RESEARCH MEMORANDUM

HEAT OF COMBUSTION OF THE PRODUCT FORMED BY THE REACTION
OF ACETYLENE AND DIBORANE (LFPL-CZ-3)

By Harrison Allen, Jr. and Stanley Tannenbaum

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON
RESEARCH MEMORANDUM

HEAT OF COMBUSTION OF THE PRODUCT FORMED BY THE REACTION
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SUMMARY

The heat of combustion of the product formed by the reaction of acetylene and diborane was found to be 20,100±100 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 chemical analyses both of the sample and of the combustion products indicated combustion in the bomb calorimeter to have been 97 percent complete. The estimated net heat of combustion for complete combustion would therefore be 20,700±100 Btu per pound.

INTRODUCTION

At the request of the Bureau of Aeronautics, Department of the Navy, the NACA is participating in a project (Project ZIP) aimed at the discovery and evaluation of certain high-energy fuels. The NACA has determined fundamental combustion parameters and heats of combustion for fuel samples submitted by companies participating in the project as contractors to the Bureau of Aeronautics, Department of the Navy.

A sample of material formed by the reaction of acetylene and diborane (LFPL-CZ-3) was received from the Callery Chemical Company. The heat of combustion of this material has been measured in a Parr oxygen-bomb calorimeter using the procedure supplied by the Parr Instrument Company (ref. 1). Although the precision of the data is not equal to that obtained for hydrocarbons or the alkylsilanes (ref. 2) which have been studied at this laboratory, this special release memorandum has been prepared to make the data available as soon as possible.

TEST SPECIMEN

A group of samples, sealed in glass bulbs, was obtained from the Callery Chemical Company along with analytical data (table I). The
liquid weight varied from 0.2 to 0.4 gram per sample, and several samples contained small amounts of suspended solids. The material was a yellow moderately viscous liquid.

In all cases there was a small amount of carbonization at the point where the bulb was sealed off. However, this involved an insignificant amount of material.

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 supplied by the Parr Instrument Company. The samples were contained in glass bulbs filled so that at room temperature the liquid occupied the entire volume. The steps followed in achieving combustion were (1) to attach the bulb to the iron ignition wire with a preweighed piece of cellulose tape, (2) to place a perforated nickel crucible around the bulb, (3) to fill the bomb with 25 atmospheres of oxygen, and then (4) to energize the ignition wire. 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 completeness of combustion. It was then washed with distilled water and the washings were filtered. The filtrate was titrated to determine nitric acid formed during the combustion. The last step was to titrate for boric acid (ref. 3) using a Fisher titrimeter.

RESULTS AND DISCUSSION

The results of three determinations of the heat of combustion of LFPL-CZ-3 and the analysis of the combustion products are given in table III. 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. Only runs 1 and 2 (of the five runs) were used to obtain the average values, since in run 3 an experimental error must have been made to give such a low heat of combustion value. In the two other runs not included in table III the combustion was not complete; however, these values still averaged 22,250 Btu per pound. Therefore value 3 in table III must be assumed to be due to an experimental error. In all cases, however, slight
amounts of black material were found among the combustion products. The average gross heating value for runs 1 and 2 was 22,324±100 Btu per pound.

Both the analysis of the combustion products and the NACA quantitative analysis of LFPL-CZ-3 (table II) gave carbon and boron percentages which were somewhat below the values reported by the Callery Chemical Company. The NACA quantitative analysis is considered to be quite accurate and is believed to be the analysis that would be found if the combustion was 100 percent complete. Therefore, in comparing this quantitative analysis with the analysis of the combustion products, it is estimated that the combustion in the Parr bomb is 97 percent complete.

In order to convert the uncorrected gross value to a corrected net heat of combustion value, it is necessary to know the chemical composition of the compound. Therefore, since the Callery Chemical Company supplied only a boron, carbon and partial hydrogen analysis, it was assumed that the remaining percentage (21 percent) was hydrogen.

Using the analysis obtained from the combustion products and the above assumption, the empirical formula for the reaction product of acetylene and diborane is B$_2$C$_4$H$_{18}$. The following corrections are then made:

1. Conversion from a constant-volume process to a constant-pressure process, add 3.5 kilocalories per mole.

2. Correction for the heat of hydration of boron oxide to boric acid and the heat of solution of part of the acid so formed, subtract 16.56 kilocalories per mole (ref. 4).

Corrections 1 and 2 result in a value of 1076.3 kilocalories per mole or 22,059.6 Btu per pound for the reaction:

\[ \text{B}_2\text{C}_4\text{H}_{18}(l) + 10 \text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s) + 9 \text{H}_2\text{O}(l) + 4 \text{CO}_2(g) \]

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 21 percent hydrogen, subtract 1965.6 Btu per pound of LFPL-CZ-3.

Thus, the net heat of combustion to gaseous water, gaseous carbon dioxide, and solid boric oxide becomes 20,094±100 Btu per pound, which is rounded off to 20,100±100 Btu per pound. If the combustion is assumed 97 percent complete, a more reasonable value would be 20,700±100 Btu per pound.
Using the carbon and boron analysis supplied by the Callery Chemical Company and assuming that the remaining percentage (14.26 percent) is hydrogen, the empirical formula for the reaction product of acetylene and diborane is $\text{B}_2\text{C}_4\text{H}_{10}$, which would be expected if the reaction went as follows:

$$\text{B}_2\text{H}_6 + 2 \text{C}_2\text{H}_2 \rightarrow \text{CH}_2=\text{CH}-\text{BH}_2-\text{BH}_2-\text{CH}=\text{CH}_2 \quad (\text{B}_2\text{C}_4\text{H}_{10})$$

Considering the $\text{B}_2\text{C}_4\text{H}_{10}$ formula in applying the corrections for converting the determined gross value to a corrected net heat of combustion value, one would get a net heat of combustion of 20,659±100 Btu per pound. Assuming 97 percent combustion a more accurate value would be 21,300±100 Btu per pound.

It is of interest to note that the net heat of combustion of diborane alone is 31,373 Btu per pound (ref. 5), and the net heat of combustion of acetylene alone is 20,734 Btu per pound (ref. 6). Thus, the reaction product of acetylene and diborane designated LFPL-CZ-3 does not have an outstandingly high heat of combustion.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, November 10, 1953

REFERENCES


TABLE I. - ANALYSIS OF PRODUCT

LFPL-CZ-3 REPORTED BY CALLERY CHEMICAL COMPANY

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percent</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>56.09</td>
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<tr>
<td>Boron</td>
<td>29.65</td>
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<tr>
<td>Active hydrogen</td>
<td>3.33</td>
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TABLE II. - ANALYSIS OF PRODUCT

LFPL-CZ-3 DETERMINED BY NACA

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percent</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>55.41</td>
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<tr>
<td>Boron</td>
<td>25.77</td>
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</table>

TABLE III. - HEAT OF COMBUSTION DATA FOR REACTION

PRODUCT OF ACETYLENE AND DIBORANE (LFPL-CZ-3)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gross uncorrected heating values, Btu/lb</th>
<th>Analysis of combustion products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carbon, percent</td>
</tr>
<tr>
<td>1</td>
<td>22,354.8</td>
<td>53.72</td>
</tr>
<tr>
<td>2</td>
<td>22,293.4</td>
<td>53.51</td>
</tr>
<tr>
<td>3</td>
<td>21,736.8</td>
<td>53.66</td>
</tr>
<tr>
<td>Average (1 and 2)</td>
<td>22,324±100</td>
<td>53.62</td>
</tr>
<tr>
<td>Corrected net value</td>
<td>20,100±100</td>
<td>25.36</td>
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</tbody>
</table>
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Abstract

The heat of combustion of the product formed by the reaction of acetylene and diborane was found to be 20,100±100 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 chemical analyses both of the sample and of the combustion products indicated combustion in the bomb calorimeter to have been 97 percent complete. The estimated net heat of combustion for complete combustion would therefore be 20,700±100 Btu per pound.