

RESEARCH PAPER RP1629

Part of Journal of Research of the National Bureau of Standards, Volume 34,
January 1945

HEATS OF COMBUSTION OF BENZENE, TOLUENE, ETHYL- BENZENE, *o*-XYLENE, *m*-XYLENE, *p*-XYLENE, *n*-PRO- PYLBENZENE, AND STYRENE

By Edward J. Prosen, Roger Gilmont, and Frederick D. Rossini

ABSTRACT

The heats of combustion of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-propylbenzene, and styrene were measured with a bomb calorimeter. The following values were obtained for 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: Benzene, 3267.09 ± 0.43; toluene, 3909.31 ± 0.49; ethylbenzene, 4564.09 ± 0.72; *o*-xylene, 4552.10 ± 1.02; *m*-xylene, 4551.10 ± 0.62; *p*-xylene, 4552.09 ± 0.91; *n*-propylbenzene, 5217.37 ± 0.68; styrene 4394.14 ± 0.82. With the factor 1/4.1833, the corresponding values in kilocalories per mole are benzene, 780.98 ± 0.10; toluene, 934.50 ± 0.12; ethylbenzene, 1091.03 ± 0.17; *o*-xylene, 1088.16 ± 0.24; *m*-xylene, 1087.92 ± 0.15; *p*-xylene, 1088.16 ± 0.22; *n*-propylbenzene, 1247.19 ± 0.16; styrene, 1050.40 ± 0.20.

CONTENTS

	Page
I. Introduction.....	65
II. Unit of energy, molecular weights, etc.....	65
III. Method and apparatus.....	66
IV. Chemical materials and procedure.....	66
1. Source and purity of the hydrocarbons.....	66
2. Chemical procedure.....	67
V. Calorimetric procedure.....	67
VI. Results of the present investigation.....	67
1. Energy equivalent of the calorimeter.....	67
2. Combustion experiments.....	67
3. Values of the heats of combustion.....	67
VII. Discussion.....	71
VIII. References.....	71

I. INTRODUCTION

This paper describes the calorimetric and chemical apparatus and procedure and gives the data obtained in an experimental investigation on the heats of combustion of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-propylbenzene, and styrene.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

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

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

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.

III. METHOD AND APPARATUS

The same method and apparatus were used as in the investigations recently reported from this laboratory [4, 5, 6, 7]. The calorimeter systems *C* and *D* are described in detail in section III-2 of reference [4], in sections V and VII-1 of reference [6], and in sections V and VI-1 of reference [7].

IV. CHEMICAL MATERIALS AND PROCEDURE

1. SOURCE AND PURITY OF THE HYDROCARBONS

The benzene (series I), toluene (series I), and ethylbenzene (series I), were samples prepared by Timmermans [8] and were reported to have the following freezing points: Benzene, 5.50° C [8]; toluene —95.02° C [9]; ethylbenzene, —95.12° C [10]. From these values, and the freezing points for zero impurity [13], the amounts of impurity in the given samples are estimated to be 0.0006, 0.0005, and 0.004 mole fraction, respectively.

The *m*-xylene (series I) was from a sample fractionated from petroleum by White and Rose [11] and was reported to have a freezing point of —48.00° C. With this value and the freezing point for zero impurity, the amount of impurity in the *m*-xylene (series I) is estimated to be 0.0035 mole fraction.

The benzene (series II), toluene (series II), ethylbenzene (series II), *o*-xylene (series I), *m*-xylene (series II), *p*-xylene (series I) and *n*-propylbenzene (series I and II), were purified in connection with the work of the American Petroleum Institute Research Project 6 at this Bureau. The styrene (series I) was purified by Madorsky and Wood [12] in connection with the work of the Rubber Section at this Bureau. From time-temperature freezing and melting curves, performed by A. R. Glasgow, Jr., of the API Research Project 6 at this Bureau, the amounts of impurity in these samples are estimated to be as follows, in mole fraction, [13]: Benzene, 0.0004; toluene, 0.0004; ethylbenzene 0.0014; *o*-xylene, 0.0011; *m*-xylene, 0.0023; *p*-xylene, 0.0008; *n*-propylbenzene, 0.0035; styrene, 0.0002.

From the foregoing information, it appears that all the samples were adequately pure for the measurements of the present investigation.

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

2. CHEMICAL PROCEDURE

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, 7]. No products of incomplete combustion were found in any of the experiments.

V. CALORIMETRIC PROCEDURE

The procedures used in the combustion experiments and the calibration 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, 6, 7].

VI. RESULTS OF THE PRESENT INVESTIGATION

1. ENERGY EQUIVALENT OF THE CALORIMETER

The calorimeter systems C and D used in the present investigation are described in sections V and VII-1 and table 1 of reference [6] and in sections V and VI-1 and table 1 of reference [7]. The electric-energy equivalent of system C was [6].

$$E_s(C) = 137,717.4 \pm 13.9 \text{ int. j/ohm,}$$

and that of system D was [7]

$$E_s(D) = 136,489.6 \pm 14.5 \text{ int. j/ohm.}$$

2. COMBUSTION EXPERIMENTS

The results of the combustion experiments on benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-propylbenzene, and styrene are given in table 1. The symbols at the heads of the columns are as previously defined [4, 6]. For simplicity in presenting and handling the data, all the values of the constant B are given in terms of calorimeter system C .

3. VALUES OF THE HEATS OF COMBUSTION

In table 2 are given the final results for the eight hydrocarbons whose heats of combustion were measured in the present investigation. The columns in table 2 give the value of the constant B for 28° C, in ohms per gram of carbon dioxide, as defined by eq 4 of reference [4]; $-\Delta U_B$, the heat evolved in the bomb process at 28° C, in international kilojoules per mole of hydrocarbon; $-\Delta U_R^\circ$, the decrement in internal energy for the ideal reaction of combustion at 28° C, with all the reactants and products in their thermodynamic standard reference states, calculated by the method of Washburn [15], modified to apply to 28° C and, for the gases, with reference to the energy content at zero pressure; $-\Delta Hc^\circ$, the decrement in heat content (or heat evolved in the combustion at constant pressure) for the reaction of combustion of the liquid hydrocarbon at 28° C, with all the re-

o-XYLENE

I.....		6	6	{	2.56145 to 2.84853	0.001975 to .002005	0.001020 to .002414	0.000339 to .001013	0.243578 to .270838	0.000398 to .000432	0.000036 to .000043	} 0.0937814	±0.000080
--------	--	---	---	---	--------------------------	---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	-------------	-----------

m-XYLENE

I.....	4			{	2.69689 to 3.49627	0.001949 to .001961	0.000269 to .002293	0.000272 to .000365	0.253313 to .328151	0.000396 to .000417	0.000013 to .000020	} 0.0937606	±0.000074
II.....		4		{	2.41763 to 2.55490	.001968 to .001993	.002432 to .002674	.000307 to .000368	.229895 to .242860	.000406 to .000425	.000037 to .000041		
All.....			8									} .0937612	±.000045
												} .0937610	±.000038

p-XYLENE

I.....		4	4	{	2.45155 to 2.89045	0.001971 to .001991	0.001495 to .002379	0.000378 to .000453	0.233106 to .274844	0.000411 to .000429	0.000042 to .000047	} 0.0937811	±0.000065
--------	--	---	---	---	--------------------------	---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	-------------	-----------

n-PROPYLBENZENE

I.....	6			{	2.68609 to 2.82867	0.001955 to .001957	0.001548 to .002322	0.000346 to .000369	0.256966 to .270502	0.000389 to .000407	0.000013 to .000015	} 0.0955214	±0.000067
II.....		5		{	2.20403 to 3.15647	.001973 to .002048	.000624 to .002314	.000395 to .001189	.213581 to .305509	.000409 to .000427	.000041 to .000054		
All.....			11									} .0955456	±.000038
												} .0955363	±.000033

STYRENE

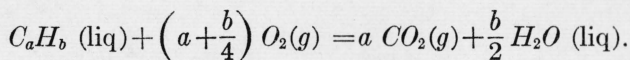
I.....		5	5	{	2.42198 to 3.27703	0.001975 to .001986	0.001090 to .002566	0.000315 to .000360	0.222408 to .300718	0.000402 to .000416	0.000032 to .000041	} 0.0905542	±0.000053
--------	--	---	---	---	--------------------------	---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	---------------------------	-------------	-----------

• The numbers in columns *C* and *D* indicate the number of experiments performed with calorimeter systems *C* and *D*, respectively, (see text).

TABLE 2.—Values of the heats of combustion

Substance (liquid)	B at 28.00° C	$-\Delta U_B$ at 28° C	$-\Delta U_B^\circ$ at 28° C	$-\Delta H^\circ_e$ (liq) at 28° C	$-\Delta H^\circ_e$ (liq) at 25° C	
	<i>Ohm/g CO₂</i>	<i>Int. kj/mole</i>	<i>Int. kj/mole</i>	<i>Int. kj/mole</i>	<i>Int. kj/mole</i>	<i>kcal/mole</i>
Benzene.....	0.0897742 ±0.0000062	3264.70 ±0.43	3263.05 ±0.43	3266.81 ±0.43	3267.09 ±0.43	780.98 ±0.10
Toluene.....	.0920579 ±0.000058	3905.70 ±0.49	3903.87 ±0.49	3908.88 ±0.49	3909.31 ±0.49	934.50 ±0.12
Ethylbenzene.....	.0940301 ±0.0000108	4559.29 ±0.72	4557.27 ±0.72	4563.53 ±0.72	4564.09 ±0.72	1091.03 ±0.17
<i>o</i> -Xylene.....	.0937814 ±0.0000160	4547.23 ±1.02	4545.27 ±1.02	4551.53 ±1.02	4552.10 ±1.02	1088.16 ±0.24
<i>m</i> -Xylene.....	.0937610 ±0.0000076	4546.24 ±0.62	4544.26 ±0.62	4550.52 ±0.62	4551.10 ±0.62	1087.92 ±0.15
<i>p</i> -Xylene.....	.0937811 ±0.0000130	4547.22 ±0.91	4545.25 ±0.91	4551.51 ±0.91	4552.09 ±0.91	1088.16 ±0.22
<i>n</i> -Propylbenzene.....	.0955363 ±0.0000066	5211.36 ±0.68	5209.20 ±0.68	5216.71 ±0.68	5217.37 ±0.63	1247.19 ±0.16
Styrene.....	.0905542 ±0.0000106	4390.75 ±0.82	4388.63 ±0.82	4393.64 ±0.82	4394.14 ±0.82	1050.40 ±0.20

actants and products in their thermodynamic standard reference states; and, finally, the same quantity, $-\Delta H_c^\circ$, for the reaction of combustion at 25° C. The foregoing values of $-\Delta U_R^\circ$ and $-\Delta H_c^\circ$ apply to the reaction



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 (or weighted 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 (or weighted mean) of the series of experiments for determining the energy equivalent of the calorimeter with electric energy or with standard benzoic acid, and (d) an uncertainty of 0.010 percent in the determination of the absolute value of the energy equivalent, with electric energy or with standard benzoic acid [14].

VII. DISCUSSION

The values of the heats of combustion of benzene, toluene, ethylbenzene, *n*-propylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, and styrene obtained in this investigation will, in other reports from this laboratory, be compared with the existing data, combined with values of the heats of formation of water and carbon dioxide to calculate the heats of formation of these hydrocarbons, used in the calculation and estimation of the heats of isomerization and formation of some higher alkyl benzenes, and utilized to calculate values for certain important specific reactions, such as the dehydrogenation of ethylbenzene to styrene.

VIII. REFERENCES

- [1] E. F. Mueller and F. D. Rossini, *Am. J. Physics* **12**, 1 (1944).
- [2] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, *J. Am. Chem. Soc.* **63**, 845 (1941).
- [3] F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.* **29**, 416 (1939).
- [4] E. J. Prosen and F. D. Rossini, *J. Research NBS* **27**, 289 (1941) RP1420.
- [5] E. J. Prosen and F. D. Rossini, *J. Research NBS* **27**, 519 (1941) RP1439.
- [6] E. J. Prosen and F. D. Rossini, *J. Research NBS* **33**, 255 (1944) RP1607.
- [7] E. J. Prosen and F. D. Rossini, *J. Research NBS* **33**, 439 (1944) RP1619.
- [8] J. Timmermans, Bureau International des Étalons Physicochimique, University of Brussels, Brussels, Belgium.
- [9] B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, *J. Research NBS* **26**, 591 (1941) RP1397.
- [10] J. D. White and F. W. Rose, Jr., *BS J. Research* **10**, 639 (1933) RP554.
- [11] J. D. White and F. W. Rose, Jr., *BS J. Research* **9**, 711 (1933) RP501.
- [12] I. Madorsky and L. A. Wood, National Bureau of Standards. Unpublished data.
- [13] A. R. Glasgow, Jr., and F. D. Rossini, National Bureau of Standards. Unpublished data.
- [14] R. S. Jessup. *J. Research NBS* **29**, 247 (1942) RP1499.
- [15] E. W. Washburn. *BS J. Research* **10**, 525 (1933) RP546.

WASHINGTON, August 15, 1944.