Heats of Combustion and Isomerization of Six Nonanes

By Walter H. Johnson, Edward J. Prosen, and Frederick D. Rossini

The heats of isomerization of six of the nonanes were determined by measurement of the ratios of the heats of combustion in the liquid state of purified samples of these compounds by the procedure previously described for other hydrocarbons. The data yield the following values for the heat of isomerization in the liquid state at 25° C, \( \Delta H^\circ \), of \( n \)-nonane into the other nonanes, in kilocalories per mole: \( n \)-Nonane, 0.00; 3,3-diethylpentane, \(-0.01 \pm 0.33\); 2,2,3,3-tetramethylpentane, \(-0.70 \pm 0.31\); 2,2,4,4-tetramethylpentane, \(-1.11 \pm 0.25\); 2,2,3,4-tetramethylpentane, \(-0.62 \pm 0.35\). These data were combined with the value previously reported for the heat of combustion of \( n \)-nonane to obtain values for the heats of combustion of the other five nonanes in the liquid state at 25° C.

I. Introduction

In continuation of the program of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types \([1, 2, 3, 4, 5, 6, 7]\) calorimetric measurements have been made that yield values for the differences in the heats of combustion, or the heats of isomerization, of six of the isomeric nonanes in the liquid state at 25° C. These heats of isomerization were combined with the value \([8]\) previously reported for the heat of combustion of \( n \)-nonane to obtain values for the heats of combustion of the other five nonanes in the liquid state at 25° C.

II. Unit of Energy, Molecular Weights, Uncertainties

The unit of energy upon which the values reported in this paper are based is the international joule, derived from mean solar seconds and the units of international ohms and international volts, in terms of which certification of standards of resistance and electromotive force is made by the Bureau. For conversion to the conventional thermochemical calorie, the following relation is used \([9]\):

\[ 1 \text{ calorie} = 4.1833 \text{ international joules}. \]

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of international atomic weights \([10]\).

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described \([11]\).

Definitions of the symbols used are given in previous papers \([1, 3, 4, 6, 7]\).

III. Method and Apparatus

The same method and apparatus were used as in the investigations recently reported from this laboratory \([1, 2, 3, 4, 5, 6, 7, 12]\). One calorimeter system was used throughout this investigation. Resistance bridge No. 404 and platinum resistance thermometer No. 373,730 were used for all the experiments reported here.

No products of incomplete combustion were found in any of the experiments.

IV. Materials

The compounds used in the present investigation were samples from the API–NBS series of highly purified hydrocarbons, which are being prepared through a cooperative undertaking of
the American Petroleum Institute and the National Bureau of Standards [15, 16, 17].

These samples of API–NBS hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the API Research Project 44 on the “Collection, Analysis, Calculation, and Compilation of Data on the Properties of Hydrocarbons.” The samples were purified at the National Bureau of Standards by the American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord.

2,2,3,3-4-Tetramethylpentane, 2,2,4,4-tetramethylpentane, and 2,3,3,4-tetramethylpentane, by the National Advisory Committee for Aeronautics, through its Aircraft Engine Research Laboratory, Cleveland, Ohio, and its supported work in the Automotive Section at the National Bureau of Standards.

n-Nonane, by the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

A complete description of the purification, purity, and freezing points of the six nonanes of the present investigation is given by Streiff, Murphy, Cahill, Flanagan, Sedlak, Willingham, and Rossini [17], who reported the amounts of impurity in these samples, as determined from measurements of freezing points, to be as follows: n-Nonane, 0.0006 ± 0.0004; 3,3-diethylpentane, 0.00013 ± 0.00011; 2,2,3,3-tetramethylpentane, 0.0006 ± 0.0002; 2,2,4,4-tetramethylpentane, 0.00024 ± 0.00014; 2,2,4,4-tetramethylpentane, 0.0011 ± 0.0008; 2,3,3,4-tetramethylpentane, 0.00044 ± 0.00037, mole fraction.

As the manner of purification of these compounds [17] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the worst case the measured heat of combustion would be affected by less than 0.001 percent because of impurities in the compound.

V. Results

The experimental results of the present investigation are summarized in table 1, which gives for each of the six compounds the following data: The number of experiments performed; the minimum and maximum values of the mass of carbon dioxide formed in the combustion and of the calorimetric quantities \( k \), \( K \), \( U \), \( \Delta R_e \), \( \Delta r \), \( \Delta \alpha \) [1]; the mean value of \( B \), and its standard deviation, in ohms per gram of carbon dioxide formed, as defined by equation 4 of reference [1]. The symbols have the same significance as in the previous report [1], and the references there cited.

In table 2 are given, for the six nonanes, values of the following: The constant \( B \) in ohms per gram of carbon dioxide, as given in table 1; \( B^2 \), which is \( B \) corrected to the ideal bomb reaction by the

<table>
<thead>
<tr>
<th>Compound (liquid)</th>
<th>Number of experiments</th>
<th>Mass of carbon dioxide formed</th>
<th>( k )</th>
<th>( K )</th>
<th>( U )</th>
<th>( \Delta R_e )</th>
<th>( \Delta r )</th>
<th>( \Delta \alpha )</th>
<th>( B ) Mean</th>
<th>( B ) Standard deviation of mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Nonane</td>
<td>5</td>
<td>2.59316 ± 0.00097 to 2.5964 ± 0.00097</td>
<td>0.001979 to 0.001984</td>
<td>0.000123 to 0.000127</td>
<td>0.287491 to 0.287493</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
<tr>
<td>3,3-Diethylpentane</td>
<td>6</td>
<td>2.53502 ± 0.000974 to 2.53508 ± 0.000974</td>
<td>0.001974 to 0.001984</td>
<td>0.000867 to 0.000866</td>
<td>0.287890 to 0.287891</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
<tr>
<td>2,2,3,3-Tetramethylpentane</td>
<td>6</td>
<td>2.55440 ± 0.000974 to 2.5647 ± 0.000974</td>
<td>0.001974 to 0.001984</td>
<td>0.0001154 to 0.0001154</td>
<td>0.277571 to 0.277568</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
<tr>
<td>2,2,4,4-Tetramethylpentane</td>
<td>6</td>
<td>2.55667 ± 0.000974 to 2.5647 ± 0.000974</td>
<td>0.001974 to 0.001984</td>
<td>0.0001518 to 0.0001518</td>
<td>0.290464 to 0.290462</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
<tr>
<td>2,2,4,4-Tetramethylpentane</td>
<td>5</td>
<td>2.55278 ± 0.000974 to 2.5897 ± 0.000974</td>
<td>0.001974 to 0.001984</td>
<td>0.0008941 to 0.0008941</td>
<td>0.289900 to 0.289900</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
<tr>
<td>2,3,3,4-Tetramethylpentane</td>
<td>7</td>
<td>2.55035 ± 0.000976 to 2.6706 ± 0.000976</td>
<td>0.001976 to 0.001965</td>
<td>0.0006777 to 0.0006777</td>
<td>0.283888 to 0.283888</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
<tr>
<td>2,3,3,4-Tetramethylpentane</td>
<td>5</td>
<td>2.53247 ± 0.000977 to 2.58449 ± 0.000977</td>
<td>0.001977 to 0.001961</td>
<td>0.0005586 to 0.0005574</td>
<td>0.286688 to 0.286688</td>
<td>0.000351 to 0.000349</td>
<td>0.000284 to 0.000293</td>
<td>0.000131 to 0.000132</td>
<td>0.0008 ± 0.0008</td>
<td>0.00000082 ± 0.00000082</td>
</tr>
</tbody>
</table>
TABLE 2.—Heats of isomerization and combustion in the liquid state

<table>
<thead>
<tr>
<th>Compound</th>
<th>B, at 28.00° C</th>
<th>B, at 28.00° C</th>
<th>Ratio of the heats of combustion in the ideal bomb process, B,J/B,J</th>
<th>Difference in the heats of combustion in the ideal bomb process (−ΔU°)</th>
<th>Int. kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Nonane</td>
<td>0.1130685 ±0.0000164</td>
<td>0.1130214 ±0.0000164</td>
<td>1.000000</td>
<td>0.00</td>
<td>0.02 ±1.39</td>
</tr>
<tr>
<td>3,3-Diethylpentane</td>
<td>0.1130482 ±0.0000196</td>
<td>0.1130214 ±0.0000198</td>
<td>0.999967 ±0.0000227</td>
<td>0.02 ±1.39</td>
<td>2.92 ±1.31</td>
</tr>
<tr>
<td>2,2,3,3-Tetramethylpentane</td>
<td>0.1136049 ±0.0000052</td>
<td>0.1136779 ±0.0000050</td>
<td>0.999615 ±0.000152</td>
<td>2.35 ±1.04</td>
<td>4.65 ±1.04</td>
</tr>
<tr>
<td>2,2,4,4-Tetramethylpentane</td>
<td>0.1195948 ±0.0000062</td>
<td>0.1129554 ±0.0000102</td>
<td>0.999289 ±0.0000171</td>
<td>2.60 ±1.45</td>
<td>2.60 ±1.45</td>
</tr>
<tr>
<td>2,3,3,4-Tetramethylpentane</td>
<td>0.1138014 ±0.0000210</td>
<td>0.1129734 ±0.0000214</td>
<td>0.996575 ±0.000238</td>
<td>0.00</td>
<td>0.02 ±1.39</td>
</tr>
</tbody>
</table>

heats of isomerization and combustion in the liquid state.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of isomerization of the liquid, (H°(\text{tq})-H°(\text{liq})) at 25.00° C</th>
<th>Heat of combustion of the liquid, (-\Delta H°) at 25.00° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Nonane</td>
<td>0.00 ±0.32</td>
<td>6123.51 ±0.75</td>
</tr>
<tr>
<td>3,3-Diethylpentane</td>
<td>-0.62 ±0.35</td>
<td>6120.91 ±1.63</td>
</tr>
<tr>
<td>2,2,3,3-Tetramethylpentane</td>
<td>-0.62 ±0.33</td>
<td>6121.16 ±1.39</td>
</tr>
<tr>
<td>2,2,4,4-Tetramethylpentane</td>
<td>-0.62 ±0.35</td>
<td>6118.86 ±1.28</td>
</tr>
<tr>
<td>2,3,3,4-Tetramethylpentane</td>
<td>-0.62 ±0.35</td>
<td>6120.91 ±1.63</td>
</tr>
</tbody>
</table>

The method of Washburn [13] \(^2\) is equal to the ratio of the heat evolved, per mole of hydrocarbon, in the ideal bomb process at 28° C for each isomer to that of n-nonane; \((-\Delta U°)_n\) = \((-\Delta U°)_i\), the difference, between n-nonane and each isomer, in the heat of combustion in the ideal bomb process at 28° C; H° (liquid) = \(H°(\text{liq})\), the heat of isomerization of n-nonane into each isomer, at 25° C and 1 atmosphere, for the liquid state; and \(-\Delta H°\), the decrement in the heat content accompanying the reaction of combustion of the hydrocarbon in the liquid state in oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard states at 25° C.

The value of the heat of isomerization was obtained by means of the relation [1]:

\[\frac{B_i/B_n}{(-\Delta U°)_n} = \frac{(-\Delta U°)_n}{(-\Delta U°)_i} = 1 - \frac{B_i/B_n}{1 - B_i/B_n}\]

For this calculation, the value of \((-\Delta U°)_n\) at 28° C was taken as 6110.2 int. kJ/mole [3]. The method of Washburn correction is the same for all these compounds as they are isomers, but account is taken of the variation of the correction with the amount of sample burned. As used here, the Washburn correction was modified to apply to 28° C and to the gases at zero pressure (instead of 1 atmosphere).

The value of the heat of combustion of a given isomer was obtained by appropriately combining the heat of isomerization with the heat of combustion of n-nonane as given by the equations [8]

\[\text{C}_2\text{H}_20 \text{ (nonane, liquid)} + \text{O}_2 \text{(gas)} = 9\text{CO}_2 \text{(gas)} + 10\text{H}_2\text{O (liquid)}\]

\[\Delta H°_{28.16} = -6123.51 ±0.75 \text{ int. kJ/mole} = -1463.80 ±0.18 \text{ int. kcal/mole}\]

All the uncertainties assigned to the experimental quantities in table 2 (except the heats of combustion) are equal to twice the standard deviation of the mean. The uncertainties assigned to the values of the heats of combustion were obtained by combining [11] the uncertainty in the value of the heat of combustion of n-nonane [8] with the uncertainties in the values of the heats of isomerization. The uncertainty to be assigned to the value of the heat of isomerization of any one of the isomers into any other one may conservatively be taken as ±0.30 kcal/mole.

The experimental data of the present and previous investigations on the paraffin hydrocarbons are being correlated to yield heats of combustion.
and formation of the remaining 29 nonanes which have not been subjected to experimental measurement, with general formulas for calculating values for the decanes and higher paraffin hydrocarbons [14].

VI. References


WASHINGTON, November 6, 1946.