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HEATS OF COMBUSTION AND FORMATION AT 25° C OF THE ALKYLBENZENES THROUGH $C_{10}H_{14}$, AND OF THE HIGHER NORMAL MONOALKYLBENZENES[1]

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ABSTRACT

Values are given for the heats of combustion (in oxygen to form gaseous carbon dioxide and liquid water) and the heats of formation (from the elements, solid carbon (graphite) and gaseous hydrogen), at 25° C, for benzene, toluene, the four C_8H_{10}, the eight C_9H_{12}, and the 22 $C_{10}H_{14}$ alkylbenzenes, in both the liquid and gaseous states, and for the higher normal monoalkylbenzenes in the gaseous state.

CONTENTS

I. INTRODUCTION

As part of the work of the Bureau's Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons," this report presents values for the heats of combustion and of formation at 25° C of the alkylbenzenes through $C_{10}H_{14}$, in both liquid and gaseous states, and of the higher normal monoalkylbenzenes in the gaseous state.

II. UNITS, CONSTANTS, AND 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. Conver-

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[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."

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sion to the conventional thermochemical calorie is made by means of the relation [1][2].

4.1833 international joules = 1 calorie.

The atomic 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 [2].

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

III. DATA USED IN THE CALCULATIONS

The data used in the calculations are the following:

Heat of formation of carbon dioxide at 25° C [4].

Heat of formation of water at 25° C [5].

Heats of combustion of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, and *n*-propylbenzene, in the liquid state at 25° C [6].

Heats of combustion of isopropylbenzene, 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene, in the liquid state at 25° C [7].

Heats of combustion of *n*-butylbenzene, isobutylbenzene, *sec*-butylbenzene, and *tert*-butylbenzene, in the liquid state at 25° C [8].

Standard heats of vaporization at 25° C for benzene, toluene, the four C_8H_{10}, the eight C_9H_{12}, and the twenty-two $C_{10}H_{14}$ alkylbenzenes, from a correlation by Wagman, Taylor, Pignocco, and Rossini [9] of selected "best" values based largely on the experimental data on the heats of vaporization at 25° C of benzene, toluene, ethylbenzene, the three xylenes, the two propylbenzenes, and the three trimethylbenzenes by Osborne and Ginnings [10].

IV. METHOD OF CALCULATION

The selected values for the heats of combustion of the hydrocarbon in the liquid state at 25° C were taken as reported in reference [6] for benzene, toluene, ethylbenzene, the three xylenes, and *n*-propylbenzene, in reference [7] for isopropylbenzene, the three methylethylbenzenes, and the trimethylbenzenes, and from reference [8] for *n*-butylbenzene, isobutylbenzene, *sec*-butylbenzene, and *tert*-butylbenzene. The corresponding values for the heat of combustion of the hydrocarbon in the gaseous state at 25° C were obtained by appropriately adding the values of the heats of vaporization from reference [9].

The selected values for the heats of formation of the above hydrocarbons in the liquid and gaseous states at 25° C were obtained by appropriately combining the values of the heats of formation of water and carbon dioxide from references [4, 5] with the corresponding selected values for the heats of combustion.

The corresponding values for the higher normal monoalkylbenzenes were obtained by adding to the values for *n*-butylbenzene the appropriate increments per CH_2 group reported for the normal paraffin hydrocarbons above *n*-pentane [11].

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

The values for the heats of formation in the gaseous state at 25° C for all the $C_{10}H_{14}$ alkylbenzenes except the four butylbenzenes were calculated by a method involving the summing of contributions from component parts of the molecule (phenyl, methyl, ethyl, *n*-propyl, and isopropyl groups), together with contributions associated with the positions of the substituent groups on the benzene ring.[3] The necessary constants were evaluated by the method of least squares from the selected values of the heats of formation in the gaseous state at 25° C for toluene, ethylbenzene, *n*-propylbenzene, isopropylbenzene, the three xylenes, the three methylethylbenzenes, and the three trimethylbenzenes.

By this method, the heat of formation of an alkylbenzene hydrocarbon, with one phenyl group having methyl, ethyl, *n*-propyl, or isopropyl substituent groups, is taken as

$$n\text{C(solid, graphite)} + (n-3)\text{H}_2\text{(gas)} = \text{C}_n\text{H}_{2n-6}\text{(gas)} \qquad (1)$$

$$\Delta Hf^\circ_{298.16} = \beta_\phi + z_\text{I}\beta_\text{I} + z_\text{II}\beta_\text{II} + z_\text{III}\beta_\text{III} + z_{\text{III}_i}\beta_{\text{III}_i} + z_o\beta_o + z_m\beta_m + z_p\beta_p \text{ kcal/mole,} \qquad (2)$$

where

z_I = the number of methyl groups

z_II = the number of ethyl groups

z_III = the number of *n*-propyl groups

z_{III_i} = the number of isopropyl groups

z_o = the number of ortho pairs of substituents (being, for example, one in *o*-xylene and two in 1,2,3-trimethylbenzene)

z_m = the number of meta pairs of substituents (being, for example, one in *m*-xylene and 1,2,3-trimethylbenzenes and three in 1,3,5-trimethylbenzene)

z_p = the number of para pairs of substituents (being, for example, one in *p*-xylene and two in 1,2,4,5-tetramethylbenzene)

β_ϕ = 19.383 kcal/mole, representing the contribution of the one phenyl group

β_I = −7.508 kcal/mole, representing the contribution of one methyl group

β_II = −12.190 kcal/mole, representing the contribution of one ethyl group

β_III = −17.513 kcal/mole, representing the contribution of one *n*-propyl group

β_{III_i} = −18.443 kcal/mole, representing the contribution of one isopropyl group

β_o = 0.469 kcal/mole, representing the contribution arising from each pair of substituent groups which are in ortho positions with respect to each other

β_m = −0.225 kcal/mole, representing the contribution arising from each pair of substituent groups which are in meta positions with respect to each other

β_p = −0.327 kcal/mole, representing the contribution arising from each pair of substituent groups which are in para positions with respect to each other.

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[3] This method is similar to that previously used in reference [9] in the evaluation of the heats of vaporization of compounds for which no data exist.

The foregoing constants yield values of the heats of formation of the C_7H_8 to C_9H_{12} alkylbenzenes which differ from the selected best values by the following amounts, in kilocalories per mole: Toluene, −0.08; ethylbenzene, 0.07; *o*-xylene, 0.30; *m*-xylene, 0.02; *p*-xylene, −0.25; 1-methyl-2-ethylbenzene, −0.14; 1-methyl-3-ethylbenzene, −0.08; 1-methyl-4-ethylbenzene, 0.14; 1,2,3-trimethylbenzene, −0.14; 1,2,4-trimethylbenzene, 0.11; 1,3,5-trimethylbenzene, 0.02. As 0.12 kcal/mole is only 0.01 percent of the value of the heat of combustion of a C_9H_{12} alkylbenzene, the correlation is considered satisfactory.

The values calculated by the foregoing method for the $C_{10}H_{14}$ alkylbenzenes, except the four butylbenzenes, are believed to be uncertain by not more than about ±0.40 to ±0.70 kcal/mole, which is ±0.03 to ±0.05 percent of their heats of combustion.

V. RESULTS

In table 1 are presented the selected "best" values for the heats of combustion and formation at 25° C of the 36 alkylbenzenes through $C_{10}H_{14}$, in both the liquid and gaseous state, and for some higher normal monoalkylbenzenes in the gaseous state.

For the heats of combustion of the normal monoalkylbenzenes above *n*-propylbenzene, in the gaseous state at 25° C:

$$C_nH_{2n-6}(\text{normal alkylbenzene, gas})+(3/2)(n-1)O_2(\text{gas})=nCO_2(\text{gas})+(n-3)H_2O(\text{liq}) \tag{3}$$

$$-\Delta Hc^\circ_{298.16}=-158.990+157.443n\pm(0.4226-0.06556n+0.003428n^2)^{\frac{1}{2}}\ \text{kcal/mole};\ n>9 \tag{4}$$

Similarly, the heats of formation of the higher normal monoalkylbenzenes in the gaseous state at 25° C are:

$$nC(\text{solid, graphite})+(n-3)H_2(\text{gas})=C_nH_{2n-6}(\text{normal alkylbenzene, gas}) \tag{5}$$

$$\Delta Hf^\circ_{298.16}=45.960-4.926n\pm(0.4234-0.06611n+0.003637n^2)^{\frac{1}{2}}\ \text{kcal/mole};\ n>9 \tag{6}$$

The foregoing equations incorporate the increment per CH_2 previously reported for the normal paraffin hydrocarbons [11].

VI. COMPARISON WITH PREVIOUS DATA

Comparison of previous experimental data with the selected best values from this report is shown in table 2, in which the values from earlier investigations have been converted, insofar as significant, to the present unit of energy and atomic weights.

TABLE 1.—*Selected "Best" values for the heats of combustion and formation of the Alkylbenzenes*

Compound	Formula	Heat of combustion [a] at 25° C, $-\Delta Hc^\circ$		Heat of formation [b] at 25° C, ΔHf°	
		Liquid	Gas	Liquid	Gas
		kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
Benzene	C_6H_6	780.98 ±0.10	789.08 ±0.10	11.72 ±0.12	19.82 ±0.12
Methylbenzene (toluene)	C_7H_8	934.50 ±0.12	943.58 ±0.12	2.87 ±0.15	11.95 ±0.15
Ethylbenzene	C_8H_{10}	1091.03 ±0.17	1101.13 ±0.17	−2.98 ±0.20	7.12 ±0.20
1, 2-Dimethylbenzene (*o*-xylene).	C_8H_{10}	1088.16 ±0.24	1098.54 ±0.24	−5.84 ±0.26	4.54 ±0.26
1, 3-Dimethylbenzene (*m*-xylene).	C_8H_{10}	1087.92 ±0.15	1098.12 ±0.15	−6.08 ±0.18	4.12 ±0.18
1, 4-Dimethylbenzene (*p*-xylene).	C_8H_{10}	1088.16 ±0.22	1098.29 ±0.22	−5.84 ±0.24	4.29 ±0.24
n-Propylbenzene	C_9H_{12}	1247.19 ±0.16	1258.24 ±0.16	−9.18 ±0.20	1.87 ±0.20
Isopropylbenzene	C_9H_{12}	1246.52 ±0.23	1257.31 ±0.23	−9.85 ±0.26	0.94 ±0.26
1-Methyl-2-ethylbenzene	C_9H_{12}	1245.26 ±0.23	1256.66 ±0.25	−11.11 ±0.26	0.29 ±0.28
1-Methyl-3-ethylbenzene	C_9H_{12}	1244.71 ±0.26	1255.92 ±0.27	−11.67 ±0.28	−0.46 ±0.29
1-Methyl-4-ethylbenzene	C_9H_{12}	1244.45 ±0.32	1255.59 ±0.33	−11.92 ±0.34	−0.78 ±0.35
1, 2, 3-Trimethylbenzene	C_9H_{12}	1242.36 ±0.28	1254.08 ±0.28	−14.01 ±0.30	−2.29 ±0.30
1, 2, 4-Trimethylbenzene	C_9H_{12}	1241.58 ±0.24	1253.04 ±0.24	−14.79 ±0.27	−3.33 ±0.27
1, 3, 5-Trimethylbenzene	C_9H_{12}	1241.19 ±0.32	1252.53 ±0.32	−15.18 ±0.34	−3.84 ±0.34
n-Butylbenzene	$C_{10}H_{14}$	1403.46 ±0.27	1415.44 ±0.28	−15.28 ±0.30	−3.30 ±0.31
Isobutylbenzene	$C_{10}H_{14}$	1402.04 ±0.29	1413.59 ±0.31	−16.70 ±0.32	−5.15 ±0.34
sec-Butylbenzene	$C_{10}H_{14}$	1402.85 ±0.27	1414.57 ±0.30	−15.89 ±0.30	−4.17 ±0.33
tert-Butylbenzene	$C_{10}H_{14}$	1401.82 ±0.27	1413.32 ±0.31	−16.92 ±0.30	−5.42 ±0.34
1, 2-Diethylbenzene	$C_{10}H_{14}$	1401.80 ±0.44	1414.21 ±0.42	−16.94 ±0.42	−4.53 ±0.40
1, 3-Diethylbenzene	$C_{10}H_{14}$	1401.30 ±0.44	1413.52 ±0.42	−17.44 ±0.42	−5.22 ±0.40
1, 4-Diethylbenzene	$C_{10}H_{14}$	1401.27 ±0.44	1413.42 ±0.42	−17.47 ±0.42	−5.32 ±0.40
1-Methyl-2-*n*-propylbenzene	$C_{10}H_{14}$	1401.22 ±0.53	1413.57 ±0.52	−17.52 ±0.51	−5.17 ±0.50
1-Methyl-3-*n*-propylbenzene	$C_{10}H_{14}$	1400.72 ±0.53	1412.88 ±0.52	−18.02 ±0.51	−5.86 ±0.50
1-Methyl-4-*n*-propylbenzene	$C_{10}H_{14}$	1400.68 ±0.53	1412.77 ±0.52	−18.06 ±0.51	−5.97 ±0.50
1-Methyl-2-isopropylbenzene	$C_{10}H_{14}$	1400.55 ±0.53	1412.64 ±0.52	−18.19 ±0.51	−6.10 ±0.50
1-Methyl-3-isopropylbenzene	$C_{10}H_{14}$	1400.05 ±0.53	1411.95 ±0.52	−18.69 ±0.51	−6.79 ±0.50
1-Methyl-4-isopropylbenzene	$C_{10}H_{14}$	1400.01 ±0.53	1411.84 ±0.52	−18.73 ±0.51	−6.90 ±0.50
1, 2-Dimethyl-3-ethylbenzene	$C_{10}H_{14}$	1398.90 ±0.62	1411.63 ±0.61	−19.84 ±0.61	−7.11 ±0.60
1, 2-Dimethyl-4-ethylbenzene	$C_{10}H_{14}$	1398.36 ±0.62	1410.83 ±0.61	−20.38 ±0.61	−7.91 ±0.60
1, 3-Dimethyl-2-ethylbenzene	$C_{10}H_{14}$	1398.90 ±0.62	1411.63 ±0.61	−19.84 ±0.61	−7.11 ±0.60
1, 3-Dimethyl-4-ethylbenzene	$C_{10}H_{14}$	1398.36 ±0.62	1410.83 ±0.61	−20.38 ±0.61	−7.91 ±0.60
1, 3-Dimethyl-5-ethylbenzene	$C_{10}H_{14}$	1397.88 ±0.62	1410.24 ±0.61	−20.86 ±0.61	−8.50 ±0.60
1, 4-Dimethyl-2-ethylbenzene	$C_{10}H_{14}$	1398.36 ±0.62	1410.83 ±0.61	−20.38 ±0.61	−7.91 ±0.60
1, 2, 3, 4-Tetramethylbenzene	$C_{10}H_{14}$	1395.70 ±0.72	1408.72 ±0.71	−23.04 ±0.71	−10.02 ±0.70
1, 2, 3, 5-Tetramethylbenzene	$C_{10}H_{14}$	1395.20 ±0.72	1408.03 ±0.71	−23.54 ±0.71	−10.71 ±0.70
1, 2, 4, 5-Tetramethylbenzene	$C_{10}H_{14}$	1395.16 ±0.72	1407.92 ±0.71	−23.58 ±0.71	−10.82 ±0.70
n-Amylbenzene	$C_{11}H_{16}$		1572.88 ±0.34		−8.23 ±0.37
n-Hexylbenzene	$C_{12}H_{18}$		1730.33 ±0.36		−13.15 ±0.39
n-Heptylbenzene	$C_{13}H_{20}$		1887.77 ±0.39		−18.08 ±0.42
n-Octylbenzene	$C_{14}H_{22}$		2045.21 ±0.42		−23.00 ±0.46
n-Nonylbenzene	$C_{15}H_{24}$		2202.66 ±0.46		−27.93 ±0.50
n-Decylbenzene	$C_{16}H_{26}$		2360.10 ±0.50		−32.86 ±0.54
n-Undecylbenzene	$C_{17}H_{28}$		2517.54 ±0.55		−37.78 ±0.59
n-Dodecylbenzene	$C_{18}H_{30}$		2674.98 ±0.59		−42.71 ±0.64
n-Tridecylbenzene	$C_{19}H_{32}$		2832.43 ±0.64		−47.63 ±0.69
n-Tetradecylbenzene	$C_{20}H_{34}$		2989.87 ±0.70		−52.56 ±0.75
n-Pendadecylbenzene	$C_{21}H_{36}$		3147.31 ±0.75		−57.49 ±0.80
n-Hexadecylbenzene	$C_{22}H_{38}$		3304.76 ±0.80		−62.41 ±0.85
Δ per CH_2	CH_2		157.443		−4.926

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[a] $-\Delta Hc^\circ$ 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] ΔHf° 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.

TABLE 2.—*Comparison of previous experimental data with the selected "best" values from this report for the heats of combustion of the alkylbenzenes.*

Compound	Investigators	Year	Reference	Heat of combustion	
				Difference from value of this report [a]	Estimated uncertainty of the difference [b]
				kcal/mole	*kcal/mole*
Benzene (liquid)	Berthelot	1878	[12]	−3.8	±3.9
	Stohmann, Rodatz, and Herzberg.	1886	[15]	0.0	±1.6
	Stohmann, Kleber, and Langbein.	1889	[16]	−0.6	±1.6
	Richards, Henderson and Frevert.	1907	[17]	−2.5	±1.6
	Richards and Jesse	1910	[18]	+1.5	±1.6
	Roth and von Auwers	1915	[19]	+2.1	±1.6
	Richards and Barry	1915	[20]	−0.2	±1.6
	Richards and Davis	1920	[21]	+1.9	±1.6
Benzene (gas)	Berthelot	1881	[13]	−3.2	±3.9
	Thomsen	1886	[14]	−11.4	±7.9
	Stohmann, Rodatz, and Herzberg.	1886	[15]	−0.4	±1.6
Toluene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	+0.8	±1.9
	Schmidlin	1906	[23]	+5.6	±4.7
	Roth and von Auwers	1915	[19]	+1.6	±1.9
	Richards and Barry	1915	[20]	+2.7	±1.9
	Richards and Davis	1917	[24]	+2.5	±1.9
	Richards and Davis	1920	[21]	+2.0	±1.9
Ethylbenzene (liquid)	Jesse	1912	[25]	−10.8	±2.2
	Moureu and André	1914	[26]	+5.8	±3.3
	Richards and Barry	1915	[20]	+0.2	±2.2
	von Auwers and Kolligs	1922	[27]	+4.3	±2.2
o-Xylene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	−2.1	±2.2
	Richards and Barry	1910	[20]	+3.5	±2.2
m-Xylene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	−2.0	±2.2
	Richards and Jesse	1910	[18]	+3.7	±2.2
	Roth and von Auwers	1915	[19]	+2.5	±2.2
p-Xylene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	−2.1	±2.2
	Richards and Jesse	1910	[18]	−2.1	±2.2
n-Propylbenzene	Genvresse	1893	[28]	+3.9	±3.7
	Richards and Barry	1915	[20]	−0.7	±2.5
	Huffman and Knowlton	1944	[29]	−1.0	±0.6
Isopropylbenzene (liquid)	Genvresse	1893	[28]	+6.2	±3.7
	Richards and Barry	1915	[20]	+0.9	±2.5
	Huffman and Knowlton	1944	[29]	−1.2	±0.6
1,2,4-Trimethylbenzene (liquid)	Richards and Barry	1915	[20]	−0.9	±2.5
1,3,5-Trimethylbenzene (liquid)	Stohmann, Rodatz, and Herzberg.	1887	[22]	+11.8	±2.5
	Richards and Barry	1915	[20]	+2.4	±2.5
tert-Buthylbenzene	Richards and Barry	1915	[20]	−1.4	±2.8
	Richards and Davis	1920	[21]	+0.1	±2.8
1-Methyl-3-*n*-propylbenzene (liquid).	Genvresse	1893	[28]	+7.5	±4.2
1-Methyl-3-isopropylbenzene (liquid).	do	1893	[28]	+12.4	±4.2
1-Methyl-4-isopropylbenzene (liquid).	Stohmann, Rodatz, and Herzberg.	1887	[22]	+4.0	±2.8
	Stohmann, Kleber, and Langbein.	1890	[30]	+15.0	±2.8
1,2,4,5-Tetramethylbenzene (liquid).	Stohmann, Kleber, and Langbein.	1889	[16]	+1.2	±2.8

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[a] Insofar as significant, the previous value was converted to the present unit of energy and atomic weights. 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.

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