NOTES

The Heat of Hydrogenation of Diisobutylene

By Bryce L. Crawford, Jr., and George S. Parks

A value for the change in heat content on the hydrogenation of "diisobutylene" to 2,2,4-trimethylpentane was recently needed in connection with a thermodynamic study in this Laboratory. From a critical review of the available combustion data we were able to deduce $\Delta H^\circ_{298} = -28{,}100$ (± 3000) cal. for the reaction involving the diisobutylene and isooctane in the liquid state. In view of the uncertainty in such a value, we decided to attempt also a direct calorimetric measurement for the heat of this reaction.

A 500-cc. Pyrex flask served as the calorimeter proper and the reaction chamber; initially in a determination it contained 150 cc. of liquid diisobutylene, which was gradually hydrogenated to yield a solution of 2,2,4-trimethylpentane in diisobutylene. This reaction flask was fastened to a shaking device and was equipped with a water jacket, adjustable in temperature, so that the calorimetric procedure could be made approximately adiabatic in character. Purified hydrogen was led into it from a gas train through a flexible glass connecting-tube; and the temperature rise, coinciding in time with the adsorption of measured quantities of hydrogen, was determined by a copper–constantan thermocouple in conjunction with a White potentiometer. The temperature relations of the calorimeter and jacket were also determined by a thermocouple and the temperature adjustment of the jacket was made by regulated electrical heating. The hydrogenation process was catalyzed by freshly prepared platinum black, suspended in the olefin in the reaction flask. The process was carried out between 24 and 35°. Calibration of the calorimetric apparatus was made electrically in a series of blank experiments in which pure trimethylpentane was substituted for the olefin, correction being made for the small difference in the heat capacities of these hydrocarbons.

Three series of determinations, involving fifteen "runs," yielded an average value of $\Delta H^\circ_{298} = -28{,}580$ cal. for the reaction

$$C_8H_{16}\ (l) + H_2\ (g) = C_8H_{18}\ (l)$$

on the assumption that the trimethylpentane–diisobutylene solution is approximately perfect. As shown by Fenske, Quiggle and Tongberg [*Ind. Eng. Chem.*, **24**, 414 (1932)], the diisobutylene is really a mixture containing 4 parts of 2,4,4-trimethylpentene-1 and 1 part of 2,4,4-trimethylpentene-2. The heats of hydrogenation of these two olefins may differ by perhaps 500 cal., if we may judge by the very precise results obtained for the isomeric butenes by Kistiakowsky, Ruhoff, Smith and Vaughan [This Journal, **57**, 876 (1935)]. Considering this factor and also the experimental errors incidental to the measurements, we believe that the maximum error in the above ΔH°_{298} value, when this is assigned to the hydrogenation of the 2,4,4-trimethylpentene-1, is within 800 cal. Such a result is considerably more reliable than that obtainable from the combustion data, although at present much less accurate than the hydrogenation values obtained by Kistiakowsky and collaborators with their vapor phase apparatus at 355°K. It might be noted in this connection that our value for diisobutylene is probably most comparable, on theoretical grounds, with theirs for isobutene (about $-28{,}140$ cal. per mole calculated to 298°K.).

Before concluding, we wish to thank Mr. Benjamin Holt and Mr. Harold Scheeline for their help in the measurements.

Department of Chemistry
Stanford University
Stanford University, Calif.

Received December 16, 1935

The Preparation of the Isomeric Hexanes

By Paul L. Cramer and Maurice J. Mulligan

In connection with the studies in this Laboratory of the aliphatic hydrocarbons, the isomeric hexanes have been prepared in large amounts and of a high degree of purity, and it seemed desirable to indicate the methods of preparation and also to present their physical constants, which in a few instances vary somewhat from previously recorded values, Table I.

The general alcohol–olefin–paraffin method was employed in their syntheses. The alcohols were prepared by the usual methods and their dehydrations were carried out by the procedures indicated in Table I. The main side reaction product

TABLE I

Dehydration of alcohols			Olefins		Hexanes			
Alcohol	T., °C.	Catalyst	B. p., °C.	Yield, %	Name	B. p., °C.	d^{20}_4	n^{20}_D
Ethyl-*n*-propylcarbinol	350	Al_2O_3	63–68	92	*n*-Hexane	68.74–68.78	0.6595	1.3752
Dimethyl-*n*-propylcarbinol	122	I_2	64–66	94	2-Methylpentane	60.22–60.26	.6532	1.3718
Methyldiethylcarbinol	120	I_2	65–69	95	3-Methylpentane	63.16–63.21	.6642	1.3775
Pinacol	130–150	HBr	70.4	55	2,3-Dimethylbutane	57.82–58.02	.6612	1.3750
Pinacolyl[a]	400	...	40.8–41	96	2,2-Dimethylbutane	49.80–49.82	.6493	1.3692

[a] Alcohol converted to the acetate and the ester pyrolyzed to obtain the olefin.

formed in the dehydration of pinacol[1] is pinacolone, which was utilized in the preparation of pinacolyl alcohol. *t*-Butylethylene was prepared by the thermal decomposition of pinacolyl acetate.[2] Eighty per cent. of the acetate was converted to the olefin and acetic acid by one passage through the reaction tube, packed with glass wool, and the unchanged acetate was recovered in nearly theoretical amounts. The olefins were readily hydrogenated to the corresponding hexanes by means of platinum oxide catalyst[3] and the products were finally purified by washing with sulfuric acid and refluxing over sodium.

The fractionation of the hexanes was carried out in a small glass spiral column having an efficiency of twenty theoretical plates, and the boiling points, appropriately corrected, are those of at least 95% of the chemically purified products. The densities were determined by the pycnometric method, and the refractive indices were obtained by means of an Abbe refractometer.

(1) Kyriakides, THIS JOURNAL, **36**, 980 (1914).

(2) Whitmore and Rothrock, *ibid.*, **55**, 1106 (1933).

(3) Adams and Shriner, *ibid.*, **45**, 2171 (1923).

RESEARCH DIVISION
GENERAL MOTORS CORPORATION
DETROIT, MICHIGAN

RECEIVED NOVEMBER 2, 1935

The Vapor Pressure of Silicon Tetrachloride

BY K. KEARBY

The vapor pressure of silicon tetrachloride has been measured by Regnault,[1] Becker and Meyer,[2] and Stock, Somieski and Wintgen.[3] The values obtained by the first and last of these investigators are in fair agreement. Those of Becker and Meyer are much higher, namely, by 50% at 0°, 20% at 10° and 10% at 20°. Their measurements were made on a sample of silicon tetrachloride which they considered of excellent quality. The measurements of Stock, Somieski and Wintgen were made on only 0.3 g. of silicon tetrachloride which they considered pure, but they do not describe the method of purifying it. Thus it is seen that considerable discrepancy exists among the available data.

Recently[4] the author had occasion to prepare some very pure silicon tetrachloride and make a few vapor pressure measurements on it. Later, with a view of clearing up the above situation, additional measurements were made.

Materials and Apparatus

A kilogram of silicon tetrachloride, 99.3% pure, was refluxed over mercury in a current of pure, dry nitrogen for four hours. It was then fractionally distilled in a series of wetted wall, glass fractionating columns, using large reflux ratios. Three fractionations were made in an atmosphere of pure nitrogen, and three *in vacuo*. The last fraction yielded about 25 cc. of pure silicon tetrachloride which was sealed off in several thin bulbs which were attached to the evacuated system. Freshly distilled mercury was used in the manometer, the pressures on which were read with a cathetometer accurate to 0.1 mm. The manometer and the tube to which it was attached, containing the bulb of silicon tetrachloride, were thoroughly evacuated and torched before breaking the bulb of silicon tetrachloride. This apparatus was placed in a thermostat constant within 0.02°. Temperatures were measured on a calibrated thermometer accurate to 0.02°.

The pressures thus measured, expressed in millimeters of mercury at 0° and a force of gravity of 980.665 cm. per sec. per sec. are given in the table.

TABLE I

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
0	77	35	346
5	98	40	419
10	124	45	501
15	153	50	599
20	191	55	709
25	235	60	839
30	287		

These results can be expressed, with a maximum deviation of 1%, by the empirical equation $\log p = 7.6414 - 1572.3/T$. From this equation the

(1) H. V. Regnault, *Mem. de l'acad. royale des Sciences de l'Institut de France*, **26**, 339 (1862).

(2) W. Becker and J. Meyer, *Z. anorg. allgem. Chem.*, **43**, 251 (1905).

(3) A. Stock, Somieski and Wintgen, *Ber.*, **50**, 1754 (1917).

(4) S. S. Kistler and K. Kearby, *Acta Physicochimica (U. R. S. S.)*, **1**, 354 (1934).