includes some excess energy as the minimum-energy process $B_2Cl_4 + h\nu \rightarrow BCl^+ + BCl_3 + e$ results in a calculated heat of formation of BCl^+ of 12.8 eV compared with 11.7 eV from BCl_3.

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Carborane Formation in Alkyne–Borane Gas-Phase Systems. III. Flash Reactions of Small Boranes[1]

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Thermally induced flash reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene, and dimethylacetylene have been studied, and the volatile products, consisting almost exclusively of parent or alkyl closed-cage carboranes and hydrocarbons, have been individually isolated and characterized. Both the total carborane yield and the relative yields of B_3 and B_4 carboranes are largest in reactions of dimethylacetylene and least in those of acetylene. Derivatives of 1,2-$C_2B_3H_5$ are formed in significant amounts from alkylacetylenes but not from acetylene. The results are compared with previous work on borane–alkyne systems, particularly the electric-discharge and flash reactions of diborane with acetylene, and implications in regard to reaction pathways are discussed. The pentaborane(11)–dimethylacetylene system is exceptional; flash reactions are not observed in 1:1 mixtures, but a 2:1 alkyne:borane ratio results in flash reaction below room temperature in which largely noncarborane products are obtained.

The gas-phase explosions or electric-discharge reactions of small boron hydrides with acetylene yield amorphous solids and volatile products consisting largely of polyhedral carboranes.[2-6] The carborane-forming processes in these systems are not understood and would constitute a formidable problem for any detailed investigation. However, in the course of exploratory studies of small-carborane chemistry it appeared useful to examine and compare the flash reactions of several small alkynes with boron hydrides in a search for possible correlations between the structures of reactants and products obtained. Accordingly, the 100° flash reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene, and dimethylacetylene were carried out in sealed bulbs under similar conditions. Volatile products were isolated by fractionation and vapor-phase chromatography and identified as described below.

Results

General.—With the exception of the B_5H_{11}–$C_2(CH_3)_2$ reaction, which proved anomalous (see below), mixtures of B_4H_{10} or B_5H_{11} with C_2H_2, HC_2CH_3, or $C_2(CH_3)_2$ flashed within 6 min at 100° without breakage of the Pyrex reactor. The products in each case consisted of dark nonhomogeneous solids, which were not investigated, and volatile species which were separated by glpc and individually characterized (Table I). The more significant results are summarized as follows.

(1) All organoboron products identified in these reactions are *closo*-carboranes or alkyl-*closo*-carboranes.

(2) The same carborane cage systems (not necessarily the same derivatives) which were produced in high-energy reactions of B_2H_6 and/or B_5H_9—*e.g.*, 1,5-

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[1] (a) Part II: R. N. Grimes, C. L. Bramlett, and R. L. Vance, *Inorg. Chem.*, **7**, 1066 (1968). (b) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (c) Abstracted from the Ph.D. dissertations of C. L. B. and R. L. V., University of Virginia, 1967 and 1968, respectively.

[2] I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

[3] I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963).

[4] R. N. Grimes, *ibid.*, **88**, 1070 (1966).

[5] R. N. Grimes, *ibid.*, **88**, 1895 (1966).

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

TABLE I

FLASH REACTIONS OF B_4H_{10} AND B_5H_{11} WITH ALKYNES AT 100°[a]

Reactants, mmol/500 ml	Total volatile carboranes, mmol/mmol of borane reactant	Volatile carborane products[b]				Other volatile products, mmol/mmol of borane reactant[c]
		$C_2B_3H_5$ derivatives[e]	1,6-$C_2B_4H_6$ derivatives	2,4-$C_2B_5H_7$ derivatives	1,6-$C_2B_8H_{10}$ derivatives	
B_4H_{10}, 3.58[d] C_2H_2, 3.58[d]	0.033	2-CH_3- [4]	Parent [4]	Parent [35] 1-CH_3- [9] 2-CH_3- [17] 3-CH_3- [9] 5-CH_3- [4]	Parent [11] B-CH_3- [7]	None detected
B_4H_{10}, 3.42 HC_2CH_3, 3.42	0.048	Parent [12] 2-CH_3- [21] C,3-$(CH_3)_2$- [12][f] Other [7][g]	1-CH_3- [2]	Parent [17] 2-CH_3- [20] 1,7-$(CH_3)_2$- [9]	None detected	Ethylene, 0.080 Propylene, 0.010 Unknown, <0.003
B_4H_{10}, 3.56 $C_2(CH_3)_2$, 3.56	0.067	Parent [17] 2-CH_3- [8] C,3-$(CH_3)_2$- [8][f] Other [21][h]	1-CH_3- [2] Other [13][i]	Parent [8] 1,7-$(CH_3)_2$- [2] 1-C_2H_5- [17] Other [4][j]	None detected	Ethylene, 0.105 Propylene, 0.019 *cis*- and *trans*-2-butene, 0.024[l] Unknown, <0.001
B_5H_{11}, 3.49 C_2H_2, 3.50	0.036	Parent [18] 2-CH_3- [4]	Parent [4]	Parent [38] 1-CH_3- [8] 3-CH_3- [4] 5-CH_3- [4]	Parent [13] B-CH_3- [7]	Ethane, 0.020 B_5H_9, 0.0009 Unknown, <0.001
B_5H_{11}, 2.68 HC_2CH_3, 2.70	0.045	Parent [17] 2-CH_3- [16] C,3-$(CH_3)_2$- [3][f] Other [10][k]	1-CH_3- [7]	Parent [21] 2-CH_3- [21] 1,7-$(CH_3)_2$- [5]	None detected	Propylene, 0.037 B_5H_9, 0.003 Unknown, 0.012[m]

[a] Data from typical experiments. No reactants were recovered in any system except 2.8% of the original C_2H_2 in the B_4H_{10}–C_2H_2 reaction. [b] Mole per cent of total volatile carboranes given in brackets. [c] Exclusive of H_2. [d] Reported previously;[6] included for comparison. [e] Derivatives of 1,5-$C_2B_3H_5$ except where otherwise indicated. [f] Derivative of 1,2-$C_2B_3H_5$. [g] Molecular weights from mass spectra of pure compounds (mol per cent of total volatile carboranes in parentheses): 104 (4), 104 (3). [h] Molecular weights (mol per cent): 90 (3), 104 (3), 104 (6), 118 (5), 146 (4). [i] Molecular weights (mol per cent): 116 (3), 102 (8), 130 (2). [j] Molecular weights (mol per cent): 114 (2), 128 (2). [k] Molecular weights (mol per cent): 104 (6), 104 (4). [l] *cis* and *trans* isomers were not separated. [m] Total of five components.

$C_2B_3H_5$, 1,2-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$—are found in the present work as parent or alkylated species.[7] In addition, 1,6-$C_2B_8H_{10}$ and its B-methyl derivative are obtained.

(3) Total carborane yields based on borane consumed are greatest in reactions of dimethylacetylene and least in those of acetylene. At the same time, methyl- and dimethylacetylene tend to bias the reaction toward smaller carborane products.

(4) Although at least one well-characterized[4,5] derivative of 1,2-$C_2B_3H_5$ is obtained from methyl- and dimethylacetylene, acetylene itself does not produce this cage structure in reactions with B_4H_{10} or B_5H_{11} (in sharp contrast to B_2H_6–C_2H_2 flash reactions[5]).

Reaction of B_5H_{11} with $C_2(CH_3)_2$.—Equimolar mixtures of B_5H_{11} and dimethylacetylene repeatedly failed to flash at 100° and instead reacted slowly to give products (Table II) qualitatively identical with those obtained at 50° in an earlier investigation.[1a] However, reproducible experiments using a 2:1 excess of the alkyne, with the reactants partially in a liquid state, did result in a flash reaction near 0°. These results (Table II) are unusual in comparison with other borane–alkyne flash reactions in that an open-cage carborane (*nido*-C,-C′-dimethyldicarbahexaborane(8)) and a trialkylborane are produced, the sole closed-cage species formed is only a minor product, and the reaction temperature is far lower than was found necessary for thermally induced flash reactions in similar systems.[6]

Experimental Section

Materials.—The purity of all reagents was checked by glpc and infrared analysis. B_4H_{10} and B_5H_{11} were prepared by allowing B_2H_6 (Olin Mathieson) to stand at 600 psi in a stainless steel cylinder at 25–35° for approximately 10 days and were purified by vacuum-line fractionation (B_4H_{10} and B_5H_{11} were retained in traps at −135 and −78°, respectively). Acetylene (Matheson) was purified by passage through a −135° trap, while methylacetylene (Matheson) was fractionated through traps at −95 and −150°, the fraction condensing at −150° being retained. Dimethylacetylene (K & K) was purified by distilling through a −63° trap and collecting it at −95°.

Spectra.—The instruments used were a Beckman IR-8 grating spectrophotometer, a CEC 21-103C mass spectrometer with digital readout, and a Varian A-60 nmr spectrometer. Gas infrared spectra were obtained in Pyrex cells of 3.5–7.0 ml, fitted with sodium chloride windows.

General Procedure.—Most of the experimental techniques used in this work have been described in detail in earlier papers.[1a,6] All reactions were carried out *in vacuo* in sealed greaseless Pyrex bulbs equipped with breakoff tips for opening into a vacuum system. Following the completion of each reaction, volatile materials were fractionated through a −135° trap. The fractions condensing and passing through the trap were separately chromatographed on a preparative-scale apparatus built into a high-vacuum system.[8] Individual compounds were collected in traps at −196° downstream from the column. Complete separations of products were achieved by repeated chromatography and by selective use of three different 9.5 ft × 0.25 in.

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[7] An exception is 1,2-$C_2B_4H_6$, which has been produced in a B_5H_9–C_2H_2 electric discharge[3] but was not found in this study.

[8] Owing to space limitations, the extensive chromatographic data accumulated in this work are not presented here, but these data are readily available upon request.

TABLE II

REACTIONS OF B_5H_{11} WITH DIMETHYLACETYLENE[a]

Reactants, mmol/125 ml	Reaction time, min	Temp, °C	Total volatile products, mmol	Volatile products [mol %][b]			
				nido-Carboranes	Alkanes	Boranes	Other
B_5H_{11}, 1.02 $C_2(CH_3)_2$, 1.02	70[c]	100	0.176	C,C′-$(CH_3)_2C_2B_4H_6$ [5]	*n*-C_4H_{10} [27]	B_2H_6 [<1] B_5H_9 [50] B_6H_{12} [4]	*sec*-$C_4H_9B_5H_8$ [13]
B_5H_{11}, 0.85 $C_2(CH_3)_2$, 1.68	*d*	*d*	0.127	C,C′-$(CH_3)_2C_2B_4H_6$ [8]	*n*-C_4H_{10} [31] C_2H_6 [12]	B_2H_6 [14] B_5H_9 [17]	$B(CH_3)_3$ [9] Unidentified B-alkyl-*closo*-carborane [9]

[a] Typical experiments. [b] Exclusive of H_2. [c] Slow reaction; no flash observed. [d] Flashed at ~0°.

columns: 30% tricresyl phosphate, 30% Kel-F, and 30% Apiezon L grease, all on Chromosorb W solid support. Yields were calculated from calibrated chromatographic peak areas or, in a few cases, from *PVT* data.

Flash Reactions of B_4H_{10} and B_5H_{11} with Alkynes.—In all experiments except those dealing with the B_5H_{11}–$C_2(CH_3)_2$ system, borane–alkyne mixtures in a 1:1 mole ratio flashed within 6 min following placement of the reaction bulb in a 100° oven. In each case large quantities of dark gray and brown nonvolatile solids were formed but were not investigated. Identification of the volatile products is described below.

Reactions of B_5H_{11} with $C_2(CH_3)_2$. (A) 1:1 Mole Ratio.—The above procedure gave no flash even on prolonged heating for periods of 70 min to 11 hr. In one experiment the reactor temperature was raised to 150° following 10 min at 100°; still no flash was observed and the products were identical with those obtained at 100° (Table I) and at 50°.[1a] Under the experimental conditions of all 1:1 reactions, some liquid $C_2(CH_3)_2$ was present which became greenish yellow after 10 min at 100°. Upon distillation of the products following the reaction, the liquid solidified to a green, nonvolatile, amorphous material which was not investigated.

(B) 2:1 Mole Ratio (Alkyne in Excess).—The reactants were sealed into a bulb immersed in liquid N_2, after which the bulb was allowed to warm to room temperature behind a transparent safety shield. After 5 min at a reactor temperature near 0° (as evidenced by the melting of frost on the outer surface), the liquid in the reactor began to boil. Within 10 sec following this, a flash was observed with deposition of nonhomogeneous brown solids on the lower half of the reactor and black solids on the upper half. The solid material was nonvolatile and was investigated. Repetition of the experiment with ir and vpc checks of the purity of the B_5H_{11} and $C_2(CH_3)_2$ immediately prior to the reaction (*i.e.*, without storage of the reactants at −196°) gave exactly the same results. One product of the reaction was not identified, although the infrared spectrum suggests a B-alkyl-*closo*-carborane.

Identification of Products.—The hydrocarbons, boranes, and alkylboranes listed in Tables I and II were identified from their ir and mass spectra by comparison with the literature spectra. The carborane products specifically listed have been structurally characterized[2–6] with the aid of infrared, ^1H and ^{11}B nmr, and mass spectra; their identification in this study was by comparison of their infrared spectra and glpc retention times with those of authentic samples. A new compound obtained from the tetraborane–dimethylacetylene reaction was identified as the apically substituted 1-C_2H_5-2,4-$C_2B_5H_6$ from the ir spectrum, which is very close to the known 1-CH_3- and 1,7-$(CH_3)_2$- derivatives and contains a B-alkyl stretching band at 1320 cm^{-1}, from the mass spectrum,[9] and from the proton nmr spectrum (neat liquid), which consists of three singlets at τ 5.32, 8.33, and 9.50 (area ratio 2:3:2). The singlet at τ 5.32 is assigned to equivalent cage C–H groups and those at higher field are attributed to the methyl and methylene protons, respectively, of the ethyl group (the B–H quartets were too weak to be observed). No other structure appeared compatible with these data.

In several reactions, small amounts of additional products were isolated in pure form. The infrared and mass spectra of these materials are clearly those of *closo*-carborane structures.[2,3,6,9] In most cases their mass spectra permit reasonably certain identification[9,10] of the specific cage system, but complete structural characterization appeared unnecessary for the purposes of this study and was not attempted.

Discussion

The formation of *closo*-carboranes exclusive of other volatile organoboron products (except in the reaction of B_5H_{11} with $C_2(CH_3)_2$) is consistent with previous studies on high-energy reactions.[2–6] In addition, it is surely significant that a total of only six cage systems (those in Table I plus 1,2-$C_2B_4H_6$[3]) have been found in all reactions of this type investigated to date, despite the much greater number of conceivable geometric isomers for carboranes having up to eight boron atoms. The effect is presumably thermodynamic, with less stable cage isomers undergoing rearrangement or further reaction. Illustrative of this is the pentagonal-bipyramidal $C_2B_5H_7$: although the parent compound and at least eight derivatives were obtained in this work, no evidence was found for species having cage carbons in other than the nonadjacent equatorial 2,4 positions (indeed, the other three geometrically possible isomers are unknown despite the variety of synthetic routes reported for $C_2B_5H_7$[11]).

Although a detailed interpretation of these results is not possible at present, it is interesting to compare the findings of this work with data previously obtained in this laboratory on the B_2H_6–C_2H_2 system.[5] This latter reaction provides a convenient basis for comparison in that the simplest borane and alkyne, free of attached alkyl groups, are involved. Results of this earlier work are of interest in the present discussion in three respects. First, the yield of parent 1,5-$C_2B_3H_5$ was highest in experiments in which the products were

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[9] J. F. Ditter, F. J. Gerhart, and R. E. Williams in "Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968.

[10] It is a useful fact that, since the molecular weights of parent $C_2B_nH_{n+2}$ species differ by increments of 12 units while alkyl derivatives of a given *closo*-carborane differ by 14-unit increments (*e.g.*, $C_2B_3H_5$ = 62; $CH_3C_2B_3H_4$ = 76; $C_2H_5C_2B_3H_4$ = $(CH_3)_2C_2B_3H_3$ = 90, etc.), the parent ion mass of any compound known to be a parent or alkyl-*closo*-carborane uniquely identifies the parent carborane as to formula (not, of course, as to specific isomer) for any *m/e* value up to 146 (sum of 62, the molecular weight of $C_2B_3H_5$, and 84, the lowest common denominator of 12 and 14). For example, among *closo*-carboranes and their alkyl derivatives, a parent ion mass of 100 corresponds uniquely to a methyl derivative of $C_2B_5H_7$. The general utility of this argument rests on the fact that parent and alkyl-*closo*-carboranes are usually readily distinguished from other types of organoboron species by their ir and mass spectra.[9]

[11] For a recent general review of carborane chemistry, see R. Koster and M. A. Grassberger, *Angew. Chem. Intern. Ed. Engl.*, **6**, 218 (1967).

trapped out of a flow system immediately following a glow discharge, was smaller when the products were not trapped but were recirculated through the discharge, and was almost nil in flash reactions. Second, this pattern was reversed for 2,4-$C_2B_5H_7$ and its derivatives. Third, the yield of 1,2-$C_2B_3H_5$ derivatives was nearly the same in all three experimental situations. From these observations one may conclude that the C_2B_3 carboranes are formed in early stages of the discharge and flash reactions but that 1,5-$C_2B_3H_5$ undergoes further reaction unless it is trapped immediately, while the 1,2-$C_2B_3H_5$ derivatives are relatively stable once formed. From the same evidence, it appears that the 2,4-$C_2B_5H_7$ system must form in later stages of the reaction from precursor species formed earlier. This argument presumes very similar mechanisms for the discharge and flash reactions, the justification being that virtually identical products are obtained.[5]

In the flash reactions of B_4H_{10} and B_5H_{11} with C_2H_2, the results are generally similar to the B_2H_6–C_2H_2 case, but the reactions involving higher alkynes are complicated by the presence of alkyl ligands. Lengthy speculation on such effects would be inappropriate here, but it is clear that the production of smaller (*e.g.*, B_3 and B_4) carboranes is increasingly favored as the number of alkyl groups about the alkyne triple bond is increased. Thus, in reactions of B_4H_{10}, the largest yield of three- and four-boron carboranes and, at the same time, the smallest yield of species having five or more borons are obtained from dimethylacetylene. The results are paralleled in the reactions of B_5H_{11} with acetylene and methylacetylene.

These data, like those from the B_2H_6–C_2H_2 study, suggest the early formation of small (four borons or less) organoboron intermediates which can undergo both intra- and intermolecular reactions to yield *closo*-carboranes. The presence of alkyl groups on such precursors—highly probable in reactions involving alkylacetylenes—might well hinder their interaction to give larger cage systems, thus favoring the formation of smaller carboranes. For example, one may visualize a facile conversion of three-boron intermediates containing adjacent carbons to the observed alkyl derivatives of 1,2-$C_2B_3H_5$.

The same argument may account for the greater *total* carborane yield obtained from the higher alkynes in comparison to acetylene. Since the synthesis of larger carboranes from smaller units is surely accompanied by some breakdown to nonvolatile solids, any curtailment of such processes should lead to higher yields of characterizable products.

The failure of 1:1 vapor-phase mixtures of B_5H_{11} and $C_2(CH_3)_2$ to undergo a flash reaction at 100° is evidently related to the extreme instability of B_5H_{11} with respect to loss of hydrogen *via* hydroboration and hydrogenation of the alkyne.[1a] The products obtained (especially *n*-butane, pentaborane(9), and *sec*-butylpentaborane(9)) are identical with those produced[1a] from the same reactants at 25–50°, suggesting that low-energy (*i.e.*, nonexplosive) processes which occur during the warming of the reactor to 100° consume enough of the reactants to prevent flashing.

Although a flash reaction involving the same reactants with the alkyne in 2:1 excess was expected at 100° by analogy with other systems containing excess alkyne with a borane,[5,6] its occurrence below room temperature was surprising. Liquid-phase interactions are clearly involved (see Experimental Section), and it may be noted that borane–alkyne reactions in the liquid phase or in solution often follow a different course from the corresponding vapor-phase systems, frequently giving alkylboranes and other noncarborane organoboron products.[12]

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(12) See, for example, G. F. Clark and A. K. Holliday, *J. Organometal. Chem.* (Amsterdam), **2**, 100 (1964); G. Zweifel and H. Arzoumanian, *J. Am. Chem. Soc.*, **89**, 291 (1967); D. J. Pasto, *ibid.*, **86**, 3039 (1964); L. I. Zakharkin and A. I. Kovredov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 393 (1964); and H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.