[Contribution from the Mallinckrodt Chemical Laboratory of Harvard University]

Heats of Organic Reactions. II. Hydrogenation of Some Simpler Olefinic Hydrocarbons

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In the first paper of this series,[1] which in the following will be designated as I, a calorimeter for the study of reactions in the gaseous phase at elevated temperatures and also some measurements of the heat of hydrogenation of ethylene were described. The present paper deals with the heat of hydrogenation of some simple homologs of ethylene, while the next one will be devoted to some of the more complex unsaturated hydrocarbons.

The calorimeter described in I has proved itself so satisfactory that it was used in the present research without further improvements. Only one change, purely of method, was made. It consisted in bracketing a gas run by two electric energy equivalent determinations, a procedure opposite to that used in the study of ethylene. While thus in a given time fewer measurements can be performed, the scattering of single values is so considerably reduced that an over-all improvement results. Some slight modifications in the gas measuring procedure have also been effected, as, for instance, the use of argon instead of nitrogen in the flame (eliminating the necessity of correcting for nitrogen oxides), and altogether the average deviations have been reduced to less than 0.1%. This value is so small that the possible systematic errors of the method or impurity of the compounds used are more serious than the accidental deviations. The former may arise chiefly from incomplete reduction on the copper catalyst and from side reactions which might occur concurrently with the main reaction. The test for the completeness of hydrogenation was originally performed, as described in I, by a reaction with bromine in the vapor phase. However, it was found that the substitution reaction with higher hydrocarbons is so prominent that the method is unreliable for a determination of olefinic hydrocarbons present in quantities of less than 0.5 cc. in one liter of gas mixture. Another procedure was therefore adopted which consists in condensing out the hydrocarbons from the effluent mixture and adding to them, while cold, a standardized solution of bromine in carbon tetrachloride. After allowing the mixture to warm slowly to room temperature, the excess bromine is titrated in the usual manner upon addition of potassium iodide. Such tests were used in most calorimetric experiments here recorded and all tests showed that hydrogenation was essentially complete. Table I shows some of the tests made with known gas mixtures. Such blank tests were made with every compound studied but propylene.

Table I

Standard bromine soln. added, cc.	0.1 *N* $Na_2S_2O_3$ for back titration, cc.	Isobutene found (cc. of gas)	Isobutene added (cc. of gas)	Isobutane added (cc. of gas)
1.0	11.3	0	0	0
0.5	5.6	0	0	456
.5	2.6	0.32	0.30	500
.5	0.05	.60	.60	500
.5	1.2	.48	.43	500
.5	5.6	0	0	500

Another test for the completeness of the reaction consisted, as discussed in I, in placing a second catalyst vessel in the gas line before it enters the calorimeter and observing the thermal effects of the mixed gas stream and of hydrogen alone. This test, which was performed with every substance studied, gave throughout negative results, thus showing that hydrogenation is complete[2] and that no thermal effects of adsorption are sufficiently prominent to cause measurable errors.

In the presence of a large excess of hydrogen, two types of side reactions are to be considered as most likely: a degradation to lower hydrocarbons and a polymerization to form molecules containing twice, or at most thrice, the number of carbon atoms present in the original substance. If these reactions are shown to be absent, a formation of heavy non-volatile products seems to be most unlikely. The test for these side reactions, made with every substance studied, consisted in placing two efficient cold traps between the

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[1] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, This Journal, **57**, 65 (1935).

[2] A rough calculation shows that the equilibrium in the hydrogenation reactions under the conditions of the calorimeter is so far on the side of the saturated hydrocarbon that no difficulties from this point are to be expected.

calorimeter and the combustion device. The first trap was cooled by Dry Ice and the second by liquid air. The gases were passed through the calorimeter for a time long enough to accumulate about 15 cc. of liquid hydrocarbon in the first trap. As was shown in I, most of the methane that may be formed passes through the traps and is detected by the weight increase of the carbon dioxide absorbers. Ethane has been found to accumulate mainly in the second trap. It was tested for by evacuating this trap while at the temperature of liquid air, and measuring the vapor pressure of the contents while cooled by solid carbon dioxide. A conversion of about 1% of the hydrocarbon to ethane is very readily detected by this method, as was shown by test runs in which this amount of ethane added to the effluent gas mixture increased the vapor pressure by about 180 mm. In runs in which no ethane was added, the vapor pressure was always found to be within 3 mm. of the vapor pressure of the pure hydrogenation product. To detect polymerization, the contents of the first trap were allowed to evaporate at atmospheric pressure from a bath kept at a temperature a few degrees higher than the boiling point of the pure saturated hydrocarbon. Polymerization products, as tested by addition of *n*-heptane[3] to butane and of trimethylethylene[3] to propane, are found when present as oily drops upon pouring some water into the trap when the evaporation is completed. Although 0.5% heavy hydrocarbon is readily detected by the method, tests with the products of hydrogenation were invariably negative.

Preparation of Compounds.—Careful preparation of compounds using all conceivable devices to ensure absence of impurities is probably the best insurance of purity, since so few methods are available which can be used to prove that an organic material, liquid or gaseous at ordinary temperatures, is pure to the extent of 99.9% or better.

Propylene—Sample A.—Commercial isopropyl alcohol was roughly fractionated, and the portion boiling at 80.5–82.5° collected. It was dehydrated by passage at the rate of 250–300 cc. per hour through a tube 70 cm. long and 2.5 cm. in diameter, filled with activated alumina[4] at 375–400°. The exit gases were passed first through a water-cooled condenser which led to a suction flask and then through a trap at −80°. The yield was approximately 90% of crude product.

Since several operations in the purification of the different hydrocarbon samples are much the same, a general description will be given here.

The crude olefin was transferred to a tank. The gas was allowed to pass through a series of scrubbing bottles as indicated in Table II, and then condensed in a bulb cooled with Dry Ice. Just before distillation, each sample, except butene-1, sample A, was filtered by forcing it at −80° through a tube packed with glass wool. After fractionation, the samples were distilled from bulb to bulb *in vacuo*, and sealed off *in vacuo* in glass containers bearing magnetic break-off devices. Propylene, on account of its high vapor pressure at room temperature, was stored in small tanks, the procedure being the same as in the case of ethylene.

Before the propylene was fractionated, it was passed through a trap at −45°; one or two cc. of liquid was condensed from about 400 g. of product. It was distilled at atmospheric pressure through a Podbielniak type column with a partial condensation head; the head was cooled by circulating alcohol which had been chilled with Dry Ice. The general distillation procedure was substantially the same as that used for ethylene.[1] The boiling point, corrected for pressure changes, of the middle fraction of the final distillation was −47.91° at 755 mm., and did not change within the accuracy of the reading instruments—about 0.01°.

Propylene—Sample B.—*n*-Propyl alcohol[5] was distilled through an all-glass column 3 meters tall and 18 mm. in diameter, packed with glass spirals.[6] The column was heated electrically and was equipped with a partial condensation type dephlegmator. Tests with carbon tetrachloride–benzene mixtures indicated that it was equivalent to 30–35 theoretical plates.[7] This column will be designated as column B. The fraction boiling at 97.5–97.6° at 762 mm. was collected; 250 g. of alcohol, 60 cc. of concentrated sulfuric acid, and 150 g. of $Al_2(SO_4)_3 \cdot 18H_2O$ were heated to boiling in a 3-liter three-necked flask fitted with a thermometer, reflux condenser and dropping funnel. The top of the reflux condenser was connected to a downward water-cooled condenser, which led to a suction flask in an ice-bath. The side arm of the suction flask led to a trap at 0°, which was followed by a trap at −80°. When the evolution of propylene began to decrease, 150 cc. of concentrated sulfuric acid was added through the dropping funnel, and the mixture heated until the evolution of gas had practically ceased. The mixture turned dark during the dehydration, and some sulfur dioxide was evolved. The yield of crude product was about 80%. The gas was passed through a trap at −45° before distillation; about 30 cc. of liquid was condensed from some 300 g. of propylene. The liquid propylene was distilled in the same manner as sample A. The boiling point, corrected for pressure changes, of the middle fraction of the final distillation was −47.64° at 764 mm. No variation during the distillation could be detected. If 0.03° per mm. is used for the value of dt/dp,[8] the boiling point,

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[3] These materials were used as they were available and should be at least as difficult to detect as any compounds which might result from the dimerization of the olefin studied.

[4] Obtained from the Alcoa Ore Co., Pittsburgh, Pennsylvania.

(5) From the du Pont Ammonia Co. The manufacturers state that no secondary butyl alcohol is present in this material.

(6) Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1933); see also Roper, Wright, Ruhoff and Smith, *ibid.*, **57**, 954 (1935).

(7) Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

(8) Burrell and Robertson, THIS JOURNAL, **37**, 2188 (1915).

TABLE II[a]

Sample	1	2	3	4	5	6	7	8	9
Propylene A	300 cc. of 10%	←50% alkali→	(0°)		(0°)	←10% alkali→	(0°)	Tower of KOH pellets	
Propylene B	Aqueous alkali	←10% alkali→	(0°)		(0°)	←50% alkali→	(0°)	Tower of KOH pellets	
Butene-2	in a bottle	←Glacial acetic acid→			water	←10% alkali→			Tower of KOH pellets
Isobutene	fitted with a	←water→			←10% alkali→			Tower of KOH pellets	
Butene-1 A	sintered glass disk	←10% alkali→			←30% alkali→			Tower of KOH pellets	
Butene-1 B	5 l. flask of water at 0° with sintered glass disk[b]	←10% alkali→	(0°)	←water→	(0°)		(0°)	Tower of KOH pellets	

[a] Unless otherwise stated, the scrubbers were Friedrich wash bottles containing 75 cc. of the washing liquid at room temperature. [b] After the washing, the iodoform test showed that the liquid in the 5-liter flask contained less than 0.1% ethyl alcohol; in Nos. 5 and 7, no alcohol could be detected.

corrected to 755 mm., is −47.91°, as is that of sample A.

Butene-2, *cis* and *trans*.—Commercial secondary butyl alcohol was distilled through column B and the fraction boiling at 98.5–98.6° collected. A mixture of 444 g. of alcohol and 165 g. of concentrated sulfuric acid was boiled in the same apparatus used for the preparation of propylene, sample B, until no further gas evolution occurred. The yield of crude product was 80%. The butene was fractionated in an all-glass column 5 meters tall and 18 mm. in diameter, packed with glass spirals[6] of not less than three-fourths turn, and not more than one and one-half turns. The column (which will be hereinafter designated as column A) was surrounded with a double-walled glass jacket through which cold alcohol circulated. The temperature of the jacket at the top of the column did not differ from that of the distilling liquid by more than a few tenths of a degree; the temperature at the bottom of the column was about 2° higher. The dephlegmator, which was of the partial condensation type, was chilled by a stream of alcohol which had been cooled with solid carbon dioxide. Temperatures were measured by means of a four-junction copper–constantan thermel, and a Leeds and Northrup type K-2 potentiometer. The glass still-pot, contained in a Dewar flask, was heated by vapors of carbon tetrachloride, boiled by means of a coil of bare nichrome wire immersed in it. The heat input seemed to be very constant, and independent of room temperature. The charge was approximately 2100 g. of crude butene-2. The reflux ratio was between 30-to-1 and 35-to-1. The results of three successive distillations are shown in Fig. 1. Sample A is from the middle portion of the low-boiling isomer. Sample B is from an earlier and completely separate series of distillations with a different column. The sample used for the heat of hydrogenation of the high-boiling isomer is a composite of samples Q + S (see distillation curve).

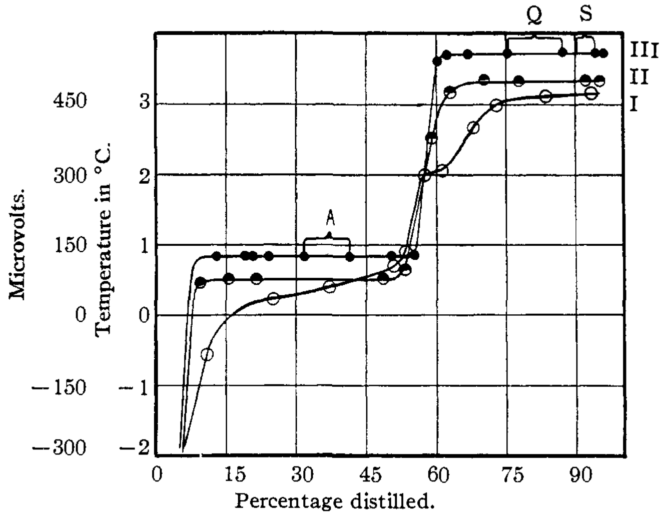

Fig. 1.—Butene-2 (curves offset vertically).

The vapor pressures of the two butene-2 isomers, which have not been determined heretofore, were measured in a static apparatus. The sample was agitated by means of a magnetic stirrer to ensure equilibrium. The temperatures, measured with a four-junction copper–constantan thermel, and a Leeds and Northrup type K potentiometer, are probably accurate to 0.03°. The pressures were read with a cathetometer with an accuracy of approximately one-tenth millimeter. The data are given in Table III. From them the following equations have been derived; these are valid from −80 to 30°.

Low Boiling: $\text{Log}_{10}\, p = (-2505.74/T) - 18.78681 \log_{10} T + 0.012991\, T + 34.25987$

High Boiling: $\text{Log}_{10}\, p = (-2379.264/T) - 15.4405 \log_{10} T + 0.0097519\, T + 46.48442$

Equations containing four constants instead of a lesser number were chosen after a series of graphical differentiations which indicated that this procedure was justified.

TABLE III

THE VAPOR PRESSURES OF THE ISOMERIC BUTENES-2

Low Boiling Isomer

Temp., °K.	p calcd.	p obsd.
143.13	0.01	
193.13	7.15	
195.20	8.55	8.75
213.13	33.67	
225.96	76.70	76.60
226.27	78.05	78.05
233.13	115.77	
243.13	176.25	
252.11	302.30	302.30
253.13	316.80	
263.13	490.50	
273.13	732.40	
273.17	733.65	733.75
274.09	760.0	
283.13	1059.4	
293.10	1490.3	1490.65
293.13	1492.0	
293.72	1521.5	1521.65
297.69	1729.3	1729.30
303.13	2059.8	
High Boiling Isomer		
303.13	1878.2	
297.54	1572.9	1572.90
293.13	1360.2	
283.13	959.6	
276.86	759.8	
273.17	658.9	658.90
273.13	657.8	
263.13	436.15	
253.13	278.45	
252.12	265.45	265.45
243.13	170.20	
233.13	98.95	
225.95	64.65	64.65
213.13	27.80	
195.02	6.70	5.70
193.13	5.65	
143.13	0.009	

The heats of vaporization from the slope of the vapor pressure curve at the boiling point are, for the low and high boiling isomers, respectively

$$\lambda_{\text{low}} = 5695 \text{ cal./mole}$$
$$\lambda_{\text{high}} = 5810 \text{ cal./mole}$$

The freezing points of the two isomers were determined using a calibrated copper-constantan single-junction thermocouple. The values are

Low boiling isomer (*trans*): −105.8°
High boiling isomer (*cis*): −139.3°

Butene-1, Sample A.—Commercial *n*-butyl alcohol was distilled through column B. The portion boiling at 117.5–117.6° was dehydrated by passing it at the rate of 250–275 cc. per hour over activated alumina in the same apparatus used for the preparation of propylene, sample A. The yield of crude product was 83% of the theoretical. The product was filtered through glass wool at −80°, and then allowed to stand in contact with sodium wire for forty-eight hours at 2°. It was distilled through column A with a reflux ratio of 15-to-1. This first distillation was not satisfactory; the boiling point rose from −6.00 to −5.85°. The lower boiling fractions were redistilled with a reflux ratio of 35-to-1. A large middle fraction was obtained, boiling at −6.67 ± 0.01° at 755 mm. Samples A-1 and A-2 are successive fractions from this distillation.

The high-boiling fractions (pot residues) from the first distillation were treated with an excess of bromine. Upon distillation, all of the material boiled below 110° at 60 mm. Butadiene tetrabromide boils at 180–181° at this pressure.

Butene-1, Sample B.—Butene-1, made in the same manner as the crude material used for the preparation of sample A, was dissolved in 100 cc. of chloroform. Bromine was added at −50° in such a way that an excess of butene was always present, except at the end of the preparation. The yield of crude material was nearly quantitative. The product was washed twice with concentrated sulfuric acid; the second washings were only slightly discolored. The dibromide was then shaken with water, dilute aqueous carbonate solution, and finally with dilute ethyl alcohol. It was dried with calcium chloride, filtered and distilled in column B at 50 mm. pressure; 1396 g. of product boiling at 80.8–81.0° was added to 500 g. of 30-mesh zinc in 2 liters of boiling 95% ethyl alcohol, contained in a flask fitted with a reflux condenser and efficient mechanical stirrer. The dibromide was added at such a rate that the alcohol was kept boiling by the heat of the reaction; the effluent butene was condensed in a trap cooled with Dry Ice, and then distilled in column A. The middle fraction boiled at −5.90° at 775 mm. This is equivalent to −6.70° at 755 mm. The discrepancy between the boiling points of samples A and B may be due to the fact that a different barometer was used in each distillation; unfortunately it was not possible to compare them.

Isobutene.—Commercial *t*-butyl alcohol was purified by partial freezing until its melting point was 21°. It was then distilled in column B; the portion boiling at 82.7–82.8° at 770 mm. was collected; 222 g. of alcohol and 15 cc. of concentrated sulfuric acid were boiled in the same apparatus as that used for the preparation of propylene, sample A, until the evolution of gas ceased. The yield was 82% of crude material. If more sulfuric acid is used, the yield is reduced, and if less, the dehydration requires an inconveniently long time. The isobutene was distilled through column A with a reflux ratio of 15-to-1. The middle fraction boiled at −6.67° at 770 mm. The freezing point of the pure isobutene was determined as in the case of the butene-2 isomers. The value found was −140.7°.

Tests for Purity.—In view of the efficiency of the stills used, the impurities which might remain in the compounds are mainly those which would form constant boiling mixtures and also compounds having very nearly the same boiling point, such as isomers or members of different hydrocarbon series with the same number of carbon atoms. For these latter impurities a gravimetric determination of the carbon-hydrogen ratio is not well suited and therefore it was not used at all. Instead the freezing curves of the compounds were determined in all cases where this was possible, while in the case of propylene and butene-1, with their low freezing points, the only test for purity is that the two samples of each prepared by different methods give identical heats of hydrogenation, as will be seen later.

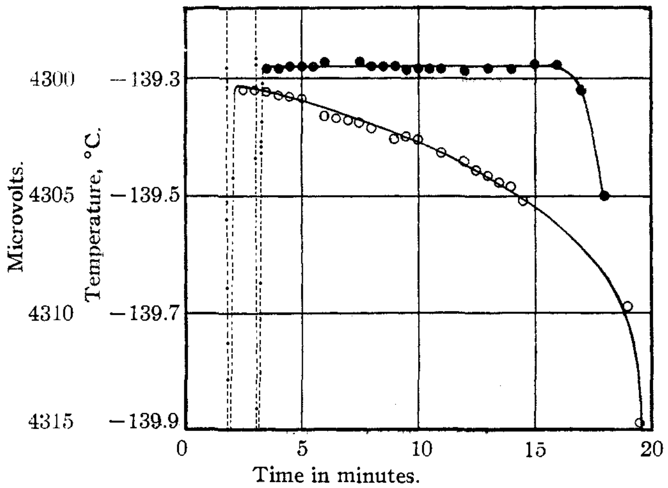

Fig. 2.—Freezing point curves of butene-2, high-boiling: ●, pure sample; ○, same with 0.5% of butene-1 added.

A study of freezing curves obtained with all-glass freezing point devices either with or without stirring showed that the use of small samples (1 cc. or less) under conditions tried gave less reliable results than the use of larger (*ca.* 40 cc.) samples.[9] For these curves the substance to be studied was distilled *in vacuo* into a glass freezing point apparatus, containing a magnetically operated stirrer, and a well for a single copper-constantan thermocouple; in a side arm was placed a small sealed tube with a weighed amount of impurity, whose effect on the freezing point was to be determined. The apparatus was sealed off from the vacuum system and a freezing curve was taken. Then the tube containing the impurity was broken, and the procedure repeated. As impurities, the alcohols from which the hydrocarbons were made, butane, and isomeric butenes were used, although with each compound studied not all, but only those which were the most likely to be present, were tried.

Figure 2 shows a typical freezing curve without and with impurity. In every case the 0.5% of the added impurity caused a much greater drift of the freezing temperature than obtained with the pure sample. These results indicate that in every case studied the original purity must be appreciably better than 99.5% and is most likely of the order of 99.9%.[9a]

A procedure was tried which involved the use of a twin freezing point apparatus of similar design to that mentioned above. The material was distilled into one side of this, and then half frozen. The liquid portion was now poured into the other side, and the freezing points of the separate halves determined. The same procedure was repeated with added impurity. This method did not prove to be as satisfactory as that discussed above.

The possibility still remains that a substance here not tried but present in the preparations forms a constant boiling mixture and also a solid solution with one or more of the compounds prepared. This is a rather improbable coincidence,[10] but it should be regarded as an uncertainty of the present research.

The Results

In Table IV are assembled all results obtained on the five substances described on the preceding pages. No experiments have been omitted for any reason whatsoever from this table. The correction to the uniform temperature of 83° was made using the same ΔC_p as in the case of ethylene (see I). This figure cannot be justified, but the true differences of heat capacities are unknown and the whole correction is so small that no significant error could have been thus committed. The average deviations from the means are on the whole about ±20 cal., with the exception of one value on propylene (Run No. 19) which differs from the average by several hundred calories. This discrepancy has been ascribed to an unnoticed leak in the gas combustion line and this one value has not been used in forming averages. The "probable errors" from the accidental errors alone are of the same order of magnitude as the above average deviations. In addition one must consider the effect of probable impurities

(9) Mair, *Bur. Stand. J. Res.*, **9**, 457 (1932); Shepard, Henne and Midgley, This Journal, **53**, 1948 (1931).

(9a) Professor G. S. Parks, of Stanford University, who has been determining the heat capacities of our samples A and Q + S of the two butenes-2, has kindly informed us that in his judgment both compounds are better than 99.9% pure.

(10) Washburn, *Ind. Eng. Chem.*, **22**, 985 (1930).

Table IV

Run	Sample	Flow C_nH_{2n}, cc./min.	Flow H_2, cc./min.	Mole C_nH_{2n}, converted	Mean temp. of calorimeter in μv. 83°C. = 0μv.	− ΔH	− ΔH corr. to 355°K., in calories
				Propylene			
16	B	32	296	0.035027	+ 50	30,125	30,125
17	B	45	448	.035162	+150	30,096	30,095
18	A	29	450	.035152	+150	30,108	30,107
19	A	45	192	.034730	+150	30,467	
20	A	32	296	.035045	−300	30,128	30,130
21	A	23	190	.034909	−300	30,101	30,103
22	A	23	442	.034887	−200	30,130	30,131
			Average 30,115 ± 13 cal./mole				
				Butene-1			
23	A-1	29	295	0.034786	+100	30,339	30,338
24	A-1	29	294	.034813	− 50	30,323	30,323
25	A-1	22	198	.034661	− 50	30,327	30,327
26	A-2	44	206	.034815	+300	30,379	30,377
27	A-2	46	478	.034909	+350	30,322	30,320
28	A-2	23	420	.034665	−100	30,359	30,360
29	B	32	302	.034807	−250	30,317	30,319
30	B	21	152	.034608	−300	30,396	30,398
31	B	45	448	.034912	−150	30,309	30,310
			Average 30,341 ± 25 cal./mole				
			Butene-2, Low Boiling Isomer				
32	A	41	294	0.045802	+ 50	27,645	27,645
33	A	32	294	.045775	+425	27,600	27,597
34	A	32	294	.038161	− 50	27,610	27,610
35	A	32.5	293	.038148	−125	27,617	27,618
36	A	20	379	.037958	−375	27,586	27,588
37	A	46	222	.038234	+100	27,641	27,640
38	B	32	294	.038151	+ 50	27,664	27,664
39	B	32	295	.038095	− 50	27,604	27,604
			Average 27,621 ± 21 cal./mole				
			Butene-2, High Boiling Isomer				
40		32	295	0.036892	+175	28,566	28,565
41		32.5	296	.036948	−100	28,560	28,561
42		44	225	.037008	− 50	28,580	28,580
43		20	381	.036757	−400	28,530	28,532
44		44	224	.036975	+125	28,612	28,611
			Average 28,570 ± 19 cal./mole				
				Isobutene			
45		32	290	0.037115	+ 50	28,412	28,412
46		31	292	.037170	+600	28,373	28,369
47		21	128	.037032	+150	28,380	28,381
48		24	431	.037081	−250	28,369	28,371
49		45	458	.037279	+100	28,384	28,383
50		45	191	.037219	+ 50	28,419	28,419
			Average 28,389 ± 18 cal./mole				

nd of side reactions. The latter is not large ecause the heats of polymerization and of degadation (see I) do not differ very greatly from he heats of hydrogenation. The impurities will ause at most an error numerically equal to their oncentration, as in the case of butane. Allowng 0.1% impurity, thus 0.1% error, which is ossibly excessive, and also 0.1% of side reactions, thus about 0.03% error from this latter source, one arrives at a total error of about 0.2% or 60 calories. We believe that this estimate is not too optimistic.

It is advantageous to correct the above values of the heats of hydrogenation to standard temperatures, but the knowledge of the heat capacities of the compounds involved is so inadequate that the calculation could hardly be anything but a guess. This calculation will not be attempted here therefore and only the following estimate will be made. The difference in heat contents of ethane and of ethylene counting from absolute zero at the temperature of the calorimeter is only about 600 calories (see I). This difference is probably sensibly constant for all other pairs of compounds here considered, as evidenced for instance by the empirical rule of Parks and Huffman,[11] that the difference in entropies of olefinic and saturated hydrocarbons is constant (2.7 E. U.). Even allowing a 100% variation in relative heat content, one still obtains sensibly accurate values, namely, 1800 ± 600 cal., as the correction to absolute zero and 250 ± 140 cal. as the correction to 298°K.

There are not many data in the literature with which to compare the present results. From the experimental heats of combustion[12] one finds the following: −32.2 kg. cal. for propylene, and −32.1 for isobutene. These values, as in the case of ethylene, are probably uncertain to the extent of several kg. cal. and thus do not afford a good means of comparison. The results of Frey and Huppke[13] on propylene and the butenes, as the authors themselves point out, are unsuited for calculation of the heats of reaction because of the short temperature range covered and of the quite noticeable side reactions present. One can only draw inferences from this work if one assumes the entropy difference to be constant for all reactions there studied. In this case the heats of hydrogenation follow the same order as here reported, except in the case of isobutene, which appears to be too low.

Conclusion.—The number of cases studied is as yet too small to permit the formulation of generally valid conclusions and a detailed discussion of the significance of our results will be presented in the following paper. It may be pointed out here, however, that the results already obtained certainly do not support the idea of constant bonding energies (referred to ordinary temperatures or to zero absolute[14]) if under the latter idea a precise rule is to be assumed. The deviations from constant bonding energies are in the same direction as found by Rossini[15] in the case of alcohols, namely increased instability of lower homologs, thus opposite to that found by the same author for saturated hydrocarbons.

We wish to thank Mr. M. A. Dolliver who has ably assisted us in preparations of the compounds used. Likewise we acknowledge our indebtedness to Mr. Edwin E. Roper, Mr. W. R. Smith and Dr. George F. Wright for their valuable work in connection with the long and tedious distillation of butene-2.

Summary

1. The values of the heat of hydrogenation of the following compounds have been determined:

Hydrocarbon	Heat of hydrogenation cal./mole
Propylene	−30,115
Butene I	−30,341
Butene II, *trans* (low boiling isomer)	−27,621
Butene II, *cis* (high boiling isomer)	−28,570
Isobutene	−28,389

These results do not bear out the theory of constant bonding energies.

2. No side reactions have been observed witl the copper catalyst used, and the results are accurate to about ±60 cal.

3. The *cis* and *trans* isomers of butene-2 hav been carefully separated. The boiling and freezing points are:

	B. p., °C.	F. p., °C.
Butene-2 (high boiling)	+3.73	−139.3
Butene-2 (low boiling)	+0.96	−105.8

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[11] Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., N. Y., 1932, p. 79.

[12] Kharasch, *Bur. Stand. J. Res.*, **2**, 359 (1929).

[13] Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

[14] The data on zero point energies are too insecure to permit calculation of the stability of all these compounds counting from th non-vibrating state as the point of reference.

[15] Rossini, *Bur. Stand. J. Res.*, **13**, 189 (1934).