THE HEAT OF COMBUSTION OF TETRAETHYLDIBORANE

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SUMMARY

The net heat of combustion of a sample of tetraethyl diborane was found to be 20,400 ± 130 Btu per pound for the reaction of liquid fuel to gaseous carbon dioxide, gaseous water, and solid boric oxide. The measurements were made in a Parr oxygen bomb calorimeter and the combustion is believed to have been 99 percent complete. A more reasonable value for the net heat of combustion would therefore be 20,600 ± 130 Btu per pound.

INTRODUCTION

At the request of the Bureau of Aeronautics, Department of the Navy, the NACA is participating in a project aimed at the discovery and evaluation of certain high-energy fuels. A part of the work that the NACA will perform in this project is the determination of the fundamental flame velocity, heat of combustion, and possibly other combustion properties of fuel samples submitted by companies participating in the project as contractors to the Bureau of Aeronautics.

A sample of tetraethyl diborane was received and the heat of combustion of this material has been measured in a Parr oxygen bomb calorimeter.

TEST SPECIMENS

Two groups of samples (A and B), along with analytical data (table I), were obtained from the manufacturer in sealed glass bulbs. They were kept at dry-ice temperature until introduced into the bomb. The liquid weight varied from 0.2 to 0.35 gram, and several samples contained small amounts of dark insoluble material.

The A samples were used for preliminary investigations; the reported values are for the B samples.
APPARATUS AND PROCEDURE

The apparatus consisted of a Parr adiabatic calorimeter equipped with an Illium constant-volume bomb and a mercury thermometer which could be read to ±0.005° F. The bomb was calibrated using standard benzoic acid. The samples were contained in glass bulbs filled so that at room temperature the liquid occupied the entire volume. The method used in making a determination was to attach the bulb to the iron ignition wire with a preweighed piece of cellulode tape, place a perforated nickel crucible around the bulb, and fill the bomb with 25 atmospheres of oxygen. The heat generated by the burning of the ignition wire and cellulose tape caused the liquid to rupture the glass bulb and burn.

Carbon dioxide formed in the combustion was absorbed in Ascarite after the gas had been dried by passage through Anhydrone. When all the gas had been flushed out with fresh oxygen, the bomb was opened and examined for signs of incomplete combustion. It was then washed with distilled water and the washings were filtered. The filtrate was then titrated to determine nitric acid formed during the combustion. The last step was to titrate for boric acid (ref. 1).

RESULTS AND DISCUSSION

The results from four determinations of the heat of combustion of sample B tetraethyldiborane and the analysis of the combustion products are given in table II. The heats of combustion are the gross uncorrected values determined directly in the bomb with gaseous carbon dioxide, liquid water, and solid boric acid as the combustion products and with part of the boric acid dissolved in the water present in the bomb. The value for this gross heating value is 22,048 ±130 Btu per pound. The determined percent carbon, as carbon dioxide, was much below the theoretical and manufacturer's values for tetraethyldiborane, whereas the percent boron was somewhat higher than the theoretical value.

In all cases, slight amounts of black material were found among the combustion products. However, experience indicates that such an amount of residue is associated with a combustion efficiency of perhaps 99 percent. It is therefore difficult to understand the discrepancy in the analytical data of tables I and II other than by the assumption that some change occurred in the material between the time it was
analyzed and the time the glass bulbs were filled. In previous studies of dimethylaminodiborane (ref. 2) and alkylsilanes (refs. 3 and 4), excellent agreement was obtained between the calculated carbon content of the compounds and that recovered as carbon dioxide after combustion.

The determined gross heating value from table II is $22,048 \pm 130$ Btu per pound, which is equivalent to 1715.3 kilocalories per mole. The following corrections were then made:

1. Conversion from a constant-volume process to a constant-pressure process, $+4.1$ kilocalories per mole

2. Correction for the heat of hydration of boric oxide to boric acid and the heat of solution of part of the acid so formed, $-16.0$ kilocalories per mole (ref. 5)

Corrections (1) and (2) result in a value of 1703.4 kilocalories per mole or 21,892 Btu per pound for the reaction

$$\text{B}_2\text{H}_2(\text{C}_2\text{H}_5)_4(l) + 15 \text{O}_2(g) \rightarrow 8 \text{CO}_2(g) + 11 \text{H}_2\text{O}(l) + \text{B}_2\text{O}_3(s)$$

A further correction is needed to yield the net heat of combustion.

3. Correction for the latent heat of vaporization of the water formed during combustion, assuming that the sample contains the theoretical concentration of hydrogen (15.9 percent), $-1488$ Btu per pound of tetraethyldiborane

Thus, the heat of combustion to gaseous water, gaseous carbon dioxide, and solid boric oxide becomes $20,404 \pm 130$ Btu per pound, which is rounded off to $20,400 \pm 130$ Btu per pound. If the combustion is assumed 99 percent complete, a more reasonable value would be $20,600 \pm 130$ Btu per pound.

Two determinations were recorded for samples A, which showed a heating value 615 Btu per pound lower than the value for samples B.

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REFERENCES


### TABLE I. - ANALYSES OF TETRAETHYLDIBORANE SAMPLES

REPORTED BY MANUFACTURER

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon, percent</th>
<th>Boron, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mfr.</td>
<td>Theory</td>
</tr>
<tr>
<td>A</td>
<td>70.0</td>
<td>68.7</td>
</tr>
<tr>
<td>B</td>
<td>72.0</td>
<td>68.7</td>
</tr>
</tbody>
</table>

### TABLE II. - HEAT OF COMBUSTION DATA FOR

SAMPLE B TETRAETHYLDIBORANE

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gross uncorrected heating values, Btu/lb</th>
<th>Analysis of combustion products</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Carbon, percent</td>
</tr>
<tr>
<td>1</td>
<td>21,996</td>
<td>66.03</td>
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<tr>
<td>2</td>
<td>22,170</td>
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<tr>
<td>3</td>
<td>22,105</td>
<td>65.63</td>
</tr>
<tr>
<td>4</td>
<td>21,920</td>
<td>66.05</td>
</tr>
<tr>
<td>Average</td>
<td>22,048 ±130</td>
<td>65.9</td>
</tr>
</tbody>
</table>

Theoretical Corrected net value

| Analysis of combustion products | 68.7 | 15.5 |

Gas lost during analysis.