U. S. Department of Commerce — National Bureau of Standards

RESEARCH PAPER RP1665

Part of Journal of Research of the National Bureau of Standards, Volume 35,

August 1945

HEATS OF COMBUSTION AND ISOMERIZATION OF THE EIGHT C_9H_{12} ALKYLBENZENES

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

ABSTRACT

The heats of isomerization of the eight C_9H_{12} alkylbenzenes were determined by measurement of the ratios of the heats of combustion in the liquid state of purified samples of these compounds by the procedure previously described for the hexanes, heptanes, and octanes. The data yield the following values for the heat of isomerization in the liquid state at 25° C, $\Delta H°$, of *n*-propylbenzene into each of the C_9H_{12} alkylbenzenes, in kilocalories per mole: *n*-propylbenzene, 0.00; isopropylbenzene, -0.67 ± 0.16; 1-methyl-2-ethylbenzene, -1.93 ± 0.16; 1-methyl-3-ethylbenzene, -2.48 ± 0.19; 1-methyl-4-ethylbenzene, -2.74 ± 0.26; 1,2,3-trimethylbenzene, -4.83 ± 0.22; 1,2,4-trimethylbenzene, -5.61 ± 0.16; 1,3,5-trimethylbenzene, -6.00 ± 0.26. These data were combined with the value previously reported for the heat of combustion of *n*-propylbenzene to obtain values for the heats of combustion of each of the C_9H_{12} alkylbenzenes in the liquid state at 25° C.

CONTENTS

I. INTRODUCTION

In continuation of the program of determining the heats of combustion, formation, and isomerization of hydrocarbons of various types [1, 2, 3, 4],[1] calorimetric measurements have been made that yield values for the differences in the heats of combustion, or the heats of isomerization, of the eight C_9H_{12} alkylbenzenes in the liquid state at 25° C. These heats of isomerization are combined with the values previously reported for the heat of combustion of *n*-propylbenzene [3] to obtain values for the heats of combustion of each of the C_9H_{12} alkylbenzenes in the liquid state at 25° C.

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

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, UNCERTAINTIES

The unit of energy upon which the values reported in this paper are based is the international joule, derived from mean solar seconds and from the units of international ohms and international volts in terms of which certification of standards of resistance and electromotive force is made by the National Bureau of Standards. For conversion to the conventional thermochemical calorie, the following relation is used [5]:

1 calorie=4.1833 international joules.

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 atomic weights [6].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [7].

Definitions of the symbols used are given in the previous papers [1, 2, 3, 4].

III. METHOD AND APPARATUS

The same method and apparatus were used in the present investigation as in the work on the hexanes [1], heptanes [2], and octanes [4], with the exception that a chronograph was used to record the time during the first 5 minutes of the reaction period. The chronograph had two pens, one recording seconds and the other the taps of a telegraph key. The telegraph key was tapped when the resistance of the platinum resistance thermometer in the calorimeter passed certain previously selected values.

IV. MATERIALS

The compounds used in the present investigation were samples from the API–NBS series of highly purified hydrocarbons, which are being prepared through a cooperative undertaking of the American Petroleum Institute and the National Bureau of Standards. A complete description of the purification and determination of the purity of these compounds will appear in other reports [8, 9]. The amounts of impurity in these samples, as determined from measurements of freezing points made by A. R. Glasgow, Jr., E. T. Murphy, and A. J. Streiff, at this Bureau, were as follows: *n*-Propylbenzene, 0.0029 ± 0.0008; isopropylbenzene, 0.0005 ± 0.0002; 1-methyl-2-ethylbenzene, 0.0024 ± 0.0007; 1-methyl-3-ethylbenzene, 0.0022 ± 0.0015; 1-methyl-4-ethylbenzene, 0.0005 ± 0.0002; 1,2,3-trimethylbenzene, 0.0008 ± 0.0004; 1,2,4-trimethylbenzene, 0.0036 ± 0.0020; 1,3,5-trimethylbenzene, 0.0007 $\pm$ 0.0003, mole fraction [8, 9].

As the manner of purification of these compounds [8, 9] was such as to leave substantially only close-boiling isomeric impurities in the respective compounds, it is calculated that in the worst case the measured heat of combustion would be affected by less than 0.002 percent because of impurities in the compound.

V. RESULTS

The experimental results of the present investigation are summarized in table 1, which gives for each of the eight compounds the following data: The number of experiments performed; the minimum and

TABLE 1.—*Results of the calorimetric combustion experiments*

Compound (liquid)	Number of experiments	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B Mean	B Standard deviation of mean
		g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g* CO_2	*Ohm/g* CO_2
n-Propylbenzene	6	2.24788 to 3.08669	0.001962 to .001989	0.001055 to .003260	0.000304 to .000520	0.216719 to .297432	0.000416 to .000429	0.000006 to .000008	0.0962420	±0.0000061
Isopropylbenzene	7	2.83771 to 3.12459	.001959 to .001979	.001052 to .001871	.000350 to .000462	.273359 to .300887	.000399 to .000427	.000004 to .000007	0.0961908	±.0000024
1-Methyl-2-ethylbenzene	5	3.20071 to 3.67189	.001969 to .001980	.000088 to .001029	.000270 to .000283	.307939 to .353211	.000409 to .000421	.000004 to .000008	0.0960945	±.0000020
1-Methyl-3-ethylbenzene	7	2.83024 to 3.43990	.001970 to .001982	.000439 to .002043	.000264 to .000315	.272266 to .330713	.000413 to .000431	.000004 to .000007	0.0960510	±.0000046
1-Methyl-4-ethylbenzene	7	3.01930 to 3.24097	.001954 to .001991	.000787 to .001505	.000240 to .000382	.290443 to .311654	.000400 to .000423	.000004 to .000007	0.0960313	±.0000085
1,2,3-Trimethylbenzene	6	2.91747 to 3.39652	.001971 to .001985	.000952 to .001620	.000299 to .000390	.280049 to .326051	.000419 to .000427	.000004 to .000007	0.0958698	±.0000062
1,2,4-Trimethylbenzene	5	3.09067 to 3.32189	.001973 to .001984	.000551 to .001084	.000325 to .000403	.296058 to .318221	.000410 to .000422	.000004 to .000005	0.0958099	±.0000025
1,3,5-Trimethylbenzene	6	2.65951 to 3.43334	.001970 to .001980	.000147 to .002285	.000320 to .000389	.254702 to .328818	.000414 to .000420	.000004 to .000006	0.0957790	±.0000086

maximum values of the mass of carbon dioxide formed in the combustion and of the calorimetric quantities k, K, U, ΔR_c, Δr_i, Δr_n [1]; the mean value of B, and its standard deviation, in ohms per gram of carbon dioxide formed, as defined by equation 4 of reference [1]. The symbols in table 1 have the same significance as in the previous report [1] and the references there cited.

In table 2 are given, for the eight C_9H_{12} alkylbenzenes, values of the following: The constant B in ohms per gram of carbon dioxide, as given in table 1; $B°$, which is B corrected to the ideal bomb reaction by the method of Washburn [10];[2] B_i°/B_n°, which is equal to the ratio of the heat evolved, per mole of hydrocarbon, in the ideal bomb process at 28° C for each isomer to that of n-propylbenzene; $(-\Delta U_R^\circ)_n-(-\Delta U_R^\circ)_i$, the difference, between n-propylbenzene and each isomer, in the heat of combustion in the ideal bomb process at 28° C; H_i° (liquid)$-H_n^\circ$ (liquid), the heat of isomerization of n-propylbenzene into each isomer, at 25° C and 1 atmosphere, for the liquid state; and $-\Delta Hc°$, the decrement in heat content accompanying the reaction of combustion of the hydrocarbon in the liquid state in oxygen to form gaseous carbon dioxide and liquid water, with all the reactants and products in their thermodynamic standard states at 25° C. The value of the heat of isomerization was obtained by means of the relation [1]:

$$(-\Delta U_R^\circ)_n-(-\Delta U_R^\circ)_i=(-\Delta U_R^\circ)_n\ (1-B_i^\circ/B_n^\circ) \qquad (1)$$

For this calculation, the value of $(-\Delta U_R^\circ)_n$ at 28° C was taken as 5209.2 int. kj/mole [3]. The value for the heat of combustion of a given isomer was obtained by appropriately combining the heat of isomerization with the heat of combustion of n-propylbenzene as given by the equations:

$$C_9H_{12}\ (n\text{-propylbenzene, liquid})+12O_2\ (\text{gas})=9\ CO_2\ (\text{gas})+6H_2O\ (\text{liquid}). \qquad (2)$$

$$\Delta H^\circ_{298.16}=-5217.37\pm0.68\ \text{int. kj/mole}=-1247.19\pm0.16\ \text{kcal/mole}. \qquad (3)$$

The experimental data of the present and the previous investigations on the alkylbenzenes [3] are being compared with the data of earlier investigations in a report [11] that will include selected "best" values for the heats of combustion and formation, for both the liquid and gaseous states, at 25° C, of all the isomeric alkylbenzenes through $C_{11}H_{16}$ with general formulas for calculating values for the higher alkylbenzenes.

[2] The Washburn correction is the same for all these compounds as they are isomers, but account is taken of the variation of the Washburn correction with amount of sample burned. As used here, the Washburn correction was modified to apply to 28° C and to the gases at zero pressure (instead of 1 atmosphere).

TABLE 2.—*Heats of isomerization and combustion in the liquid state*

Compound (liquid)	B at 28.00° C	$B°$ at 28.00° C	Ratio of the heats of combustion in the ideal bomb process, $B°_i/B°_n$, at 28.00° C	Difference in the heats of combustion in ideal bomb process, $(-\Delta U°_R)_n-(-\Delta U°_R)_i$, at 28.00° C	Heat of isomerization of the liquid, $H°_{i\,(\mathrm{liq})}-H°_{n\,(\mathrm{liq})}$, at 25.00° C		Heat of combustion, $-\Delta H°_c$, at 25.00° C	
	Ohm/g CO_2	*Ohm/g* CO_2		*Int. kj/mole*	*Int. kj/mole*	*kcal/mole*	*Int. kj/mole*	*kcal/mole*
n-Propylbenzene	0.0962420±0.0000122	0.0962016±0.0000122	1.000000	0.00	0.00	0.00	5217.37±0.68	1247.19±0.16
Isopropylbenzene	.0961908± .0000048	.0961498± .0000048	.999462±0.000131	2.80±0.68	−2.80±0.68	−0.67±0.16	5214.57± .96	1246.52± .23
1-Methyl-2-ethylbenzene	.0960945± .0000040	.0960523± .0000040	.998448± .000128	8.08± .67	−8.08± .67	−1.93± .16	5209.29± .95	1245.26± .23
1-Methyl-3-ethylbenzene	.0960510± .0000092	.0960097± .0000092	.998005± .000153	10.39± .80	−10.39± .80	−2.48± .19	5206.98±1.05	1244.71± .25
1-Methyl-4-ethylbenzene	.0960313± .0000170	.0959900± .0000170	.997800± .000209	11.46±1.09	−11.46±1.09	−2.74± .26	5205.91±1.28	1244.45± .31
1,2,3-Trimethylbenzene	.0958698± .0000124	.0958287± .0000124	.996124± .000174	20.19± .91	−20.19± .91	−4.83± .22	5197.18±1.14	1242.36± .27
1,2,4-Trimethylbenzene	.0958099± .0000050	.0957683± .0000050	.995496± .000132	23.46± .69	−23.46± .69	−5.61± .16	5193.91± .97	1241.58± .23
1,3,5-Trimethylbenzene	.0957790± .0000172	.0957380± .0000172	.995181± .000211	25.10±1.10	−25.10±1.10	−6.00± .26	5192.27±1.29	1241.19± .31

VI. REFERENCES

[1] E. J. Prosen and F. D. Rossini, J. Research NBS **27,** 289 (1941) RP1420.
[2] E. J. Prosen and F. D. Rossini, J. Research NBS **27,** 519 (1941) RP1439.
[3] E. J. Prosen, R. Gilmont, and F. D. Rossini, J. Research NBS **34,** 65 (1945) RP1629.
[4] E. J. Prosen and F. D. Rossini, J. Research NBS **34,** 163 (1945) RP1635.
[5] E. F. Mueller and F. D. Rossini, Am. J. Physics **12,** 1 (1944).
[6] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, J. Am. Chem. Soc. **63,** 845 (1941).
[7] F. D. Rossini and W. E. Deming, J. Wash. Acad. Sci. **29,** 416 (1939).
[8] A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham, and F. D. Rossini, National Bureau of Standards, API Research Project 6. Unpublished data.
[9] A. J. Streiff, E. T. Murphy, C. B. Willingham, V. A. Sedlak, and F. D. Rossini, National Bureau of Standards, API Research Project 6. Unpublished data.
[10] E. W. Washburn, BS J. Research **10,** 525 (1933) RP546.
[11] E. J. Prosen, W. H. Johnson, and F. D. Rossini, National Bureau of Standards. Unpublished data.

WASHINGTON, April 3, 1945.