413. *Thermochemistry of Organoboron Compounds. Part VII.* The Heats of Reaction of Diborane with Acetone and with Propan-2-ol.*

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The heats of reaction of diborane with acetone and with propan-2-ol at 25° have been measured with use of an isothermal-jacket calorimeter. Both these reactions give di-isopropoxyborine as product. The measured heats of reaction have been used to derive the heat of formation of di-isopropoxyborine, giving $\Delta H_f^\circ[(\mathrm{Pr^iO})_2\mathrm{BH,liq}] = -183\cdot85 \pm 1\cdot5$ kcal./mole.

BROWN, SCHLESINGER, and BURG [1] have reported that diborane in excess reacts rapidly and quantitatively with simple aldehydes and ketones in the liquid phase, to produce dialkoxyborines. The reaction of diborane with alcohols, which also produces dialkoxyborines, was studied by Burg and Schlesinger [2] in 1937.

Part VI of this series described an isothermal-jacket calorimeter, adapted to the measurement of heats of reaction involving diborane gas; this same experimental procedure was used in the present study on the reactions of diborane with acetone and with propan-2-ol. In both these reactions the product is di-isopropoxyborine. The thermochemical studies have provided independent values for the heat of formation of the product, in close agreement with one another.

EXPERIMENTAL

Preparation of Compounds.—Diborane, prepared by the method of Brown and Subba Rao,[3] was purified and handled as described in Part VI.

Acetone was a commercial sample, dried over calcium sulphate, and purified by fractional distillation through a gauze-packed column.

Propan-2-ol was an " AnalaR " sample, dried over calcium hydride, and fractionally distilled from calcium hydride through a gauze-packed column.

Hexane was B.D.H. material " for spectroscopic purposes," dried by lithium aluminium hydride, and purified by fractional distillation.

Calorimeter.—The calorimeter assembly has been described in detail in Part VI. The reaction vessel in the present experiments, however, consisted of two Pyrex containers (50 and 25 ml. capacity) connected together, and similar to the vessel used by Prosen, Johnson, and Pergiel [4] in their measurements of the heat of hydrolysis of diborane.

RESULTS

Acetone.—The experiments were carried out by passing a measured volume of diborane either into acetone dissolved in hexane, or into pure liquid acetone, contained in the twin reaction vessel. The amount of diborane consumed in each experiment was determined from the volume of diborane introduced into the calorimeter, less that escaping the reaction vessel to be trapped in an acetone-filled bubbler in the exit-line from the calorimeter.

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* Part VI, *J.*, 1961, 2472.

[1] Brown, Schlesinger, and Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.

[2] Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **55**, 4020.

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

[4] Prosen, Johnson, and Pergiel, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 43.

The thermochemical results, summarized in Table 1a, relate to the reaction

$$B_2H_6(g) + (4 + m)\text{Acetone–Hexane (solvent)} \longrightarrow 2[(Pr^iO)_2BH] + m[\text{Acetone}]\text{–Hexane (solvent)}, \qquad (1a)$$

and those in Table 1b to the reaction

$$B_2H_6(g) + (4 + m)\text{Acetone(liq)} \longrightarrow 2[(Pr^iO)_2BH] + m[\text{Acetone}] \text{ (solution)}, \qquad (1b)$$

where m in each case indicates the excess of acetone used.

Because of the ready hydrolysis of diborane, care was taken to keep the glass reaction vessel and the reactants thoroughly dry. As described in Part VI, the glass filling lines, reaction vessel, and solvent sample were pretreated with diborane before each experiment but, despite these precautions, small amounts of hydrogen were formed during the acetone hydroboration. The $\Delta H_{\text{obs.}}$ values have therefore been " corrected," to allow for the thermal effect of the hydrolysis, occurring as a side-reaction to the main reaction (1a or b). The corrections were small.

The values ΔH_1 listed in Tables 1a and b refer to the " idealized " reaction

$$B_2H_6(g) + 4\text{Acetone(liq)} \longrightarrow 2[(Pr^iO)_2BH,\text{liq}], \qquad (1c)$$

and are derived from the ΔH_{obs} values by making allowance for the heat effects due to the presence of the solvent. Measurements were made with a simple Dewar-vessel solution calorimeter of the heat of mixing of acetone with hexane over a wide range of concentration. The solution-heat corrections due to this are listed under $\Delta H_{\text{soln.}}$ (acetone–hexane) in Table 1a. We have not measured the heat of solution of di-isopropoxyborine, either in hexane or in acetone. The corrections are based on the assumption that, in hexane, di-isopropoxyborine has the same heat of solution as in acetone, and that the heat of mixing of di-isopropoxyborine with acetone is negligible.

TABLE 1a.

Diborane + Acetone–Hexane.

Expt. no.:	1	2	3	4
B_2H_6 added (mmole)	3·783	3·667	3·743	3·123
B_2H_6 escaping reaction	0·040	0·072	0·132	0·040
B_2H_6 consumed	3·743	3·595	3·611	3·083
Acetone added (mmole)	35·9	35·9	35·9	131·3
Acetone, excess	20·8	21·5	21·4	119·0
Gas evolved (ml.)	20·8	nil	6·9	17·8
$\Delta H_{\text{obs.}}$ (kcal./mole of B_2H_6)	−139·9	−140·9	−143·0	−137·4
$\Delta H_{\text{corr.}}$,,	−140·9	−140·9	−143·3	−138·5
$\Delta H_{\text{soln.}}$ (acetone–hexane)	5·9	5·9	5·9	2·0
$\Delta H_{\text{soln.}}$ (product–hexane)	2·9	2·9	2·9	1·0
ΔH_1 (kcal./mole of B_2H_6)	−137·9	−137·9	−140·3	−137·5

ΔH_1, mean = $-138{\cdot}4 \pm 0{\cdot}8$ kcal./mole.

TABLE 1b.

Diborane + Acetone.

Expt. no.:	1	2	3	4
B_2H_6 added (mmole)	3·502	3·600	3·765	3·632
B_2H_6 escaping reaction	0·037	0·017	nil	nil
B_2H_6 consumed	3·465	3·583	3·765	3·632
Gas evolved (ml.)	10	15	12	12
$\Delta H_{\text{obs.}}$ (kcal./mole of B_2H_6)	−136·6	−136·5	−134·9	−135·7
$\Delta H_{\text{corr.}} = \Delta H_1$	−137·0	−137·1	−135·4	−136·2

ΔH_1, mean = $-136{\cdot}4 \pm 0{\cdot}6$ kcal./mole.

The average ΔH_1 from the two sets of experiments is $-137{\cdot}4$ kcal./mole; we attach an uncertainty interval of ± 2 kcal./mole to this figure, bearing in mind that a strict measure of error limits is impracticable pending measurements of estimated corrections for heats of solution. The heat of formation of di-isopropoxyborine may be derived from the thermochemical equation (reaction 1c), thus:

$$\Delta H_f{}^\circ[(Pr^iO)_2BH,\text{liq}] = \tfrac{1}{2}\Delta H_1 + \tfrac{1}{2}\Delta H_f{}^\circ(B_2H_6,g) + 2\Delta H_f{}^\circ(\text{Acetone,liq}), \qquad (2)$$

by using the values[5] $\Delta H_f°(B_2H_6,g) = 6{\cdot}73 \pm 0{\cdot}52$ kcal./mole, and[6] $\Delta H_f°(\text{acetone,liq}) = -59{\cdot}34 \pm 0{\cdot}3$ kcal./mole; thence we obtain

$$\Delta H_f°[(\text{Pr}^i\text{O})_2\text{BH,liq}] = -184{\cdot}01 \pm 1{\cdot}3 \text{ kcal./mole.}$$

Propan-2-ol.—The thermochemical results, summarized in Table 2, refer to the reaction

$$B_2H_6(g) + (4 + m)\text{Pr}^i\text{OH(liq)} \longrightarrow [2(\text{Pr}^i\text{O})_2\text{BH,liq} + m\text{Pr}^i\text{OH,liq}] + 4H_2(\text{g,sat.Pr}^i\text{OH}). \qquad (3)$$

The reaction occurs readily at 25° when gaseous diborane is passed into an excess of propan-2-ol, but the rate of reaction is markedly less than that of diborane with acetone under similar conditions. Reaction times of 30 min. or more were required, and the rate of passage of diborane was kept low to prevent escape of diborane from the reaction zone. The values ΔH_2 refer to the idealized reaction

$$B_2H_6(g) + 4\text{Pr}^i\text{OH(liq)} \longrightarrow 4H_2(g) + 2(\text{Pr}^i\text{O})_2\text{BH(liq)} \qquad (3')$$

and are derived from $\Delta H_{\text{obs.}}$ by making correction for the heat loss from the reaction vessel caused by the saturation of the hydrogen with alcohol vapour; the heat of solution of di-isopropoxyborine in propan-2-ol was assumed to be negligible.

TABLE 2.

Diborane + Propan-2-ol.

Expt. no.:	1	2
B_2H_6 added (mmole)	3·988	3·997
B_2H_6 escaping reaction	0·040	0·038
B_2H_6 consumed	3·948	3·959
$\Delta H_{\text{obs.}}$ (kcal./mole of B_2H_6)	−67·2	−67·0
ΔH_2 (kcal./mole of B_2H_6)	−70·0	−69·8

The heat of formation of di-isopropoxyborine may now be derived from the thermochemical equation (reaction 3′):

$$\Delta H_f°[(\text{Pr}^i\text{O})_2\text{BH,liq}] = \tfrac{1}{2}\Delta H_2 + \tfrac{1}{2}\Delta H_f°(B_2H_6,g) + 2\Delta H_f°(\text{Pr}^i\text{OH,liq}) \qquad (4)$$

by using the value[7] $\Delta H_f°(\text{Pr}^i\text{OH,liq}) = -76{\cdot}04 \pm 0{\cdot}2$ kcal./mole; thence we obtain

$$\Delta H_f°[(\text{Pr}^i\text{O})_2\text{BH,liq}] = -183{\cdot}67 \pm 0{\cdot}8 \text{ kcal./mole,}$$

in satisfactory agreement with that determined from the heat of hydroboration of acetone.

DISCUSSION

The only previous study on the heats of formation of dialkoxyborines was that of Cooper and Masi[8] who measured the heat of hydrolysis of dimethoxyborine, from which they derived $\Delta H_f°[(\text{MeO})_2\text{BH,liq}] = -145{\cdot}8$ kcal./mole. The value now reported for di-isopropoxyborine is consistent with this, in that the increment in $-\Delta H_f°(\text{liq})$ in passing from $(\text{MeO})_2\text{BH}$ to $(\text{Pr}^i\text{O})_2\text{BH}$ is almost equal to the difference $2\Delta H_f°[\text{MeOH(liq)} - \text{Pr}^i\text{OH(liq)}]$.

It is noteworthy that the diborane–acetone experiments were carried out in the presence of an excess of acetone relative to di-isopropoxyborine formed, allowing the possibility of further reaction to form tri-isopropyl borate, $B(\text{OPr}^i)_3$. The thermochemical evidence indicates that this does not occur (at 25°) to any significant extent. The heat of formation of tri-isopropyl borate has not been measured, but can be estimated from that of tri-n-propyl borate, for which[9,7] $\Delta H_f°[B(\text{OPr})_3,\text{liq}] = -270{\cdot}0$ kcal./mole. The

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[5] Prosen, Johnson, and Pergiel, *J. Res. Nat. Bur. Stand.*, 1958, **61**, 247.

[6] Pennington and Kobe, *J. Amer. Chem. Soc.*, 1957, **79**, 300.

[7] Skinner and Snelson, *Trans. Faraday Soc.*, 1961, **57**, 2125.

[8] Cooper and Masi, *J. Phys. Chem.*, 1960, **64**, 682.

[9] Charnley, Skinner, and Smith, *J.*, 1952, 2288.

estimated value is $\Delta H_f^\circ[B(OPr^i)_3,liq] \simeq -282$ kcal./mole. Hence, for the reaction $B_2H_6(g) + 6Acetone(liq) \longrightarrow 2[B(OPr^i)_3,liq]$ the calculated heat of reaction, per mole of diborane consumed, is $\Delta H = -215$ kcal./mole. The observed heat of reaction of diborane with acetone is slightly less than two-thirds of this calculated figure.

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