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HEATS OF COMBUSTION OF FOUR CYCLOPENTANE AND FIVE CYCLOHEXANE HYDROCARBONS

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

ABSTRACT

The heats of combustion of cyclopentane, methylcyclopentane, ethylcyclopentane, *n*-propylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, *n*-propylcyclohexane, and *n*-butylcyclohexane were measured with a bomb calorimeter. The following values were obtained for $-\Delta Hc°_{298.16}$, the heat of combustion at 25° C and constant pressure of the liquid hydrocarbon in gaseous oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard reference states, in international kilojoules per mole (with the corresponding value in terms of the conventional thermochemical calorie being given in parentheses):

Cyclopentane, 3290.34 ±0.72 (786.54 ±0.17)
Methylcyclopentane, 3937.07 ±0.75 (941.14 ±0.18)
Ethylcyclopentane, 4591.17 ±0.94 (1097.50 ±0.22)
n-Propylcyclopentane, 5244.75 ±1.18 (1253.74 ±0.28)
Cyclohexane, 3919.26 ±0.70 (936.88 ±0.17)
Methylcyclohexane, 4564.52 ±0.95 (1091.13 ±0.23)
Ethylcyclohexane, 5221.71 ±1.46 (1248.23 ±0.35)
n-Propylcyclohexane, 5874.79 ±1.15 (1404.34 ±0.27)
n-Butylcyclohexane, 6529.21 ±1.22 (1560.78 ±0.29).

CONTENTS

I. INTRODUCTION

In continuation of the program of the Bureau's thermochemical laboratory of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types, calorimetric measurements have been made of the heats of combustion of nine cycloparaffin hydrocarbons, including the first four members of the normal alkylcyclopentane series and the first five members of the normal alkycyclohexane series. This report gives the details of the experimental work and results.

II. UNITS AND CONSTANTS

The unit of energy upon which the experimental values of this investigation are based is the international joule determined by the standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau.

The following relation was used to convert the values to the conventional thermochemical calorie [1][1]:

4.1833 international joules=1 calorie.

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 [2].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [3]. In other cases, reasonable estimates of the uncertainty were made.

Definitions of the symbols used are given in previous papers [4, 5, 6, 7, 8].

III. METHOD, APPARATUS, AND PROCEDURE

The method and apparatus used in this investigation are described in previous papers [4, 5, 6, 7, 8]. Calorimeter system *F* was used in the experiments on all the compounds of the present work except those on *n*-butylcyclohexane. Calorimeter system *D*, described in reference [6], was used in these latter experiments. Calorimeter system *F* differed from system *D* in that a new bomb and heater, made of the same design as those of system *D*, were used. Resistance bridge No. 404 and platinum resistance thermometer No. 373,730 were used for all the experiments reported here.

The method of sealing the samples of hydrocarbons in glass ampoules, the ignition of the hydrocarbons in the bomb, the purification of the oxygen used for combustion, the examination of the products of combustion, and the determination of the amount of reaction were the same as previously described [4, 5, 6]. No products of incomplete combustion were found in any of the experiments.

The procedure used in the combustion experiments and the method of determining the ignition energy and of correcting for the formation of nitric acid were the same as previously described [4, 5, 6].

IV. MATERIALS

The 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, and calculation of data on the properties of hydrocarbons." The samples were purified by the API Research Project 6 on the "Analysis, purification, and properties of hydrocarbons," from material supplied by the following laboratories:

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

Cyclopentane, ethylcyclopentane, *n*-propylcyclopentane, ethylcyclohexane, *n*-propylcyclohexane, *n*-butylcyclohexane, and half of the methylcyclohexane, by the API Research Project 45 on the "Synthesis and properties of hydrocarbons of low molecular weight" at the Ohio State University, under the supervision of Cecil E. Boord.

Cyclohexane, and half of the methylcyclohexane, by the Barrett Division of the Allied Chemical & Dye Corporation.

Methylcyclopentane, by the Houdry Process Corporation, through the courtesy of E. A. Smith.

A complete description of the purification and determination of purity of these compounds are given in other reports [10, 11]. The mole fractions of impurity in these samples, as determined by A. R. Glasgow, Jr., E. T. Murphy, and A. J. Streiff from time-temperature freezing and melting curves and as described in reference [12], were as follows: Cyclopentane, 0.0002 ± 0.0001; methylcyclopentane, 0.0016 ± 0.0006; ethylcyclopentane, 0.0008 ± 0.0003; *n*-propylcyclopentane, 0.0019 ± 0.0010; cyclohexane, 0.00003 ± 0.00002; methylcyclohexane, 0.0010 ± 0.0008; ethylcyclohexane, 0.0011 ± 0.00008; *n*-propylcyclohexane, <0.003 (preliminary value); *n*-butylcyclohexane <0.003 (preliminary value) [10, 11].

As the manner of purification of these compounds [10, 11] 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 0.005 percent because of impurities in the compound.

V. RESULTS

The energy equivalents of calorimeter systems *C* and *D* are (see section VI–1 of reference [6]):

$$E_s(C) = 137717.4 \pm 13.9 \text{ int. j/ohm.}$$
$$E_s(D) = 136489.6 \pm 14.5 \text{ int. j/ohm.}$$

The results of the experiments to determine the energy equivalent of calorimeter system *F*, through its ratio to that of calorimeter system *C* by the combustion of benzoic acid, are given in table 1. The symbols at the heads of the columns are as defined in references [4, 5, 6]. The energy equivalent of calorimeter system *F*, together with its estimated over-all uncertainty, is

$$E_s(F) = 0.992496\ E_s(C)$$
$$= 136684.0 \pm 19.0 \text{ int. j/ohm.}$$

For convenience and clarity the data are all reported in terms of the energy equivalent of calorimeter system *F*.

The results of the combustion experiments on cyclopentane, methylcyclopentane, ethylcyclopentane, *n*-propylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane, *n*-propylcyclohexane, and *n*-butylcyclohexane are given in table 2. The symbols at the heads of the columns are as defined in references [4, 5, 6]. The value of *B* for *n*-butylcyclohexane is given in terms of calorimeter system *F*, with the ratio of $E_s(F)$ to $E_s(D)$.

TABLE 1.—*Energy equivalent calorimeter system F*

Experiment number	Mass of benzoic acid[a]	k	K	U	ΔR_c	Δr_i	Δr_n	B'	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g of benzoic acid*	*Ohm/g of benzoic acid*
1	1.51711	0.001985	0.001082	0.000296	0.293732	0.000410	0.000005	0.1933711	0.0000317
2	1.51864	.001979	.001140	.000280	.293998	.000418	.000007	.1933434	.0000040
3	1.52204	.001976	.001194	.000338	.293638	.000413	.000005	.1933385	−.0000009
4	1.51768	.001965	.001190	.000355	.293768	.000420	.000005	.1933141	−.0000253
5	1.51642	.001963	.000998	.000379	.293537	.000412	.000004	.1933299	−.0000095
Mean								0.1933394	
Standard deviation of the mean								±.0000094	

[a] NBS Standard Sample 39f.

TABLE 2.—*Results of the calorimetric combustion experiments*

Compound (liquid)	Number of experiments	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	$\bar{B}$ Mean	$\bar{B}$ Standard deviation of mean
Cyclopentane	5	2.65418 to 2.70407	0.001973 to .001981	0.001141 to .001268	0.000248 to .000333	0.290298 to .295649	0.000418 to .000430	0.000011 to .000012	0.1091973	±0.0000075
Methylcyclopentane	6	2.69351 to 2.75965	.001972 to .001992	.000946 to .001200	.000251 to .000331	.293636 to .300909	.000423 to .000429	.000011 to .000012	.1088836	±.0000045
Ethylcyclopentane	6	2.68285 to 3.00924	.001965 to .001987	.000819 to .001248	.000245 to .000334	.292316 to .327896	.000419 to .000427	.000010 to .000013	.1088346	±.0000062
n-Propylcyclopentane	7	2.67656 to 2.76082	.001970 to .001980	.001006 to .001314	.000213 to .000362	.291493 to .300782	.000417 to .000427	.000010 to .000011	.1087869	±.0000080
Cyclohexane	6	2.50354 to 2.77753	.001964 to .001974	.000915 to .001763	.000270 to .000346	.271925 to .301417	.000410 to .000431	.000006 to .000009	.1083894	±.0000029
Methylcyclohexane	6	2.50695 to 2.99699	.001965 to .001972	.000251 to .001746	.000290 to .000413	.271685 to .324614	.000411 to .000430	.000009 to .000012	.1082005	±.0000064
Ethylcyclohexane	5	1.68309 to 2.68037	.001955 to .001986	.001236 to .004197	.000214 to .000422	.182730 to .290810	.000413 to .000427	.000008 to .000010	.1083063	±.0000121
n-Propylcyclohexane	6	2.61019 to 2.75202	.001968 to .001976	.001047 to .001425	.000301 to .000368	.283102 to .298494	.000419 to .000429	.000007 to .000009	.1083144	±.0000052
n-Butylcyclohexane	6	2.63440 to 2.77833	.001982 to .002005	.001013 to .001432	.000243 to .000333	.286302 to .301826	.000407 to .000417	.000037 to .000040	[a].1083424	±.0000064

[a] This value has been converted to apply to calorimeter system *F* (see text).

In table 3 are given the final results for the four cyclopentane and five cyclohexane hydrocarbons whose heats of combustion were measured in the present investigation. The columns give the value of B for 28° C, in ohms per gram of carbon dioxide, as given in table 2; $B°$, which is B corrected to the ideal bomb reaction [8]; $-\Delta U°$, the decrement in internal energy for the ideal reaction of combustion at 28° C, with all reactants and products in their thermodynamic standard reference states of unit fugacity, in international kilojoules per mole of hydrocarbon; $-\Delta Hc°$, the decrement in heat content or enthalpy (or heat evolved in the combustion at constant pressure) for the reaction of combustion of the liquid hydrocarbon at 28° C, with all the reactants and products in their thermodynamic standard reference states; and finally, the same quantity, $-\Delta Hc°$, for the reaction of combustion at 25° C. The foregoing values of $-\Delta U°$ and $-\Delta Hc°$ apply to the reaction.

$$C_aH_b(\text{liq})+\left(a+\frac{b}{4}\right)O_2(\text{g})=aCO_2(\text{g})+\frac{b}{2}H_2O(\text{liq}).$$

TABLE 3.—*Values of the heats of combustion*

Compound (liquid)	B at 28° C	$B°$ at 28° C	$-\Delta U°$ at 28° C
	Ohm/g CO_2	*Ohm/g* CO_2	*Int. kj/mole*
Cyclopentane	0.1091973 ±0.0000150	0.1091668 ±0.0000150	3283.44 ±0.72
Methylcyclopentane	.1088836 ±0.0000090	.1088531 ±0.0000090	3928.81 ±0.75
Ethylcyclopentane	.1088346 ±0.0000124	.1088039 ±0.0000124	4581.54 ±0.94
n-Propylcyclopentane	.1087869 ±0.0000160	.1087564 ±0.0000160	5233.76 ±1.18
Cyclohexane	.1083894 ±0.0000058	.1083590 ±0.0000060	3910.98 ±0.70
Methylcyclohexane	.1082005 ±0.0000128	.1081707 ±0.0000128	4554.88 ±0.95
Ethylcyclohexane	.1083063 ±0.0000242	.1082772 ±0.0000240	5210.70 ±1.46
n-Propylcyclohexane	.1083144 ±0.0000104	.1082841 ±0.0000104	5862.41 ±1.15
n-Butylcyclohexane	.1083424 ±0.0000128	.1083121 ±0.0000128	6515.47 ±1.22

Compound (liquid)	$-\Delta Hc°$ (liq) at 28° C	$-\Delta Hc°$ (liq) at 25° C	
	Int. kj/mole	*Int. kj/mole*	*kcal/mole*
Cyclopentane	3289.70 ±0.72	3290.34 ±0.72	786.54 ±0.17
Methylcyclopentane	3936.32 ±0.75	3937.07 ±0.75	941.14 ±0.18
Ethylcyclopentane	4590.30 ±0.94	4591.17 ±0.94	1097.50 ±0.22
n-Propylcyclopentane	5243.77 ±1.18	5244.75 ±1.18	1253.74 ±0.28
Cyclohexane	3918.49 ±0.70	3919.26 ±0.70	936.88 ±0.17
Methylcyclohexane	4563.64 ±0.95	4564.52 ±0.95	1091.13 ±0.23
Ethylcyclohexane	5220.71 ±1.46	5221.71 ±1.46	1248.23 ±0.35
*n*Propycyclohexane	5873.68 ±1.15	5874.79 ±1.15	1404.34 ±0.27
n-Butylcyclohexane	6527.99 ±1.22	6529.21 ±1.22	1560.78 ±0.29

The over-all uncertainty assigned to each final value of the heat of combustion of a given compound was taken as the square root of the sum of the squares of the following: (a) Twice the standard deviation of the mean of the series of combustion experiments, (b) an uncertainty of 0.010 percent in the determination of the absolute value of the amount of reaction, (c) twice the standard deviation of the mean of the series of experiments for determining the energy equivalent of the calorimeter with electric energy and of the series of experiments to determine the ratios of the energy equivalents, and (d) an uncertainty of 0.010 percent in the determination of the absolute value of the energy equivalent, with electric energy.

Following the usual practice of the Bureau's Thermochemical Laboratory, the values reported in this investigation are being utilized in the calculation of the heats of formation for the same compounds, in the gaseous as well as the liquid state, and in the evaluation by the method of increments per CH_2 group [9] of the values of the heats of combustion and formation for the higher normal alkylcyclopentanes and normal alkylcyclohexanes.

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