

in the measurements, we have found 20,900, 19,620 and 18,850 cal., respectively, for the ΔF_{298}° in the process of dehydrogenating *n*-butane to yield butene-1, *cis*-butene-2 and *trans*-butene-2. The ΔF_{298}° of formation of *n*-butane¹¹ (p. 64) recalculated with Rossini's new combustion value is -4580 (=300) cal. We thus obtain 16,320, 15,040 and 14,270 cal. for the ΔF_{298}° of formation of butene-1, *cis*-butene-2 and *trans*-butene-2, respectively, from the elements. These values, though not as reliable, are in good agreement with those just found in Table IV and serve to place the normal butenes in the same order of thermodynamic stability.

Before concluding, we wish to take this opportunity to thank the investigators in the chemical laboratory of Harvard University for the remark-

ably pure butene samples, without which this study would have been impossible.

Summary

1. The heat capacities of the four isomeric butenes have been measured between liquid air temperatures and their respective boiling points.

2. The entropies of *cis*-butene-2, *trans*-butene-2 and isobutene at 298.1°K. have been calculated from these heat capacities in conjunction with other data. An estimate has been made for the entropy of butene-1.

3. The free energies of formation of these four butenes have also been calculated. The order of increasing thermodynamic stability is apparently: butene-1, *cis*-butene-2, *trans*-butene-2, isobutene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Heats of Organic Reactions III. Hydrogenation of Some Higher Olefins

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The first and second communications¹ of this series have dealt with a calorimeter for the determination of the heats of hydrogenation of organic compounds in the vapor phase and with the results thus far obtained on ethylene and some of its simpler homologs. The present paper is concerned with further measurements on ethylene homologs of higher molecular weight. While this line of inquiry is not yet completed, some regularities of rather general applicability can be noted and will be discussed after the presentation of the results. However, before proceeding to this main subject, it is desirable to devote some space to a renewed consideration of the accuracy of the method developed; this is being reviewed because, as has been recently pointed out,² there exists a considerable discrepancy between the observed position of the thermal equilibrium in the ethane-ethylene-hydrogen system and that which is calculated using the new value for the heat of hydrogenation and computing entropies and heat capacities statistically.

(1) (a) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, *THIS JOURNAL*, **57**, 65 (1935), hereinafter called I; (b) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935), hereinafter called II.

(2) Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935).

This conclusion has also been reached independently by Topley and Teller,³ who have made a more exhaustive consideration of all possible sources of error in the calculations; these authors conclude in effect that the true heat of hydrogenation is lower at least by 900 and more likely by some 1500 calories than that given in the first paper of this series. Smith and Vaughan, on the other hand, are inclined to attribute the discrepancy to an incorrect calculation of the rotational entropy of ethane.

On the Reliability of the Method

The situation described above clearly indicates the desirability of further search for possible experimental errors. Besides those which have been adequately dealt with in the first and second publications, an error could result if the compounds used were irreversibly adsorbed on the catalyst. If this hypothetical exothermic process, probably accompanied by partial hydrogenation and polymerization, were to take place at a steady rate during all measurements on a given compound, self-consistent results would be obtained, but they would be too high. To test this rather un-

(3) Topley and Teller, *J. Chem. Soc.*, 876 (1935).

likely possibility, ethylene-hydrogen mixtures as used in I were passed through a tube filled with a copper catalyst maintained at 80°. The catalyst had been made in the same manner as that previously used and was tested for its activity. Upon passage of gases for a few minutes, the tube was taken out of the line and weighed without air being admitted; then it was replaced and gas flow resumed for a longer time, whereupon it was weighed again. The two weights were found to agree to within 0.2 mg. although in the meantime 2.5 g. of ethylene had been hydrogenated. This test proves, we believe, that no steady accumulation of irreversibly adsorbed ethylene takes place under our experimental conditions. It may be added here that similar tests—with invariably negative results—have now been performed on several of the compounds and catalysts to be discussed later.

To eliminate completely the possibility of "chemical" errors, the heat of hydrogenation of ethylene on a platinum catalyst was determined. The catalyst was made by precipitating hot platinum chloride solution by hydrazine hydrate and was supported on asbestos (*ca.* 5% Pt). After repeated decantation it was dried and then heated in a hydrogen stream at 200° for several hours to remove volatile impurities and was then reactivated by a short treatment with oxygen. The remainder of the technique was that described in I except, as stated in II, the electric calibrations preceded and followed each chemical run. Three values were obtained, the average being 32,739 \pm 17 cal./mole at 82°. This is to be compared with 32,792 \pm 39 obtained previously for ethylene from the same tank on copper catalyst. The difference is well within our experimental errors, the two figures being close enough to show conclusively that no significant "chemical" errors have marred the determination of the heat of hydrogenation of ethylene.

As this paper will show, the results obtained thus far on quite a number of compounds form such a consistent picture that the only large errors yet possible are the systematic ones. Their elimination, however, is possible through a re-determination, by the present method, of an accurately known thermal quantity. As such, the heat of formation of water was chosen and was determined with as few changes in the technique as possible. In the calorimeter proper only one was made: the copper catalyst was replaced by a

small amount of the platinum catalyst described above. The gas stream consisted of the usual excess hydrogen with about 7% oxygen metered in the same manner as were the hydrocarbons previously. Large additional tubes of Dehydrite preceded the calorimeter; beyond the latter the combustion furnace was replaced by weighing tubes similarly filled with Dehydrite. The remainder of the procedure and apparatus was the same as described in I and suitable blank runs were made to test new details of the technique. Two runs, made under identical conditions of gas flow, gave 58,042 and 58,053 cal. per mole of water vapor at 85°. The close agreement of these figures is fortuitous because the error of weighing alone amounted to about 0.1%; the water samples collected were limited to *ca.* 0.7 g. each as the temperature change of the calorimeter in the runs was kept approximately the same as in experiments on hydrocarbons. Converting the mean of the above, 58,048 cal./mole, to 25° and liquid water with the aid of data given in "I. C. T.," one obtains 68,380 cal. with an experimental uncertainty of about 150 cal. This is to be compared to Rossini's⁴ figure of 68,313 \pm 10 cal. Comment is superfluous.

The last, but not the least, link in the chain of evidence in favor of the present measurements is the agreement of the herein reported heat of hydrogenation of *n*-heptene-1 with that determined on the same sample but *entirely independently* by Professor H. E. Bent and his collaborators.⁵ These workers use a liquid phase calorimeter at 25°. Correcting their figure to gas phase by means of their own new data and to 82° with the aid of an estimated $\Delta C_p = -4.2$ cal./degree, they find an agreement with our figure of much better than 1%.

With this bulk of additional information we feel that we have conclusively demonstrated the precision and accuracy of our measurements. We have now no hesitancy whatsoever in maintaining that the heat of hydrogenation of ethylene, as given in the first paper of the series, is correct in absolute magnitude to better than 0.2%—the uncertainty of our determination of ΔH for water formation.

Significant errors in the determination of the thermal equilibrium in the ethane system are also unlikely because of the accumulation of consistent

(4) Rossini, *Bur. Standards J. Research*, **6**, 1 (1931).

(5) Privately communicated; *THIS JOURNAL*, **58**, 165 (1936).

independent data;⁶ although Topley and Teller's presentation makes them appear somewhat more consistent than is evident upon a detailed study of individual experiments. Thus this whole problem acquires new interest. Accepting tentatively the argument of Topley and Teller that any reasonable readjustment of the vibrational frequencies in ethane and ethylene molecules cannot eliminate the discrepancy, one is led inevitably to the conclusion that the calculations must be wrong in the matter of rotational entropies. The size of the molecules involved being fairly accurately known, only the internal rotational entropy of ethane is in doubt. In both published calculations it has been assumed that ethane has free rotation above about 250°K.—a conclusion due to Eucken and Weigert.⁷ It is supported by their own measurements of the heat capacity of ethane at low temperatures which were made by a none too certain method. Because of this and of the impasse reached in the statistical calculation of the thermal equilibrium, it seems to us that the free internal rotation of ethane down to such low temperatures as claimed by Eucken has by no means been proved and requires further study; on the other hand, it is not impossible that Topley and Teller were too conservative in estimating the effect of all other errors in the calculation.

Experimental Details

No changes in calorimetric procedure, as compared with that described in I and II, were made. A system was devised for introducing compounds boiling above room temperature into the calorimeter. The hydrogen stream was split, the main part flowing through the same system as described previously; the other part was by-passed through the automatic flow regulating device, otherwise used for gaseous hydrocarbons; it then entered an efficient spiral wash bottle filled with the liquid hydrocarbon, immersed in a large water thermostat regulated to $\pm 0.02^\circ$. From here the hydrogen, now saturated with the hydrocarbon vapor, passed through an all-glass valve to rejoin the main stream. The glass valve and all the tubing before and after the calorimeter were heated electrically to prevent condensation. By changing either the flow of hydrogen through the wash bottle or the temperature of the water thermostat, the amount of hydrocarbon entering the calorimeter was readily adjusted and kept constant in a run.

(6) See summarizing table in Topley and Teller's paper, Ref. 3.

(7) Eucken and Weigert, *Z. physik. Chem.*, **B24**, 277 (1934).

When dealing with more complex molecules than those discussed in II, it was soon found that the freezing point apparatus there described was not sufficiently flexible. It underwent a number of changes; the final form included devices for seeding and for a better control of the rate of cooling. The first consisted of a small well in the freezing tube, the bottom of the well just reaching below the surface of the liquid; the seeding was accomplished by introducing a few drops of liquid air into it. In the matter of cooling rate control, we have followed the designs of Skau⁸ and others, mounting a copper shield with an air interspace around the freezing tube. The shield was provided with a heating coil and with a thermocouple, the other junction of which was in the freezing tube. The whole was surrounded by an insulating layer and was immersed in the liquid air bath.

The experiments testing for degradation and polymerization (see Paper II) gave some trouble also because higher hydrocarbons in a stream of hydrogen form fogs of fine solid particles which pass through Dry-Ice and liquid-air traps even though these are filled with glass wool. A final large trap tightly packed with cotton solved this difficulty.

Preparation of Compounds

More space is devoted to the method of preparation and purification than their novelty would warrant. This is done in the belief that the descriptions which follow form an essential link in the chain of evidence for the high purity of these compounds. Column A (see II), which has been used almost always in the final distillation, was equipped with the same four-junction thermel employed in the butene preparations. This thermel was calibrated with the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ transition point (32.38°) and boiling water, the latter in the column itself; a quadratic equation was adapted to these temperatures. Also, the single-junction thermocouple used in the freezing-point determinations was calibrated against subliming carbon dioxide and boiling oxygen, the microvolt readings being compared to values of Southard and Andrews;⁹ a quadratic equation was adapted to the differences and the table of Ref. 9 used with these corrections.⁹ The deviations of the boiling and freezing points, unless otherwise stated, represent the magnitude of random fluctuations in absence of systematic drift. The boiling points were obtained in the still head and therefore the absolute temperature may be appreciably in error. Initial freezing points are given in this section, more detailed discussion being reserved for the following one.

n-Heptene-1.¹⁰—*n*-Butyl bromide was distilled through Column B, and the fraction boiling at 101.47 – 101.64° at

(8) Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

(9) Southard and Andrews, *J. Franklin Inst.*, **207**, 323–339 (1929).

(10) (a) Waterman and de Kok, *Rec. trav. chim.*, **52**, 298 (1933); (b) Wilkinson, *J. Chem. Soc.*, 3057 (1931).

770 mm. was collected. Allyl alcohol was prepared by the method described in "Organic Syntheses."¹¹ The crude mixture of alcohol and formic acid was neutralized with strong (about 50%) sodium hydroxide; approximately 900 g. of alkali was required for twice the quantities given in "Organic Syntheses." The solution was distilled through a 91-cm. indented column until the sp. gr. of the distillate was 0.998. The yield was 1780 g. of alcohol having a sp. gr. of 0.900—54% calculated on the glycerine. Allyl bromide was prepared by a modification of the method of "Organic Syntheses."¹² When additional sulfuric acid was introduced to the hydrobromic-sulfuric acid mixture resulting from the reduction of bromine with sulfur dioxide, the yield was 55%. When no additional acid was used, the yield was 76%, and when 100 g. of copper turnings was dissolved beforehand in the mixed acids, the yield was further increased—in some cases by as much as 10%.¹³ In each preparation, about 25 moles of allyl alcohol was used with the mixed acids from 2971 g. of bromine. The crude bromide was worked up in the usual manner and finally fractionated through a column 2 meters tall and 32 mm. in diameter packed with glass cylinders. This column will be designated as Column C. The fraction boiling at 70.36–70.46° at 770 mm. was used for the preparation of heptene-1.

The Grignard reagent was prepared by adding 822 g. of *n*-butyl bromide in 2500 cc. of ether to 170 g. of magnesium turnings over a period of about five hours. The ether solution of the Grignard reagent was filtered by forcing it through a tube packed with glass wool; 726 g. of allyl bromide diluted with ether to 2 liters was added over a period of three to five hours at a temperature of 5 to 10° until the reaction mixture no longer gave a test for Grignard reagent. The end of the reaction was also marked by a change of color of the solution from yellowish-brown to gray.¹⁴ The reaction mixture was poured on ice, and acetic acid was added until the solution was acid to litmus. The lower layer was saturated with sodium chloride; the upper layer was drawn off and stirred with alkali until it was alkaline to litmus. The ether layer was dried with potassium carbonate, filtered, and distilled through Column C. The combined residues from three runs were distilled through Column B. The yield of material to this point was 85% (on butyl bromide). The fraction boiling at 93–94° was refluxed with sodium and then distilled. It was finally fractionated through Column A. The main portion boiled at 93.06 ± 0.01° at 757 mm. (0°) and had a refractive index of n_D^{20} 1.3997. The freezing point was -119.1°.

Pentenes-2.—The mixture of the *cis* and *trans* pentenes-2 was kindly given to us by Professors E. P. Carr and M. L. Sherrill of Mt. Holyoke College. The characteristic data supplied us are: b. p. 36.2–36.5° at 760 mm.; n_D^{20} 1.3796. They had been distilled but in a column not efficient enough to effect any considerable separation of the isomers. The fraction used in this work was the middle one and should correspond in composition to the equilibrium mixture.

unsym-Methylisopropylethylene.—Dimethyl-*i*-propylcarbinol was prepared by adding an appropriate quan-

tity of acetone (b. p. 55.95–56.05° at 760 mm.) to the Grignard reagent prepared from *i*-propyl bromide (b. p. 59.12–59.22° at 760 mm.). A considerable quantity of propane seemed to be produced during the reaction along with a small quantity of propylene. The reaction product was worked up in the usual manner. The yield of unpurified carbinol was about 40%. The combined product from nine five-mole runs was systematically fractionated. The boiling point fluctuated, and some water seemed to be formed. However, when a small quantity of potassium carbonate was added to the still pot, this difficulty was removed. The freezing point was -11.1°. A small quantity of the purified material was dehydrated; the residue had a fruity odor, suggesting the presence of mesityl oxide.¹⁵ The carbinol was then refluxed with 15 g. of sodium for two hours, after which it had turned a dark brown. The alcohol was distilled from the sodium and fractionated in Column B. The boiling point at 755 mm. was 117.91–117.95°, and the freezing point was -10.6°. Further treatment of a small sample with sodium did not cause darkening to occur.

Five hundred sixty-seven grams of purified carbinol was dehydrated by passing it over activated alumina¹⁶ at 300° at the rate of 18 g. per minute. The water was removed and the olefin was then separated from the residual alcohol by distillation. The recovered alcohol was passed over the alumina again. After three cycles, the yield of crude olefin was 86%. The product was washed with water and dilute alkali, dried over potassium carbonate, filtered, and distilled through a 91-cm. column. The material consisted largely of *unsym*-methyl-*i*-propylethylene, as can be seen from the following distillation data on a test run.

T., °C.	to 60	60–68	68–80	80–117	117–119
Distil., g.	34	4	4	1	12 (residual carbinol)

The olefin was finally fractionated in Column A. The boiling point of the middle fraction was 55.87 ± 0.01° at 762 mm. (0°), and the refractive index was n_D^{20} 1.3897. The pot residues had a slight odor of the parent carbinol. This suggested the possibility of a constant boiling mixture of the olefin and the latter. Part of the olefin was then mixed with methyl alcohol and re-fractionated as the methyl alcohol azeotrope in Column A. The boiling point was 44.22 ± 0.01° at 762 mm. (0°). The product was extracted ten times with an equal volume of ice water, dried with potassium carbonate, filtered, and distilled. Its refractive index was n_D^{20} 1.3898. This material slowly froze to a glass in liquid air.

Cyclohexene.¹⁷—Commercial cyclohexanol was distilled through Column B, and the fraction boiling at 160.40–160.55° at 765 mm. was collected; 800 g. of this material mixed with 24 cc. of concentrated sulfuric acid was boiled in the dehydrating apparatus¹⁸ until no more hydrocarbon would come over. The temperature of the water in the reflux condenser was maintained at about 75°. The preparation required two to three hours. The prod-

(15) Laughlin, Nash and Whitmore, *THIS JOURNAL*, **56**, 1395 (1934).

(16) See II, p. 877.

(17) "Organic Syntheses," Coll. Vol. I, p. 177.

(18) See II, p. 877.

(11) "Organic Syntheses," Coll. Vol. I, p. 34.

(12) *Ibid.*, p. 24.

(13) Breckport, *Bull. soc. chim. Belg.*, **39**, 462 (1930).

(14) See Ref. 10b.

uct was washed with water, dilute alkali, dried over potassium carbonate, and distilled through a 91-cm. column packed with glass cylinders. The yield to this point was 78%. The product was finally fractionated through Column A. The boiling point of the main fraction was $83.63 \pm 0.01^\circ$ at 767 mm. (0°) and the index of refraction was n_D^{20} 1.4465. The freezing point was -103.4° .

Trimethylethylene and unsym-Methylethylethylene.—Commercial *t*-amyl alcohol was purified by partial freezing in a large ice cream freezer. From approximately 40 liters of starting material, 2 liters of product was obtained after six crystallizations. The partially purified alcohol was refluxed with 5–10 mole % of sodium, and then distilled from the residue which consisted of unreacted sodium mixed with a dark brown material. It was then fractionally distilled in Column B.¹⁹ The boiling range was 102.37 – 102.47° at 770 mm., and the freezing point was -8.72 .²⁰ Timmermans²¹ gives 102.35° at 760 mm. and -8.55° . Inasmuch as the molar freezing point depression calculated from the heat of fusion²² is 10.4° , the alcohol was probably substantially free from impurities—particularly the straight chain amyl alcohols, which would yield straight chain olefins on dehydration.

Five hundred twenty-eight grams of this purified alcohol mixed with 20 cc. of concentrated sulfuric acid was boiled in the apparatus used for the preparation of propylene Sample B²³ until no more hydrocarbon distilled. The temperature of the water in the reflux condenser was about 40° . The combined product from 1320 g. of alcohol was shaken with aqueous alkali, dried with anhydrous potassium carbonate, filtered and distilled on the steam-bath. The yield was 89% of material boiling up to 50° ; nothing more would distil over. The olefin was washed four times with 50-cc. portions of 75% methyl alcohol, in which it is almost insoluble, and then shaken ten times with 100-cc. portions of cold water. It was then dried with potassium carbonate, refluxed for three days over 60 g. of thinly sliced sodium, distilled, and finally fractionated in Column A.²⁴ The main fraction of trimethylethylene boiled at $38.68 \pm 0.01^\circ$ at 762 mm. (0°), and had an index of refraction of n_D^{20} 1.3869. The freezing point was -133.6° .

A smaller fraction was also obtained which boiled from 31.21 to 31.28° at 762 mm. (0°) (mostly 31.21 to 31.24°), and had an index of refraction of n_D^{20} 1.3777. These constants agree with those given for *unsym*-methylethylethylene.²⁵ While the compound, as indicated by the boiling range, was not entirely pure, it seems likely that it contained only branched chain pentenes as impurities—most probably only trimethylethylene. A simple calculation,

(19) See II, p. 877.

(20) It is possible that several treatments of the crude commercial alcohol with sodium, with careful fractional distillations intervening, would have given a product with as high a freezing point. Fractional distillation alone of the crude product gave material freezing at about -11° , and treatment with sodium, when it was not followed by a careful fractionation, did not change this figure appreciably. However, when the commercial alcohol was refluxed with sodium, and then fractionated through Column B, the freezing point was -9.9° .

(21) Timmermans, *J. chim. phys.*, **29**, 529 (1932).

(22) "International Critical Tables," Vol. V, p. 132.

(23) See II, p. 877.

(24) See II, p. 878.

(25) Professors Carr and Sherrill have communicated the following values to us: b. p. $31.05 \pm 0.05^\circ$ at 760 mm.; n_D^{20} 1.3777.

assuming Raoult's law, indicates that 0.1% of trimethylethylene will change the boiling point of *unsym*-methylethylethylene by 0.07° . This fraction was not of sufficient size to permit a freezing point determination.

Tetramethylethylene.—Two hundred four grams of dimethyl-*t*-propylcarbinol and 10 cc. of 50% (by volume) sulfuric acid was distilled through a 80-cm. indented column under such conditions of boiling and refluxing that the temperature of the distilling liquid was 68 – 73° . The product from several runs was combined, washed with water, dilute alkali, dried with potassium carbonate, filtered and distilled through a 91-cm. column.

The yield of olefins, almost entirely tetramethylethylene, at this point was 83%. They were mixed with methyl alcohol and distilled through Column B until the boiling point rose to 65° . The boiling point of the azeotrope was 52.2° at 762 mm. The product was washed five times with an equal volume of ice water, dried with potassium carbonate, filtered, and distilled. It was finally fractionated in Column A. The boiling point of the middle fraction was $73.39 \pm 0.01^\circ$ at 762 mm. (0°). The refractive index was n_D^{20} 1.4124. The freezing point was -74.2° .

Cyclohexane.—This material was purified in order that a standard would be available for comparison with the products from the hydrogenations of cyclohexene, cyclohexadiene and benzene.²⁶

Du Pont Co. cyclohexane²⁷ was purified by partial freezing until the freezing point no longer increased, remaining constant at $+6.5^\circ$ on a 0.1° thermometer. This material was then distilled in Column A. The boiling point of the middle fraction was $80.92 \pm 0.01^\circ$ at 762 mm. (0°), and n_D^{20} 1.4260. The freezing point was 6.42° (no drift whatever); the addition of 0.1% benzene caused the initial freezing point to drop to 6.01° and during the freezing the temperature dropped steadily.

The Results

The compounds studied will be discussed individually since there were too many differences in the various tests to permit a general presentation. The "double catalyst" experiment (see I, p. 71) was performed with all compounds, save *unsym*-methylethylethylene and the mixture of the pentenes-2, and will not be mentioned specifically. In every run it also was determined that hydrogenation was at least 99.9% complete. This was done by use of the bromine addition method (see II, p. 876) for all hydrocarbons except cyclohexene (see the results under cyclohexene for this exception). The applicability to every compound of this procedure was justified by control experiments. In correcting the ΔH values to 355°K ., the previously used $\Delta C_p = -4.2$ cal./deg. was employed; the correction never amounted to more than 10 cal. No runs have been omitted

(26) For the data on the latter two compounds, see the following paper, IV.

(27) This, we were assured, contains no benzene.

from the tabulations save those few which definitely failed because of technical imperfections. The several samples given in some of the Tables indicate different "cuts" from the distillation.

***n*-Heptene-1.**—Table I, which needs no explanations, gives the results of all calorimetric experiments.

TABLE I
n-Heptene-1

Run	Moles heptene	H ₂ flow mole/min.	C ₇ H ₁₄ flow moles/min.	-Δ <i>H</i> at 355°K., cal./mole
1	0.037048	0.0142	14.8 (10 ⁻⁴)	30,175
2	.037026	.0140	14.8 (10 ⁻⁴)	30,158
3	.037131	.0181	19.0 (10 ⁻⁴)	30,170
4	.037055	.0141	11.2 (10 ⁻⁴)	30,063
5	.036826	.0157	14.3 (10 ⁻⁴)	30,118
Average				30,137 ± 37

Runs 1 to 4. Sample No. H-5

Run 5. Sample No. H-6-7

The experiment testing for degradation and polymerization (see I and II) gave completely negative results. Tests were made for methane, by combustion of non-condensable gases, and for slightly volatile polymerization products by fractionation of the contents of the Dry-Ice trap in a small column.

It proved impossible to test for the absence of impurities by the freezing curve method, as the rate of crystallization of *n*-heptene-1 was very slow. After seeding, the temperature of the sample kept increasing for as long as one-half hour before beginning to decrease, and the readings of the thermocouple depended too much upon the rate of heat flow. The only seemingly satisfactory experiment gave a constant "flat" at -119.1°. Similar studies were also made on the hydrogenation product and a fairly constant value of -90.3° was obtained; but contamination of this material with 0.5% 2,3-dimethylbutane gave a "flat" of almost identical form, although the initial point was -90.4°. The drift in each case was about 0.1° to 80% frozen material. The freezing curve of Eastman *n*-heptane was also determined and found to be 0.05° lower than that of our own "pure" sample (by hydrogenation), but the "flat" was more pronounced. The n^{20} D of both our "pure" heptane and the Eastman product was 1.3874. The strongest evidence in favor of the purity of our *n*-heptene-1 comes from Professor G. S. Parks who has studied the pre-melting heat capacity and has informed us privately that the sample is approximately 99.85% pure. We estimate the all inclusive probable error as 60 cal.

unsym-Methylethylethylene.—Because of the smallness of the sample, only two runs were possible and no tests, other than that for completeness of reaction, were made. The all inclusive error is within 100 cal.

TABLE II
unsym-METHYLETHYLETHYLENE

Run	Moles C ₆ H ₁₀	H ₂ flow, mole/min.	C ₆ H ₁₀ flow, moles/min.	-Δ <i>H</i> at 355°K., cal./mole
1	0.037370	0.0146	13.5 (10 ⁻⁴)	28,528
2	.037474	.0150	13.7 (10 ⁻⁴)	28,455
Average				28,491 ± 36

Pentene-2 (Mixture).—On account of the closeness of the boiling points of the two isomers and the size of our sample, it was deemed inadvisable to attempt a separation at the present. Only two runs were performed. No degradation-polymerization experiments were done in view of the previously obtained negative results on the butenes-2 (see II). The all inclusive error is 100 cal.

TABLE III

PENTENES-2 (MIXTURE)

Run	Moles C ₅ H ₁₀	H ₂ flow, mole/min.	C ₅ H ₁₀ flow, moles/min.	-Δ <i>H</i> at 355°K., cal./mole
1	0.039468	0.0124	14.3 (10 ⁻⁴)	27,982
2	.039524	.0149	14.3 (10 ⁻⁴)	27,925
Average				27,954 ± 28

unsym-Methylisopropylethylene.—The calorimetric data are presented in Table IV. No methane was found in the degradation-polymerization experiment, and likewise no polymerization was detectable, the entire contents of the trap immersed in Dry-Ice distilling at 61° and leaving no residue.

As the criterion of the purity of the unsaturated material we have only the boiling range, as the compound could not be crystallized, notwithstanding many efforts. However, the heats of hydrogenation of the straight distillation product and of the azeotrope preparation were identical; furthermore the hydrogenation product gave a

TABLE IV

unsym-METHYL ISOPROPYL ETHYLENE

Run	Moles C ₆ H ₁₂	H ₂ flow, mole/min.	C ₆ H ₁₂ flow, moles/min.	-Δ <i>H</i> at 355°K., cal./mole
1	0.039549	0.0140	14.8 (10 ⁻⁴)	27,988
2	.039572	.0157	20.4 (10 ⁻⁴)	28,042
3	.039481	.0137	15.1 (10 ⁻⁴)	27,958
4	.039197	.0126	8.97 (10 ⁻⁴)	28,000
Average				27,997 ± 24

Runs 1 and 2. Sample MIE-4

Runs 3 and 4. Sample MIE1A-2A (methyl alcohol azeotrope)

very sharp freezing point at -127.8° (with no observable drift). Addition of *ca.* 0.1% of tetramethylethylene lowered the freezing point *ca.* 1.0° and caused definite drift; n_D^{20} 1.3746. The all inclusive error is therefore within 100 cal.

Cyclohexene.—The test for the completeness of the reaction by the bromine method failed in the case of cyclohexene. Instead, 1 cc. of the hydrogenation product was boiled briefly with 0.1 cc. of concd. sulfuric acid; in the absence of unsaturates no color developed, but the presence of 0.1% of cyclohexene was readily denoted by a yellow coloration. This procedure was standardized with control experiments. The degradation-polymerization experiment gave negative results. The freezing point of cyclohexene was not excellent, the drift amounting to 0.2° to 80% frozen material and this was not appreciably increased by the addition of 0.5% cyclohexane, although in the latter case the initial point was 0.2° lower (-103.6°). However, the hydrogenation product had a "flat" freezing curve at $+6.40^{\circ}$ and n_D^{20} 1.4260 (compare with our pure cyclohexane). In view of the high freezing point lowering of cyclohexane this shows a very high degree of purity—of the order of $99.9 + \%$. It is possible, therefore, to conclude that if any impurity were present in the cyclohexene it must have been some of the six-carbon ring compounds which cannot be separated by distillation. In view of the preparative method, they would have to have been produced by disproportionation, in which case their presence could have but little effect on the heat of hydrogenation. The all inclusive error is within 100 cal.

TABLE V
CYCLOHEXENE

Run	Moles C ₆ H ₁₀	H ₂ flow, mole/min.	C ₆ H ₁₀ flow, moles/min.	$-\Delta H$ at 355°K., cal./mole
1	0.036954	0.0154	13.3 (10 ⁻⁴)	28,588
2	.036981	.0144	13.3 (10 ⁻⁴)	28,603
3	.036587	.0087	7.12 (10 ⁻⁴)	28,577
4	.036571	.0121	7.10 (10 ⁻⁴)	28,602
Average				28,592 \pm 10

Trimethylethylene.—The degradation-polymerization experiment showed that no side reactions were occurring, tests being made for CH₄, C₂H₆, C₃H₈ and polymerization products. The freezing "flat" of the starting material was excellent and addition of 0.5% unsym-methylethylene caused appreciable drift. The all inclusive error is not more than 60 cal.

TABLE VI

TRIMETHYLETHYLENE				
Run	Moles C ₃ H ₆	H ₂ flow, mole/min.	C ₃ H ₆ flow, moles/min.	$-\Delta H$ at 355°K., cal./mole
1	0.039627	0.0136	16.0 (10 ⁻⁴)	26,896
2	.039606	.0136	16.1 (10 ⁻⁴)	26,923
3	.038834	.0139	7.21 (10 ⁻⁴)	26,919
4	.043733	.0138	20.0 (10 ⁻⁴)	26,936
5	.039700	.0126	16.0 (10 ⁻⁴)	26,916
Average				26,920 \pm 10

Tetramethylethylene.—The copper catalyst used with all other compounds here discussed was found to be ineffective with this substance. Instead the platinum catalyst already described was employed. The degradation-polymerization experiment gave negative results for all likely side reactions. The freezing "flat" of the starting material was very good and a pronounced drift was obtained upon addition of 0.5% tetramethylethane. The hydrogenation product also gave a flat freezing curve at -128.6° , although it was not as good as the curve obtained with the product from *unsym*-methylisopropylethylene. The two thus differ by 0.8° although they should be identical. Upon addition of 0.1–0.2% impurity

TABLE VII

TETRAMETHYLETHYLENE				
Run	Moles C ₄ H ₈	H ₂ flow, mole/min.	C ₄ H ₈ flow, moles/min.	$-\Delta H$ at 355°K., cal./mole
1	0.041221	0.0133	15.0 (10 ⁻⁴)	26,670
2	.041701	.0131	15.3 (10 ⁻⁴)	26,632
3	.037280	.0127	9.62 (10 ⁻⁴)	26,633
4	.041898	.0136	20.1 (10 ⁻⁴)	26,596
Average				26,633 \pm 19

Runs 1, 2, 3. Sample TTME-4

Run 4. Sample TTME-4 + 3

to the hydrogenation product of *unsym*-methylisopropylethylene the initial freezing point was lowered by approximately 1° , indicating a heat of fusion of 40–80 cal./mol. Also the duration of the freezing "flat" (eight minutes) of the uncontaminated compound when correlated with the uniform rate of cooling before freezing ($0.33^{\circ}/\text{min.}$) leads to a figure of *ca.* 100 cal./mol. Furthermore the freezing points given here are some 7° higher than that given in "I. C. T.," vol. I, indicating extremely large freezing point lowerings. On the other hand, the heats of fusion of many similar compounds, given in the literature,²⁸ suggest 2000 cal./mole as a likely value for λ_F . The situation is thus unsatisfactory. As the compounds concerned were either contaminated or disposed of before we appreciated this situation, we are un-

(28) See, for example, Landolt-Börnstein, *z. g.* 11 b. p. 1481.

able to clear it up. The all inclusive error is probably within 100 cal.

Discussion

It is, of course, unfortunate that, due to unavoidable chemical difficulties, some of the results are not as accurate as the calorimetric measurements themselves would make them. Nevertheless, in all cases the probable errors are too small to affect the essential conclusions to be drawn from them. In fact, these experimental uncertainties are probably not larger than those which result from the comparison of values obtained at 355°K. without their correction to absolute zero. With the present state of our knowledge of the heat capacities of gaseous hydrocarbons at low temperatures such correction, however, could be nothing but a guess.

In the series of ethylene homologs (see also Papers II and I) very obvious regularities stand out. The substitution of alkyl radicals in ethylene has a pronounced stabilizing effect on the resulting compounds compared with the corresponding saturated hydrocarbons. The size of the substituted straight chain radical has very little, if any, effect upon this stabilization. Thus we find that monosubstituted compounds, propylene, butene-1 and heptene-1, have a heat of hydrogenation lower by 2700 (± 100) cal. than ethylene. Whether the slight difference between propylene and heptene on one side and butene on the other is real and is due to the alternating even-odd effect, is very doubtful. The substitution of the second group in the *cis* or *iso* position (butene-2, cyclohexene, methylethylethylene and isobutene) lowers the heat of hydrogenation by an additional 1700 (± 100) cal., the differential effect of the two positions being too small to be considered real. It is interesting to note that while the increase in length of the straight chain has no effect on the heat of hydrogenation, a branching of it on the carbon adjacent to the double bond has quite a considerable one; thus *unsym*-methylisopropylethylene has a heat of hydrogenation lower by 500 cal. than *unsym*-methylethylethylene. We have, however, only one example of the effect of branched chains and further study is under way.

Two substituted radicals in the *trans* position are found to stabilize the unsaturated hydrocarbon in regard to the paraffin by an additional 950 cal. Only one case (butene-2-*trans*) is here available directly but the data on pentenes-2 may also

be thus tentatively interpreted. If one assumes that the heat of hydrogenation of *cis*-pentene is the same as that of *cis*-butene; also, that the pentenes in the sample studied were present in the same proportions, as were found for butenes (*ca.* 35-65%), then the experimental figure of 27,960 cal. for the mixture of pentenes leads to a value of 27,630 cal. for the *trans*-pentene-2. This is nearer to the heat of hydrogenation of *trans*-butene, 27,620 cal., than one might expect because of the uncertainty of the starting material but shows that one may extend the *cis-trans* difference rule to longer (straight) chains. With branched chains one might expect, of course, different relations. Thus, taking an extreme case, the heat of transformation of isostilbene (*cis*) into stilbene (*trans*) was found to be $\Delta H_{800^\circ} = ca. -3000$ cal.²⁹

It is most unlikely that the heat capacities of the *cis* and the *trans* butenes-2 differ enough to explain the observed change of 950 cal. in the heat of hydrogenation and it is therefore to be ascribed to a difference in interaction energies of the methyl groups in the *cis* and the *trans* position. We are inclined to consider the high-boiling isomer as the *cis* compound because of the following considerations: (1) this assignment is consistent with the synthesis of Lucas; (2) the heat of hydrogenation of the high boiling compound is identical with that of the cyclohexene. Each of these arguments by itself cannot be considered very strong, but together, we believe, they constitute sufficient evidence for a tentative selection. Furthermore, it is much more likely that the methyl groups repel, rather than attract, each other, and inasmuch as in the *cis* position they are nearer together than in the *trans*, this is also consistent with the choice made. The precise orientation of the methyl groups in butane is unknown, but the average distance of the methyl groups is probably between those in the *cis*- and in the *trans*-butenes. Therefore, neither the heat of hydrogenation of the *cis* nor that of the *trans* compounds should be regarded as typical of the *sym*-disubstituted ethylenes; instead, a value somewhat below 28,500 but above 27,500 cal. should be selected. If this argument is accepted, one sees that the substitution of two groups in ethylene on the same carbon atom has a somewhat smaller effect in reducing the heat of hydrogenation. According to the new data of Rossini³⁰ on

(29) Kistiakowsky and Smith, *THIS JOURNAL*, **56**, 638 (1934).

(30) Rossini, *J. Chem. Phys.*, **3**, 438 (1935).

the heats of combustion of butane and isobutane, it is found nevertheless that isobutene is energetically the most stable of the four isomeric butenes. The greater stability of isobutane as compared with that of the straight chain isomer is rather unexpected, however, if the methyl groups repel each other as is here assumed. The strengthening of some other bonds in the molecule must evidently more than compensate this effect.

The introduction of a third substituent alkyl group lowers the heat of hydrogenation further by 700 to 1600 cal. and a fourth brings it down 300 cal. more. It is true that these latter relations are established on the basis of one compound each, but the general applicability of other regularities appears sufficiently well founded so that one may, with some feeling of security, regard these as also applicable to longer substitution groups.

Considering the results as a whole, it is clear that changes in the groups adjacent to the carbon-carbon double bond have profound effects on the energetics of it. In this connection particularly interesting will be a study of the effect of highly branched substituents and such work is planned with the expectation that still lower heats of hydrogenation will be found. The action of an increasing number of substituents is not additive. This precludes the quantitative application of a very interesting suggestion of Eyring³¹ that the varying heats of hydrogenation may be due to different strengths of the carbon-hydrogen bonds in the primary, secondary and tertiary position.

In conclusion we wish to thank Mr. M. A. Dolliver for his able assistance in preparation of organic materials. It is also a pleasant duty to thank Dr. J. B. Conant and Professor E. P. Kohler for many valuable suggestions and criticisms which have materially helped the progress of this work, which was made possible by a grant from the Rockefeller Foundation.

Errata and Addenda

I

(1) Fig. 2, p. 68, Abscissa should be labelled "secs."

(31) Eyring, THIS JOURNAL, 64, 3191 (1932), and a private communication.

(2) Fig. 3, p. 70, "heat capacity" should read "electric energy equivalent."

II

(1) P. 878, vapor pressure equation for low-boiling isomer should read.

$$\log_{10} p = -2505.074/T - 18.78681 \log_{10} T + 0.012991 T + 54.25987$$

(2) In summary, p. 882, under 1, the temperature of 355°K. should be specified.

Summary

1. The reliability of the calorimetric measurements is discussed and some new experiments presented. It is concluded that the originally given estimate of the errors in the case of ethylene is fully justified.

2. The heats of hydrogenation of the following substances have been determined at 355°K. as:

	ΔH , cal./mole
<i>n</i> -Heptene-1	-30,137 \pm 37 (60)
<i>unsym</i> -Methylethylethylene	-28,491 \pm 36 (100)
Pentenes-2 (<i>cis</i> and <i>trans</i>)	-27,954 \pm 28 (100)
<i>unsym</i> -Methylisopropylethylene	-27,997 \pm 24 (100)
Cyclohexene	-28,592 \pm 10 (100)
Trimethylethylene	-26,920 \pm 10 (60)
Tetramethylethylene	-26,633 \pm 19 (100)

The deviations represent calorimetric precision, while the bracketed figures are a crude attempt to estimate total errors.

3. Some generalizations regarding the effects of substitution on the energetics of an ethylenic double bond are proposed. It appears that with increasing number of substituent alkyl groups, the heat of hydrogenation is lowered in a progressive manner. Mono-substitution produces a decrease of 2.7 Cal.; di-substitution 4.2 (*cis*) to 5.2 (*trans*); tri-substitution 5.9 and tetra-substitution 6.2. Thus the differential effect grows smaller with increasing number of substituents. The effect is independent of the chain length of the normal alkyl radical substituted, but branched groups appear to have greater influence.

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