

## RESEARCH PAPER RP1093

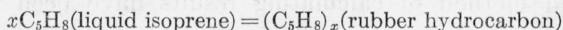
Part of *Journal of Research of the National Bureau of Standards*, Volume 20,  
May 1938

## HEAT OF COMBUSTION OF ISOPRENE

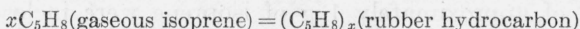
By Ralph S. Jessup

## ABSTRACT

The heat of combustion of isoprene has been measured by means of a bomb calorimeter which was calibrated with benzoic acid. The mass of isoprene burned in each experiment was determined from the mass of  $\text{CO}_2$  formed in combustion. As the result of seven measurements the value  $3156.9 \pm 1.6$  international kilojoules per mole was obtained for the heat of combustion of liquid isoprene at  $25^\circ \text{C}$  and under a constant pressure of 1 atmosphere, the products of combustion being liquid water and gaseous  $\text{CO}_2$ . Using the value 25.9 international kilojoules per mole calculated by Bekkedahl, Wood, and Wojciechowski for the heat of vaporization of isoprene, the heat of combustion of gaseous isoprene is calculated to be  $3182.8 \pm 1.7$  international kilojoules per mole at  $25^\circ \text{C}$  and under a constant pressure of 1 atmosphere, the products of combustion being liquid water and gaseous  $\text{CO}_2$ . Combining the data on isoprene with data reported previously on the heat of combustion of rubber hydrocarbon, there are obtained for the heats evolved in the reactions



and



at  $25^\circ \text{C}$  and a constant pressure of 1 atmosphere, the values  $(74.8 \pm 6.2)x$  and  $(100.7 \pm 6.3)x$  international kilojoules respectively.

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## I. INTRODUCTION

The work described in this paper was done as part of an investigation of thermodynamic properties of rubber hydrocarbon and related substances. In previous papers data have been reported on the heat of combustion [8]<sup>1</sup> and on the entropy and free energy of formation of rubber hydrocarbon [1]. Recently, data on the entropy of isoprene have been reported by Bekkedahl and Wood [2], who discuss the chemical similarity of isoprene and rubber hydrocarbon, and point out the desirability of a knowledge of the free energy of forma-

<sup>1</sup> Numbers in brackets relate to the literature references given at the end of this paper.

tion of isoprene for use in studying the thermodynamics of reactions involving the two substances. In order to use the entropy data in calculating the free energy of formation, an accurate value for the heat of combustion of isoprene is required.

## II. PREVIOUS WORK

The only data on the heat of combustion of isoprene which have been found in the literature are those of Lebedev, Chochlovkin, and Kalacheva [10]. They report 11 measurements of the heat of combustion of liquid isoprene, the results of which range from 11,142 to 11,215 calories per gram, the mean result being 11,165 calories per gram. These authors do not give sufficient data to permit an estimate of the accuracy of their results, and they do not define their energy unit, so that accurate conversion of their data to the energy unit used for the entropy data is not possible. For these reasons a new determination of the heat of combustion of isoprene was desirable. If it is assumed that the calorie used by Lebedev, Chochlovkin, and Kalacheva is equal to 4.1833 international joules, their value for the heat of combustion of isoprene becomes 46.7 international kilojoules per gram, a value which is nearly 1 percent higher than that obtained in the present work.

## III. APPARATUS AND METHOD

The bomb calorimeter and accessory apparatus, experimental procedure, and method of calculating results have been described in detail [4, 7, 9].

Samples of approximately 1 g of isoprene were inclosed in thin-walled glass bulbs which were flattened on opposite sides and filled completely with the liquid in the manner described by Richards and Barry [11]. The samples were ignited by means of an electric fuse of iron wire, as described previously [7]. The volume of the bomb used was determined to be 377 cm<sup>3</sup>. One cm<sup>3</sup> of water was placed in the bomb before each experiment.

In most experiments the mass of isoprene burned was determined in two ways: (1) By weighing the sample of isoprene, and (2) by absorbing the CO<sub>2</sub> formed in combustion in Ascarite (a sodium hydroxide-asbestos mixture) and weighing it, and passing the remaining gas through a copper tube heated to redness to oxidize any CO which might be present, absorbing the resulting CO<sub>2</sub> in Ascarite and weighing [12, 7]. The mass CO<sub>2</sub> obtained by oxidizing the CO was very small, usually less than 0.01 percent of the total CO<sub>2</sub> formed in the bomb.

## IV. CALIBRATION OF CALORIMETER

The calorimeter was calibrated with benzoic acid (NBS Standard Sample 39e), using for the heat of combustion of this material the value 26,414 international joules per gram mass under standard conditions [9]. These standard conditions are:

Temperature to which reaction is referred.....	30° C.
Initial absolute pressure of oxygen at 30° C.....	30 atm.
Mass of benzoic acid per liter of bomb volume.....	3 g.
Mass of water placed in bomb per liter of bomb volume..	3 g.

The results of the calibration experiments are given in table 1. The uncertainty of the mean of the nine experiments (defined as  $2 \sqrt{\frac{\sum \Delta^2}{n(n-1)}}$ , or about three times the "probable error") is 0.026 percent.

In the calibration experiments the final temperature of the calorimeter was 30° C, and as the value used for the heat of combustion of benzoic acid is that for 30° C, the values obtained for the energy equivalent of the calorimeter are for the initial system at the mean temperature of the experiments. In other words, the observed values of energy equivalent represent the energy per degree required to raise the temperature of the calorimeter from its initial to its final temperature (30° C) when the bomb contains 1 g of water, the charge of benzoic acid, and oxygen under a pressure of 30 atmospheres at 30° C. The values given in table 1 for the energy equivalent of the calorimeter are the observed values minus the heat capacity of the charge of benzoic acid (specific heat=1.26 j/g° C). In each experiment on isoprene the final temperature of the calorimeter was very nearly 30° C, and the value used for the energy equivalent was the mean value given in table 1, plus the heat capacity of the charge of isoprene (specific heat=2.25 j/g° C). Since the energy equivalent of the calorimeter is that of the initial system the observed values for the heat of combustion of the isoprene are for the final temperature of the calorimeter, or 30° C.

TABLE 1.—*Calibration of bomb calorimeter*

Experiment	Observed-energy equivalent at 28.5° C	Deviation from mean		Experiment	Observed-energy equivalent at 28.5° C	Deviation from mean	
		int. j° C	Percent			int. j° C	Percent
1.....	13498.6	-1.0	-0.007	7.....	13501.2	+1.6	+0.012
2.....	13490.4	-9.2	-0.068	8.....	13510.2	+10.6	+0.079
3.....	13500.1	+0.5	+0.004	9.....	13499.3	-0.3	-0.002
4.....	13495.5	-4.1	-0.030	Mean.....	13499.6	±3.2	±0.024
5.....	13499.5	-0.1	-0.001				
6.....	13501.4	+1.8	+0.013				

## V. MATERIAL

The isoprene used was prepared by Bekkedahl, Wood, and Wojciechowski [3] by cracking dipentene vapor and was purified by fractional distillation. Their ebulliometric measurements on the freshly distilled isoprene indicated that the material was of a very high degree of purity. However, the measurements of CO<sub>2</sub> formed in combustion in the present investigation showed that the samples absorbed significant amounts of impurity upon exposure to the air during the filling of the glass bulbs used to contain the combustion samples. The isoprene was kept in glass bottles, closed in some cases by ground-glass stoppers, in others by cork stoppers, and it is possible that there was also some contamination of the isoprene as a result of leakage of air past the stoppers. Correlation of the results of the CO<sub>2</sub> determinations with the heat of combustion measurements indicated that there was little or no heat of mixing or combination of the impurity with the isoprene, the effect of the impurity being merely to reduce the heat

of combustion and the amount of  $\text{CO}_2$  formed in combustion in the same proportion. For this reason values of heat of combustion of the isoprene obtained by using the mass of  $\text{CO}_2$  formed in combustion as a measure of the mass of isoprene burned, should be fairly reliable in spite of the relatively large amounts of impurity in the samples.

The oxygen used was ordinary commercial oxygen from which combustible impurities were removed by passing the gas over copper oxide maintained at a temperature of 700 to 800° C. The oxygen was then passed through Ascarite before being admitted to the bomb in order to remove any  $\text{CO}_2$  which might be present.

## VI. RESULTS AND CONCLUSIONS

The results of heat of combustion measurements on several samples of isoprene are shown in table 2. Columns 1, 2, and 3 of this table give the sample number, experiment number, and mass (weight in vacuo) of isoprene burned in the experiment. Column 4 gives the

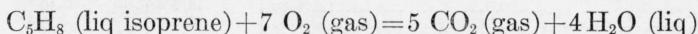
TABLE 2.—*Results of measurements on isoprene*

Sample	Experiment	Mass of charge	$\frac{\text{CO}_2 \text{ found}}{\text{CO}_2 \text{ calc}} = r$	Observed heat of combustion, $Q_B$	$\frac{Q_B}{r}$	Approximate Washburn correction	$-\Delta U_R$	Remarks
1	2	3	4	5	6	7	8	9
$A_1$ -----	1	0.89065 g	0.99796	int. j/g 46, 211	int. j/g 46, 305	int. j/g -12	int. j/g 46, 293	Freshly distilled.
$A_2$ -----	2	1.10090	.98303	45, 588	46, 375	-12	46, 363	Same sample as $A_1$ but had been kept in a bottle at room temperature 17 days.
$B$ -----	3	1.18103	-----	44, 724	-----	-----	-----	Had been kept in a bottle for unknown length of time.
$C_1$ -----	{ 4	1.09362	-----	46, 318	-----	-----	-----	} Freshly distilled.
	5	0.96029	.99397	46, 304	46, 585	-13	46, 572	
$C_2$ -----	{ 6	1.13093	-----	46, 218	-----	-----	-----	} Same lot of material as $C_1$ but had been kept in a bottle in icebox for 7 days.
	7	1.33751	.99235	46, 224	46, 580	-13	46, 567	
$D$ -----	8	1.18985	-----	46, 100	-----	-----	-----	Freshly distilled into anti-oxidant.
$E_1$ -----	{ 9	1.07797	.99254	45, 921	46, 266	-11	46, 255	} Freshly distilled, bulbs filled immediately.
	10	1.00322	.99251	45, 919	46, 266	-11	46, 255	
$E_2$ -----	11	1.00296	.99229	45, 917	46, 274	-12	46, 262	Same lot of material as $E_1$ , bulb filled about 3 hours later.
$E_3^a$ -----	{ 12	0.86821	.99268	46, 202	46, 543	-13	46, 530	} Same lot of material as $E_1$ , bulbs filled about 26 hours later.
	13	1.06559	.99240	45, 910	46, 262	-11	46, 251	
$E_4^a$ -----	14	0.97403	.99249	45, 906	46, 253	-11	46, 242	Same lot of material as $E_1$ , bulb filled 4 days later.
$F$ -----	{ 15	1.11085	-----	46, 028	-----	-----	-----	} Freshly distilled, bulbs filled immediately.
	16	1.14830	-----	46, 054	-----	-----	-----	
	17	1.00289	-----	45, 996	-----	-----	-----	
	18	1.18388	.99380	46, 019	46, 306	-10	46, 296	

<sup>a</sup> Samples  $E_3$  and  $E_4$  were kept outdoors in a bottle at temperatures ranging from -3 to +11° C for 1 and 4 days, respectively.



ratio,  $r$ , of the mass of carbon dioxide formed in the complete combustion of the sample to the amount calculated from the mass of sample, assuming that the sample was pure isoprene. The atomic weights used in this calculation are  $C=12.01$ ,  $H=1.0078$ ,  $O=16.000$ . Column 5 of table 2 gives the observed heat of combustion per gram of isoprene ( $Q_B$ ) under the conditions of the bomb process, when the amount of isoprene burned is taken as the mass determined by weighing the sample of isoprene. Column 6 gives values of  $Q_B/r$ , that is, the heat of combustion of isoprene under the conditions of the bomb process when the mass of isoprene burned in each experiment is calculated from the observed mass of carbon dioxide formed in combustion of the isoprene. The values of  $Q_B/r$  are therefore the values of  $Q_B$  corrected on the assumption that the departures from unity of the corresponding values of  $r$  are due to inert impurity in the isoprene. Column 7 gives Washburn's approximate correction [13], and column 8 the value of  $-\Delta U_B$ , that is, the energy decrease per gram of pure isoprene for the reaction



at 30° C and under a total pressure of 1 atmosphere, assuming again that the departures from unity of the ratio  $r$  are due to inert impurity.

Table 2 shows that the values of  $r$  are considerably lower than unity. There is also evidence that  $r$  decreased with time when the isoprene was kept in stoppered bottles, as previously mentioned. For example, for sample *A* the value of  $r$  dropped from about 0.998 to 0.983 when the sample was kept at room temperature for 17 days, and for sample *C* the value of  $r$  dropped from about 0.994 to 0.992 when the sample was kept in an icebox for 7 days. On the other hand, the value of  $r$  for sample *E* did not show any appreciable decrease when the sample was exposed to temperatures ranging from  $-3$  to  $+11^\circ$  C for 4 days.

It was thought that the departures from unity of the values of  $r$  might be caused by oxidation of the isoprene. To test this hypothesis a sample was distilled into a vessel containing an antioxidant, and one determination was made of the heat of combustion of the sample (experiment 8). Unfortunately, the attempt to measure the mass of  $CO_2$  formed in combustion in this experiment was unsuccessful due to loss of part of the  $CO_2$ . However, the value obtained for the heat of combustion per gram of sample ( $Q_B$ ) was so low as to indicate that this sample of isoprene contained more rather than less impurity than most of the other samples. It was concluded, therefore, that the impurity was not oxygen or an oxidation product but was probably water absorbed from the atmosphere. This conclusion is supported by unpublished data obtained by Bekkedahl and Wood in combustion analyses of sample *E*. The isoprene they used was contained in glass bulbs which were filled at the same time as some of those used in the calorimetric combustion experiments. The value for the ratio  $r$  obtained in their first experiment was 0.9926, which is in good agreement with the values of  $r$  for sample *E* in table 2. Their value for the hydrogen content of the sample was 11.83 percent as compared with the theoretical value 11.84 percent for pure isoprene. In a second combustion analysis part of the carbon dioxide was lost, but the observed hydrogen content was 11.79 percent. The fact that the carbon content of the isoprene was low and the hydrogen content

was nearly that for pure isoprene indicates that the impurity in the sample was water, since the hydrogen content of water is nearly the same as that of isoprene.

It will be seen from table 2 that the values  $-\Delta U_R$  for most of the experiments are in satisfactory agreement, but that the values for experiments 5, 7, and 12, although consistent among themselves, are higher by about 0.63 percent than those for the remaining experiments. This is shown more clearly in table 3, where the results of experiments 5, 7, and 12 are listed separately from those of the other experiments.

TABLE 3.—Comparison of the results of experiments 5, 7, and 12 with those of other experiments

Experiment	$-\Delta U_R$		Deviation from mean	
	int. j/g	int. j/g	int. j/g	Percent
1.-----	46, 293	+28		+0.061
2.-----	(46, 363)			
9.-----	46, 255	-10		-.022
10.-----	46, 255	-10		-.022
11.-----	46, 262	-3		-.006
13.-----	46, 251	-14		-.030
14.-----	46, 242	-23		-.050
18.-----	46, 296	+31		+0.067
Mean-----	46, 265		±17	±.037
5.-----	46, 572	+16		+0.034
7.-----	46, 567	+11		+0.024
12.-----	46, 530	-26		-.056
Mean-----	46, 556		±18	±.039

The difference between the mean of experiments 5, 7, and 12 and the mean of the other group of experiments in table 3 was found to be about 85 percent of the energy of evaporation of isoprene, and this suggested that the glass bulbs used to contain the liquid isoprene had broken in experiments 5, 7, and 12 and allowed liquid to evaporate to fill the bomb with saturated isoprene vapor before the beginning of the calorimetric experiments. Unfortunately, an accurate calculation of the effect of evaporation of isoprene in the bomb is not possible, because no data are available on either (a) the effect on the partial pressure of the isoprene of the increase in concentration of water in the liquid phase resulting from evaporation of part of the isoprene, and possibly also from absorption of water from the water-saturated atmosphere in the bomb; or on (b) the effect of the pressure of the oxygen in the bomb on the density of the saturated isoprene vapor. However, it is possible to make fairly reasonable assumptions regarding the possible effects of factors (a) and (b), and to calculate the thermal effect of evaporation of isoprene in the bomb on the basis of these assumptions. In table 4 are given the results of recalculating the data of experiments 5, 7, and 12 on the assumption that the bomb was filled with isoprene vapor. The amount of isoprene in the vapor phase was calculated in the following three ways: (1) The effect of the factors (a) and (b) mentioned above was neglected. The vapor pressure of pure isoprene at the initial temperature of the calorimeter in each experiment was calculated from a vapor-pressure equation of the form  $\log p = a - b/T$ , where the constants were determined from values of boiling point and change of

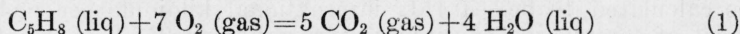
boiling point with pressure reported by Bekkedahl, Wood, and Wojciechowski [3]. The actual pressure of the isoprene vapor in the bomb was assumed to be lower than the vapor pressure of pure isoprene by an amount calculated by means of Henry's law from the amount of impurity (assumed to be water) indicated by the observed values of  $r$  (table 2). The specific volume of the isoprene vapor was calculated by means of the relation  $PV/T = \text{constant}$ , where the constant was determined from the values of  $V$  and  $T$  at  $P=1$  atmosphere [3]. (2) The liquid isoprene was assumed to have absorbed an amount of water sufficient to reduce the density of isoprene in the vapor phase to 80 percent of the density of vapor in equilibrium with pure liquid isoprene. The effect of the presence of oxygen in the bomb on the density of the isoprene vapor was neglected. (3) The presence of the oxygen in the bomb was assumed to have caused complete evaporation of the isoprene.

TABLE 4.—Results of three methods of recalculating the data of experiments 5, 7, and 12

Experiment	Recalculated values of $-\Delta U_R$ at 30° C		
	Method 1	Method 2	Method 3
	int. j/g	int. j/g	int. j/g
5.....	46,278	46,332	46,227
7.....	46,354	46,391	46,214
12.....	46,208	46,268	46,189
Mean.....	46,280	46,330	46,210

It will be seen from table 4 that the mean of the results recalculated by method 1 are in agreement within 0.03 percent with the mean of the first group of values given in table 3. The mean results obtained by methods 2 and 3 differ from the mean of the first group of values in table 3 by +0.14 and -0.12 percent, respectively. As the effects of the two factors neglected in method 1 are relatively small and of opposite sign they will partially cancel, and it may be concluded that the result obtained by method 1 is not seriously in error. The agreement of this result with the mean of the first group of values in table 3 may therefore be considered as confirmation of the hypothesis that the high values of  $-\Delta U_R$  obtained in experiments 5, 7, and 12 were due to breaking of the glass bulbs containing the isoprene and the consequent evaporation of part of the isoprene.

In view of the above discussion, it appears justifiable to discard the results of experiments 5, 7, and 12, and to adopt as the value for the decrease in energy for the reaction



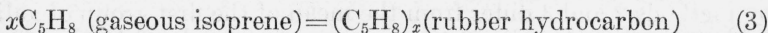
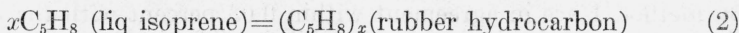
at 30° C and under a pressure of 1 atmosphere, the value of  $-\Delta U_R$  obtained from the first group of experiments of table 3, namely, 46,265 international joules per gram (weight in vacuo), or 3151.2 international kilojoules per mole of  $\text{C}_5\text{H}_8$ . The corresponding value of  $-\Delta H$  for the above reaction is obtained by adding the value of  $-\Delta(pv)$  for the reaction, 5.1 international kilojoules per mole, to the value of  $-\Delta U_R$ , giving for  $-\Delta H$  the value 3156.3 international kilojoules per mole.

The uncertainty of the mean of the results given in the first group in table 3, defined as  $2\sqrt{\frac{\sum\Delta^2}{n(n-1)}}$ , is 0.035 percent. Combining this with the uncertainty of the energy equivalent of the calorimeter, 0.026 percent, and the estimated uncertainty, 0.023 percent, in the value used for the heat of combustion of benzoic acid, there is obtained for the uncertainty of the value given for the heat of combustion of liquid isoprene

$$\sqrt{(0.023)^2 + (0.026)^2 + (0.035)^2} = 0.049 \text{ percent.}$$

Using for the specific heats at constant pressure of liquid isoprene, gaseous oxygen, gaseous  $\text{CO}_2$ , and liquid water the values 153.3 [2], 29.18 [5], 36.62 [5], and 75.18 [6] international joules per mole, respectively, there is obtained the value  $-0.126$  kilojoule per mole degree centigrade for the temperature coefficient ( $=d/dT(-\Delta H)$ ) of the heat of combustion of isoprene at constant pressure. Hence the value derived from this investigation for the heat of combustion of liquid isoprene at  $25^\circ\text{C}$  and a constant pressure of 1 atmosphere to form liquid water and gaseous  $\text{CO}_2$  is  $3156.9 \pm 1.6$  international kilojoules per mole. Adding to this the value for the heat of vaporization of isoprene calculated by Bekkedahl, Wood, and Wojciechowski [3],  $25.9 \pm 0.3$  kilojoules per mole, there is obtained the value  $3182.8 \pm 1.7$  international kilojoules per mole for the heat of combustion of gaseous isoprene at  $25^\circ\text{C}$  and at a constant pressure of 1 atmosphere, the products of combustion being liquid water and gaseous  $\text{CO}_2$ .

The data on the heat of combustion of isoprene can be combined with data reported previously [8] for the heat of combustion of rubber to calculate the heats evolved in the reactions.



Several values were reported in the reference cited for the heats of combustion of different samples of rubber. The value reported for the heat of combustion of "steam purified" rubber, which was the purest of the samples on which measurements were made, was  $45239 \pm 90$  international joules per gram (weight in vacuo), or  $(3081.3 \pm 6.0)x$  international kilojoules per mole at  $30^\circ\text{C}$ . Using the value  $128.7x$  joules per mole degree centigrade reported by Bekkedahl and Matheson [1] for the specific heat of rubber hydrocarbon at  $27.5^\circ\text{C}$ , and the values given previously in this paper for the specific heats of gaseous oxygen, gaseous carbon dioxide, and liquid water, the temperature coefficient of the heat of combustion of rubber hydrocarbon is calculated to be  $-0.151x$  international kilojoule per mole. The heat of combustion of rubber hydrocarbon at  $25^\circ\text{C}$  is therefore calculated to be  $(3082.1 \pm 6.0)x$  international kilojoules per mole. Combining this value with the values given previously for the heats of combustion of liquid and gaseous isoprene there are obtained the values  $(74.8 \pm 6.2)x$  and  $(100.7 \pm 6.3)x$  for the heats evolved in the reactions (2) and (3), respectively, at  $25^\circ\text{C}$  and a constant pressure of 1 atmosphere.



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WASHINGTON, February 4, 1938.