U. S. Department of Commerce
National Bureau of Standards

Research Paper RP1728
Volume 37, July 1946

Part of Journal of Research of the National Bureau of Standards

Heats of Formation and Combustion of the Normal Alkylcyclopentanes and Cyclohexanes and the Increment per CH_2 Group for Several Homologous Series of Hydrocarbons[1]

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

Values are presented for the heats of formation and combustion at 25° C for the normal alkylcyclopentanes and the normal alkylcyclohexanes, in the liquid state through normal butyl and in the gaseous state through normal hexadecyl, with equations to yield values for all the higher members of both series in the gaseous state.

The increment per CH_2 group is compared for the lower members of several normal alkyl homologous series, including paraffins, monoolefins (1-alkene), alkylbenzenes, alkylcyclopentanes, alkylcyclohexanes, and alkyl acetylenes (1-alkyne).

I. Introduction

A value was recently presented for the increment in energy content per CH_2 group for the members of the normal paraffin hydrocarbons above pentane [1].[2] This new value of the increment per CH_2 group, which was based on many new data on the heats of combustion and vaporization of the normal paraffin hydrocarbons [2, 3, 4, 5, 6], replaced the previous and less precise one presented in 1934 [7]. With the new value for the increment per CH_2 group, values have been calculated for the heats of formation and combustion of the higher normal monoolefins (1-alkene) [8] and the higher normal alkylbenzenes [9].

In the present paper, values are presented for the heats of formation and combustion of the normal alkylcyclopentanes and normal alkylcyclohexanes, and a comparison is made of the increment per CH_2 group for the lower members of several normal alkyl homologous series, including paraffins, monoolefins (1-alkenes), alkylbenzenes, alkylcyclopentanes, alkylcyclohexanes, and alkyl acetylenes (1-alkyne).

[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons."

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

Contents

II. Heats of Formation and Combustion of the Normal Alkylcyclopentanes and Cyclohexanes

In table 1, values are given for the heats of combustion and formation at 25° C of the normal alkylcyclopentanes, in the liquid state through normal butyl and in the gaseous state through normal hexadecyl.

TABLE 1.—*Values for the heats of combustion and formation of the alkylcyclopentanes*

Compound	Formula	Heat of combustion[a] at 25° C, $-\Delta Hc°$		Heat of formation[b] at 25° C, $\Delta Hf°$	
		Liquid	Gas	Liquid	Gas
		kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
Cyclopentane	C_5H_{10}	786.54 ±0.17	793.39 ±0.17	−25.31 ±0.18	−18.46 ±0.18
Methylcyclopentane	C_6H_{12}	941.14 ±0.18	948.72 ±0.18	−33.08 ±0.20	−25.50 ±0.20
Ethylcyclopentane	C_7H_{14}	1097.50 ±0.22	1106.21 ±0.23	−39.08 ±0.24	−30.37 ±0.25
n-Propylcyclopentane	C_8H_{16}	1253.74 ±0.28	1263.56 ±0.28	−45.21 ±0.30	−35.39 ±0.30
n-Butylcyclopentane	C_9H_{18}	1410.10 ±0.34	1421.10 ±0.33	−51.22 ±0.37	−40.22 ±0.36
n-Amylcyclopentane	$C_{10}H_{20}$		1578.54 ±0.34		−45.15 ±0.37
n-Hexylcyclopentane	$C_{11}H_{22}$		1735.99 ±0.36		−50.07 ±0.39
n-Heptylcyclopentane	$C_{12}H_{24}$		1893.43 ±0.39		−55.00 ±0.42
n-Octylcyclopentane	$C_{13}H_{26}$		2050.87 ±0.42		−59.92 ±0.46
n-Nonylcyclopentane	$C_{14}H_{28}$		2208.32 ±0.46		−64.85 ±0.50
n-Decylcyclopentane	$C_{15}H_{30}$		2365.76 ±0.50		−69.78 ±0.55
n-Undecylcyclopentane	$C_{16}H_{32}$		2523.20 ±0.55		−74.70 ±0.59
n-Dodecylcyclopentane	$C_{17}H_{34}$		2680.65 ±0.60		−79.63 ±0.64
n-Tridecylcyclopentane	$C_{18}H_{36}$		2838.09 ±0.64		−84.55 ±0.70
n-Tetradecylcyclopentane	$C_{19}H_{38}$		2995.53 ±0.70		−89.48 ±0.75
n-Pentadecylcyclopentane	$C_{20}H_{40}$		3152.97 ±0.75		−94.41 ±0.80
n-Hexadecylcyclopentane	$C_{21}H_{42}$		3310.42 ±0.80		−99.33 ±0.86
△ per CH_2	CH_2		157.443		−4.926

[a] $-\Delta Hc°_{298.16}$ represents the heat evolved in the combustion of the given hydrocarbon, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure, with all reactants and products in their appropriate standard reference states.

[b] $\Delta Hf°_{298.16}$ represents the increment in the heat content or enthalpy of the process of forming the given hydrocarbon in the state indicated, from its elements, at 25° C, with all reactants and products in their appropriate standard reference states.

Values of the heats of combustion in the gaseous state at 25° C for the normal alkylcyclopentanes from normal butyl to normal hexadecyl (given in table 1), and for all the higher members, are given by the equations:

$$C_nH_{2n}(\text{gas, normal alkylcyclopentane})+(3n/2)O_2(\text{gas})=nCO_2(\text{gas})+nH_2O(\text{liquid}); \quad (1a)$$

$$-\Delta Hc°_{298.16}=4.114+157.443_n\pm(0.3605-0.05864n+0.003428n^2)^{1/2}\ \text{kcal/mole};\ n>8. \quad (1b)$$

Similarly, values of the heats of formation in the gaseous state at 25° C for all the normal alkylcyclopentanes above normal propyl are given by the equations:

$$nC(\text{solid, graphite})+nH_2(\text{gas})=C_nH_{2n}(\text{gas, normal alkylcyclopentane}); \quad (2a)$$

$$\Delta Hf°_{298.16}=4.114-4.926n\pm(0.3605-0.05864n+0.003637n^2)^{1/2}\ \text{kcal/mole};\ n>8. \quad (2b)$$

In table 2, values are given for the heats of combustion and formation at 25° C of the normal alkylcyclohexanes, in the liquid state through normal butyl and in the gaseous state through normal hexadecyl.

Values of the heats of combustion in the gaseous state at 25° C for all the normal alkylcyclohexanes above normal propyl are given by the equations:

$$C_nH_{2n}(\text{gas, normal alkylcyclohexane})+(3n/2)\,O_2(\text{gas})=nCO_2(\text{gas})+nH_2O(\text{liquid}); \quad (3a)$$

$$-\Delta Hc°_{298.16}=-1.690+157.443n\pm(0.4216-0.06358n+0.003428n^2)^{1/2}\ \text{kcal/mole};\ n>9. \quad (3b)$$

Similarly, values of the heats of formation in the gaseous state at 25° C for all the normal alkylcyclohexanes above normal propyl are given by the equations:

TABLE 2.—*Values for the heats of combustion and formation of the alkylcyclohexanes*

Compound	Formula	Heat of combustion[a] at 25° C, $-\Delta Hc°$		Heat of formation[b] at 25° C, $\Delta Hf°$	
		Liquid	Gas	Liquid	Gas
		kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
Cyclohexane	C_6H_{12}	936.88 ±0.17	944.79 ±0.17	−37.34 ±0.19	−29.43 ±0.19
Methylcyclohexane	C_7H_{14}	1091.13 ±0.23	1099.59 ±0.23	−45.45 ±0.25	−36.99 ±0.25
Ethylcyclohexane	C_8H_{16}	1248.23 ±0.35	1257.90 ±0.35	−50.72 ±0.37	−41.05 ±0.37
n-Propylcyclohexane	C_9H_{18}	1404.34 ±0.27	1415.12 ±0.27	−56.98 ±0.30	−46.20 ±0.30
n-Butylcyclohexane	$C_{10}H_{20}$	1560.78 ±0.29	1572.74 ±0.30	−62.91 ±0.32	−50.95 ±0.33
n-Amylcyclohexane	$C_{11}H_{22}$		1730.18 ±0.37		−55.88 ±0.40
n-Hexylcyclohexane	$C_{12}H_{24}$		1887.63 ±0.39		−60.80 ±0.43
n-Heptylcyclohexane	$C_{13}H_{26}$		2045.07 ±0.42		−65.73 ±0.46
n-Octylcyclohexane	$C_{14}H_{28}$		2202.51 ±0.45		−70.65 ±0.49
n-Nonylcyclohexane	$C_{15}H_{30}$		2359.96 ±0.49		−75.58 ±0.54
n-Decylcyclohexane	$C_{16}H_{32}$		2517.40 ±0.53		−80.51 ±0.58
n-Undecylcyclohexane	$C_{17}H_{34}$		2674.84 ±0.58		−85.43 ±0.63
n-Dodecylcyclohexane	$C_{18}H_{36}$		2832.28 ±0.62		−90.36 ±0.68
n-Tridecylcyclohexane	$C_{19}H_{38}$		2989.73 ±0.67		−95.28 ±0.73
n-Tetradecylcyclohexane	$C_{20}H_{40}$		3147.17 ±0.72		−100.21 ±0.78
n-Pentadecylcyclohexane	$C_{21}H_{42}$		3304.61 ±0.77		−105.14 ±0.83
n-Hexadecylcyclohexane	$C_{22}H_{44}$		3462.06 ±0.83		−110.06 ±0.88
Δ per CH_2	CH_2		157.443		−4.926

[a] $-\Delta Hc°_{298.16}$ represents the heat evolved in the combustion of the given hydrocarbon, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure, with all reactants and products in their appropriate standard reference states.

[b] $-\Delta Hf°_{298.16}$ represents the increment in the heat content or enthalpy of the process of forming the given hydrocarbon in the state indicated, from its elements, at 25° C, with all reactants and products in their appropriate standard reference states.

$$n\text{C (solid, graphite)} + n\text{H}_2\text{(gas)} = \text{C}_n\text{H}_{2n}\text{(gas, normal alkylcyclohexane)}; \quad (4a)$$

$$\Delta Hf°_{298.16} = -1.690 - 4.926n \pm (0.4216 - 0.06358n + 0.003637n^2)^{1/2} \text{ kcal/mole}; \; n > 9. \quad (4b)$$

In the foregoing equations, n is the total number of carbon atoms per molecule.

The values of heats of formation and heats of combustion given in tables 1 and 2 and by equations 1, 2, 3, and 4 were derived from the following data:

Heats of combustion in the liquid state at 25° C of the first four members of the series of normal aklylcyclopentanes and the first five members of the series of normal alkylcyclohexanes [10].

Heats of vaporization of the first five members of each of the seris of normal alkylcyclopentanes and normal alkylcyclohexanes [4, 5].

Increment per CH_2 group for the gaseous normal paraffin hydrocarbons above pentane [1].

Comparison of previous experimental data with the selected "best" values from this report is shown in table 3, in which the values from earlier investigations have been converted, insofar as significant, to the present unit of energy and atomic weights.

TABLE 3.—*Comparison of previous experimental data with the values of this report for the heats of combustion of the alkylcyclopentanes and alkylcyclohexanes*

Compound	Investigators	Year	Reference	Heat of combustion: Difference from value of this report	Heat of combustion: Estimated uncertainty of the difference
				kcal/mole[a]	*kcal/mole*[b]
Cyclopentane (liquid).	Huffman	1943	[17]	+0.12	±0.33
Methyl cyclopentane (liquid).	Zubow	1898	[13]	−2.62	±.94
	Moore, Renquist, and Parks.	1940	[14]	−0.46	±.44
Ethyl cyclopentane (liquid).	Moore, Renquist, and Parks.	1940	[14]	−.65	±.43
Cyclohexane (liquid)	Zubow	1898	[13]	−.07	±.94
	Richards and Barry.	1915	[15]	+3.76	±1.89
	Roth and Von Auwers.	1915	[16]	+1.77	±1.89
	Moore, Renquist, and Parks.	1940	[14]	−0.16	±0.35
	Huffman	1943	[17]	−.26	±.32
Methylcyclohexane (liquid).	Zubow	1898	[13]	+1.31	±1.09
	Moore, Renquist, and Parks.	1940	[14]	−0.33	±0.51

[a] Insofar as significant, the previous value was converted to the present unit of energy and atomic weight. A negative sign in this column indicates that the earlier value is less than that of the present report; a positive sign, higher.

[b] The uncertainties have been assigned by the present authors where estimates of the uncertainties were not given by the previous authors.

III. Increment per CH_2 Group for Several Homologous Series of Hydrocarbons

Figure 1 gives a plot of the deviations from linearity with number of carbon atoms in the normal alkyl radical of the values of the heats of formation of several homologous series of hydrocarbons, expressed as the value of δ in the following relation:

$$\Delta Hf^{\circ}_{298.16}\ [\text{gas, Y}-(CH_2)_m-\text{H}] = A'+Bm+\delta \text{ kcal/mole.} \quad (5)$$

Here $(CH_2)_m-H$ is a normal alkyl radical (methyl, ethyl, normal propyl, normal butyl, etc.) attached to any end group Y (methyl, vinyl, phenyl, cyclopentyl, cyclohexyl); A' is a constant peculiar to the end group, Y; B is a constant for all normal alkyl series, independent of Y; and δ is a term which has a small finite value for the lower members, being largest for $m=0$, and becomes zero for the higher members, beginning near $m=4$.

The new data yield more accurate values of the deviations for the paraffin and monoolefin series than those previously reported [7, 11], and give, for the first time, values of the deviations for the alkylbenzenes, alkylcyclopentanes, and alkylcyclohexanes. The new data also disclose for the first time a small, but significant, alternation in magnitude of the deviations with even or odd numbers of carbon atoms in normal alkyl radical. This effect is particularly noticeable in going from $m=1$ through $m=2$ to $m=3$. Although the uncertainties are relatively large, this alternation is believed to be definitely established because each of the five series exhibits the effect.

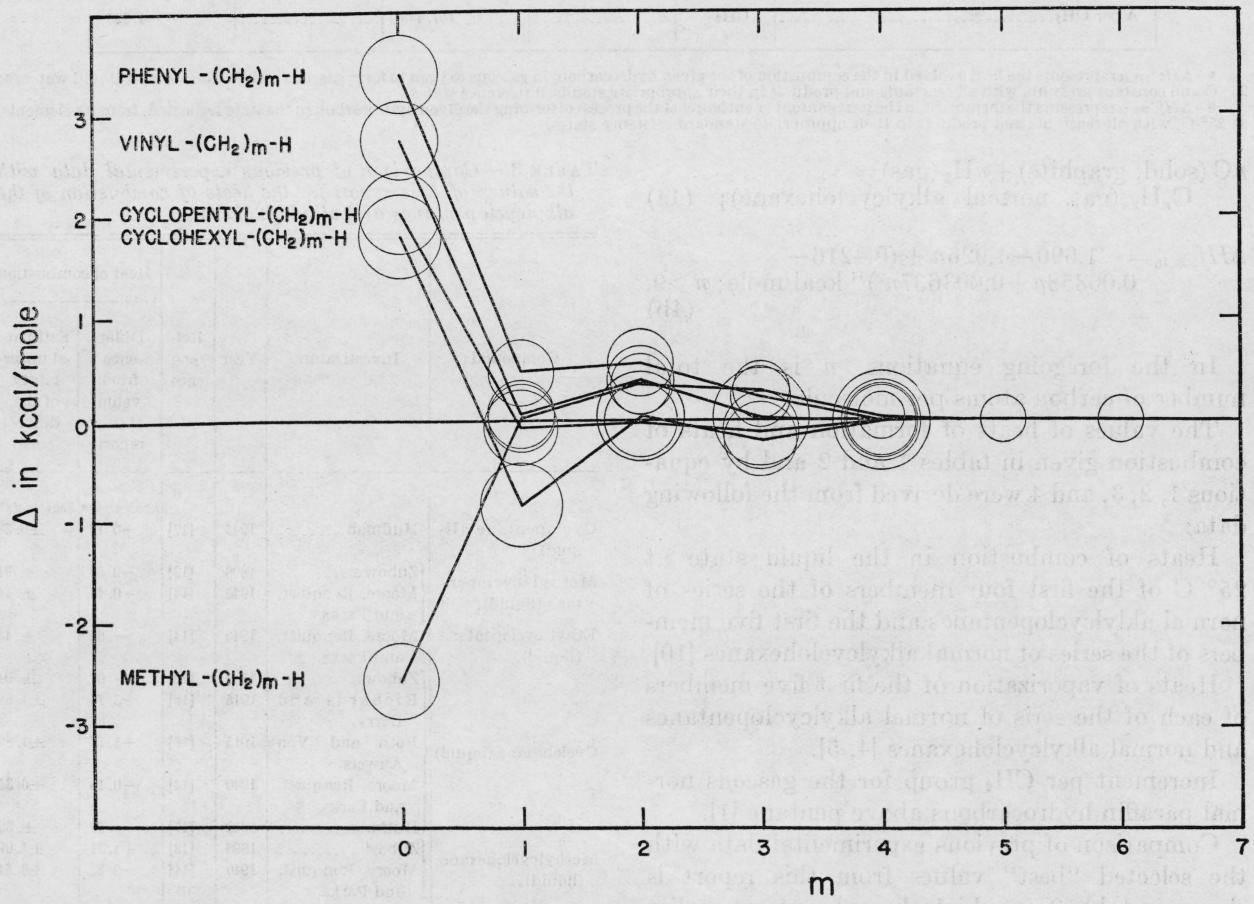

FIGURE 1.—*Plot of the deviations from linearity with number of carbon atoms, m, in the normal alkyl radical of the heats of formation of the lower members of several homologous series of hydrocarbons, expressed as the value of δ in the following relation:*

$$\Delta Hf^{\circ}_{298.16}\left[\text{gas, Y}-(CH_2)_m-\text{H}\right] = A'+Bm+\delta \text{ kcal/mole.}$$

TABLE 4.—*Values of the deviations from linearity with number of carbon atoms, m, in the normal alkyl radical of the heats of formation of the lower members of several homologous series of hydrocarbons*

Series	Structure	Values of A', B, and δ in the equation for the heat of formation in the gaseous state at 25° C $\Delta Hf° = A' + Bm + \delta$, kcal/mole							
		A'	B	δ, in kcal/mole					
				$m=0$	$m=1$	$m=2$	$m=3$	$m=4$	$m=5$
		kcal/mole	*kcal/mole per CH_2 group*						
Normal paraffins	Methyl$-(CH_2)_m-H$	−15.334	−4.926	−2.55 ±0.37	+0.02 ±0.33	+0.37 ±0.30	+0.30 ±0.28	+0.04 ±0.23	0.00 ±0.23
Monoolefins (1-alkene)	Vinyl$-(CH_2)_m-H$	9.740	−4.926	+2.76 ±0.37	+.07 ±0.33	+.39 ±0.33	+.04 ±0.48	.00 ±0.47	.00 ±0.47
Normal alkylbenzenes	Phenyl$-(CH_2)_m-H$	16.404	−4.926	+3.42 ±0.38	+.47 ±0.34	+.57 ±0.33	+.24 ±0.30	.00 ±0.35	.00 ±0.35
Normal alkylcyclopentanes	Cyclopentyl$-(CH_2)_m-H$	−20.516	−4.926	+2.05 ±0.40	−.06 ±0.37	−.01 ±0.36	−.10 ±0.37	.00 ±0.39	.00 ±0.39
Normal alkylcyclohexanes	Cyclohexyl$-(CH_2)_m-H$	−31.246	−4.926	+1.82 ±0.41	−.82 ±0.40	+.05 ±0.45	−.18 ±0.37	.00 ±0.37	.00 ±0.37

Table 4 gives, for each of the five series, the numerical values of the constants A' and B and of the term δ in equation 5, for the lower members of the series. The uncertainty assigned to the value of δ in each case includes the uncertainty associated with the extrapolation of the linear part of relations, equation 5, to lower values of m.

The values of δ in equation 5, for $m=0$, are characteristic of the end group in each series, and can be seen to vary regularly with changes in the number of hydrogen atoms and number and kind of carbon atoms bonded to the main or attaching carbon atom of the end group. The values of δ for $m=0$ for several end groups (including ethyl, isopropyl, *tert*-butyl, isopropenyl, and ethynyl, in addition to those given in table 4 and fig. 1) are shown in table 5 in relation to the number of carbon-hydrogen bonds and the number and kind of carbon-carbon bonds associated with the main or attaching carbon atom of the end group, not including the attaching bond. The value of δ for $m=0$ for an ethyl end group was obtained by noting that this is the same as the value of δ for $m=1$ for a methyl end group. The value of δ for $m=0$ for an isopropyl end group was calculated from the values previously reported [1] for propane, 2-methylpropane, 2-methylbutane, 2-methylpentane, 2-methylhexane, and 2-methylheptane. The value δ for $m=0$ for a tertiary butyl end group was calculated from the values of heats of formation previously reported [1] for isobutane, 2,2-dimethylpropane, 2,2-dimethylbutane, 2,2-dimethylpentane, and 2,2-dimethylhexane. The value of δ for $m=0$ for an isopropenyl end group was calculated from the values of heats of formation previously reported [8] for propene, 2-methylpropene, 2-methyl-1-butene, and 2-methyl-1-pentene. The value of δ for $m=0$ for an ethynyl end group was obtained from unpublished values for the heats of formation of the normal acetylenes (1-alkynes) [12].

TABLE 5.—*Relation between the value of the deviation from linearity for $m=0$ and the number and kind of bonds associated with the main or attaching carbon atom of the end group*

End group	Value of δ for m=0	Bonds associated with the main or attaching carbon atom of the given end group (not including the attaching bond)				
		C−H	C−C (paraffin)	C=C (phenyl)	C=C (olefin)	C≡C (acetylene)
	kcal/mole					
Methyl	−2.55 ±0.37	3				
Ethyl	0.02 ±0.33	2	1			
Cyclohexyl	1.82 ±0.41	1	2			
Cyclopentyl	2.05 ±0.40	1	2			
Isopropyl	2.05 ±0.50	1	2			
tert-Butyl	2.55 ±0.50		3			
Vinyl	2.76 ±0.37	1			1	
Phenyl	3.42 ±0.38			2		
Isopropenyl	3.68 ±0.40		1		1	
Ethynyl	4.94 ±0.55					1

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WASHINGTON, February 19, 1946.