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.

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The Preparation of the Isomeric Hexanes

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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