U. S. Department of Commerce
National Bureau of Standards

Research Paper RP1812
Volume 39, July 1947

Part of the Journal of Research of the National Bureau of Standards

Heats of Combustion and Isomerization of the Eight C_8H_{16} Alkylcyclohexanes

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The heats of isomerization of the eight C_8H_{16} alky cyclohexanes 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, $\Delta H°$, of ethylcyclohexane into the dimethyl cyclohexanes, in kilocalories per mole: Ethylcyclohexane, 0.00; 1,1-dimethylcyclohexane, -1.58 ± 0.28; *cis*-1,2-dimethylcyclohexane, 0.08 ± 0.25; *trans*-1,2-dimethylcyclohexane, -1.46 ± 0.27; *cis*-1,3-dimethylcyclohexane, -2.57 ± 0.22; *trans*-1,3-dimethylcyclohexane, -0.85 ± 0.21; *cis*-1,4-dimethylcyclohexane, -0.83 ± 0.21; *trans*-1,4-dimethylcyclohexane, -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 dimethylcyclohexanes in the liquid state at 25° C. (For the two isomers of 1,3-dimethylcyclohexane, 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 C_8H_{16} 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 dimethylcyclohexanes 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

[1] Figures in brackets indicate the literature references at the end of this paper.

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, ΔR_c, Δr_i, Δr_n, [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 C_8H_{16} alkylcyclohexanes, values of the following: The constant B, in ohms per gram of carbon dioxide, as given in table 1; $B°$, which is B corrected to the ideal bomb reaction by the method of Washburn [13][2]; $B_i°/B_n°$, which 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 ethylcyclohexane; $(-\Delta U°)_n-(-\Delta U°)_i$, the difference, between ethylcyclohexane and each isomer, in the heat of combustion in the ideal bomb process at 28° C; $H_i°$ (liquid)$-H_n°$ (liquid), the heat of isomerization of ethylcyclohexane into each isomer, at 25° C and 1 atmosphere, for the liquid state, and $-\Delta H_c°$, 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]:

$$(-\Delta U°)_n-(-\Delta U°)_i=(-\Delta U°)_n(1-B_i°/B_n°).$$

For this calculation, the value of $(-\Delta U°)_n$ at 28° 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]:

$$C_8H_{16} \text{ (ethylcyclohexane, liquid)} + 12O_2\text{(gas)} = 8CO_2\text{(gas)} + 8H_2O \text{ (liquid)}.$$

$$\Delta H°_{298.16} = -5221.71 \pm 1.46 \text{ int. kj/mole} = -1248.23 \pm 0.35 \text{ kcal/mole}.$$

[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° C and to the gases at zero pressure (instead of 1 atmosphere).

TABLE 1.—*Results of the calorimetric combustion experiments*

	Number of experiments	Mass of of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B	
									Mean	Standard deviation of mean
		g	*Min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g* CO_2	*Ohm/g* CO_2
Ethylcyclohexane	6	2.65972 to 2.96025	0.001981 to .002003	0.000859 to .001287	0.000251 to .000323	0.288605 to .321191	0.000248 to .000263	0.000009 to .000009	0.1084307	±0.0000080
1, 1-Dimethylcyclohexane	5	2.67588 to 2.85326	.001990 to .002011	.000660 to .001259	.000286 to .000299	.290033 to .309281	.000254 to .000265	.000006 to .000011	.1082938	±.0000094
cis-1, 2-Dimethylcyclohexane	5	2.63272 to 2.94480	.001990 to .001999	.000417 to .001355	.000264 to .000293	.285754 to .319481	.000250 to .000272	.000009 to .000010	.1084379	±.0000074
trans-1, 2-Dimethylcyclohexane	6	2.72767 to 2.82471	.001986 to .001997	.000776 to .001036	.000286 to .000318	.295635 to .306092	.000252 to .000257	.000009 to .000009	.1083037	±.0000086
cis-1, 3-Dimethylcyclohexane [a]	6	2.77695 to 2.85646	.001977 to .001986	.000846 to .000989	.000219 to .000293	.300654 to .309318	.000254 to .000268	.000004 to .000004	.1082071	±.0000054
trans-1, 3-Dimethylcyclohexane [b]	4	2.66184 to 2.86883	.001985 to .001997	.000627 to .001219	.000259 to .000307	.288666 to .311099	.000249 to .000265	.000005 to .000005	.1083564	±.0000041
cis-1, 4-Dimethylcyclohexane	5	2.69279 to 2.73107	.001988 to .002008	.001015 to .001163	.000242 to .000358	.292047 to .296131	.000253 to .000285	.000009 to .000010	.1083583	±.0000042
trans-1, 4-Dimethylcyclohexane	5	2.64243 to 2.81077	.001989 to .002001	.000870 to .001325	.000238 to .000288	.286155 to .304383	.000252 to .000261	.000010 to .000011	.1082172	±.0000049

[a] 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].

[b] 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*

Compound	B at 28° C	B° at 28° C	Ratio of the heats of combustion in the ideal bomb process, B_i°/B_n°, at 28.00° C	Difference in the heats of combustion in the ideal bomb process, $(-\Delta U^\circ)_n-(-\Delta U^\circ)_i$, at 28.00° C	Heat of isomerization of the liquid, $H_i^\circ(\text{liq})-(H_n^\circ(\text{liq})$, at 25.00° C		Heat of combustion of the liquid, $-\Delta Hc^\circ$, at 25.00° C	
	Ohm/g CO_2	*Ohm/g* CO_2		*Int. kj/mole*	*Int. kj/mole*	*kcal/mole*	*Int. kj/mole*	*kcal/mole*
Ethylcyclohexane	0.1084307±0.0000160	0.1084002±0.0000160	1.000000	0.00	0.00	0.00	5221.71±1.46	1248.23±0.35
1,1-Dimethylcyclohexane	.1082938±0.0000188	.1082632±0.0000186	0.998736±0.000227	6.59±1.18	−6.59±1.18	−1.58±0.28	5215.12±1.88	1246.65±0.45
cis-1,2-Dimethylcyclohexane	.1084379±0.0000148	.1084075±0.0000150	1.000067±0.000202	−0.35±1.05	0.35±1.05	0.08±0.25	5222.06±1.80	1248.31±0.43
trans-1,2-Dimethylcyclohexane	.1083037±0.0000172	.1082732±0.0000172	0.998828±0.000217	6.11±1.13	−6.11±1.13	−1.46±0.27	5215.60±1.85	1246.77±0.44
cis-1,3-Dimethylcyclohexane [a]	.1082071±0.0000108	.1081765±0.0000108	.997936±0.000178	10.75±0.93	−10.75±0.93	−2.57±0.22	5210.96±1.73	1245.66±0.41
trans-1,3. Dimethylcyclohexane [b]	.1083564±0.0000082	.1083258±0.0000082	.999314±0.000166	3.57±0.86	−3.57±0.86	−0.85±0.21	5218.14±1.69	1247.38±0.40
cis-1,4-Dimethylcyclohexane	.1083583±0.0000084	.1083280±0.0000084	.999334±0.000167	3.47±0.87	−3.47±0.87	−0.83±0.21	5218.24±1.70	1247.40±0.41
trans-1,4-Dimethylcyclohexane	.1082172±0.0000098	.1081868±0.0000098	.998031±0.000173	10.26±0.90	−10.26±0.90	−2.45±0.22	5211.45±1.72	1245.78±0.41

[a] 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].

[b] 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].

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 C_8H_{16} 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

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WASHINGTON, February 17, 1947.