EQUILIBRIUM CONSTANTS IN THE REACTIONS

3-METHYLHEXANE = 2-METHYLHEXANE

AND

2,3-DIMETHYLPENTANE = 2,4-DIMETHYLPENTANE

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## ABSTRACT

Equilibrium constants have been measured for the reactions,
3-methylhexane = 2-methylhexane, and 2,3-dimethylpentane =
2,4-dimethylpentane. The values were determined by direct
equilibration employing sulfuric acid at 60°, chlorosul-
fonic acid at -33.4° and an equimolar mixture of the two
at 0°.

The results are:

|  | 3MH = 2MH | | | 23MP = 24MP | | |
|---|---|---|---|---|---|---|
| Temp.° | $X_{2MH}^{eq}$ | K | $\Delta F°$ | $X_{2MH}^{eq}$ | K | $\Delta F°$ |
| 60 | 0.595 | 1.47 | -255 | 0.596 | 1.48 | -260 |
| 0 | .628 | 1.69 | -285 | .706 | 2.40 | -475 |
| -33.4 | .655 | 1.90 | -306 | .728 | 2.68 | -470 |

Sulfuric acid and chlorosulfonic acid specifically interconvert methylalkanes.[2,3,4] Change of chain branching as in the conversion

(2) R.L. Burwell, Jr. and G.S. Gordon, III, J. Am. Chem. Soc., 70, 3128 (1948); Gordon and Burwell, ibid., 71, 2355 (1949).
(3) R.L. Burwell, Jr., Robert B. Scott, Lucien G. Maury and Allen S. Hussey, Technical Report No. 2 of this project.
(4) R.L. Burwell, Jr., Lucien G. Maury and Robert B. Scott, Technical Report No. 4 of this project.

of the 2- and 3-methylhexane pair to the 2,3- and 2,4-dimethylpentane pair occurs much more slowly. It, thus, seemed desirable to test the applicability of this discovery to the determination of the equilibrium constants of the following two reactions by direct equilibration.

$$\text{3-Methylhexane} \rightleftharpoons \text{2-Methylhexane} \tag{1}$$

$$\text{2,3-Dimethylpentane} \rightleftharpoons \text{2,4-Dimethylpentane} \tag{2}$$
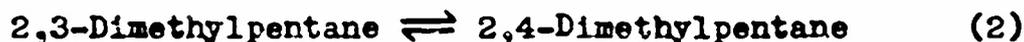
Voorthuijsen[5] determined the equilibrium constants of these

(5) J.J.B. Voorthuijsen, Rec. trav. chim., 66, 323 (1947).

reactions by direct equilibration of all heptanes by aluminum chloride at 20°. The more specific nature of the reaction with sulfuric acid offered hope of increased assuracy. The equilibrium constants have accordingly been measured at 60°, 0° and -33.4°.

## Experimental

The preparation of the hydrocarbons has been described.[3] The infrared absorption spectra were indistinguishable from those of the Bureau of Standards standard samples and no ultraviolet absorption was exhibited at wave lengths longer than 2200 A.

As isomerizing agents, 96.04% sulfuric acid was employed at 60°, an equimolar mixture of this acid and freshly distilled Eastman Kodak

Practical Grade Chlorosulfonic acid was employed at $0^c$, and the chlorosulfonic acid alone was employed at $-33.4°$. Thermostating was by a water bath at $60°$, by an ice-water mixture at $0°$ and by refluxing ammonia at $-33.4°$.

The value of the equilibrium constant was first approximated from the relative initial rates of isomerization of the two hydrocarbons involved by the relation $K = k_1/k_{-1}$. Mixtures of known composition on either side of the estimated equilibrium composition were prepared and subjected to the isomerizing conditions. According to the observed changes in composition, the estimated equilibrium composition was revised and new mixtures prepared. These were then subjected to isomerizing conditions. By this means, it was possible to employ short times of contact and relatively mild condition and, thus, to minimize side reactions.

Reaction flasks and stirring procedures have been described.[8] To avoid preferential vapor loss of one component, ratios of gas to liquid volume were kept low, never exceeding 15 to 1.

The flask and acid were brought to temperature before the hydrocarbon mixture was added. After "emulsification" by magnetic stirring for the desired time, stirring was stopped and a sample of the hydrocarbon layer was pipetted into a cold 30% solution of potassium hydroxide. The hydrocarbon layer was then removed and stored over solid potassium hydroxide before analysis. Precautions were taken throughout to prevent change in composition of the hydrocarbon sample after removal from the thermostated reactor either by isomerization or preferential vapor loss.

Analysis.- An infrared spectrometric technique was employed[3] using a pair of matched cells and substitution against a standard mixture. As appropriate, this was 59.18 mole% 2-methylhexane and 40.82 mole% 3-methylhexane or 62.13 mole% 2,4-dimethylpentane and 37.87 mole% 2,3-dimethylpentane. In the first system, measurements were made at 7.43, 8.63, 10.43, 11.09 and 12.98 m. ons; in the second, at 8.68, 9.02, 9.96, 10.46, 12.38 and 12.78.

In the methylhexane system, a plot of log % transmission vs. %2-methylhexane was prepared at each of the five wave lengths. The standard mixture was always in Cell A and the transmission was always adjusted to read 100% with Cell A in the beam. The plots were prepared from readings with the various synthetic mixtures prepared for isomerization runs in Cell B. Average deviations from smooth curves was less then 0.1%. Analyses could be performed on synthetic mixtures giving agreeing results to this accuracy at all wave lengths. With products of isomerization runs, particularly those extending over longer periods of time, there was some spread in the values determined for each wave length owing to side reactions.

## Results and Discussion

By exposing mixtures of hydrocarbons in the vicinity of the equilibrium mixture to isomerizing conditions for relatively short times, the position of the steady state has been located with minimum interference by side reactions. We feel that the position of the steady state, so located, is accurate to within a few tenths of 1%. The experimental data are shown in Tables I and II.

However, as Bates has pointed out,[6] in the presence of side

(6) J.R. Bates, J. Am. Chem. Soc., 68, 511 (1946).

## Table I

### The 2-Methylhexane-3-Methylhexane Equilibrium

| Temp. ° | Reaction Time, Hours | Reactant Mixture, % 2-Methylhexane | Product Mixture, Av. % 2MH | Average Deviation% |
|---|---|---|---|---|
| 60 | 1.00 | 56.7 | 58.0 | 0.4 |
| | 1.00 | 60.4 | 60.0 | .3 |
| | .50 | 59.2 | 59.5 | .1 |
| | .50 | 59.8 | 59.6 | .3 |
| 0 | .67 | 65.6 | 64.6 | .8 |
| | .33 | 63.5 | 62.8 | .4 |
| | .25 | 62.7 | 62.8 | .2 |
| -33.4 | .67 | 60.5 | 62.0 | .4 |
| | 1.00 | 65.3 | 65.5 | .7 |
| | .50 | 65.7 | 65.5 | .3 |
| | 1.00 | 65.4 | 65.5 | .2 |

## Table II

### The 2,3-Dimethylpentane-2,4-Dimethylpentane Equilibrium

| Temp. ° | Reaction Time, Hours | Reactant Mixture, %2,4-Dimethylpentane | Product Mixture, Av. % 2,4MH | Average Deviation% |
|---|---|---|---|---|
| 60. | .16 | 60.2 | 60.0 | 0.1 |
| | .16 | 59.5 | 59.6 | .2 |
| | .16 | 59.8 | 59.7 | .2 |
| 0. | .16 | 70.5 | 70.6 | .1 |
| | .16 | 70.8 | 70.6 | .1 |
| | .16 | 70.6 | 70.6 | .1 |
| −33.4 | .16 | 74.2 | 73.0 | .2 |
| | .16 | 71.4 | 72.2 | .2 |
| | .16 | 72.7 | 72.8 | .1 |
| | .16 | 73.1 | 72.9 | .1 |

reactions, the steady state does not necessarily correspond to the equilibrium composition. Since the interconversion of 2- and 3-methylhexane proceeds about 10 times as fast as the formation of dimethylpentanes,[3] the error introduced into the equilibrium constant is small.[5] Furthermore, at 60°, at any rate, if the mechanism advanced[3] is correct, no error is introduced. The small spread in the analyses at different wave lengths (Tables I and II) would indicate that no serious error was introduced by side reactions.

Computed equilibrium compositions and constants are presented in Table III where they are compared with the values of Voorthuijsen,[5]

## Table III

### Equilibrium Results

| Temp. ° | 3MH = 2MH[a] | | | 23MP = 24MP[b] | | |
|---|---|---|---|---|---|---|
| | $X_{2MH}^{eq}$ | $\underline{K}$ | $\Delta \underline{F}^{o}$ cal. | $X_{24MP}^{eq}$ | $\underline{K}$ | $\Delta \underline{F}^{o}$ |
| 60[c] | 0.595 | 1.47 | -255 | 0.596 | 1.48 | -260 |
| 0[c] | .628 | 1.69 | -285 | .706 | 2.40 | -475 |
| -33.4[c] | .655 | 1.90 | -306 | .728 | 2.68 | -470 |
| 25[d] | | 1.35 | -180 | | 1.90 | -380 |
| 20[e] | | 1.63 | -284 | | 1.50 | -236 |
| 60[f] | | 1.05 | -29 | | 0.25 | +921 |
| 0[f] | | 1.27 | -130 | | .29 | +668 |
| -33.4[f] | | 1.49 | -191 | | .33 | +525 |

[a] 2MH and 3MH are 2- and 3-methylhexane, respectively.

[b] 23MP and 24MP are 2,3- and 2,4-dimethylpentane, respectively.

[c] Results of this investigation.

[d] Voorthuijsen (ref. 5).

[e] Roebuck and Evering (ref. 7).

[f] Rossini, et al. (ref. 8).

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the recent values of Roebuck and Evering,[7] and the computed values

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(7) A.K. Roebuck and B.L. Evering, ibid., 75, 1631 (1953). These
    values were obtained by direct equilibration with sulfuric acid.

of Rossini.[8]

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(8) American Petroleum Institute, Research Project 44 at the
    National Bureau of Standards, "Selected Values of Properties of
    Hydrocarbons." F.R. Rossini, E.J.R.Prosen and K.S. Pitzer,
    J. Res. Nat. Bureau of Standards. 27, 529 (1941). The values
    of $\triangle F^0$ for the vapor state were corrected by the Antoine
    Equation from the first cited reference to the liquid state
    assuming Raoult's Law.
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In terms of the experimental procedures employed, the experi-
mental results of previous investigators should not be taken as
diverging seriously from our results since the deviation in $K$
corresponds to a deviation in $X^{eq}$ of but a few %. Similarly the
computed results of Rossini[8] may be taken as in quite satisfactory
agreement for the equilibrium between the methylhexanes. The dis-
crepancy in the case of the dimethylpentanes is larger and amounts
to about 1000 cal. in terms of $\triangle \underline{F}^0$.

To within the accuracy of the data, the values of $\triangle \underline{F}^0$ for
the methylhexane reaction are representable by $\triangle \underline{H}^0 = -436$ cal.
and $\triangle \underline{S}^0 = +0.55$ cal./deg. Standard states are the pure liquids.

The rate of change of $\triangle \underline{F}^0$ with temperature is too large to
permit an accurate computation of values of $\triangle \underline{H}^0$ and $\triangle \underline{S}^0$ from
the data for the dimethylpentanes. $\triangle \underline{S}^0$ changes sign in the
vicinity of 0° at which temperature $\triangle \underline{H}^0$ has a value of about
-475 cal.

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