HEATS OF FORMATION AND COMBUSTION OF 1,3-BUTA-DIENE AND STYRENE [1]

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ABSTRACT

Values are given for the heats of formation from the elements, and for the heats
of combustion, of 1,3-butadiene and styrene, in both the liquid and gaseous states,
at 25° C.

CONTENTS

I. INTRODUCTION

The previously published value from this laboratory for the heat
of formation of 1,3-butadiene from its elements [1] [2] is based on a
combination of values of the heat of hydrogenation of 1,3-butadiene
to n-butane [2], the heat of combustion of n-butane [3], the heat of
formation of water from its elements [4], and the heat of formation of
carbon dioxide from its elements [5]. Because a new "best" value
for the heat of formation of carbon dioxide [6] and new data on the
heat capacities of n-butane [7] and 1,3-butadiene [8, 25, 26] have be-
come available, a revised value for the heat of formation of 1,3-
butadiene can be calculated. From this value, a new value for the
heat of combustion of 1,3-butadiene is obtained.

The existing values for the heats of combustion and formation of
styrene are based on old measurements of the heat of combustion
[17, 18, 19, 20, 21, 22]. New data on the heat of combustion of styrene
obtained in this laboratory [16] yield a more reliable value for its heat
of formation from the elements, as well as for its heat of combustion.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values presented in this paper
are based is the international joule determined by standards of resist-

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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 and Analysis of
Data on the Properties of Hydrocarbons.
[2] Figures in brackets indicate the literature references at the end of this paper.

ance (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 [9]:

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

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 [10].

The uncertainties assigned to the various quantities dealt with were derived, where possible, by a method previously described [11]. In other cases, reasonable estimates of the uncertainty were made.

III. 1,3-BUTADIENE

The selected value previously used [1] for the heat of hydrogenation of 1,3-butadiene to n-butane, at 25° C, was obtained from the selected value for the heat of hydrogenation at 82° C [2] corrected to the new atomic weight of carbon and converted to 25° C [1], using an estimated value for the difference in heat capacities of 1,3-butadiene and n-butane, with the known heat capacity of hydrogen [23]. The conversion of the heat of hydrogenation from 82° to 25° C had previously been taken as

$$C_4H_6(\text{gas, 1,3-butadiene}) + 2H_2(\text{gas}) = C_4H_{10}(\text{gas, } n\text{-butane}) \quad (1)$$
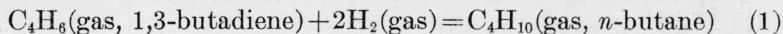
$$\Delta H°_{355.16} - \Delta H°_{298.16} = -0.500 \pm 0.100 \text{ kcal/mole.} \quad (1a)$$

Fortuitously, the previous estimate is substantially in accord with the new data on the heat capacities of 1,3-butadiene and n-butane [7, 8, 25, 26], which yield nearly the same value for the conversion, but with a considerably smaller uncertainty:

$$\Delta H°_{355.16} - \Delta H°_{298.16} = -0.520 \pm 0.020 \text{ kcal/mole.} \quad (1b)$$

Therefore, the new value for the heat of hydrogenation of 1,3-butadiene to n-butane at 25° C is as follows:

$$\Delta H°_{298.16} = -56.560 \pm 0.150 \text{ kcal/mole.} \quad (1c)$$

A revised value for the heat of formation of n-butane from its elements, taking into account the new value for the heat of formation of carbon dioxide [6], has been calculated [12]:

$$4C(\text{c, graphite}) + 5H_2(\text{gas}) = C_4H_{10}(\text{gas, } n\text{-butane}) \quad (2)$$
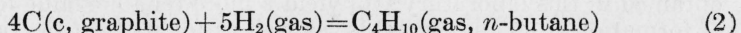
$$\Delta H°_{298.16} = -29.812 \pm 0.179 \text{ kcal/mole.} \quad (2a)$$

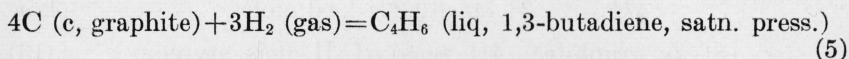Combination of eq 1c and 2 yields for the heat of formation of gaseous 1,3-butadiene at 25° C:

$$4C(\text{c, graphite}) + 3H_2(\text{gas}) = C_4H_6(\text{gas, 1,3-butadiene}) \quad (3)$$
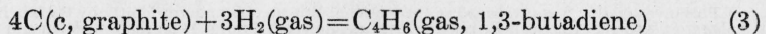
$$\Delta H°_{298.16} = 26.748 \pm 0.233 \text{ kcal/mole.} \quad (3a)$$

The heat of vaporization of 1,3-butadiene, from the liquid at saturation pressure to the gas at zero pressure, at 25° C, is reported [13] as:

$$C_4H_6 \text{ (liq, 1,3-butadiene, satn. press.)} =$$
$$C_4H_6 \text{(gas, 1,3-butadiene, zero press.)} \quad (4)$$
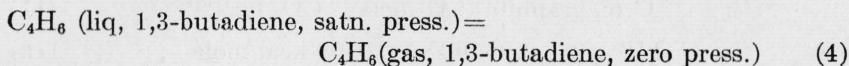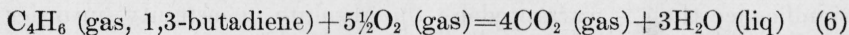
$$\Delta H_{298.16} = 5.119 \pm 0.010 \text{ kcal/mole.} \quad (4a)$$

Therefore, the heat of formation, from the elements in their standard reference states, of 1,3-butadiene in the liquid state at saturation pressure at 25° C is

$$4C \text{ (c, graphite)} + 3H_2 \text{ (gas)} = C_4H_6 \text{ (liq, 1,3-butadiene, satn. press.)} \quad (5)$$
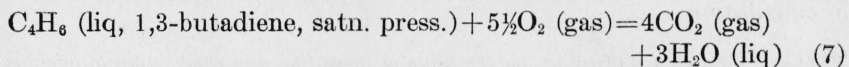
$$\Delta H_{298.16} = 21.629 \pm 0.234 \text{ kcal/mole.} \quad (5a)$$

Combination of eq 1c with the heat of formation of water from its elements [4, 24] and with the heat of combustion of *n*-butane [3, 12] yields the following values for the heats of combustion of gaseous and liquid 1,3-butadiene, with all the reactants and products in their standard reference states unless otherwise indicated:
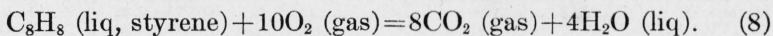
$$C_4H_6 \text{ (gas, 1,3-butadiene)} + 5\tfrac{1}{2}O_2 \text{ (gas)} = 4CO_2 \text{ (gas)} + 3H_2O \text{ (liq)} \quad (6)$$

$$\Delta H°_{298.16} = -607.907 \pm 0.225 \text{ kcal/mole.} \quad (6a)$$

$$C_4H_6 \text{ (liq, 1,3-butadiene, satn. press.)} + 5\tfrac{1}{2}O_2 \text{ (gas)} = 4CO_2 \text{ (gas)} + 3H_2O \text{ (liq)} \quad (7)$$

$$\Delta H_{298.16} = -602.788 \pm 0.226 \text{ kcal/mole.} \quad (7a)$$

IV. STYRENE

The new calorimetric data on the heat of combustion of styrene [16] yield

$$C_8H_8 \text{ (liq, styrene)} + 10O_2 \text{ (gas)} = 8CO_2 \text{ (gas)} + 4H_2O \text{ (liq).} \quad (8)$$

$$\Delta H°_{298.16} = -1050.40 \pm 0.20 \text{ kcal/mole.} \quad (8a)$$

The old data on the heats of combustion of styrene yield values which differ from the foregoing value by the following amounts, in percent: Stohmann, et al. [17], -0.15 ± 0.20; Auwers, et al. [18], $+0.05 \pm 0.10$; Lemoult [19], $+1.1 \pm 0.6$; Moureu and André [20], -0.13 ± 0.20; Landrieu, et al. [21], $+0.37 \pm 0.20$; Luschinsky [22], -0.13 ± 0.10.

The heat of vaporization of styrene, at 25° C, to the gas at zero pressure, may be taken as [14, 15]:

$$C_8H_8 \text{ (liq, styrene)} = C_8H_8 \text{ (gas, styrene)} \quad (9)$$
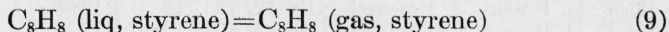
$$\Delta H°_{298.16} = 10.39 \pm 0.10 \text{ kcal/mole.} \quad (9a)$$

Combination of eq 8 and 9 yields for the heat of combustion of gaseous styrene

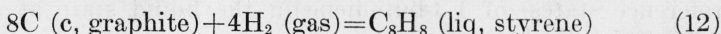$$C_8H_8 \text{ (gas, styrene)} + 10O_2 \text{ (gas)} = 8CO_2 \text{ (gas)} + 4H_2O \text{ (liq)} \quad (10)$$
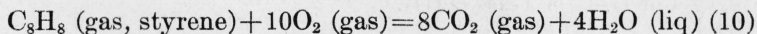
$$\Delta H°_{298.16} = -1060.79 \pm 0.22 \text{ kcal/mole.} \quad (10a)$$

The new "best" value for the heat of formation of carbon dioxide is [6]:

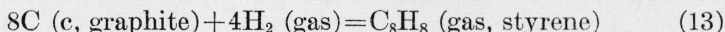$$C \text{ (c, graphite)} + O_2 \text{ (gas)} = CO_2 \text{ (gas)} \tag{11}$$
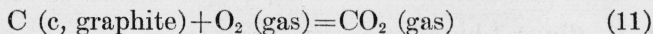
$$\Delta H^\circ_{298.16} = -94.0518 \pm 0.0108 \text{ kcal/mole} \tag{11a}$$

Combination of eq 9, 10, and 11 with the value for the heat of formation of water [4] yields the following values for the heats of formation of styrene in the liquid and gaseous states:

$$8C \text{ (c, graphite)} + 4H_2 \text{ (gas)} = C_8H_8 \text{ (liq, styrene)} \tag{12}$$

$$\Delta H^\circ_{298.1} = 24.716 \pm 0.221 \text{ kcal/mole} \tag{12a}$$

$$8C \text{ (c, graphite)} + 4H_2 \text{ (gas)} = C_8H_8 \text{ (gas, styrene)} \tag{13}$$

$$\Delta H^\circ_{298.16} = 35.106 \pm 0.243 \text{ kcal/mole} \tag{13a}$$

V. TABULAR SUMMARY

The foregoing values for the heats of formation and of combustion of 1,3-butadiene and styrene, in both the liquid and gaseous states, are summarized in table 1. Individual values are given to a greater significance than is warranted by the absolute uncertainty, in order to retain the precision of small differences and to permit recovery of the original starting value unchanged in proceeding around a cycle in calculation.

TABLE 1.—*Summary of values for the heats of formation and combustion of gaseous and liquid 1, 3-butadiene and styrene, at 25° C.*

Compond	State	Heat of combustion [a] at 25° C $-\Delta Hc^\circ{}_{298.16}$	Heat of formation [b] at 25° C $\Delta Hf^\circ{}_{298.16}$
		kcal/mole	*kcal/mole*
1, 3-Butadiene	Gas	607. 907 ±0. 225	26. 748 ±0. 233
Do	Liquid [c]	602. 788 ±0. 226	21. 629 ±0. 234
Styrene	Gas	1060. 79 ±0. 22	35. 106 ±0. 243
Do	Liquid	1050. 40 ±0. 20	24. 716 ±0. 221

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

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

[c] At saturation pressure.

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