692. *Thermochemistry of Organoboron Compounds. Part VIII.** *The Heats of Reaction of Diborane with Ethylene, Isobutene, Butadiene, and Isoprene.*

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The heats of reaction of diborane with ethylene, isobutene, butadiene, and isoprene have been measured at 25° in 1,2-dimethoxyethane as solvent. From the results, values were derived for the heats of formation (ΔH_f°) of liquid triethylboron, and tri-isobutylboron, $-45{\cdot}4$ and $-81{\cdot}9 \pm 1{\cdot}2$ kcal./mole, respectively.

The available heats of formation of alkylborons are discussed in terms of the empirical bond-energy and bond-interaction scheme recently suggested by Allen. The scheme is applied to calculate the heats of possible reactions occurring on hydroboration of butadiene (and isoprene): the experimental thermochemistry of these reactions is consistent with the view that the initial products are low polymers of $-CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}BH-$ or similar units.

Bennett and Skinner [1] recently obtained values for the heats of formation of trihexylboron, triheptylboron, and trioctylboron from measurements of the heats of addition of diborane to hex-1-ene, hept-1-ene, and oct-1-ene. These terminal olefins react rapidly at room temperature in ether solvents,[2,3] *viz.*:

$$6R{\cdot}CH{=}CH_2 + B_2H_6 \longrightarrow 2B(CH_2{\cdot}CH_2R)_3,$$

and proved to be suited to direct calorimetric study. The present paper reports an extension of these calorimetric studies to the addition of diborane to ethylene, isobutene, butadiene, and isoprene.

Experimental

Preparation of Compounds.—Diborane was prepared as described by Brown and Rao [2] and purified by low-temperature distillation in an all-glass system. Ethylene was supplied by the British Oxygen Company, Ltd., and was 98·3% pure; the major impurities were nitrogen (1·2%) and carbon dioxide (0·3%). Isobutene was a high-purity sample from the Phillips Petroleum Co., supplied to us by Dr. P. H. Plesch. Butadiene was supplied by Imperial Chemical Industries Limited and stated to be 99·3% pure, the impurities being but-1-ene (0·4%) and but-2-ene (0·3%). Isoprene was a sample of 99·8% purity, presented by the Dunlop Rubber Co.

" Diglyme " (diethylene glycol dimethyl ether) and " monoglyme " (1,2-dimethoxyethane) were supplied by the Ansul Chemical Co. and purified by fractional distillation over calcium hydride; they were redistilled from lithium aluminium hydride and stored under dry nitrogen.

Calorimeter.—The calorimeter, of the isothermal-jacket type, was described in detail in Part VI. The reaction vessel was the same as used in Part VII. The calorimeter was calibrated electrically by the substitution method.

Procedure.—The general procedure was to mix known amounts of olefin and diborane in monoglyme in the glass reaction vessel inside the calorimeter, and to measure the ensuing change in temperature of the system with time.

Units and Auxiliary Quantities.—Heat quantities are given in thermochemical calories, defined by 1 cal. ≡ 4·1840 abs. joule.

The following values were accepted for the molar volumes of the pure gases at N.T.P.; diborane = 22·15 l.; ethylene = 22·26 l.; isobutene = 21·60 l.; and butadiene = 21·50 l.

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* Part VII, *J.*, 1962, 2150.

[1] Bennett and Skinner, *J.*, 1961, 2472.

[2] Brown and Subba Rao, *J. Org. Chem.*, 1957, **22**, 1136; *J. Amer. Chem. Soc.*, 1959, **81**, 6428.

[3] Brown, *Tetrahedron*, 1961, **12**, 117.

The diborane samples were assumed to have an average purity of 99·5% (as determined by hydrolysis of random samples). The following standard heats of formation were accepted:

ΔH_f° (B_2H_6,g.) = 6·73 ± 0·52 kcal./mole; [4]
ΔH_f° (C_2H_4,g.) = 12·50 ± 0·10 kcal./mole; [5]
ΔH_f° ($Me_2C{=}CH_2$,g.) = −4·04 ± 0·26 kcal./mole; [5]
ΔH_f° ($CH_2{=}CH{-}CH{=}CH_2$,g.) = 26·33 ± 0·30 kcal./mole; [5]
ΔH_f° ($CH_2{=}CMe{-}CH{=}CH_2$,g.) = 18·10 ± 0·30 kcal./mole.[5]

RESULTS

Diborane and Ethylene.—Two sets of experiments were made on the diborane–ethylene reaction. In the first set, a measured volume of ethylene was passed into a solution of diborane in monoglyme, contained in the reaction vessel in the calorimeter. The diborane was present in excess ($m > 0$) with respect to the equation:

$$(m + 1)B_2H_6 \text{ (monoglyme)} + 6C_2H_4 \text{ (g.)} \longrightarrow [m(B_2H_6) + 2B(C_2H_5)_3] \text{ (monoglyme)}. \quad (1)$$

The measured heats of reaction, ΔH_1, calculated per 6 moles of ethylene consumed, were found to diminish as the value of m approached zero. In the presence of an excess of diborane however, eqn. (1) is inaccurate,[6] the products of reaction being a mixture of BEt_3, $BHEt_2$, and BH_2Et. Despite this, we have accepted the value of ΔH_1 obtained by extrapolation of the observed heats of reaction to $m = 0$ as a valid measure: the results are summarised in the Table.

Expt. no.	1	2	3	4	5
C_2H_4 used (mmoles)	11·73	11·69	17·05	15·48	18·59
Value of m	0·70	0·70	0·33	0·33	0·20
ΔH_1, obs. (kcal./$6C_2H_4$)	−169·8	−169·8	−165·0	−164·8	−164·6

Extrapolation to $m = 0$ gives $\Delta H_1 = -164·3 \pm 1$ kcal./mole.

The heat of solution of diborane in monoglyme was measured by Bennett,[7] who obtained $\Delta H_{\text{soln}} = -6·4 \pm 0·2$ kcal./mole. Hence, for the reaction involving B_2H_6 and C_2H_4 as gases, *i.e.*,

$$B_2H_6\text{(g.)} + 6C_2H_4\text{(g.)} + \text{monoglyme} \longrightarrow [2B(C_2H_5)_3], \text{ soln., monoglyme,} \quad (2)$$

the heat of reaction, $\Delta H_2 = -170·7 \pm 1·2$ kcal./mole.

In view of the unsatisfactory feature involved in extrapolating the value ΔH_1, a second set of experiments was made by a different procedure. In these, a measured volume of diborane was passed into a saturated solution of ethylene in monoglyme, the solvent being resaturated with ethylene at the end of the reaction period: the observed heat of reaction, ΔH_3, now refers to the system:

$$[xC_2H_4], \text{ sat. soln. monoglyme} + B_2H_6\text{(g.)} + 6C_2H_4\text{(g.)} \longrightarrow [xC_2H_4 + 2B(C_2H_5)_3]\text{,soln. monoglyme} \quad (3)$$

and, since the heat of solution of C_2H_4 in monoglyme should not differ significantly from that in monoglyme containing a small amount of dissolved triethylboron, the observed reaction heat should be identical with ΔH_2.

The measured heats are summarised as annexed. The mean value is in fair agreement with ΔH_2 obtained in the first set of experiments. We accept $\Delta H_3 = -170·5 \pm 2$ kcal./mole as representative of the results from both sets of experiments.

Expt. no.	1	2	3	4	5	6
B_2H_6 used (mmole)	2·476	2·469	2·500	2·238	2·463	2·516
ΔH_3, obs. (kcal./mole of B_2H_6)	−173·3	−171·5	−168·1	−170·5	−169·5	−168·9

Mean value: $\Delta H_3 = -170·3$ kcal./mole.
2 × Standard deviation of mean = ±1·6 kcal./mole.

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[4] Johnson, Prosen, and Pergiel, *J. Res. Nat. Bur. Standards*, 1958, **61**, 247.
[5] A.P.I. Tables, Project 44, Carnegie Institute of Technology, Pittsburgh, 1953 onwards.
[6] Brown, Tsukamoto, and Bigley, *J. Amer. Chem. Soc.*, 1960, **82**, 4703.
[7] Bennett, Ph.D. Thesis, Manchester University, 1961.

For the idealised reaction:

$$B_2H_6(g.) + 6C_2H_4(g.) \longrightarrow 2B(C_2H_5)_3(liq.), \qquad (4)$$

the heat of reaction, ΔH_4, is related to ΔH_3 by

$$\Delta H_4 = \Delta H_3 - 2\Delta H_{soln.}, \qquad (5)$$

where $\Delta H_{soln.}$ is the heat of solution of liquid triethylboron in monoglyme. The latter was not measured, but was estimated on the basis of the known heat of solution of trihexylboron [1] in diglyme, and of tri-isobutylboron in monoglyme (see below), $\Delta H_{soln.} \sim 1{\cdot}0 \pm 0{\cdot}3$ kcal./mole. Hence, $\Delta H_4 = -172{\cdot}5 \pm 2{\cdot}1$ kcal./mole.

The heat of formation of $B(C_2H_5)_3$,liq., may be derived from ΔH_4 through the thermochemical equation

$$\Delta H_f^\circ(BEt_3,liq.) = \tfrac{1}{2}\Delta H_4 + \tfrac{1}{2}\Delta H_f^\circ(B_2H_6,g.) + 3\Delta H_f^\circ(C_2H_4,g.), \qquad (6)$$

whence $\Delta H_f^\circ(BEt_3,liq.) = -45{\cdot}4 \pm 1{\cdot}2$ kcal./mole. The result compares reasonably well with the value $-47{\cdot}2 \pm 3{\cdot}7$ kcal./mole obtained by Johnson, Kilday, and Prosen [8] from measurements of the heat of combustion using a bomb-calorimeter.

Diborane and Isobutene.—This reaction was studied by adding a known volume of diborane to a solution of an excess of isobutene in monoglyme, *viz.*:

$$(6 + x)C_4H_8,\ \text{monoglyme solution} + B_2H_6(g.) \longrightarrow [2B(C_4H_9)_3 + xC_4H_8],\ \text{monoglyme solution.} \qquad (7)$$

The measured heats of reaction, ΔH_7, per mole of B_2H_6 consumed, are annexed.

Expt. no.	1	2	3	4	5	6
C_4H_8 added (mmole)	18·63	22·41	21·74	22·58	24·87	22·92
B_2H_6 used (mmole)	2·440	2·878	2·846	2·797	2·815	2·748
Value of x	1·64	1·78	1·63	2·08	2·84	2·33
ΔH_7 (kcal./mole of B_2H_6)	−117·4	−115·3	−115·8	−117·0	−115·2	−115·6

Mean value, $\Delta H_7 = -116{\cdot}1$ kcal./mole.
2 × Standard deviation of mean = $\pm 0{\cdot}8$ kcal./mole.

Measurements were also made of the heat of solution of isobutene vapour in monoglyme, yielding $\Delta H_{soln.} = -4{\cdot}55 \pm 0{\cdot}2$ kcal./mole, and of the solution heat of liquid tri-isobutylboron, $\Delta H_{soln.} = 1{\cdot}40 \pm 0{\cdot}1$ kcal./mole; the latter was obtained by using the solution heat calorimeter previously described by Bennett and Skinner.[1] Hence, for the idealised reaction

$$6C_4H_8(g.) + B_2H_6(g.) \longrightarrow 2B(C_4H_9)_3,liq., \qquad (8)$$

the reaction heat, $\Delta H_8 = -146{\cdot}2 \pm 1{\cdot}5$ kcal./mole from which we derive $\Delta H_f^\circ[B(C_4H_9)_3,liq.] = -81{\cdot}9 \pm 1{\cdot}2$ kcal./mole.

According to Brown,[3] the hydroboration of 2-methylbut-1-ene leads almost exclusively (99%) to attachment of boron to the terminal $=CH_2$ group; analogy suggests that the hydroboration of isobutene yields tri-isobutylboron, with little (if any) formation of t-butylboron.

Diborane and Butadiene.—The addition of diborane to dienes has been investigated recently by Zwiefel, Nagase, and Brown,[9] who concluded that a series of competing addition reactions occur with the formation of complex polymeric organoboranes. The diene–diborane reactions, because of their complexity, are less promising from the thermochemical viewpoint than the olefin–diborane reactions, and our studies of them have been no more than exploratory.

The calorimeter was set up with monoglyme in the reaction vessel and allowed to reach a steady thermal state. A measured volume of gaseous butadiene was then dissolved in the solvent, followed by a measured volume of diborane, and the calorimeter temperature was

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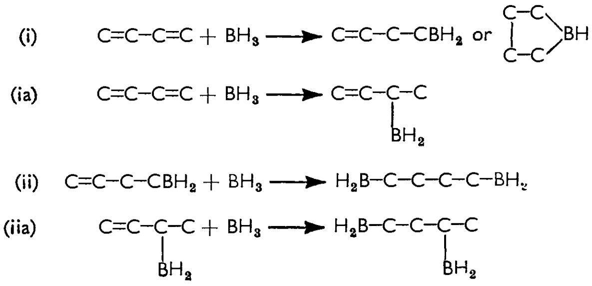
[8] Johnson, Kilday, and Prosen, *J. Res. Nat. Bur. Standards*, 1961, **65**, *A*, 215.

[9] Zweifel, Nagase, and Brown, *J. Amer. Chem. Soc.*, 1962, **84**, 183.

recorded throughout. At the end of the experiment, the products were hydrolysed with water, and the volume of hydrogen evolved was measured.

The reaction is considered to involve the steps:



followed by the addition of each of these products to butadiene, to form polymeric organoboranes. The latter may still contain ⁻BH linkages, which are hydrolysed by water, evolving hydrogen.

The calorimetric results are summarised in Table 1. It appears that the heat of reaction per mole of B_2H_6 added increases as the ratio H_2/BH_3 diminishes (Fig. 1), but it is not simply related to the ratio diene/BH_3. By extrapolation of the results plotted in Fig. 1, the value $\Delta H \sim -160 \pm 10$ kcal./mole is indicated when the ratio H_2/BH_3 becomes zero, *i.e.*, when reaction of B⁻H with diene proceeds to completion.

TABLE 1.

Hydroboration of butadiene.

Expt.	Diene (mmoles)	BH_3 (mmoles)	H_2 (mmoles)	$\frac{\text{Diene}}{BH_3}$	$\frac{H_2}{BH_3}$	$-\Delta H$ (kcal./mole of B_2H_6)
1	6·09	6·19	5·61	0·98	0·91	98·1
2	4·87	4·92	4·09	0·99	0·83	97·3
3	6·92	6·55	5·03	1·06	0·77	100·6
4	6·31	5·73	—	1·10	—	115·0
5	6·34	5·68	4·0	1·12	0·70	115·7
6	12·06	5·76	2·44	2·09	0·42	132·1
7	11·83	5·64	1·31	2·10	0·23	141·5
8	16·83	5·81	2·88	2·90	0·50	132·7
9	16·94	5·83	2·88	2·91	0·49	133·5

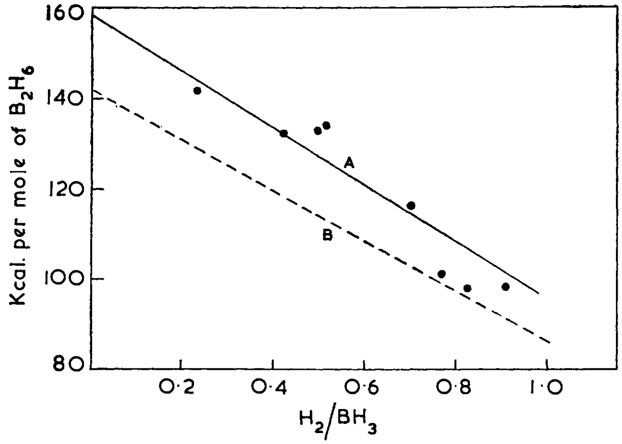
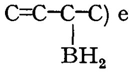


FIG. 1. Butadiene–diborane reaction.

It is clear that the butadiene–diborane reaction does not stop at the first stage (formation of $C{=}C{-}C{-}CBH_2$ and in part, $C{=}C{-}\underset{BH_2}{\underset{|}{C}}{-}C$) even when the diene/$BH_3$ ratio is only 1·0, since in this event the H_2/BH_3 ratio should be 2·0, and was invariably found to be $<1{\cdot}0$. The initial product must therefore either re-arrange by cyclisation, or by forming $-CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}BH-$ and becoming part of a chain polymer



On increasing the ratio diene/BH_3 from 1·0 to 2·0 and up to 3·0, conditions should favour more complete reaction of the B–H links.

This is borne out in Table 1, which shows that the ratio H_2/BH_3 falls to 0·5 or less as diene/BH_3 increases from 1·0 to 2·0. However, the H_2/BH_3 ratio did not continue to fall as the diene/BH_3 ratio was increased from 2·0 ⟶ 3·0. It seems that some B–H linkages become entangled in the polymer structures sufficiently to prevent, or seriously retard, their further reaction with the excess of butadiene.

Diborane and Isoprene.—These studies followed the pattern described for the butadiene–diborane reaction, except that the isoprene was dissolved in the monoglyme before the reaction was started and the temperature changes recorded.

The results are summarised in Table 2.

TABLE 2.

Hydroboration of isoprene.

Expt.	Diene (mmoles)	BH_3 (mmoles)	H_2 (mmoles)	Diene/BH_3	H_2/BH_3	$-\Delta H$ (kcal./mole of B_2H_6)
1	6·5	6·72	6·50	0·97	0·97	80·4
2	6·3	6·21	4·73	1·01	0·76	87·8
3	6·3	6·17	4·38	1·02	0·71	92·1
4	11·0	5·69	2·67	1·93	0·47	102·1
5	11·0	5·67	2·11	1·94	0·37	108·0
6	13·2	6·49	3·29	2·04	0·51	102·7
7	12·0	5·59	2·46	2·15	0·44	95·7
8	17·5	5·68	2·94	3·08	0·52	99·6
9	20·2	6·47	3·51	3·12	0·54	97·2

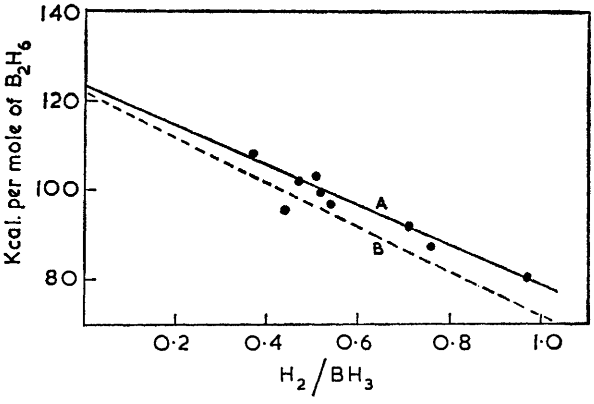


FIG. 2. Isoprene–diborane reaction. (A) Experimental. (B) Calculated.

Extrapolation of these values, plotted in Fig. 2, gives $\Delta H \sim -126 \pm 5$ kcal./mole of B_2H_6 for the complete reaction, *i.e.*, when the ratio H_2/BH_3 becomes zero. As in the hydroboration of butadiene, increasing the diene/BH_3 ratio from 2 to 3 does not seem to increase the degree of hydroboration of the diene.

DISCUSSION

Table 3 lists the heats of formation now available for alkylborons, which have been obtained either from heats of combustion or from heats of hydroboration.

TABLE 3.

Heats of formation of alkylborons.

Compound	Method	Ref.	ΔH_f° (liq.) (kcal./mole)	ΔH_v° (kcal./mole)	ΔH_f° (gas) (kcal./mole)
BMe_3	C	8	-34.8 ± 5.4	4.8 ± 0.2	-30.0 ± 5.5
BEt_3	C	8	-47.2 ± 3.7	8.8 ± 0.2	-38.4 ± 3.8
	HB	*	-45.4 ± 1.2		-36.6 ± 1.4
BBu^n_3	C	8	-83.2 ± 2.5	14.8 ± 0.5	-68.4 ± 3
BBu^i_3	HB	*	-81.9 ± 1.2	13.8 ± 0.5	-68.1 ± 1.7
BBu^s_3	C	10	-75.0 ± 6	14.3 ± 0.5	-60.7 ± 6.5
$B(C_6H_{13})_3$	HB	1	-117.2 ± 2.3	21.2 ± 0.5	-96.0 ± 2.8
$B(C_7H_{15})_3$	HB	1	-135.0 ± 1.8	24.4 ± 0.5	-110.6 ± 2.3
$B(C_8H_{17})_3$	HB	1	-153.3 ± 1.8	27.6 ± 0.5	-125.7 ± 2.3
$B(sec.-C_8H_{17})_3$	HB	1	-149.3 ± 3.5	26.6 ± 0.5	-122.7 ± 4

* This research. C = combustion. HB = hydroboration.

To derive the values ΔH_f°(gas), the heats of vaporisation at 25°, ΔH_v°, given by Furukawa and Park[11] for BMe_3 and BEt_3 were used; for the remainder, we have assumed that $\Delta H_v^\circ(BR_3) = \Delta H_v^\circ(HCR_3)$, and calculated the latter from an empirical formula given by Greenshields and Rossini[12] (the attached error limits of ± 0.5 kcal./mole are arbitrary). The ΔH_f°(liq.) quoted for the hexyl, heptyl, and octyl compounds differ slightly from those given originally;[1] they have been corrected to allow for Brown's finding[3] that the hydroboration of 1-olefins does not lead exclusively to addition of boron to the terminal $=CH_2$, and that *ca.* 6% of addition occurs at the 2-position.

The internal consistency of these ΔH_f°(g.) values may be tested by comparing the experimental with calculated values obtained by application of the bond-energy and bond-interaction scheme described by Allen[13] and Skinner.[14] The scheme leads to the equation:

$$\Delta H_f^\circ[B(C_nH_{2n+1})_3,g.],\text{ calc.} = \Delta H_f^\circ(BMe_3,g.) + 3(n-1)[\Delta H_f^\circ(C_2H_6,g.) - \Delta H_f^\circ(CH_4,g.)] - b_3\Gamma - c_4\Delta - b_3'\Gamma_B - c_4'\Delta_B + [S]. \quad (9)$$

where b_3 is the number of C–C–C interactions, b_3' the number of B–C–C interactions, c_4 the number of C_3 trios, c_4' the number of BC_2 trios, and $[S]$ the total steric repulsion correction in the molecule. The interaction parameters Γ and Δ have been previously defined[14] and given the values 2·58 and —0·55 kcal./mole, respectively. For the parameters Γ_B and Δ_B, we suggest (provisionally) the values 0·7 and —1·1 kcal./mole, respectively, and have accepted (provisionally) a value —27·6 kcal./mole for $\Delta H_f^\circ(BMe_3,g.)$: hence, eqn. (9) now becomes:

$$\Delta H_f^\circ[B(C_nH_{2n+1})_3,g.],\text{ calc.} = -20.55 - 7.05n - 2.58b_3 + 0.55c_4 - 0.7b_3' + 1.1c_4' + [S]. \quad (10)$$

Comparison of the ΔH_f° calculated from eqn. (10) with the experimental data is made in Table 4 below. The agreement between calculated and observed values is satisfactory, in view of the large uncertainty limits attached to the experimental values. The steric repulsion corrections, $[S]$, in the isobutyl, s-butyl, and s-octyl compounds are considered due to the close approach (within 2 Å) of certain non-bonded hydrogen atoms in these molecules (shown diagrammatically in Ia and b). In BBu^s_3, there are six steric interactions,* three of the type $S_{11}(12^2)$, and three of type $S_{11}(2^22^3)$, in the symbolism used by Skinner[14] in discussing similar steric interactions in paraffins: if we adopt the paraffin

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* These can be demonstrated by scale models made with units manufactured by W. Buchi, Glasapparatefabrik, Flawil, Switzerland.

[10] Hasely, Garrett, and Sisler, *J. Phys. Chem.*, 1956, **60**, 1136.

[11] Furukawa and Park, unpublished data referred to in ref. 8.

[12] Greenshields and Rossini, *J. Phys. Chem.*, 1958, **62**, 271.

[13] Allen, *J. Chem. Phys.*, 1959, **31**, 1039.

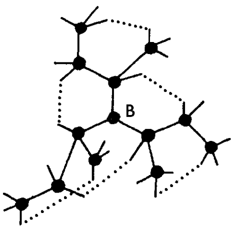
[14] Skinner, *J.*, 1962, 4396.

TABLE 4.

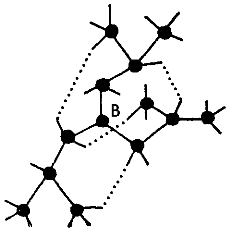
Calculated and observed ΔH_f° values.

Molecule	n	b_3	c_4	b_3'	c_4'	$[S]$ (kcal./mole)	ΔH_f°(g.) (kcal./mole) calc.	obs.
BMe_3	1	0	0	0	0	0·0	−27·6	−30·0 ± 5·5
BEt_3	2	0	0	3	0	0·0	$-36{\cdot}7_5$	−38·4 ± 3·8 −36·6 ± 1·4
BBu^n_3	4	6	0	3	0	0·0	$-66{\cdot}3_3$	−68·4 ± 3
BBu^i_3	4	9	3	3	0	*ca.* 3	−69·4	−68·1 ± 1·7
BBu^s_3	4	6	0	6	3	*ca.* 3·8	−61·3	−60·7 ± 6·5
$B(C_6H_{13})_3$	6	12	0	3	0	0·0	$-95{\cdot}8_1$	−96·0 ± 2·8
$B(C_7H_{15})_3$	7	15	0	3	0	0·0	$-110{\cdot}6_0$	−110·6 ± 2·3
$B(C_8H_{17})_3$	8	18	0	3	0	0·0	−125·4	−125·7 ± 2·3
B(sec.-$C_8H_{17})_3$	8	18	0	6	3	*ca.* 3·8	−120·4	−122·7 ± 4

values for these terms, the total steric correction in BBu^s_3 (and in BOc^s_3) may be evaluated at *ca.* 3·8 kcal./mole. The correction for BBu^i_3 is less easy to estimate, since the steric interactions are here due to close approach of C–H bonds 1,5 to one another and have not been evaluated in paraffins. There are four " close approaches " (to within *ca.* 2 Å) in the conformation we have chosen as the least hindered: we have assumed each of these makes a repulsion-energy contribution of *ca.* $\frac{3}{4}$ kcal./mole.



(Ia) (BBu^s_3)
Six 1,4-C–H interactions.



(Ib) (BBu^i_3)
Four 1,5-C–H interactions.

With the provisional evaluation of the parameters Γ_B and Δ_B (eqn. 9), the Allen scheme can be applied to calculate approximate ΔH_f° values for complex organoboranes such as may be present in the products of hydroboration of butadiene. One of the simpler of these, according to Koster,[15] is 1,1′-tetramethylenebisborolane, $C_4H_8B{\cdot}[CH_2]_4{\cdot}BC_4H_8$, although it now appears [9] that this results as a redistribution product on distillation of the initial product mixture. Application of Allen's scheme to the borolane derivative gives:

$$\Delta H_a^\circ[\square\!\!\!>\!\mathrm{B\text{–}CCCC\text{–}B}\!<\!\!\!\square,\mathrm{g.}],\ \text{calc.} = 2\Delta H_a^\circ[\mathrm{BMe_3,g.}] + 3\Delta H_a^\circ[\mathrm{C_2H_6,g.}] + 6\mathrm{B_{CC}} \\ - 12\mathrm{B_{CH}} + 6(\Gamma + \Gamma_\mathrm{B}) - 2\mathrm{S_R} \quad (11)$$

where ΔH_a° measures heat of atomisation (at 25°), $\mathrm{B_{CC}}$ and $\mathrm{B_{CH}}$ are " effective " bond energy terms,[14] and $\mathrm{S_R}$ is the ring-strain of the borolane ring. Equation (11) may readily be recast into the more convenient form:

$$\Delta H_f^\circ[\square\!\!\!>\!\mathrm{B\text{–}C_4\text{–}B}\!<\!\!\!\square,\mathrm{g.}] = 2\Delta H_f^\circ[\mathrm{BMe_3,g.}] + 3\Delta H_f^\circ[\mathrm{C_2H_6,g.}] + 6[\Delta H_f^\circ(\mathrm{C_2H_6}) \\ - \Delta H_f^\circ(\mathrm{CH_4})] - 6\Delta H_f^\circ(\mathrm{CH_4}) - 6(\Gamma + \Gamma_\mathrm{B}) + 2\mathrm{S_R} \quad (12)$$

which, if we assume $S_\mathrm{R} \sim 6$ kcal./mole, leads to $\Delta H_f^\circ[\square\!\!\!>\!\mathrm{B\text{–}C_4\text{–}B}\!<\!\!\!\square,\mathrm{g.}] = -30{\cdot}4$ kcal./mole. We further assume, approximating, that the heat of vaporisation of an organoborane is given (in kcal./mole) by the sum for the number of boron and carbon

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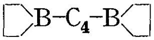
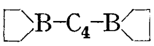
[15] Koster, *Angew. Chem.*, 1959, **71**, 520; 1960, **72**, 626.

atoms in the molecular formula: whence we obtain $\Delta H_f°$[,liq.] ~ —44·4 kcal./mole, and we can now calculate the heat of the specific hydroboration reaction:

$$3CH_2{=}CH{-}CH{=}CH_2(g.) + B_2H_6(g.) \longrightarrow$$  (liq.); (13)

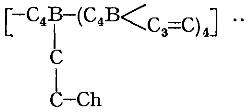
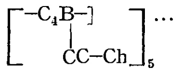
$$\Delta H \text{ (calc.)} = -130{\cdot}1 \text{ kcal./mole.}$$

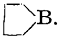
Heats of a number of possible hydroboration reactions of butadiene, calculated in the above manner, are listed in Table 5. A further datum, $\Delta H_f°(Me_2BH,g.) \sim -12{\cdot}4$ kcal./mole, was required in constructing Table 5, and was obtained from $\Delta H_f°(BH_3,g.) = 18{\cdot}0$ kcal./mole,[16] by assuming that $\Delta H_f°(Me_2BH,g.) = \frac{2}{3}\Delta H_f°(BMe_3,g.) + \frac{1}{3}\Delta H_f°(BH_3,g.)$.

TABLE 5.

Calculated heats of hydroboration of butadiene

$nC_4H_6(g.) + B_2H_6(g.) \longrightarrow$ Products(liq.).

	Reaction *	ΔH (calc.) kcal./mole of B_2H_6	$\frac{\text{Diene}}{BH_3}$	$\frac{H_2}{BH_3}$
$2C_4H_6 + B_2H_6$	$\longrightarrow$ 2CpBH	−74	1·0	1·0
$3C_4H_6 + B_2H_6$	$\longrightarrow$ CpB–C_4–BCp	−130	1·5	0·0
$4C_4H_6 + B_2H_6$	$\longrightarrow$ 2CpB–CCC=C	−130	2·0	0·0
$5C_4H_6 + 2\frac{1}{2}B_2H_6$	$\longrightarrow [-C_4BH-]_5$	−86	1·0	1·0
$6C_4H_6 + 2\frac{1}{2}B_2H_6$	$\longrightarrow [(C_4BH)_4{-}C_4B{<}_{C_3=C}]$	−97	1·2	0·8
$7C_4H_6 + 2\frac{1}{2}B_2H_6$	$\longrightarrow [(C_4BH)_3{-}(C_4B{<}_{C_3=C})_2]$	−108	1·4	0·6
$8C_4H_6 + 2\frac{1}{2}B_2H_6$	$\longrightarrow [(C_4BH)_2{-}(C_4B{<}_{C_3=C})_3]$	−119	1·6	0·4
$9C_4H_6 + 2\frac{1}{2}B_2H_6$	$\longrightarrow [(C_4BH){-}(C_4B{<}_{C_3=C})_4]$	−130	1·8	0·2
$10C_4H_6 + 2\frac{1}{2}B_2H_6$	$\longrightarrow [-C_4B{<}_{C_3=C}]_5$	−142	2·0	0·0
$4C_4H_6 + B_2H_6$	$\longrightarrow 2(C{=}CCC)_2BH$	−86	2·0	1·0
$6C_4H_6 + B_2H_6$	$\longrightarrow 2(C{=}CCC)_3B$	−143	3·0	0·0
$11C_4H_6 + 2\frac{1}{2}B_2H_6$		−161	2·2	0·0
$15C_4H_6 + 2\frac{1}{2}B_2H_6$		−234	3·0	0·0

* CpB =  Ch = Cyclohex-2-enyl.

Zweifel, Nagase, and Brown[9] reported that the main products of room-temperature hydroboration of butadiene (diene/BH_3 ratio = 1 are polymers of $-[CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}BH]-$, mainly pentamers and hexamers; special interest, therefore, attaches to the set of reactions in Table 5 leading to $-[CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}BH]_5-$ and its derivatives. The calculated heats of these reactions, for diene/BH_3 ratios from 1·0 to 2·0, and H_2/BH_3 ratios from 1·0 to 0·0, are plotted (broken line) in Fig. 1, for direct comparison with the measured heats of reaction. The experimental line lies some 10—15 kcal./mole of B_2H_6 above the theoretical, and is of similar slope. The smallness of the gap between the lines implies that the principal reaction occurring is hydroboration, and that polymerisation of the excess of butadiene does not occur to any appreciable extent: *

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* The addition of butadiene to ethylene occurs only to 20% at 200° and 200—400 atm., according to Joshel and Butz.[17]

[16] JANAF Thermochemical Data, ed. D. R. Stull, Dow Chemical Co., Midland, Mich., 1960 onwards.

[17] Joshel and Butz, *J. Amer. Chem. Soc.*, 1941, **63**, 3350.

heats of reaction considerably in excess of those observed would be expected in this event (cf. the calculated reaction heats for the formation of the cyclohexene derivatives listed at the foot of Table 5).

The calculated ΔH values for the comparable reactions of isoprene with diborane are similarly plotted (broken line) in Fig. 2. In these, however, the ΔH refer to reaction systems in which the isoprene was present initially in monoglyme solution [in calculating ΔH, the heat of solution of liquid isoprene in monoglyme was assumed, $\Delta H_{\text{soln.}} = 0{\cdot}5$ kcal./mole, so that ΔH_f° (isoprene, monoglyme soln.) $= 12{\cdot}3$ kcal./mole]. As with butadiene, the theoretical line lies below the experimental, the separation between the two in this case being no more than 5—10 kcal./mole. The thermochemistry of these diene–diborane reactions thus appears to be consistent in the main essentials with the proposed mechanism of Zweifel *et al.*[9]

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