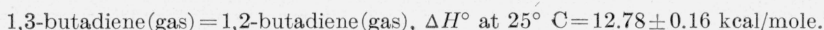


Heat of Isomerization of the Two Butadienes

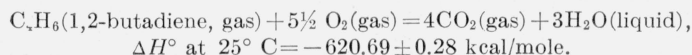
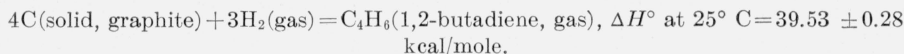
By Edward J. Prosen, Frances W. Maron, and Frederick D. Rossini

The heat of isomerization of 1,3-butadiene to 1,2-butadiene, in the gaseous state at 25° C was determined by measurement of the ratio of their heats of combustion in oxygen to form carbon dioxide and water. The combustion of the gaseous hydrocarbon occurred in a flame at constant pressure in a glass calorimetric reaction vessel of improved design. A complete description of the new calorimetric reaction vessel is given.

The following experimental value is reported for the reaction of isomerization:



Using the value for the heat of formation of 1,3-butadiene previously reported, the following calculated values are given for the reactions of formation and combustion of 1,2-butadiene:



I. Introduction

This work, sponsored by the Office of Rubber Reserve, is part of a thermochemical investigation of monomeric compounds of importance in the national synthetic rubber program, and is also a part of the work of the thermochemical laboratory of this Bureau on the determination of the heats of formation of compounds of importance to industry and science.

Calorimetric measurements have been made that yield a value for the difference in the heats of combustion at constant pressure of 1,3-butadiene and 1,2-butadiene in the gaseous state at 25° C. Combination of this value, which is the heat of isomerization in the gaseous state at 25° C, with the previously reported value for the heat of formation of 1,3-butadiene [1],¹ yields values for the heats of formation and combustion of 1,2-butadiene.

II. Unit of Energy, Molecular Weights, Uncertainties

The unit of energy upon which values reported in this paper are based is the absolute joule,

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

derived from mean solar seconds, and absolute ohms and volts, in terms of which certification of standard resistances and standard cells is made by this Bureau. For conversion to the conventional thermochemical calorie, the following relation [2,3] is used:

$$1 \text{ calorie} = 4.1840 \text{ absolute joules.}$$

The atomic weights were taken as O=16.0000, H=1.0080, and C=12.010 from the 1947 table of international atomic weights [4].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by the method previously described [5].

III. Method

The aim of this investigation was to determine as precisely as possible the heat of isomerization of 1,3-butadiene (gas) to 1,2-butadiene (gas) at constant pressure and 25° C. This was done by determining the ratio of the heats of combustion of these isomers [6]. The value of the difference between this ratio and unity, multiplied by an accepted value for the heat of combustion of 1,3-butadiene, gives the heat of isomerization of 1,3-butadiene to 1,2-butadiene. In principle, the

ratio of the heats of combustion of these isomers was determined as the inverse ratio of the masses of carbon dioxide, whose formation in the combustion of the respective isomers produced identical increases in temperature in the standard calorimeter system, measured as increases in resistance of the platinum resistance thermometer as determined on the given resistance bridge. With this procedure, the energy equivalent of the calorimeter system or the heat of combustion of one of the isomers need be known only approximately, and other systematic errors tend to cancel out.

The method of reducing the experimental observations was as follows: Let

ΔR_c = the corrected increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the given platinum thermometer at a mean temperature of 25° C, as measured with the given resistance bridge;

m_{CO_2} = the mass of carbon dioxide formed in the combustion of the hydrocarbon, in grams;

E_s = the energy equivalent, over the "standard" interval of temperature, of the "standard" calorimeter system, obtained as the ratio of a given quantity of electric energy to the value of ΔR_c produced by it, expressed as joules per ohm;

q_i = the energy introduced into the calorimeter in the "ignition" process, consisting of sparking, igniting the flame, and extinguishing the flame, but not including any part of the heat of combustion, expressed in joules;

q_g = the energy introduced into the calorimeter by gases entering or leaving at a temperature different from 25° C.

q_v = the energy (negative) introduced into the calorimeter by the process of evaporating such water as leaves or remains in the calorimeter in the gaseous state.

q_c = the energy introduced into the calorimeter by the "standard calorimetric process" of combustion.

The total energy, q , introduced into the calorimeter by the actual combustion process in an experiment is

$$q = E_s \Delta R_c = q_c + q_g + q_v + q_i. \quad (1)$$

Letting

$$B = \frac{q_c}{E_s m_{CO_2}}, \quad (2)$$

we obtain the following relation from which B is calculated for any given experiment:

$$B = \left(\frac{\Delta R_c}{m_{CO_2}} \right) \left[1 - \frac{(q_g + q_v + q_i)}{E_s \Delta R_c} \right]. \quad (3)$$

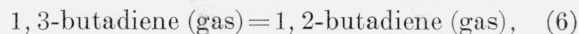
For any two isomers, the ratio of the heats evolved per gram of carbon dioxide is equal to the ratio of their heats of combustion per mole. If the subscripts a and b refer to 1,3-butadiene and 1,2-butadiene, respectively, and $-\Delta Hc^\circ$ is the heat evolved in the standard combustion of one mole of the hydrocarbon, then

$$B_b/B_a = (-\Delta Hc^\circ)_b / (-\Delta Hc^\circ)_a, \quad (4)$$

and

$$(-\Delta Hc^\circ)_a - (-\Delta Hc^\circ)_b = (-\Delta Hc^\circ)_a (1 - B_b/B_a). \quad (5)$$

For the reaction of isomerization,



the standard heat of isomerization is

$$\Delta H^\circ (\text{isomerization}) = -(-\Delta Hc^\circ)_a (1 - B_b/B_a). \quad (7)$$

It may be seen from eq 3 and 7 that the heat of isomerization derived by this procedure is not sensitive to the value of E_s or of $(-\Delta Hc^\circ)_a$. The total amount of energy in one experiment is about 60,000 j, and the largest variation in the value of $q_v + q_g + q_i$ is about 150 j. Therefore, an error of 1 percent in the value of E_s , used in eq 3, would cause an error of not more than 0.002 percent in the value of B_b/B_a . This corresponds to an error of 0.01 kcal/mole in the value of ΔH° (isomerization). Similarly, an error of 0.1 percent in the value of $(-\Delta Hc^\circ)_a$ used in eq 5 would cause an error of 0.01 kcal/mole in the value of ΔH° (isomerization).

IV. Apparatus

1. Calorimeter Assembly and Thermometric System

The calorimeter assembly used in this investigation was similar to that used in other investiga-

tions in this laboratory [6, 7], with some improvements added. The jacket of the calorimeter was maintained near 27.00°C , at a temperature constant within $\pm 0.002^{\circ}\text{C}$, by means of an automatic regulator. In all experiments, the calorimeter uniformly contained 3627.56 ± 0.02 g of water, together with the stirrer, platinum resistance thermometer, calorimeter heater, and the glass reaction vessel with its metal support. The stirrer was operated at a substantially constant speed of 276 rpm with a belt drive from a synchronous motor.

The calorimeter heater consisted of about 65 ohms of enameled constantan resistance wire, No. 30 AWG, wound on a Pizein-coated, thin, copper cylinder, the whole covered with Pizein [7].

The thermometer system consisted of a platinum resistance thermometer No. 262,214 and Mueller resistance bridge No. 404 [8].

2. Reaction Vessel

An improved glass reaction vessel was designed and made for this and subsequent investigations involving combustions in a flame at constant pressure. The new reaction vessel is shown in figure 1.

In the combustion of hydrocarbons other than methane and ethane in a flame in a glass reaction vessel, it is necessary to mix some "primary" oxygen with the combustible gas before it reaches the flame, in order to prevent deposition of unburned carbon in the burner tube. For a given rate of flow of the combustible gas, the flame velocity is required to be such that the flame will neither flash back inside the burner tube, nor blow off from the burner tip. For a given combustible gas burning in an atmosphere of oxygen, the position of the flame at the burner tip is determined largely by the amount of "primary" oxygen mixed with the combustible gas. In the previous design of reaction vessel [7], the admixture of primary oxygen was determined largely by the size of the Bunsen openings at the base of the burner tip. The size of the Bunsen openings could be changed only by cutting the reaction vessel apart. As changes were always required for different types of hydrocarbons, this was a cumbersome arrangement. In the new design, the primary oxygen is introduced through a sep-

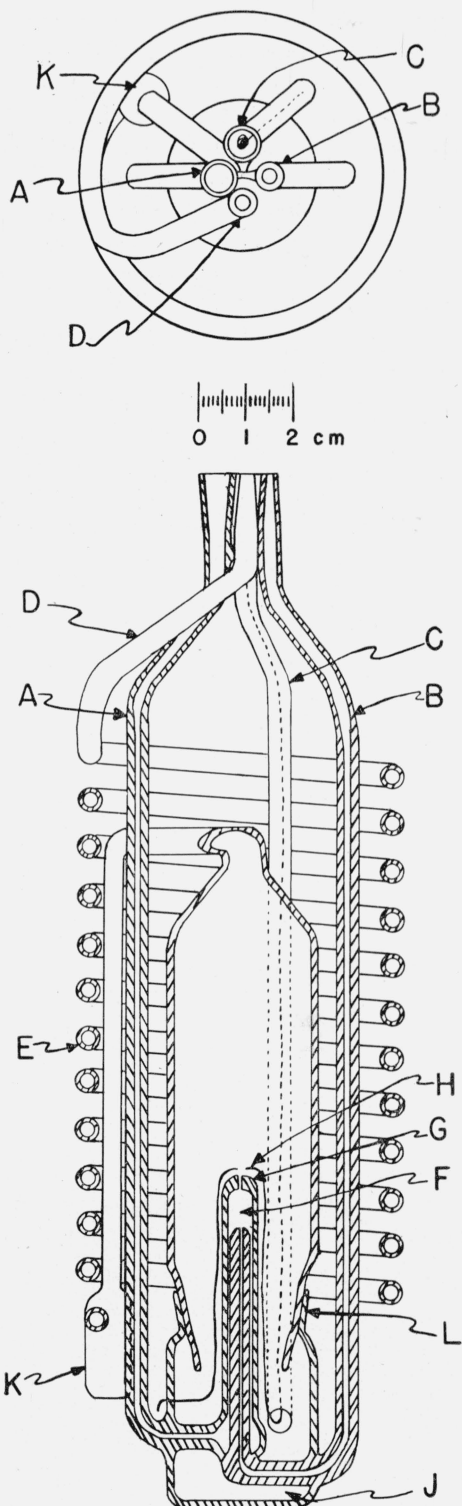


FIGURE 1. Diagram of the reaction vessel.

arate line, and the fraction of primary oxygen in the combustible mixture reaching the flame at the burner tip is easily controlled by regulating separately the rate of flow of the combustible gas and of the oxygen.

In the present investigation, a rate of flow of butadiene equal to 29 ml/min (or 0.0012 mole/min) was found to be satisfactory. The primary oxygen was adjusted to produce a blue flame with a sharp inner cone. The primary oxygen supplied about 30 percent of the oxygen required for complete combustion of the hydrocarbon. The total oxygen (primary plus secondary) was about 150 percent of that required for complete combustion. (In order to avoid possible damage to the glass reaction vessel, preliminary tests of the amount of primary oxygen required for the satisfactory combustion of a given hydrocarbon, at given rates of flow, were made with a similar burner tube made of brass and provided with a glass chimney.)

The method of operation of the new reaction vessel is as follows: The hydrocarbon enters through inlet tube *A*, the primary oxygen through *B*, and the secondary oxygen through *C*. The hydrocarbon and primary oxygen mix in the chamber *F* and emerge through a hole (about 0.5 mm diameter) in the quartz tip *G*. Sparking across the platinum wires *H*, above the tip, ignites the mixture, which burns in a steady flame in the atmosphere of secondary oxygen supplied through the inlet *C*. One of the platinum wires enters through the secondary oxygen inlet tube *C*; the other is grounded to the calorimeter can. The gap between the platinum wires is about 3 mm. The gaseous products of combustion leave the combustion chamber at the top, are cooled to the temperature of the calorimeter in their passage through the glass spiral *E*, and leave the calorimeter through the outlet *D*. Most of the water vapor condenses to liquid, which collects at the bottom of the vessel at *J*, or in the bulb *K*, at the bottom of the spiral. The vessel is constructed to come apart at the joint *L*, to facilitate adjusting the spark gap and cleaning the vessel.

3. Sparking System

A new sparking system was assembled for this investigation. It consisted of a high-tension coil (Delco-Remy 538-z), a condenser having a capacity of 0.2 microfarad, and breaker points operated by a hexagonal cam driven by a synchronous motor

having a speed of 1,800 rpm. Four dry cells were used as a source of energy. The spark gap at the burner tip was about 3 mm, and the normal time of sparking was 15 sec.

V. Chemical Procedure

1. Source and Purity of the Butadienes

The sample of 1,3-butadiene used was from a lot of 1,3-butadiene labeled Research Grade, Phillips Petroleum Co. The purity of this material, sampled from the vapor phase, was determined by measurements of freezing points by A. R. Glasgow, Jr. to be 99.83 ± 0.06 mole percent [9].

The 1,2-butadiene used was a sample 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. It was made available through the American Petroleum Institute Research Project 44 at the National Bureau of Standards on "Data on properties of hydrocarbons" and was purified at the National Bureau of Standards by the American Petroleum Institute Research Project 6 on the "Analysis, purification, and properties of hydrocarbons" from material supplied by the Standard Oil Development Co. through W. J. Sweeney. A complete description of the purification and purity of this compound is given by Streiff, Murphy, Zimmerman, Soule, Sedlak, Willingham, and Rossini [10], who reported the purity by measurement of freezing points, to be 99.94 ± 0.05 mole percent.

It is calculated that in the extreme case, the heat of combustion would be affected by less than the following amounts because of the impurities: 0.012 percent for impurities in 1,3-butadiene; and 0.003 percent for impurities in 1,2-butadiene.

The butadiene was withdrawn in the vapor phase from its container, passed through a tube of anhydrous calcium sulfate followed by a small amount of anhydrous magnesium perchlorate to remove traces of water, and fed directly into the reaction vessel in the calorimeter for the combustion.

2. Purification of the Oxygen Used for Combustion

The oxygen used for combustion, including both the primary and secondary streams, was commer-

cial oxygen that was freed of combustible impurities by passage through copper oxide at about 550° C. The oxygen in both lines was freed of carbon dioxide and water before entering the calorimeter by passage through tubes containing, successively, ascarite, magnesium perchlorate, and phosphorus pentoxide.

3. Purity of the Reaction of Combustion

As a check on the purity of the reaction of combustion, both the water and carbon dioxide formed in the combustion were collected and the masses determined for each experiment. In eight combustion experiments with 1,3-butadiene, the mean value of the ratio, r , of one-fourth of the number of moles of carbon dioxide to one-third of the number of moles of water, was found to be 1.00024, with a standard deviation of ± 0.00022 . Similarly for six experiments with 1,2-butadiene, the mean value of r was found to be 0.99994, with a standard deviation of ± 0.00019 .

Samples of the products of combustion were analyzed for carbon monoxide by the Gas Chemistry Section of this Bureau [11]. In no case was the total amount of carbon monoxide greater than 0.004 percent of the amount of carbon dioxide formed in the combustion.

The effect of any possible incomplete combustion during the ignition or extinction of the flame was eliminated by the procedure, described below, of determining the "ignition" energy in separate experiments in which the flame was allowed to burn only long enough to produce a steady flame, and then was extinguished. With this procedure, the heat of combustion was in reality determined from the portion of the combustion when the flame was in a steady state, any constant errors associated with the ignition and extinction of the flame cancelling out.

4. Determination of the Amount of Reaction

For each calorimetric combustion experiment, the amount of reaction was determined from the mass of carbon dioxide formed, taking 1 mole or 44.010 g of carbon dioxide as equivalent to one-fourth mole of butadiene.

VI. Calorimetric Procedure

1. Calorimetric Combustion Experiments

The following procedure was followed in preparing the calorimeter for all experiments: The

calorimeter jacket was brought to temperature, near 27.00° C, where it was automatically maintained constant, within about $\pm 0.002^\circ$ C, throughout the whole experiment. The standard mass of water, 3627.56 ± 0.02 g, was weighed into the calorimeter can on the pan of a 5-kg balance, having a sensitivity at this load of 0.008 g per scale division, using the same weights in all experiments. The calorimeter can was placed in the calorimeter jacket, the dry reaction vessel with the heater around it was lowered into the can, the cover was placed on the can, the jacket was covered, the stirrer was connected, and the platinum resistance thermometer inserted into the calorimeter can through the hole in the jacket cover. The hydrocarbon and primary and secondary oxygen lines were connected to the reaction vessel through flexible glass spirals. The weighed absorption tubes for water and carbon dioxide, a guard tube containing magnesium perchlorate and ascarite, a sampling bulb, and a flowmeter were connected to the outlet side of the reaction vessel through a three-way stopcock near the vessel. This stopcock permitted oxygen to bypass the reaction vessel at the end of a combustion to flush any water and carbon dioxide in the lines into the absorption tubes. The calorimeter was brought to near the starting temperature by electrical heating, and a period of about 20 min was allowed for equilibrium to be established. The calorimetric observations were begun when the calorimeter reached the selected starting temperature. The standard temperature rise was about 4 degrees for the combustion experiments, and the final temperature was slightly below the jacket temperature.

The calorimetric observations during an experiment consisted of: (a) a fore period of 20 min during which the reaction vessel, containing oxygen at atmospheric pressure, remained closed, and readings of the resistance of the platinum thermometer were taken every 2 min; (b) a "reaction" period during which the reaction took place, with a period allowed for equilibrium to be reestablished in the calorimeter, and during which readings of the resistance of the platinum thermometer were taken about every 15 sec or every minute, depending on the shape of the time-temperature curve; and (c) an after period of 20 min during which the reaction vessel remained closed, the calorimeter temperature was slightly

below the jacket temperature, and readings of the resistance of the platinum thermometer were taken every 2 min.

The manipulation of the apparatus controlling the reaction during a combustion experiment was as follows: Before the calorimetric experiment, the two absorption tubes for water and carbon dioxide were flushed with hydrogen and weighed by a method previously described [12, 13, 14]. The hydrocarbon inlet tube was flushed with helium to remove oxygen from this line and the rest of the reaction vessel then flushed and left filled with oxygen at atmospheric pressure. During the fore period, the rates of flow of the primary and secondary oxygen and gaseous hydrocarbon were regulated through bypass flowmeters. At the end of the fore period, the three-way stopcock outlet on the reaction vessel was opened to the absorption tubes, the primary and secondary streams of oxygen were turned into the vessel, the spark was turned on, and the hydrocarbon was then turned into the vessel. The sparking was continued for 15 sec, or until the flame was started, as indicated by the flowmeter at the end of the line. The flame was allowed to burn until a final temperature slightly below the jacket temperature was reached, when the flame was extinguished by turning off the hydrocarbon. The time of combustion was usually about 22 min. The primary and secondary streams of oxygen were left on for an additional 10 min and then cut off. The reaction vessel was closed by setting the three-way stopcock at the outlet such that the oxygen would bypass the reaction vessel but would flow through the absorption tubes. Thus, all the water vapor not in the calorimetric reaction vessel was swept into the absorption tube. An additional period of about 6 min was allowed for equilibrium to be established before starting the after period. After the experiment, the absorption tube for water was flushed with hydrogen and weighed to obtain the amount of water carried out of the calorimeter as vapor. The absorption tubes were replaced on the train and the reaction vessel flushed with oxygen overnight to carry all the water and carbon dioxide into the absorption tubes. Both tubes were then flushed with hydrogen and weighed. The mass of carbon dioxide produced was used to determine the amount of reaction, and the stoichiometric ratio of the masses of carbon dioxide

and water was used to check the purity of the reaction of combustion.

The corrected increase in temperature of the calorimeter system, ΔR_c , expressed as the increase in resistance in ohms of the given platinum thermometer at a mean temperature of 25° C, was taken as the difference in the resistance of the thermometer between the beginning of the after period and the end of the fore period, corrected for heat of stirring and thermal leakage [15].

2. Determination of the "Ignition" Energy

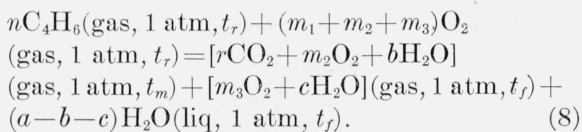
Experiments to determine the energy associated with the ignition and extinction of the flame ("ignition" energy experiments) were performed in the same manner as the regular combustion experiments, except that the flame was allowed to burn only long enough to be sure a steady flame was attained. The flame was usually left burning for about 40 seconds. The initial temperature in these experiments was a fraction of a degree below the jacket temperature, and the rise of temperature was about 0.1 deg. Experiments were also performed in which only sparking energy was added to the calorimeter.

The mean value for the "ignition" energy, which is the energy associated with the process of ignition and extinction of the flame, but not including any part of the heat of combustion, obtained from seven experiments with 1,3-butadiene and two experiments with 1,2-butadiene, with an average of 0.0005 mole of butadiene burned in each experiment, was found to be 33.1 j, with a standard deviation of ± 2.8 j. In separate experiments in which no hydrocarbon was burned and sparking alone for the standard time occurred, the sparking energy was found to be 31.1 j with a standard deviation of ± 0.8 j. In making these calculations, the value of E_s , the standard energy equivalent, was taken as 154,446 abs j/ohm.

For the present experiments, the ignition energy for the standard time (15 sec) of sparking was taken as the weighted mean of the foregoing values, 31.3 j with a standard deviation of 0.8 j.

3. Reduction to the Standard Calorimetric Process

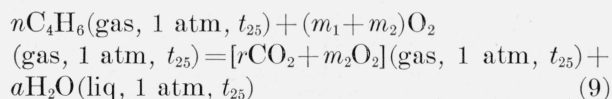
The process that actually takes place in the calorimetric reaction vessel during a combustion experiment is the following:



The energy evolved in this reaction and including the ignition energy is $q = E_s \Delta R_c$. In the foregoing equation, t_r is the temperature of the room; t_m and t_f are the mean and final temperatures, respectively, of the calorimeter; n is the number of moles of hydrocarbon entering the calorimeter; $(m_1 + m_2 + m_3)$ is the number of moles of oxygen

entering the calorimeter; $m_1 = \frac{11}{2}n$ is the number of moles entering during the actual combustion period and being used in the combustion; m_2 is the excess number of moles entering during the actual combustion period and leaving the calorimeter as a mixture with $r = 4n$ moles of carbon dioxide and b moles of water vapor; m_3 is the number of moles of oxygen entering the calorimeter during the flushing immediately following the actual combustion period and leaving the calorimeter as a mixture with c moles of water vapor; $(a - b - c)$ is the number of moles of water left in the calorimeter in the liquid state; and $a = 3n$ is the total number of moles of water formed in the combustion. The quantity c also includes a very small amount of water left in the calorimeter in the gaseous state.

It is desirable to correct the results of each calorimetric experiment to a common basis for comparison. This can be done by adjusting all results to the basis of a "standard calorimetric process" defined by the equation



The energy evolved in this reaction is q_c .

For the present experiments the various quantities have the values

$$m_1 = \frac{11}{2}n, \quad m_2 = \frac{11}{4}n, \quad r = 4n, \quad \text{and} \quad a = 3n.$$

The difference between the energy, q_c , evolved

in the standard calorimetric process expressed by eq 9, and that evolved in the actual calorimetric process expressed by eq 8, but including the energy of ignition, is $q_c - q = -(q_g + q_v + q_i)$.

The energy associated with the adjustment of the composition of the carbon dioxide-oxygen mixture issuing from the calorimeter in the individual experiments to the average composition as expressed in the "standard calorimetric process" is negligible. The quantities q_g and q_v were evaluated by the relations:

$$\begin{aligned}
q_g &= C_1[n(t_r - t_{25})] + \\
& C_2[m_1(t_r - t_{25}) + m_2(t_r - t_m) + m_3(t_r - t_f)] + \\
& C_3[b(t_{25} - t_m) + c(t_{25} - t_f)] + \\
& C_4[(a - b - c)(t_{25} - t_f)] + C_5[r(t_{25} - t_m)], \\
q_v &= -(b + c)[\Delta H_v];
\end{aligned}$$

where $C_1 = 80.1$, $C_2 = 29.4$, $C_3 = 33.6$, $C_4 = 75.3$, and $C_5 = 37.1$ are the approximate heat capacities of butadiene(gas), oxygen(gas), $\text{H}_2\text{O}(\text{gas})$, $\text{H}_2\text{O}(\text{liq})$, and $\text{CO}_2(\text{gas})$, respectively, in j/deg mole, and $\Delta H_v = 43,992$ abs j/mole is the heat of vaporization of water at 25°C and saturation pressure.

To obtain the values of the standard heat of reaction, ΔH° , from the standard calorimetric process indicated by eq 9, it is only necessary to take account of the change in heat content with pressure at constant temperature for each gas from its given pressure to zero pressure, so that each substance will have the heat content of the thermodynamic standard state. Since this correction will not be significantly different for the two isomers, the ratio of the values of ΔH for the standard calorimetric process will also be the ratio of the values of ΔH° for the standard thermodynamic process.

VII. Results of the Present Investigation

The results of the calorimetric combustion experiments for 1,3-butadiene and 1,2-butadiene are given in tables 1 and 2, respectively. For these calculations, the value of E_s , the energy equivalent, was taken as approximately 154,446 j/ohm. The value of B were calculated from eq 3.

TABLE 1. Results of calorimetric combustion experiments on 1,3-butadiene

Experiment	ΔR_c	Mass of carbon dioxide	q_o	q_s	q_i	B	Deviation from mean
	<i>Ohms</i>	<i>g</i>	<i>j</i>	<i>j</i>	<i>j</i>	<i>Ohms/g CO₂</i>	<i>Ohms/g CO₂</i>
1.....	0.388048	4.17091	+16.5	-342.3	31.3	0.0934941	-0.0000514
2.....	.381756	4.10179	-2.4	-331.2	31.3	.0935478	+.0000023
3.....	.381025	4.09487	+0.1	-360.3	31.3	.0935695	+.0000240
4.....	.397671	4.27289	-2.8	-355.4	31.3	.0935637	+.0000182
5.....	.384888	4.13689	-16.8	-352.2	31.3	.0935665	+.0000210
6.....	.390584	4.19985	-18.6	-362.7	31.3	.0935390	-.0000065
7.....	.391438	4.20192	-23.9	-236.5	31.3	.0935099	-.0000356
8.....	.378484	4.07076	-17.2	-389.7	31.3	.0935735	+.0000280
Mean.....						0.0935455	-----
Standard deviation of the mean.....						±.0000104	-----

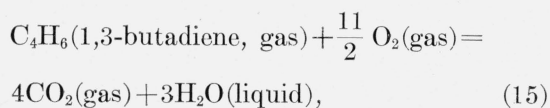
TABLE 2. Results of calorimetric combustion experiments on 1,2-butadiene

Experiment	ΔR_c	Mass of carbon dioxide	q_o	q_s	q_i	B	Deviation from mean
	<i>Ohms</i>	<i>g</i>	<i>j</i>	<i>j</i>	<i>j</i>	<i>Ohms/g CO₂</i>	<i>Ohms/g CO₂</i>
1.....	0.384743	4.04783	-13.2	-304.9	31.3	0.0955079	-0.0000048
2.....	.380613	4.00684	-5.5	-345.8	31.3	.0955080	-.0000047
3.....	.388498	4.09171	-10.1	-368.8	31.3	.0954977	-.0000150
4.....	.395315	4.16322	-7.7	-383.4	31.3	.0955137	+.0000010
5.....	.397521	4.18337	-10.8	-352.4	31.3	.0955377	+.0000250
6.....	.388279	4.08829	-16.6	-354.3	31.3	.0955112	-.0000015
Mean.....						0.0955127	-----
Standard deviation of the mean.....						±.0000055	-----

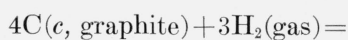
From these data, the ratio of the heat of combustion of 1,2-butadiene to that of 1,3-butadiene is

$$(-\Delta H_c^\circ)_b / (-\Delta H_c^\circ)_a = B_b / B_a = 1.021029 \pm 0.000256. \quad (14)$$

The values previously reported [1] for the heats of combustion and formation of 1,3-butadiene (gas) are



$$-\Delta H_c^\circ_{298.16} = 607.91 \pm 0.23 \text{ kcal/mole.}$$



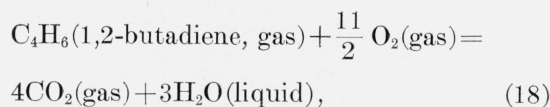
$$\Delta H_f^\circ_{298.16} = 26.75 \pm 0.23 \text{ kcal/mole.} \quad (16)$$

The heat of isomerization at 25° C thus becomes (from eq 7):

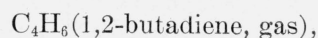
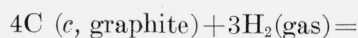
$$1,3\text{-butadiene (gas)} = 1,2\text{-butadiene (gas)} \quad (17)$$

$$\Delta H^\circ (\text{isomerization}) = 12.78 \pm 0.16 \text{ kcal/mole.}$$

The heats of combustion and formation of 1,2-butadiene become:



$$-\Delta H_c^\circ_{298.16} = 620.69 = 0.28 \text{ kcal/mole.}$$



$$\Delta H_f^\circ_{298.16} = 39.53 \pm 0.28 \text{ kcal/mole.} \quad (19)$$

VIII. References

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