

Benzamides, prepared in the customary manner from the pyrrolidine, benzoyl chloride (1 cc. per g. of amine) and 10% sodium hydroxide solution (10 cc. per g. of amine), were recrystallized from 60–80% ethanol and finally from ethanol alone (see Table II).

When equal weights of the pyrrolidine and phenyl isothiocyanate were mixed, considerable heat was evolved and the mixture usually solidified upon cooling. After being washed with 50% ethanol the phenylthioureas were crystallized from chloroform-ethanol. These derivatives are likewise listed in Table II.

Summary

1. It has been found that diethylamine is a suitable catalyst for the addition of nitroparaffins to α,β -unsaturated ketones.

2. Substituted pyrrolidines were the principal products when a number of γ -nitroketones were reduced over Raney nickel, both in the presence and absence of ammonia.

GREENCASTLE, INDIANA

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Experimental Vapor Heat Capacities and Heats of Vaporization of *n*-Hexane and 2,2-Dimethylbutane¹

BY GUY WADDINGTON AND DONALD R. DOUSLIN

The current thermodynamic program of the Petroleum and Natural Gas Division of the Bureau of Mines includes the measurement of the heat capacities of hydrocarbon vapors. Incidental to the determination of vapor heat capacities accurate values of the heats of vaporization are obtained. A recent publication² describes the flow calorimeter and cycling vaporizer used for determining the above properties.

This paper gives the results of measurements of the vapor heat capacities and heats of vaporization of *n*-hexane and 2,2-dimethylbutane.

Experimental

The Apparatus and Experimental Method.—

The flow calorimeter and vapor cycling system have been described recently in considerable detail, hence only a brief account of the method and apparatus will be given here.

A measured constant flow of hydrocarbon vapor is produced in a glass vaporizing vessel thermally isolated from its surroundings. Normally the vapor is passed through the calorimeter, then condensed and returned to the vaporizer as liquid. The boiling temperature is kept constant by carefully controlling the pressure of helium gas in the static portion of the system. The dependence of rate of flow on the power input to the vaporizer heater is determined by diverting the stream of vapor into a suitable collecting vessel for a measured time interval and weighing the condensed sample of hydrocarbon. From properly corrected values of mass, power and time, accurate values of the heat of vaporization are obtained.

To ascertain the heat capacity of the vapor the temperature rise produced in the flowing vapor by the measured power input to the calorimeter heater is determined. Two platinum resistance thermometers situated directly in the vapor

stream are used to measure the temperature of the vapor after it has passed the heater. By measuring the resistances of the thermometers before and after supplying energy to the heater a value of the temperature increase, accurate to a few thousandths of a degree, is obtained. From the mass of vapor flowing through the calorimeter per unit of time, the power supplied to the calorimeter heater, and the temperature increase of the vapor, values of the apparent heat capacities are calculated. The apparent heat capacities differ from true heat capacities because of heat losses in the calorimeter. By making measurements at four flow rates, covering the range 0.05 to 0.25 mole per minute, data are obtained by which corrections may be made for heat losses. The design of the calorimeter is such that the relationship $C_{P(\text{obs.})} = C_P + k/F$ accurately represents the experimental data, where C_P is the true heat capacity, F is the flow rate and k a constant for a given set of operating conditions. From this it follows that a plot of $C_{P(\text{obs.})}$ vs. $1/F$ extrapolated linearly to zero value of $1/F$ gives the correct value of C_P . To obtain accurate values of C_P^0 , the heat capacity of the vapor in the ideal gas state, heat capacities are determined at two or more pressures and the results extrapolated linearly to zero pressure. The validity of the linear extrapolation has been checked experimentally for a number of compounds.

In the case of 2,2-dimethylbutane the mode of carrying out the heat capacity measurements at 1 atmosphere pressure differed from the other measurements reported in this paper and from the work reported earlier.² Instead of maintaining a fixed boiling temperature in the vaporizer, for a series of measurements at different flow rates, the helium pressure in the system was maintained constant. Because of the pressure head between the vaporizer and the condensers the boiling temperatures were different at different flow rates. This necessitated a correction for the temperature

(1) Approved for publication by the Director of the Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Guy Waddington, Samuel S. Todd and Hugh M. Huffman, *THIS JOURNAL*, **69**, 22 (1947).

coefficient of the heat of vaporization and modified the pressure correction described previously.² The net result of this difference in experimental procedure is that the consistency between the 1-atmosphere measurements and the 293-mm. measurements (carried out one year later) is slightly inferior to that of other compounds studied with this apparatus. This reveals itself when values of $C_P^1 - C_P^0$ are plotted against temperature.

Materials.—The 2,2-dimethylbutane was Phillips Petroleum Company's "Pure Neohexane." After distillation through a 77-plate column at a reflux ratio of 60:1 it had the following constants: d^{20}_4 0.6490; n^{20}_D 1.3687. A melting point determination indicated a purity of 99.70 mole per cent. assuming the impurities to be liquid-soluble, solid-insoluble.

The *n*-hexane, while ostensibly Phillips Petroleum Company's Technical Grade, was a special cut³ which, after dearomatization with silica gel and distillation through a 100-plate column at a reflux ratio of 150:1, had the following properties: d^{20}_4 0.6595, n^{20}_D 1.3748. The purity determined by the freezing point method was 99.77 mole per cent.

Heats of Vaporization.—The determination of the flow of vapor is also a method of obtaining heats of vaporization which differs in some aspects from other modern methods capable of yielding accurate results. To check the accuracy of the method of measuring heats of vaporization used in this work, measurements were made on benzene⁴ at four temperatures, several experiments being carried out at each temperature. The results of all experiments are given in Table I. Rates of flow were in the range 0.05 to 0.08 mole/minute, the mass collected varied from 23 to 45 g. and the time of collection was six to eight minutes. It is seen that the values at 49.9 and 80.1° closely check the experimental points of Fiock, Ginnings and Holton⁵ at these temperatures. Moreover, it may be shown graphically that the four points are in excellent agreement with a value of 8090 cal./mole determined by Osborne and Ginnings⁶ at 25°.

A further direct comparison with results of high accuracy is available in the case of 2,2-dimethylbutane. At 25°, Osborne and Ginnings⁶ find, for this compound, a value of 6617 cal./mole. In the present work a value of 6640 cal./mole was obtained at 22.9°. Using a value of -12.6 cal./mole/deg. (derived from eq. 1) for $d(\Delta H)/dT$

(3) Obtained through the courteous cooperation of J. W. Tooke and A. E. Buell of the Phillips Petroleum Co.

(4) The purity of the sample as determined from a time-temperature freezing curve was 99.93 mole per cent. Thiophene, a common impurity in benzene, forms solid solutions with benzene hence its presence is not revealed by freezing curve studies. A bomb sulfur analysis did not indicate any significant amount of sulfur. The authors thank Mr. E. L. Garton and Miss Shirley Nix of this Station for performing the bomb sulfur analysis.

(5) E. F. Fiock, D. C. Ginnings and W. B. Holton, *J. Research Natl. Bur. Standards*, **6**, 881 (1931).

(6) N. S. Osborne and D. C. Ginnings, *Natl. Bureau of Standards*, unpublished data.

TABLE I
THE HEAT OF VAPORIZATION OF BENZENE⁷

<i>t</i> , °C.	41.6	49.9	60.9	80.1
ΔH_{vap} , cal./mole	7866	7761	7606	7348
	7870	7753	7604	7350
		7751	7608	7350
Mean	7868 \pm 2	7755 \pm 4	7606 \pm 2	7349 \pm 1
Fiock, <i>et al.</i> ⁵		7757		7353

shows these two results to agree within 3 cal. Fiock, Ginnings and Holton estimate the uncertainty of their measurements to be 0.1% or less. This would indicate a maximum uncertainty of about 0.15% for the benzene value at 80.1° from the present work with the possibility of its being less. For other compounds studied the uncertainty in the heats of vaporization should be similar to the benzene results save where impurity in the available sample may have some effect.

Table II summarizes the experimental values of the heat of vaporization for 2,2-dimethylbutane and *n*-hexane. Six⁸ experiments covering a wide range of flow rates are listed for neohexane at the normal boiling point. The ebullition is extremely violent at the highest flow rate and could conceivably lead to entrainment of liquid droplets in the vapor stream, with resulting low values for the heat of vaporization. Many investigators have taken precautions against this effect. The evidence here suggests that the presence of an ade-

TABLE II
THE HEATS OF VAPORIZATION OF 2,2-DIMETHYLBUTANE AND *n*-HEXANE

<i>t</i> , °C.	Flow, moles/min.	ΔH_{vap} , cal./mole	ΔH_{vap} , calcd. eq. 1, 2	ΔH_{vap} , calcd. Clapeyron ^a
2,2-Dimethylbutane				
49.7	0.057	6283		
	.088	6294		
	.112	6292		
	.144	6286		
	.234	6282		
	.378	6287		
	Mean	6287 \pm 7	6287	6288
25.0 (ref. 6)	6617	6616	
22.9	3 expts.	6640 \pm 4	6643	6642
<i>n</i> -Hexane				
68.7	4 expts.	6896 \pm 3	6895	6894
54.8	3 expts.	7115 \pm 3	7115	7116
35.6	3 expts.	7393 \pm 3	7394	7393
25.0 (ref. 6)	7540	7540	7543

^a Since the molal volumes of vapor employed in calculating these values are derived in part from the experimental heats of vaporization of this work and of Osborne and Ginnings⁶ the figures of this column are not an independent check of the experimental values of column 3.

(7) In this paper the following values are used: 1 cal. = 4.1833 int. joules; at. wt. carbon = 12.010; at. wt. hydrogen = 1.008; 0° C. = 273.16° K.

(8) The mean value and the mean deviation of the thirteen experiments actually performed is essentially the same as for the six listed

quate vapor space above the boiling hydrocarbon permits any liquid droplets formed by bursting bubbles to return to the liquid.

Kilpatrick and Pitzer⁹ have measured the vapor pressure of 2,2-dimethylbutane from 1.9 to 225 mm., while Willingham,¹⁰ *et al.*, have measured this property from 217 to 780 mm. Each has proposed an Antoine-type equation to represent the data. The consistency of these two equations in the region where they overlap and of the experimentally obtained value of 6640 cal./mole for the heat of vaporization at 22.9° may be checked by using the Clapeyron equation $\Delta H_{\text{vap.}} = T \Delta V dP/dT$ to obtain heats of vaporization from the two vapor-pressure equations and from the molal volumes of vapor and liquid. The equation of Kilpatrick and Pitzer leads to 6634 cal./mole while that of Willingham and co-workers yields 6642 cal./mole. The agreement is satisfactory. Vapor volumes for 2,2-dimethylbutane were calculated from the equation $PV = RT + BP$, the value of the second virial coefficient being taken as $B = -555 + 6.2 \times 10^8 T^{-1} - 7.07 \times 10^{12} T^{-4}$ (cc.). This is derived from measured heats of vaporization and the variation of heat capacity with pressure as will be shown later in this paper. The use of the Berthelot equation to calculate the volume of the vapor, in the case of this compound, also gives good agreement between calculated and experimental heats of vaporization.

The equation of Willingham, *et al.*,¹⁰ in conjunction with the Clapeyron equation and equation of state data referred to above gives a calculated heat of vaporization of 6288 cal./mole at the normal boiling point in good agreement with the experimental value of 6287 cal./mole given in Table II but disagrees with Pitzer's¹¹ experimental value of 6355 cal./mole.

The equation

$$\Delta H_{\text{vap.}} = 8149 + 2.37T - 0.0252T^2 \quad (1)$$

may be used for interpolation over the range of experimentation. The slight curvature indicated by the equation was arrived at by consideration of vapor pressure and gas imperfection data.

Table II also lists the heat of vaporization of *n*-hexane at four temperatures, that at 25° being from the work of Osborne and Ginnings⁶ while the other three are from this research. The values under $\Delta H_{\text{vap.}}$ calcd. are derived from the Clapeyron equation, using the vapor pressure data of Willingham, *et al.*,¹⁰ and the vapor volumes are obtained by use of a second virial coefficient

$$B = -2270 + 6.25 \times 10^8 T^{-1} - 1.306 \times 10^{13} T^{-4} \text{ (cc.)}$$

The close agreement implies excellent consistency of the data from three laboratories.

Use of the Berthelot equation for calculating the molal volume of the vapor of *n*-hexane leads to

(9) J. E. Kilpatrick and K. S. Pitzer, *THIS JOURNAL*, **68**, 1080 (1946).

(10) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **55**, 219 (1945).

(11) K. S. Pitzer, *THIS JOURNAL*, **68**, 2413 (1941).

a heat of vaporization 0.75% higher than the experimental value at the normal boiling point.

The empirical equation

$$\Delta H_{\text{vap.}} = 8571 + 6.372T - 0.03298T^2 \quad (2)$$

is in almost perfect agreement with the experimental values for *n*-hexane from 25° to the normal boiling point but is not of a form to give accurate values outside of the range of experiment. The figures in column 4 of Table II are from equations (1) and (2).

Lemons with Felsing¹² have measured the heat of vaporization of *n*-hexane over the temperature range covered here with an estimated accuracy of 1%. Their values average about 1% lower than those of this paper.

Vapor Heat Capacities.—Table III gives the experimental values of the molal vapor heat capacities of 2,2-dimethylbutane and *n*-hexane at the various temperatures and pressures used. At most temperatures, measurements were made at two pressures so that C_p^0 , the heat capacity of the gas in the ideal gas state, could be obtained by linear extrapolation to zero pressure. For *n*-hexane at 365.15° K., measurements were made at three pressures and show that, in the pressure range studied, the heat capacity of the vapor is a linear function of pressure. This fact also has been demonstrated for *n*-heptane.²

TABLE III
EXPERIMENTAL HEAT CAPACITIES, CAL./DEG./MOLE
2,2-Dimethylbutane

<i>P</i> , mm.	<i>T</i> , °K. →				
	341.55	353.20	376.05	412.40	449.40
293.4	38.400		41.665	45.075	48.410
760.0	38.870	39.880	41.930	45.275	48.535
<i>n</i> -Hexane					
	333.85	365.15	398.85	433.70	468.90
235.7	37.740	40.440	43.430	46.460	49.505
479.4	38.140	40.685			
760.0		40.950	43.735	46.630	49.600

Since the results are highly precise and since the evaluation of $C_p^1 - C_p^0$ depends on differences, values are given to 0.005 cal./mole/deg. although the absolute accuracy does not approach this. As with other compounds studied,² large scale plots of C_p vs. T for the 1 atm. results for the two compounds give smooth curves slightly concave toward the T axis at high temperatures but tending to curve in the opposite direction at low temperatures due to the greater contributions of gas imperfection in this region.

Heat Capacity in the Ideal Gas State.—From the data of Table III, values of C_p^0 were obtained at each temperature by linear extrapolation from the experimental points to zero pressure. These are listed in Table IV along with values of C_p^1 , the heat capacity at 1 atmosphere. The following

(12) J. F. Lemons with W. A. Felsing, *ibid.* **65**, 46 (1943).

equations may be used to obtain values of C_P^0 by interpolation without loss of accuracy, since the maximum deviation of an experimental point from the curves represented by the equations is 0.035%.

n-Hexane:

$$C_P^0 = 4.280 + 0.10573T - 1.9948 \times 10^{-5}T^2 \quad (3)$$

2,2-Dimethylbutane:

$$C_P^0 = -2.558 + 0.13724T - 5.339 \times 10^{-5}T^2 \quad (4)$$

TABLE IV

HEAT CAPACITIES IN THE IDEAL GAS STATE, CAL./DEG./MOLE

<i>T</i> , °K.	C_P^1	C_P^0	$C_P^1 - C_P^0$		
			Expt.	2nd Virial	Berthelot
<i>n</i> -Hexane					
333.85	38.60	37.35	(1.25)	(1.25)	(0.59)
365.15	40.95	40.22	0.73	0.75	.45
398.85	43.74	43.30	.44	.44	.35
433.70	46.63	46.39	.24	.25	.27
468.90	49.60	49.46	.14	.14	.21
2,2-Dimethylbutane					
341.55	38.87	38.10	0.77	0.73	0.50
353.20	39.88	39.25			.45
376.05	41.93	41.50	.43	.45	.37
412.40	45.28	44.95	.33	.29	.28
449.40	48.54	48.33	.21	.19	.22

Pitzer¹¹ has determined the heat capacity of 2,2-dimethylbutane vapor at three temperatures. The scattering of his points from the results of this work is of the magnitude of his estimated 1% accuracy. Eucken and Sarstedt's¹³ point at 451° K. is about 0.4% higher than the value reported here which is well within their claimed 2% accuracy. The accuracy of this work is estimated as probably within $\pm 0.2\%$.

In a recent paper Kilpatrick and Pitzer⁹ compare C_P^0 values derived from the one atmosphere measurements reported here with their statistically calculated heat capacities of 2,2-dimethylbutane. The correction for gas imperfection was made by use of the Berthelot equation of state. Measurements made later at 293.4 mm. showed the Berthelot correction to be inadequate, the discrepancy amounting to about 0.25 cal./deg./mole at the lowest temperature. This change brings the slopes of the calculated and experimental values into closer agreement.

Eucken and Sarstedt's¹³ value of C_P^0 for *n*-hexane at 451° K. is 2% higher and Bennowitz and Rossner's¹⁴ value at 410° K. is six calories lower than those of Table IV. Pitzer's¹⁵ values calculated by approximate statistical methods range from one cal./deg./mole higher at the lower end of the temperature range to about 0.5 cal./deg./mole higher at the upper end of the range.

(13) Eucken and Sarstedt, *Z. physik. Chem.*, **B50**, 143 (1941).

(14) K. Bennowitz and W. Rossner, *ibid.*, **B39**, 125 (1938).

(15) Kenneth S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

Gas Imperfections.—Two aspects of the foregoing experimental work are intimately related to gas imperfections. The molal volume of the vapor is related to the heat of vaporization by the exact Clapeyron equation $\Delta H_{\text{vap.}} = T(V_g - V_l)$ dP/dT while the variation of heat capacity of the vapor with pressure is given by $(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P$.

From the measured values of $\Delta H_{\text{vap.}}$ and of $(\Delta C_P/\Delta P)_T$ it is possible to determine the temperature dependency of B , in the equation of state $PV = RT + BP$. For a low-pressure vapor, B can be identified with the second virial coefficient with little error.¹⁶ The dependence of heat capacity on pressure in terms of the above equation of state becomes $(\partial C_P/\partial P)_T = -T(\partial^2 B/\partial T^2)_P$.

If B is set equal to $B_0 - A_0/T - C_0/T^n$ the variation of heat capacity with pressure at constant temperature is $2A_0/T^2 + n(n+1)C_0/T^{n+1}$. The value of n which gives a linear plot of $T^2(\Delta C_P/\Delta P)_T$ vs. $1/T^{n-1}$ will give a good fit of the experimental data. For 2,2-dimethylbutane and *n*-hexane n equals four. From this same plot A_0 and C_0 may be readily evaluated. The values of $(\Delta C_P/\Delta P)_T$ are numerically equal to $C_P^1 - C_P^0$ since it has been demonstrated experimentally that C_P is a linear function of pressure at constant temperature. To obtain the remaining constant, B_0 , in the expression for B , a molal volume of the vapor may be determined from a heat of vaporization measurement, by use of the exact Clapeyron relationship, which permits B to be evaluated from the equation of state. B_0 can now be found by difference. In this way, using all the measured heats of vaporization of Table IV to obtain mean values of B_0 , the following equations of state were determined.

$$\textit{n-Hexane: } PV = RT - (2270 - 6.25 \times 10^6 T^{-1} + 1.306 \times 10^{13} T^{-4})P \quad (5)$$

$$\text{2,2-Dimethylbutane: } PV = RT - (567 - 6.2 \times 10^3 T^{-1} + 7.07 \times 10^{12} T^{-4})P \quad (6)$$

The units are P in atm., V in cc. and T in °K.

In Table IV the results of calculating $C_P^1 - C_P^0$ from the above equations are given in the column headed "2nd Virial." The excellent agreement with experimental values for *n*-hexane is an indication of the precision of the measured values of C_P . It is also seen that use of the Berthelot equation does not give highly accurate values of C_P^0 at low temperatures.

In using the Berthelot equation Kay's¹⁷ values for the critical constants of *n*-hexane and 2,2-dimethylbutane were used. The calculated values of $C_P^1 - C_P^0$ for 2,2-dimethylbutane indicate somewhat less precision in the measured values of $C_P^1 - C_P^0$ for this compound. This is probably because the 1-atmosphere measurements were made

(16) Charles F. Curtis and J. O. Hirschfelder, *J. Chem. Phys.*, **8**, 491 (1942).

(17) Webster B. Kay, *THIS JOURNAL*, **68**, 1336 (1946).

a year earlier than the results at lower pressure, using the somewhat less satisfactory experimental procedure referred to previously. It is evident that equations (3) and (4) in conjunction with equations (5) and (6) may be used to obtain the heat capacity of either compound at any temperature and pressure in the range studied. Probably extrapolation to pressures of several atmospheres would give results adequate for many purposes.

The calculated heats of vaporization in Table II provide a further excellent check of the consistency of equations (5) and (6). The calculated values of the heats of vaporization of 2,2-dimethylbutane were obtained by use of a slightly modified version of eq. (6) derived from Osborne and Ginnings⁶ 25° heat of vaporization and the variation of $C_p^1 - C_p^0$ with temperature, thus providing calculated values of the heats of vaporization at 22.9 and 49.7° which are essentially independent of the heats of vaporization measured in this Laboratory.

Acknowledgments.—We wish to thank Mr. R. M. Gooding of this Station for the time and care spent in the purification of the compounds. We also appreciate the assistance given by Mr. Harold Coleman to Mr. Gooding in the determination of purity and physical constants. The valuable suggestions made by Dr. S. S. Todd during the progress of this work and his assist-

ance in making some of the measurements are gratefully acknowledged. The authors appreciate the encouragement and helpful advice given by Dr. H. M. Huffman.

Summary

The heat capacities of the vapors of *n*-hexane and 2,2-dimethylbutane have been measured at several pressures in the temperature range 33 to 470° K.

The experimental values of the heat capacities of the vapors in the ideal gas state deviate from the following empirical equations by less than 0.1%

$$n\text{-Hexane: } C_p^0 = 4.280 + 0.10573T - 1.9948 \times 10^{-5}T^2$$

2,2-Dimethylbutane:

$$C_p^0 = -2.558 + 0.13724T - 5.339 \times 10^{-5}T^2$$

The heats of vaporization of the two compounds have been measured and are represented with an accuracy of approximately $\pm 0.1\%$ in the range from 25° to the normal boiling points by the equations

$$n\text{-Hexane: } \Delta H_{\text{vap.}} = 8571 + 6.372T - 0.03298T^2$$

$$2,2\text{-Dimethylbutane: } \Delta H_{\text{vap.}} = 8149 + 2.37T = 0.0252T^2$$

Second virial coefficients which represent the low temperature, low pressure behavior of the vapors have been obtained from the thermal measurements.

BARTLESVILLE, OKLA.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, HOUSTON REFINERY, SHELL OIL COMPANY, INCORPORATED]

Kinetics and Mechanism of the Thermal Decomposition of *n*-Heptane¹

BY W. G. APPLEBY, W. H. AVERY^{1a} AND W. K. MEERBOTT

Introduction

During the past decade a large number of papers has appeared in the literature which deal with the thermal decomposition of paraffin hydrocarbons. Because of the labor involved in the analysis of the decomposition products, very few investigations have been reported in which complete enough analytical data were obtained to permit conclusions of general validity to be drawn regarding the kinetics and mechanism of the decomposition of the normally liquid paraffins.

If the Rice free radical chain theory predicts the products formed in the decomposition of paraffins, then no saturated compounds other than hydrogen, methane, ethane and propane should be formed in the pyrolysis at atmospheric pressure of paraffin hydrocarbons. This, in turn, would imply that the amount of unreacted paraffin remaining after pyrolysis of a liquid paraffin could be

(1) The work described here was carried out during 1942. Publication has been delayed by the pressure of other work during the war.

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determined from the weight of the liquid product remaining after suitable treatment for removing olefins. The hypothesis that, after treatment of the liquid sample to remove olefins, only unchanged charging stock should remain can be supported by determination of the refractive index of the treated sample. This line of reasoning has been tested by Dintses and co-workers.² Pure normal octane was pyrolyzed to 20% decomposition in a copper reactor. The liquid and gaseous product showed on "most careful analysis" no saturated hydrocarbons other than methane, ethane and propane. Further tests were made on fractions of Baku gasoline (containing 60% naphthenes) that had been treated with concentrated sulfuric acid before pyrolysis. In every case, treatment of the liquid product of the reaction with sulfuric acid left a material identical in refractive index and other physical properties with the original charging stock.

(2) A. I. Dintses and A. V. Frost, *J. Gen. Chem., U. S. S. R.*, **3**, 747 (1933); **4**, 610 (1934); A. I. Dintses and A. V. Zherko, *ibid.*, **6**, 68 (1936).