Heats of Combustion and Isomerization of the Eight C₈H₁₆ Alkylcyclohexanes

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

The heats of isomerization of the eight C₈H₁₆ alkylcyclohexanes 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, ΔH°, of ethylcyclohexane into the dimethyl cyclohexanes, in kilocalories per mole: Ethylcyclohexane, 0.00; 1,1-dimethylecyclohexane, -1.58 ± 0.28; cis-1,2-dimethylecyclohexane, -1.46 ± 0.27; cis-1,3-dimethylecyclohexane, -2.57 ± 0.22; trans-1,3-dimethylecyclohexane, -0.85 ± 0.21; cis-1,4-dimethylecyclohexane, -0.83 ± 0.21; trans-1,4-dimethylecyclohexane, -2.45 ± 0.22. These data were combined with the value previously reported for the heat of combustion of ethylcyclohexane to obtain values for the heats of combustion of the seven dimethylecyclohexanes in the liquid state at 25°C. (For the two isomers of 1,3-dimethylecyclohexane, the labels "cis" and "trans" are here applied to the lower and higher boiling isomers, respectively.)

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, 8]¹ calorimetric measurements have been made that yield values for the differences in the heats of combustion, or the heats of isomerization, of the eight C₈H₁₆ alkylcyclohexanes in the liquid state at 25°C. These heats of isomerization were combined with the value [7] previously reported for the heat of combustion of ethylcyclohexane to obtain values for the heats of combustion of the seven dimethylecyclohexanes in the liquid state at 25°C.

II. Unit of Energy, Molecular Weights, Uncertainties

The unit of energy upon which 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 this Bureau. For conversion to the conventional thermochemical calorie, the following relation is used [9]

1 calorie = 4.1833 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, 8, 12]. One calorimetric 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 [14, 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 API Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons," from material supplied by the following laboratories:

Ethylcyclohexane, 1,1-dimethylcyclohexane, cis-1,2-dimethylcyclohexane, trans-1,2 dimethylcyclohexane, cis-1,3-dimethylcyclohexane, and trans-1,3-dimethylcyclohexane, by the American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord.

cis-1,4-Dimethylcyclohexane and trans-1,4-dimethylcyclohexane, by the Standard Oil Development Co., Elizabeth, N. J., through William J. Sweeney.

A complete description of the purification, purity, and freezing points of the eight API-NBS hydrocarbons used in the present investigation is given by Streiff, Murphy, Cahill, Flanagan, Soule, Sedlak, Willingham, and Rossini [16, 17], who reported the amounts of impurity in these samples, as determined from measurements of freezing points, to be as follows in mole fraction: Ethylcyclohexane, 0.0010±0.0008; 1,1-dimethylcyclohexane, 0.0007±0.0003; cis-1,2-dimethylcyclohexane, 0.00017±0.00015; trans-1,2-dimethylcyclohexane, 0.0008±0.0007; cis-1,3-dimethylcyclohexane, 0.0006±0.0005; trans-1,3-dimethylcyclohexane, 0.0012±0.0007; cis-1,4-dimethylcyclohexane, 0.0006±0.0004; trans-1,4-dimethylcyclohexane, 0.0011±0.0008.

As the manner of purification [16, 17] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the extreme case the measured heat of combustion would be affected by less than 0.001 percent because of impurities.

V. Results

The experimental results of the present investigation are summarized in table 1, which gives for each of the eight 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, \( k, K, U, \Delta R_c, \Delta r_c, \Delta r_s, \) \([1]\); the mean value of \( B \), and its standard deviation, in ohms per gram of carbon dioxide formed, as defined by eq 4 of reference [1]. The symbols have the same significance as in the previous reports [1, 8] and the references there cited.

In table 2 are given, for the eight \( \text{C}_8\text{H}_{16} \) alkylcyclohexanes, values of the following: The constant \( B \), in ohms per gram of carbon dioxide, as given in table 1; \( B^0 \), which is \( B \) corrected to the ideal bomb reaction by the method of Washburn [13] \(^2\); \( B_i^0/B_e^0 \), which is equal to the ratio of the heat evolved, per mole of hydrocarbon, in the ideal bomb process at \( 28^\circ \) C for each isomer to that of ethylcyclohexane; \( (-\Delta U^c)_i - (-\Delta U^c)_n \), the difference, between ethylcyclohexane and each isomer, in the heat of combustion in the ideal bomb process at \( 28^\circ \) C; \( H^0_i \) (liquid)\( - H^0_n \) (liquid), the heat of isomerization of ethylcyclohexane into each isomer, at \( 25^\circ \) C and 1 atmosphere, for the liquid state, and \( -\Delta H^c_i \), 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 \( 25^\circ \) C.

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

\[
(-\Delta U^c)_n - (-\Delta U^c)_i = (-\Delta U^c)_n (1 - B_i^0/B_e^0).
\]

For this calculation, the value of \( (-\Delta U^c)_n \) at \( 28^\circ \) C was taken as 5210.7 int. kj/mole [7]. 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 ethylcyclohexane as given by the equations [7]:

\[
\text{C}_8\text{H}_{16} \text{ (ethylcyclohexane, liquid) + 12O}_2(gas) = 8\text{CO}_2(gas) + 8\text{H}_2\text{O (liquid).}
\]

\[
\Delta H^c_{298.16} = -5221.71 \pm 1.46 \text{ int. kj/mole} = -1248.23 \pm 0.35 \text{ kcal/mole.}
\]

\(^2\) The 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 \( 28^\circ \) C and to the gases at zero pressure (instead of 1 atmosphere).
### Table 1.—Results of the calorimetric combustion experiments

<table>
<thead>
<tr>
<th>Number of experiments</th>
<th>Mass of carbon dioxide formed</th>
<th>k</th>
<th>K</th>
<th>U</th>
<th>( \Delta R_i )</th>
<th>( \Delta R_t )</th>
<th>( \Delta R_a )</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylcyclohexane</td>
<td>6</td>
<td>( \frac{\text{mol}}{\text{g}} )</td>
<td>2.65072</td>
<td>to</td>
<td>to</td>
<td>to</td>
<td>to</td>
<td>to</td>
</tr>
<tr>
<td>1,1-Dimethylcyclohexane</td>
<td>5</td>
<td>to</td>
<td>2.96925</td>
<td>to</td>
<td>0.02003</td>
<td>0.01287</td>
<td>0.000233</td>
<td>0.32191</td>
</tr>
<tr>
<td>cis-1, 2-Dimethylcyclohexane</td>
<td>5</td>
<td>to</td>
<td>2.83326</td>
<td>to</td>
<td>0.02011</td>
<td>0.01259</td>
<td>0.000299</td>
<td>0.306921</td>
</tr>
<tr>
<td>trans-1, 2-Dimethylcyclohexane</td>
<td>6</td>
<td>to</td>
<td>2.94480</td>
<td>to</td>
<td>0.01990</td>
<td>0.00417</td>
<td>0.000264</td>
<td>0.28575</td>
</tr>
<tr>
<td>cis-1, 3-Dimethylcyclohexane</td>
<td>6</td>
<td>to</td>
<td>2.95757</td>
<td>to</td>
<td>0.01986</td>
<td>0.00776</td>
<td>0.000286</td>
<td>0.29635</td>
</tr>
<tr>
<td>trans-1, 3-Dimethylcyclohexane</td>
<td>5</td>
<td>to</td>
<td>2.82471</td>
<td>to</td>
<td>0.01967</td>
<td>0.01066</td>
<td>0.000318</td>
<td>0.30062</td>
</tr>
<tr>
<td>cis-1, 4-Dimethylcyclohexane</td>
<td>5</td>
<td>to</td>
<td>2.63184</td>
<td>to</td>
<td>0.01985</td>
<td>0.00627</td>
<td>0.000259</td>
<td>0.28866</td>
</tr>
<tr>
<td>trans-1, 4-Dimethylcyclohexane</td>
<td>5</td>
<td>to</td>
<td>2.66883</td>
<td>to</td>
<td>0.01997</td>
<td>0.01219</td>
<td>0.000307</td>
<td>0.31199</td>
</tr>
</tbody>
</table>

* This isomer, formerly labeled “trans,” has the following properties: Boiling point at 1 atm, 120.09°C; refractive index, \( n_D \) at 25°C, 1.4206; density at 25°C, 0.7620 g/ml [18].
* This isomer, formerly labeled “cis,” has the following properties: Boiling point at 1 atm, 124.45°C; refractive index, \( n_D \) at 25°C, 1.4284; density at 25°C, 0.7806 g/ml [18].

### Table 2.—Heats of isomerization and combustion in the liquid state

<table>
<thead>
<tr>
<th>Compound</th>
<th>( B ) at 28°C</th>
<th>( B' ) at 28°C</th>
<th>Ratio of the heats of combustion in the ideal bomb process, ( B'/B ), at 28.00°C</th>
<th>Difference in the heats of combustion in the ideal bomb process, ( (\Delta H_i - \Delta H_t) / \Delta H_t ) at 28.00°C</th>
<th>Heat of isomerization of the liquid, ( \Delta H_i ) (lit), at 25.00°C C</th>
<th>Heat of combustion of the liquid, ( -\Delta H_c ), at 25.00°C C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylcyclohexane</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
</tr>
<tr>
<td>1,1-Dimethylcyclohexane</td>
<td>0.1082071±0.000016</td>
<td>0.1082071±0.000016</td>
<td>0.1082938±0.000016</td>
<td>0.1082938±0.000016</td>
<td>0.1082938±0.000016</td>
<td>0.1082938±0.000016</td>
</tr>
<tr>
<td>cis-1,2-Dimethylcyclohexane</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
</tr>
<tr>
<td>trans-1,2-Dimethylcyclohexane</td>
<td>0.1082071±0.000016</td>
<td>0.1082071±0.000016</td>
<td>0.1082938±0.000016</td>
<td>0.1082938±0.000016</td>
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<td>0.1082938±0.000016</td>
</tr>
<tr>
<td>cis-1,3-Dimethylcyclohexane a</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
</tr>
<tr>
<td>trans-1,3-Dimethylcyclohexane b</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
</tr>
<tr>
<td>cis-1,4-Dimethylcyclohexane</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
<td>0.1083833±0.000016</td>
</tr>
<tr>
<td>trans-1,4-Dimethylcyclohexane</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
<td>0.1084379±0.000016</td>
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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 ethylcyclohexane [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 relation between the heats of isomerization and molecular structure of the C₆H₆ alkylcyclohexanes will be discussed in another paper [19], which also give values for the heats of formation and isomerization of these compounds in the liquid and gaseous states at 25° C, and in the gaseous state at 0° K.

VI. References

WASHINGTON, February 17, 1947.