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HEATS OF FORMATION, HYDROGENATION, AND COMBUSTION OF THE MONOOLEFIN HYDROCARBONS THROUGH THE HEXENES, AND OF THE HIGHER 1-ALKENES, IN THE GASEOUS STATE AT 25° C¹

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ABSTRACT

For ethylene, propylene, the four butenes, the six pentenes, and the 17 hexenes, and all the higher 1-alkene hydrocarbons, in the gaseous state at 25° C, values are given for the heats of formation (from the elements solid carbon (graphite) and gaseous hydrogen), the heats of hydrogenation in the gaseous state, and the heats of combustion (in oxygen to form gaseous carbon dioxide and liquid water). The values for 2 of the pentenes, 14 of the 17 hexenes, and all the higher 1-alkene hydrocarbons, were calculated by a method involving correlation of the heat of hydrogenation with structure and the use of constants evaluated from the available experimental data on 4 butenes, 4 pentenes, 3 hexenes, and 1 heptene.

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I. INTRODUCTION

In a previous report [1]² values were given for the heats of formation of the monoolefin hydrocarbons from ethylene through the pentenes in the gaseous state. At that time, the data on the heats of hydrogenation of the higher monoolefins [2, 3] could not be utilized for calculating heats of formation because of the lack of reliable experimental data on the corresponding paraffin hydrocarbons. Since then new data on the paraffin hydrocarbons above the pentanes have become available [4, 5, 6, 7, 8]. The present paper presents (a) revised values for the monoolefins through the pentenes, changed on account of slight revisions in the selected "best" values for heats of formation of water and carbon dioxide [9, 10] and of improved values of specific heat [11, 12] for converting to 25° C the heats of

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.

hydrogenation [2, 3, 18] measured at 82° C, and (b) new values for the hexenes and the higher 1-alkene hydrocarbons, utilizing data on specific heat and heat of hydrogenation of the monoolefins and new data on the heats of formation of the paraffins. For these compounds, values of the heats of formation, hydrogenation, and combustion are given for the gaseous state at 25° C. The values for 2 of the pentenes, 14 of the hexenes, and all the higher 1-alkene hydrocarbons were calculated by a method involving correlation of the heat of hydrogenation with structure and the use of constants evaluated from the available data on 4 butenes, 4 pentenes, 3 hexenes, and 1 heptene.

II. UNITS, CONSTANTS, UNCERTAINTIES

The unit of energy upon which the values presented in this paper are based is the international joule determined by standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau. Conversion to the conventional thermochemical calorie is made by means of the relation [13]

$$4.1833 \text{ international joules} = 1 \text{ calorie.}$$

The molecular weights of hydrogen, oxygen, and carbon were taken as 1.0080, 16.0000, and 12.010, respectively, from the 1941 table of International Atomic Weights [14].

The uncertainties assigned to the various quantities dealt with were derived, where possible, by a method previously described [15]. In other cases, reasonable estimates of the uncertainties were made.

III. DATA USED IN THE CALCULATIONS

The following data were used in the calculations:

Heat of formation of carbon dioxide at 25° C [9].

Heat of formation of water at 25° C [10].

Heats of combustion of ethylene and propylene at 25° C [16].

Heats of hydrogenation, at 82° C, of ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene, 2-pentene (mixture of *cis* and *trans* isomers), 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, and 1-heptene [2, 3, 17, 18].

Heats of formation of the paraffin hydrocarbons at 25° C [8].

Values of $\Delta H_{355}^{\circ} - \Delta H_{298.16}^{\circ}$ for the reaction of hydrogenation of the appropriate monoolefin hydrocarbons calculated statistically from spectroscopic and other molecular data [11, 12].

IV. METHOD OF CALCULATION

For ethylene and propylene, values of the heat of formation at 25° C were calculated both from (a) the data on the heat of combustion of the olefin [16] and the heats of formation of water [10] and carbon dioxide [9], all at 25° C, and (b) the data on the heat of hydrogenation of the olefin at 82° C [17, 18], corrected to 25° C with appropriate values of the change of the heat content with the change of temperature [10, 11, 12, 21, 22, 23], and the recently published selected "best" value for the heat of formation of the corresponding paraffin [8]. The resulting values were weighted inversely as the square of their assigned uncertainties to obtain the selected best values for the heats of formation of ethylene and propylene. The selected best values for the heats of hydrogenation of ethylene and propylene were then taken as the appropriate differences in the selected best values for the heats of formation of ethylene and ethane and propylene and propane.

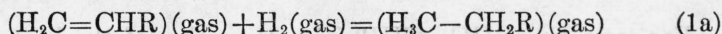
The values for the heats of formation at 25° C of 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene were calculated from the heats of hydrogenation at 82° C [2, 3, 18], corrected to 25° C with appropriate values of the change of heat content with change of temperature, combined with the selected best values of the heats of formation of the corresponding paraffins [8]. The values for *cis*-2-pentene and *trans*-2-pentene were similarly obtained by using the data on the heat of hydrogenation at 82° C of a mixture of *cis*- and *trans*-2-pentene [2], and assuming the relative amounts of the two isomers to be as given by Kistiakowsky, et al. [2] and the difference in their heats of hydrogenation at 82° C to be the same as the difference between *cis*-2-butene and *trans*-2-butene at 82° C.

The values for the 14 hexenes for which no experimental data are available were calculated by a method involving correlation of the heat of hydrogenation with molecular structure, as follows:

The monoolefin hydrocarbons were divided into classes according to the number and location of the alkyl substituents, R, on the double-bond carbon atoms, as has previously been done in connection with other properties [19, 20].

Table 1 lists the several types of monoolefins, together with the values selected for their heats of hydrogenation. The values were selected as follows:

For type I, $\text{H}_2\text{C}=\text{CHR}$, the value of the heat of hydrogenation at 25° was taken as



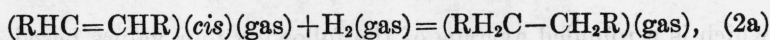
$$\Delta H^\circ_{298.16} = -30.00 \pm 0.40 \text{ kcal/mole}, \quad (1b)$$

which is a rounded average of the following four values based on experiment: 1-butene, -30.092 ± 0.081 ; 3-methyl-1-butene, -29.995 ± 0.082 ; 3,3-dimethyl-1-butene, -30.103 ± 0.153 ; 1-heptene, -29.876 ± 0.100 , kcal/mole.

TABLE 1.—Values of the heats of hydrogenation selected for the several classes of monoolefin hydrocarbons

Type	Structure	Selected value of $\Delta H_{298.16}^\circ$
I-----	$\begin{array}{c} \text{H} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	Kcal/mole -30.00 ± 0.40
IIc-----	$\begin{array}{c} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	-28.40 ± 0.50
IIIt-----	$\begin{array}{c} \text{R} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{R} \end{array}$	-27.40 ± 0.50
III-----	$\begin{array}{c} \text{H} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{R} \end{array}$	-28.10 ± 0.50
IV-----	$\begin{array}{c} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{R} \end{array}$	-26.70 ± 0.50
V-----	$\begin{array}{c} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{R} & & \text{R} \end{array}$	

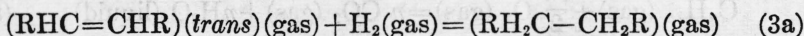
For type IIc, $\text{RHC}=\text{CHR}$ (*cis*), the value of the heat of hydrogenation at 25° C was taken as



$$\Delta H_{298.16}^\circ = -28.40 \pm 0.50 \text{ kcal/mole}, \quad (2b)$$

which is based on the experimental value for *cis*-2-butene, supported by the data on 2-pentene (*cis*+*trans*).

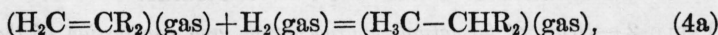
For type II_t, RHC=CHR (*trans*), the value of the heat of hydrogenation at 25° C was taken as



$$\Delta H^\circ_{298.16} = -27.40 \pm 0.50 \text{ kcal/mole}, \quad (3b)$$

which is based on the experimental value for *trans*-2-butene, supported by the data on 2-pentene (*cis*+*trans*).

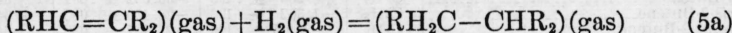
For type III, H₂C=CR₂, the value of the heat of hydrogenation at 25° C was taken as



$$\Delta H^\circ_{298.16} = -28.10 \pm 0.50 \text{ kcal/mole}, \quad (4b)$$

which is based on the experimental values for the following three compounds: Isobutene, -28.109 ± 0.80 ; 2-methyl-1-butene, -28.240 ± 0.122 ; 2,3-dimethyl-1-butene, -27.713 ± 0.124 kcal/mole.

For type IV, RHC=CR₂, the value of the heat of hydrogenation at 25° C was taken as



$$\Delta H^\circ_{298.16} = -26.70 \pm 0.50 \text{ kcal/mole}, \quad (5b)$$

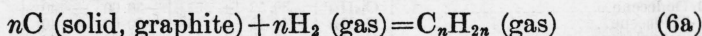
which is based on the experimental value for 2-methyl-2-butene, -26.745 ± 0.082 kcal/mole.

As there is only one hexene of type V, 2,3-dimethyl-2-butene, and as experimental data for it are available, no value for it was required to be selected for further calculation.

V. RESULTS

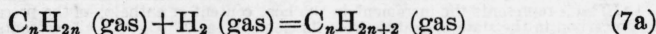
The results of the calculations are presented in table 2, which gives the values for the heats of formation, hydrogenation, and combustion of the monoolefin hydrocarbons in the gaseous state at 25° C. For the 1-alkenes above 1-pentene, the tabulated values were calculated from the following equations:

For the heat of formation—



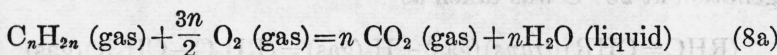
$$\Delta H^\circ_{298.16} = 19.592 - 4.926n \pm (0.3248 - 0.03884n + 0.002893n^2)^{1/2} \text{ kcal/mole; } n > 5. \quad (6b)$$

For the heat of hydrogenation—



$$\Delta H^\circ_{298.16} = -30.00 \pm 0.40 \text{ kcal/mole; } n > 5 \quad (7b)$$

For the heat of combustion—



$$\Delta H^\circ_{298.15} = -19.592 - 157.443n \pm (0.3248 - 0.03884n + 0.003102n^2)^{1/2} \text{ kcal/mole; } n > 5 \quad (8b)$$

Equations 7a and 7b correspond to eq 1a and 1b of this report. Equations 6a and 6b were obtained by combining eq 7a and 7b of this report with eq 5 and 6 from [8]. Equations 8a and 8b were obtained by appropriately combining with eq 6a and 6b the equations for the heats of formation of water and carbon dioxide.

TABLE 2.—Heats of formation, hydrogenation, and combustion of the monoolefin hydrocarbons through the hexenes, and of the higher 1-alkene hydrocarbons, in the gaseous state at 25° C

Compound (gas)	Formula	Heat of formation ¹ ΔH_f°	Heat of hydrogenation ² ΔH_h°	Heat of combustion ³ $-\Delta H_c^\circ$
		<i>Kcal/mole</i>	<i>Kcal/mole</i>	<i>Kcal/mole</i>
Ethene (ethylene).....	C ₂ H ₄	+12.496 ± 0.066	-32.732 ± 0.133	337.234 ± 0.072
Propene (propylene).....	C ₃ H ₆	+4.879 ± .122	-29.699 ± .181	491.987 ± .129
1-Butene.....	C ₄ H ₈	+0.280 ± .196	-30.092 ± .081	649.757 ± .204
<i>cis</i> -2-Butene.....	C ₄ H ₈	-1.362 ± .196	-28.450 ± .080	648.115 ± .204
<i>trans</i> -2-Butene.....	C ₄ H ₈	-2.405 ± .196	-27.407 ± .080	647.072 ± .204
2-Methylpropene (isobutene).....	C ₄ H ₈	-3.343 ± .182	-28.109 ± .080	646.134 ± .191
1-Pentene.....	C ₅ H ₁₀	-5.00 ± .43	-30.00 ± .400	806.85 ± .44
<i>cis</i> -2-Pentene.....	C ₅ H ₁₀	-6.51 ± .26	-28.491 ± .201	805.34 ± .27
<i>trans</i> -2-Pentene.....	C ₅ H ₁₀	-7.59 ± .26	-27.410 ± .201	804.26 ± .27
2-Methyl-1-butene.....	C ₅ H ₁₀	-8.68 ± .23	-28.240 ± .182	803.17 ± .24
3-Methyl-1-butene.....	C ₅ H ₁₀	-6.92 ± .22	-29.935 ± .082	804.93 ± .23
2-Methyl-2-butene.....	C ₅ H ₁₀	-10.17 ± .22	-26.745 ± .082	801.68 ± .23
1-Hexene.....	C ₆ H ₁₂	-9.96 ± .44	-30.00 ± .40	964.25 ± .45
<i>cis</i> -2-Hexene.....	C ₆ H ₁₂	-11.56 ± .53	-28.40 ± .50	962.66 ± .54
<i>trans</i> -2-Hexene.....	C ₆ H ₁₂	-12.56 ± .53	-27.40 ± .50	961.66 ± .54
<i>cis</i> -3-Hexene.....	C ₆ H ₁₂	-11.56 ± .53	-28.40 ± .50	962.66 ± .54
<i>trans</i> -3-Hexene.....	C ₆ H ₁₂	-12.56 ± .53	-27.40 ± .50	961.66 ± .54
2-Methyl-1-pentene.....	C ₆ H ₁₂	-13.56 ± .56	-28.10 ± .50	960.66 ± .57
3-Methyl-1-pentene.....	C ₆ H ₁₂	-11.02 ± .46	-30.00 ± .40	963.20 ± .47
4-Methyl-1-pentene.....	C ₆ H ₁₂	-11.66 ± .47	-30.00 ± .40	962.56 ± .48
2-Methyl-2-pentene.....	C ₆ H ₁₂	-14.96 ± .56	-26.70 ± .50	959.26 ± .57
<i>cis</i> -3-Methyl-2-pentene.....	C ₆ H ₁₂	-14.32 ± .55	-26.70 ± .50	959.00 ± .56
<i>trans</i> -3-Methyl-2-pentene.....	C ₆ H ₁₂	-14.32 ± .55	-26.70 ± .50	959.00 ± .56
<i>cis</i> -4-Methyl-2-pentene.....	C ₆ H ₁₂	-13.26 ± .56	-28.40 ± .50	960.96 ± .57
<i>trans</i> -4-Methyl-2-pentene.....	C ₆ H ₁₂	-14.26 ± .56	-27.40 ± .50	959.96 ± .57
2-Ethyl-1-butene.....	C ₆ H ₁₂	-12.92 ± .55	-28.10 ± .50	961.30 ± .56
2,3-Dimethyl-1-butene.....	C ₆ H ₁₂	-14.78 ± .27	-27.713 ± .124	959.44 ± .28
3,3-Dimethyl-1-butene.....	C ₆ H ₁₂	-14.25 ± .28	-30.103 ± .153	959.97 ± .29
2,3-Dimethyl-2-butene.....	C ₆ H ₁₂	-15.91 ± .27	-28.576 ± .124	958.31 ± .28
1-Heptene.....	C ₇ H ₁₄	-14.89 ± .44	-30.00 ± .40	1121.69 ± .45
1-Octene.....	C ₈ H ₁₆	-19.82 ± .45	-30.00 ± .40	1279.13 ± .46
1-Nonene.....	C ₉ H ₁₈	-24.74 ± .46	-30.00 ± .40	1436.58 ± .48
1-Decene.....	C ₁₀ H ₂₀	-29.67 ± .48	-30.00 ± .40	1594.02 ± .50
1-Undecene.....	C ₁₁ H ₂₂	-34.60 ± .50	-30.00 ± .40	1751.46 ± .52
1-Dodecene.....	C ₁₂ H ₂₄	-39.52 ± .52	-30.00 ± .40	1908.91 ± .55
1-Tridecene.....	C ₁₃ H ₂₆	-44.45 ± .56	-30.00 ± .40	2066.35 ± .59
1-Tetradecene.....	C ₁₄ H ₂₈	-49.38 ± .59	-30.00 ± .40	2223.79 ± .62
1-Pentadecene.....	C ₁₅ H ₃₀	-54.31 ± .62	-30.00 ± .40	2381.23 ± .66
1-Hexadecene.....	C ₁₆ H ₃₂	-59.23 ± .66	-30.00 ± .40	2538.68 ± .70
1-Heptadecene.....	C ₁₇ H ₃₄	-64.15 ± .70	-30.00 ± .40	2696.13 ± .74
1-Octadecene.....	C ₁₈ H ₃₆	-69.08 ± .75	-30.00 ± .40	2853.57 ± .79
1-Nonadecene.....	C ₁₉ H ₃₈	-74.00 ± .80	-30.00 ± .40	3011.01 ± .85
1-Eicosene.....	C ₂₀ H ₄₀	-78.93 ± .84	-30.00 ± .40	3168.45 ± .89
Δ per CH ₂ ; n > 5.....	-CH ₂ -	-4.926	0.00 ± .40	157.443

¹ $\Delta H_f^\circ_{298.15}$ 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.

² $\Delta H_h^\circ_{298.15}$ represents the increment in heat content or enthalpy of the reaction of hydrogenation of the monoolefin to form the corresponding paraffin hydrocarbon, in the gaseous state at 25° C, with all reactants and products in their appropriate standard reference states.

³ $\Delta H_c^\circ_{298.15}$ 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.

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