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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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DETERMINATION OF THE HEAT OF FORMATION OF DECABORANE

(Presented by Academician Vikt. I. Spitsyn, 18 IX 1961)

For the heat of formation of decaborane, a quantity very important in the thermochemistry of boron compounds, no reliable value was available by the time this work was begun. The literature cited only the values +8 kcal/mole ([1]) and −15.8 kcal/mole ([2]), taken from unpublished work. To determine this quantity we chose the route of thermal decomposition of decaborane, since with any other determinations (combustion in oxygen, hydrolysis, etc.) the error in the desired value $\Delta H^\circ_{\text{form}}\text{B}_{10}\text{H}_{14}$ would inevitably have been very large (because of errors in the heats of formation of the reaction products).

The thermal decomposition of decaborane into boron and hydrogen proceeds completely at 700–800°; this reaction has been used by a number of authors ([3,4]) to establish the composition of decaborane.

Experimental Part

1. Substance investigated and apparatus. In the experiments we used a sample of decaborane purified by repeated sublimation in vacuum (to a constant melting point). The substance was stored in a hermetically sealed weighing bottle. Determinations of the heat of decomposition (pyrolysis) of decaborane were carried out in a combustion-heat calorimeter with an isothermal jacket ([5]).

The calorimetric system consisted of a copper nickel-plated vessel, equipped with a stirrer and an electric heater and containing a measured amount of water (2186.0 g), a calorimetric bomb, to the head of which a quartz vessel for pyrolysis was suspended, and a calorimetric mercury thermometer. The calorimetric bomb had two insulated electrodes and two valves for inlet and outlet of gases; the volume of the internal cavity of the bomb was 260 cm^3.

Fig. 1

Figure 1a shows the design of the vessel for pyrolysis: chamber 1 is intended for placing the weighed portion of decaborane (≈ 0.8 g); the heater was introduced through tube 2. The chamber is surrounded by vacuum jacket 3. The heater (Fig. 1b) was made of tungsten wire ($d = 0.3$ mm) annealed by electric current in vacuum and consisted of two concentric spirals connected to each other and fastened on quartz capillaries.* The ends of the heater were connected by clamps to silver current leads. The heater was supplied with alternating current. To measure the work of the current, we used a previously developed installation (^{6}), the principal elements of which were precision alternating-current meters. The accuracy of determining the amount of heat Q_{el}, released by the elec- electric current in the heater of the pyrolysis vessel, in all experiments, was $±$0.05%.

The degree of decomposition of decaborane was found from quantitative determinations of the hydrogen contained in the bomb after the experiment. In the first series of determinations, the hydrogen was pumped from the bomb by Toepler pumps into a calibrated glass reservoir (volume 3228 cm^3), in which the pressure was then determined with a mercury manometer. In the second series of experiments a gravimetric method was used: the hydrogen was oxidized to water (in a furnace with copper oxide at 600°), which was then absorbed in adsorption tubes with magnesium perchlorate and phosphorus anhydride. The accuracy of determining the amount of hydrogen by both methods was about 0.2%.

2. Procedure for carrying out the experiments. In the pyrolysis vessel (Fig. 1a), the lower bulb and one-third of the upper bulb were filled with decaborane. Before the experiments (first series), the bomb was flushed with dry helium and evacuated to $2 \cdot 10^{-3}$ mm Hg; in the second series of experiments, after flushing, the bomb was filled to 1.1 atm with dry helium purified from hydrogen. The duration of the passage of electric current in the pyrolysis experiment was 7-7.5 min; 2.5 min after switching on, the current in the heater was 5 A, and the temperature of the tungsten spiral was about 1100°.

The initial temperature of the main period in all experiments was $12.14 \pm 0.03°$, and the final temperature was from 24.0 to 24.4°. In the initial, main, and final periods of the experiments, respectively 20, 60, and 40 measurements of the calorimeter temperature were made at intervals of 30 sec. The thermometer readings could be read to 0.0005 degree. The thermal value of the calorimetric system was determined electrically; in doing so, the tungsten heater in the pyrolysis vessel was replaced by a nichrome one with a resistance of 59 ohms, and the bomb was filled to 5 atm with dry helium. From 8 determinations the thermal value was calculated to be $W = 2615.4 \pm 1.1$ cal/deg. In calculating the pyrolysis experiments, a small correction for the difference in the heat capacities of the substances contained in the bomb in the pyrolysis experiments and in the

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* Resistance of the heater $R_{25°} \approx 0.6\ \Omega$.

experiments for determining the thermal value was introduced into the value of W found.

Products of pyrolysis. The solid products of pyrolysis remained practically completely in the pyrolysis vessel. In appearance they were not homogeneous: the heater was filled with a very fine black powder; in the lower and middle bulbs of the vessel there were mainly loose, slag-like black-brown pieces (some with a metallic luster) and, in addition, a small amount of coarse black powder. On the inner wall of the upper bulb of the pyrolysis vessel there was a deposit of a gray and brown substance. X-ray examination established that the fine powder removed from the heater was amorphous; the slag-like pieces contained 5-10% of a crystalline phase; and the coarse powder was mainly crystalline, having a structure similar to that of quartz.

The products of pyrolysis, on chlorination (350-400°), were almost completely converted into BCl_3; the nonchlorinated residue amounted to about 2% and had the appearance of a black powder. Since crystalline boron is distinguished by chemical inertness and is not chlorinated at 350-400°, the crystalline powder apparently represents a nonvolatile hydride of boron; the amorphous substance, according to the X-ray pattern, is amorphous boron. The formation of volatile boron hydrides was not observed: when the hydrogen was pumped out of the bomb, no condensation of any substance occurred in the trap immersed in liquid nitrogen.

Results of the experiments. The amount of heat expended on the decomposition of decaborane in the experiment, Q_{react}, was calculated from the equation:

$$Q_{\text{react}} = W \cdot \Delta\vartheta_{\text{exp}} - Q_{\text{el}},$$

where W is the thermal value of the calorimetric system, $\Delta\vartheta_{\text{exp}}$ is the rise in the temperature of the calorimeter in the experiment (with allowance for corrections for heat exchange and

(the protruding column of mercury) and Q_{el} is the heat evolved by the electric current in the heater of the pyrolysis vessel.

The measure of the progress of the decomposition reaction of decaborane was the precisely determined volume of hydrogen V_{H2}.

The ratio of the values Q_{react} to the corresponding values of V_{H2} (referred to $\vartheta = 0$°C and $P = 760$ mm Hg) in the experiments carried out proved to be constant within the possible error of this ratio, despite the fact that the percentage of hydrogen evolved in the experiments varied from 82.7 to 95.5. This result is very important, since it permits the assumption that the ratio $Q_{\text{react}}/V_{\text{H2}}$ will remain the same when complete decomposition of decaborane into boron and hydrogen is attained. Taking further into account that the pyrolysis products contained no crystalline boron, we arrive at the conclusion that the values $Q_{\text{react}}/V_{\text{H2}}$ may be referred to the decomposition of decaborane according to the equation:

$$B_{10}H_{14\,\text{(cryst)}} = 10B_{\text{(amorph)}} + 7H_{2\,\text{(gas)}}.$$

The heat of decomposition of 1 mole of decaborane under the conditions of the experiments was calculated from the equation

$$\Delta U_\text{B} = -\frac{Q_\text{react}}{V_\text{H2}} \cdot 22433 \cdot 7,$$

where 22433 and V_H2 are, respectively, the molar volume and the volume of hydrogen evolved in the experiment, in milliliters at normal conditions.

The experimental results are given in Table 1.

Table 1

Results of experiments on the pyrolysis of decaborane

No.	Q_react, cal	V_H2 (at 0°C and 760 mm), ml	ΔU_B, kcal/mole	Decomposition (by hydrogen), %
1	−88.6	955.2	14.5_6	94.2
2	−74.4	960.3	12.1_7	90.0
3	−104.4	984.6	16.6_5	95.1
4	−78.1	825.0	14.8_6	82.7
5	−84.9	942.2	14.1_5	85.2
6	−66.3	837.7	12.4_3	93.9
7	−81.7	877.3	14.6_2	95.5
8	−89.5	956.8	14.6_9	95.3
9*	−79.1	1080.8	11.5_4	88.8
10*	−86.7	1025.9	13.2_7	87.7
Average . . .			$13.8_9 \pm 1.0$	

* In experiments 9 and 10, V_H2 was calculated from the weight of water obtained by oxidation of the evolved hydrogen.

On passing from ΔU to ΔH and to the standard conditions of the reaction ($\vartheta = 25°$, $P = 1$ atm), only the quantity $\Delta nRT = 4.13$ kcal/mole proved significant. Thus, for the reaction

$$B_{10}H_{14\,\text{(cryst)}} = 10B_{\text{(amorph)}} + 7H_{2\text{(gas)}},$$

proceeding under standard conditions, $\Delta H = 18.0 \pm 1.0$ kcal/mole. The error given is twice the standard error of the mean result.

Taking $B_{(cryst)}$ as the standard state for boron and taking into account the heat of transformation $B_{(amorph)} = B_{(cryst)}$, $\Delta H = -0.4$ kcal/mole (^{1}), for the standard heat of formation of crystalline decaborane from crystalline

of boron and gaseous hydrogen, we have:

$$\Delta H^0_{\text{form}} B_{10}H_{14(\text{cryst})} = -14.0 \pm 1.0 \text{ kcal/mole}.$$

The result obtained agrees with the value -15.8 ± 1.4 kcal/mole, reported in the recently published work of Johnson, Kilday, and Prosen (7).

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