JOURNAL OF CATALYSIS 5, 428–446 (1966)

# The Mechanisms of Hydrogenolysis and Isomerization of Hydrocarbons on Metals

## II. Mechanisms of Isomerization of Hexanes on Platinum Catalysts

Y. BARRON, G. MAIRE, J. M. MULLER, AND F. G. GAULT

*From the Department of Chemistry, Université de Caen, Caen, France*

Received July 8, 1965; revised September 28, 1965

The isomerization of *n*-hexane (I), 2-methylpentane (II), and 3-methylpentane (III) were studied on various supported platinum catalysts, and the initial product distributions compared and identified with the initial distributions of the hydrogenolysis of methylcyclopentane.

These results suggest that a common cyclopentane intermediate is involved in both reactions, adsorbed on the metal sites of the catalysts. The absence of 2,3-dimethylbutane in the product distributions, the simultaneous dehydrocyclization of (I), (II), and (III) to methylcyclopentane, and the difficulty of isomerizing the 2,3-dimethylbutane under the same conditions, are consistent with the proposed mechanism.

On platinum films, another type of skeletal rearrangement also takes place: 2,3-dimethylbutane is formed from the hexanes, and benzene from methylcyclopentane. The mechanism probably involves a species adsorbed on two carbon atoms in the $\alpha,\gamma$ positions and is very similar in its effects to a carbonium ion mechanism.

Only aromatization occurs when 1,1,3-trimethylcyclopentane reacts with hydrogen on a platinum film at 300°C, and that is a further proof of the possibility of ring enlargement on metal catalysts.

### INTRODUCTION

The isomerization of saturated hydrocarbons on acidic catalysts such as silica-alumina has been extensively studied and the mechanisms of these reactions involve carbonium ions as intermediates. Similar reactions take place at a much lower temperature, when a metal has been deposited on these acidic catalysts. It is widely believed that on these "dual-function" catalysts, the only part played by the metal is to dehydrogenate the saturated hydrocarbons to olefins which are then isomerized, via carbonium intermediates, on the acidic sites. So, very little attention has been paid to a possible catalytic effect of the metal itself in the isomerization.

However, platinum-on-alumina catalysts are active in these reactions at very low temperatures (280°C), where the acidic properties of the carrier are doubtful. On the other hand, Anderson and Baker have shown that isomerization of acyclic hydrocarbons (butanes, neopentane) may occur on metal films (*1*, *2*).

In a preliminary note in this journal (*3*), we gave some arguments in favor of a mechanism of isomerization of hexanes involving cyclopentane intermediates adsorbed on the platinum itself. Since then the mechanisms of hydrogenolysis of cycloalkanes have been studied (*4*) and we are now able to develop this idea, by relating the isomerization of hexanes to the hydrogenolysis of methylcyclopentane on various supported platinum catalysts and on platinum films. The aromatization of acyclic and cyclic hydrocarbons takes place under the same conditions as isomerization and will also be considered; it will also be interesting to examine the part played by the metal in this reaction, since the mechanism of aromatization is often taken as an example of a dual mechanism.

## EXPERIMENTAL

### *Apparatus*

The reactions on evaporated films were studied with a static system; the connection of the reaction vessel (200 cc) to the source of a mass spectrometer, as described by Kemball (*5*), enabled following the reaction without any interruption; at the end of the run, the reaction mixture was trapped away and analyzed by gas chromatography. The standard reaction mixture was 6 torr of hydrocarbon and 60 torr of hydrogen.

In the experiments on supported catalysts, a microcatalytic reactor was employed, in conjunction with a gas-liquid chromatograph using hydrogen as carrier gas. The technique has been described elsewhere (*4*). The product distribution was reproducible within ±3%, and the overall conversion within ±10% over a long period of time (several weeks), on any supported catalysts, except on dispersed platinum-alumina catalysts (0.2–1%). When brought to a temperature of 300°C and above, the latter catalysts are slowly deactivated and the product distributions modified in both reactions of methylcyclopentane hydrogenolysis and hexane isomerization (*4*).

When pumice was used as a carrier, instead of alumina, the section of the microreactor had to be multiplied by a factor of 3 and the amount of catalyst by a factor of 10, so that the same temperature range could be used for the isomerization on platinum-pumice and platinum-alumina. Thus there is an apparent difference of activity between the two catalysts. This difference represents, in fact, a difference in the adsorptive properties of the carriers: It was found that hydrocarbons, when passed through the same microreactor and the same amount of solid, with a same flow rate of hydrogen, stayed 120 times longer on alumina than on pumice.

### *Catalysts*

The method of evaporating the platinum films has been previously described (*5*); the supported platinum catalysts have been prepared according to Pines, Olberg, and Ipatieff (*6*).

Platinum wire was spec. pure sample from Johnson Matthey; pure grade platinum chloride and $\gamma$ alumina were obtained from, respectively, Caplain-St-André and Woelm.

### *Materials*

3-Methylpentane and methylcyclopentane were prepared from MEK and cyclopentanone by condensation with the appropriate Grignard reagent, dehydration, and hydrogenation. Methyl isobutyl ketone was reduced to 2-methylpentane according to Huang-Minlon (*7*). 2,3-dimethylbutane, 2,2-dimethylbutane, and *n*-hexane of a high purity were obtained from Fluka.

The preparation of 1,1,3 trimethylcyclopentane has been previously described (*8*).

Any hydrocarbon was purified by gas chromatography before use and, in the experiments on platinum films, outgassed and stored in liquid nitrogen. Cylinder hydrogen was purified on platinum-alumina catalysts (supported catalysts) or diffused through a palladium thimble (platinum films).

### *Gas Chromatography*

In the microreactor technique, hydrogen was used as carrier gas and a conductivity cell as detector; the pressure at the entrance of the column and in the microreactor was 1 atm, the depression 60 cm of mercury. The reaction mixture removed from the static system was analyzed using a flame-ionization detector and nitrogen as carrier gas; the pressure at the entrance of the column was then 1.4 to 1.8 atm, according to the column used.

The five hexanes, methylcyclopentane, and benzene were well resolved on a 5-m silicone oil column at room temperature, but cyclopentane could not be separated from 2,3-dimethylbutane under these conditions. A 5-m glutaronitrile propylene carbonate column (*11*) was used to resolve both hydrocarbons, whenever they were present in the reaction mixture, i.e., in isomerization of hexanes on films; the retention times of the cyclic hydrocarbons were very high on this column, and it could be checked that 2,3-dimethylbutane and not cyclopentane was formed in the reaction. The separation of the three xylenes and toluene was performed on a 5-m Bentone column (*9*).

### *Mass Spectrometrical Analysis*

**a. In the hydrogenolysis of methylcyclopentane.** On platinum films at 270°C, the five isomeric hexanes, benzene, and hydrocarbons of lower molecular weight were formed; small amounts of hexenes and methylcyclopentenes were also present in the reaction mixture at higher temperatures, in equilibrium with the corresponding paraffins and, in the analytical data, they were included in the per cents of the corresponding saturated hydrocarbons.

Ions at masses 86, 84, and 78 were used to determine the amounts of hexanes, methylcyclopentane, and benzene at any time. The sensitivities were determined by comparing the mass spectrum of the reaction mixture at the end of the reaction, with its gas chromatographic analysis, performed after hydrogenation of the small amounts of olefins present. Thus the per cent of total hexanes, methylcyclopentane, and benzene in the gas phase were known at any time, provided that the distributions of the hexanes remained constant throughout the reaction; the error introduced with this assumption was estimated at less than 2%. An attempt was made to analyze the five hexanes continuously using various fragments; unfortunately, it was found that the fragmentation for a hexane isomer changed in the presence of the other four, so that the analysis could not be performed by solving a system of linear equations.

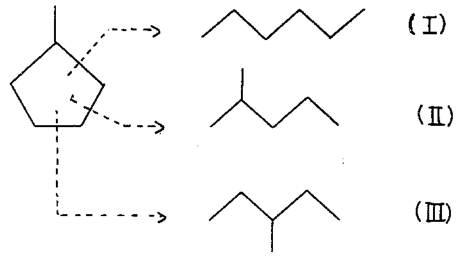
**b. In isomerization of 2-methylpentane, 3-methylpentane, and *n*-hexane.** The four other hexanes, methylcyclopentane, benzene (and small amounts of hexenes and methylcyclopentenes) were formed in isomerization. Benzene and methylcyclopentane were analyzed by the ions at masses 78 and 84, after corrections for the hexenes parent peaks and the second fragment of the hexanes.

In one experiment of isomerization of 3-methylpentane, the amounts of isomeric hexanes were determined at any time by using the ions at masses 71 and 86: At the end of the run, the reaction mixture was analyzed by gas chromatography; the relative ionic abundances at masses 86 and 71 for the mixture of isomerized hexanes could thus be calculated and the sensitivities of this mixture relative to 3-methylpentane determined by comparing the mass spectra and gas chromatographic analysis of the final reaction mixture. In this case again, it was supposed that the distribution of the isomerized hexanes was independent of time, and this assumption introduced an error of 1% to 5% in the analysis.

## RESULTS

### *A. Isomerization of Hexanes on Supported Platinum Catalysts: Comparison of the Product Distributions in the Hydrogenolysis of Methylcyclopentane and in the Isomerization of Hexanes*

*n*-Hexane (I), 2-methylpentane (II), and 3-methylpentane (III) were obtained as the main reaction products in the hydrogenolysis of methylcyclopentane on supported platinum catalysts at 290–330°C. In the same conditions, any of these three hexanes gave the other two by isomerization and was simultaneously dehydrocyclized to methylcyclopentane.



Less than 2% of 2,3-dimethylbutane was formed in both reactions. Cracking to hydrocarbons of lower molecular weight and dehydrocyclization to benzene also occurred, especially at higher temperatures.

The distributions of the hexanes obtained in hydrogenolysis and in isomerization will be compared at the same contact time and initially. We take $x_1$, $x_2$, and $x_3$ as the concentrations of (I), (II), and (III), expressed as mole fractions of the reaction mixture; the ratios $r_3 = x_2/x_1$, $r_2 = x_3/x_1$, $r_1 = x_2/x_3$, obtained in the hydrogenolysis of methylcyclopentane will be considered in the following sections. The isomerization of *n*-hexane (I) will be characterized by the ratio $r'_1 = x_2/x_3$ of the two main reaction products; similarly, $r'_2 = x_3/x_1$ will be envisaged in the isomerization of (II), and $r'_3 = x_2/x_1$ in that of (III). Thus the ratios $r_1$, $r_2$, $r_3$, obtained in hydrogenolysis will be compared to the ratios $r'_3 = x_2/x_1$, $r'_2 = x_3/x_1$, $r'_1 = x_2/x_3$ obtained in the isomerization of, respectively, *n*-hexane (I), 2 methylpentane (II), and 3 methylpentane (III).

### 1. *Comparison for the Same Contact Time*

In the first series of experiments the three hexanes (I), (II), (III), and methylcyclopentane were successively passed on the same amount of a 1% platinum-alumina catalyst, under the same flow conditions. The product distributions were thus compared for the same contact time; varying the temperature of the microreactor varied the conversion and the product distributions.

For every experiment at a given temperature, the ratios $r'_1$, $r'_2$, $r'_3$ obtained in isomerization of hexanes, were very close to the ratios $r_1$, $r_2$, $r_3$ obtained in the hydrogenolysis of methylcyclopentane. Such an experiment is represented in an $XOY$ diagram (Fig. 1a) by three plots: $X_1 = r'_1$, $Y_1 = r_1$; $X_2 = r'_2$, $Y_2 = r_2$; $X_3 = r'_3$, $Y_3 = r_3$. All the plots, corresponding to various temperatures between 269° and 325°C, are grouped near the bisectrix in the diagram.

Figures 1b and 1c represent similar experiments on 10% platinum-alumina (286–360°C) and on 10% platinum-pumice (270–345°C). It is of interest that the product distributions, though widely varying from one catalyst to another, and especially from a 1% to a 10% platinum-alumina catalyst are very close in isomerization and hydro-

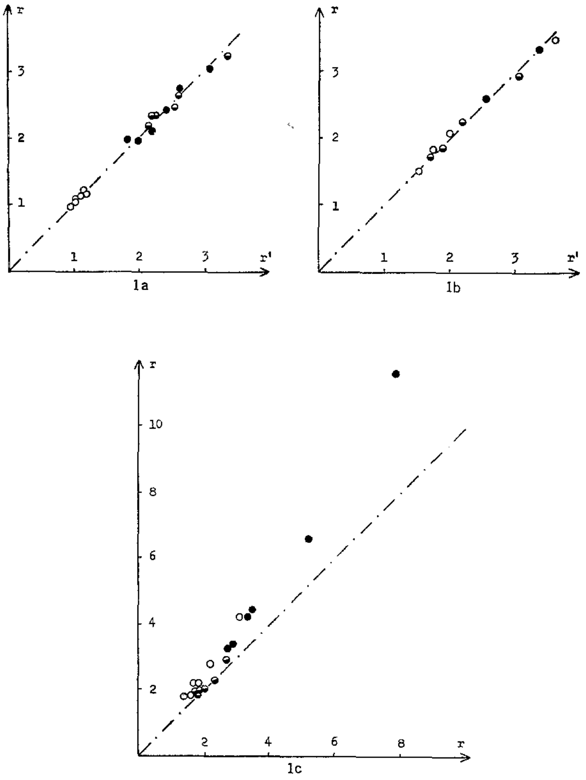


FIG. 1. Comparison of hydrogenolysis and isomerization for a same contact time: (1a), 1% platinum on alumina; (1b), 10% platinum on pumice; (1c), 10% platinum on alumina. ○, $Y_2 = r_2$ (hydrogenolysis); $X_2 = r'_2$ (isomerization of II); ◒, $Y_1 = r_1$ (hydrog.); $X_1 = r'_1$ (isom. of I); ●, $Y_3 = r_3$ (hydrog.); $X_3 = r'_3$ (isom. of III).

genolysis. However, at the lower temperatures on 10% platinum-alumina, the differences between $r_2$, $r_3$ and $r'_2$, $r'_3$ were beyond the experimental errors.

In any case, the observed distributions were very different from the equilibrium distribution.

### *2. Comparison of the Initial Distributions of Hydrogenolysis and Isomerization*

In the preceding experiments, the conversion was never negligible and readsorption of the primary products took place. It thus seemed necessary to determine the initial product distributions in hydrogenolysis and isomerization.

In the hydrogenolysis of methylcyclopentane, the ratios $r_1$, $r_2$, and $r_3$ were determined as functions of the conversion

$$\rho = \frac{x_1 + x_2 + x_3}{x_1 + x_2 + x_3 + x_4}$$

$x_4$ being the mole fraction of methylcyclopentane.

Similarly, in the isomerization of *n*-hexane, 2-methylpentane, and 3-methylpentane, $r'_1$, $r'_2$, $r'_3$ were determined as functions of, respectively,

$$\rho'_1 = \frac{x_2 + x_3}{x_1 + x_2 + x_3} \quad \rho'_2 = \frac{x_1 + x_3}{x_1 + x_2 + x_3}$$

$$\rho'_3 = \frac{x_1 + x_2}{x_1 + x_2 + x_3}$$

**a. 0.2% Platinum on alumina.** Figures 2a to 2c represent the product distributions obtained in hydrogenolysis and isomerization on a 0.2% platinum-alumina catalyst at 300°C. The initial values for the different

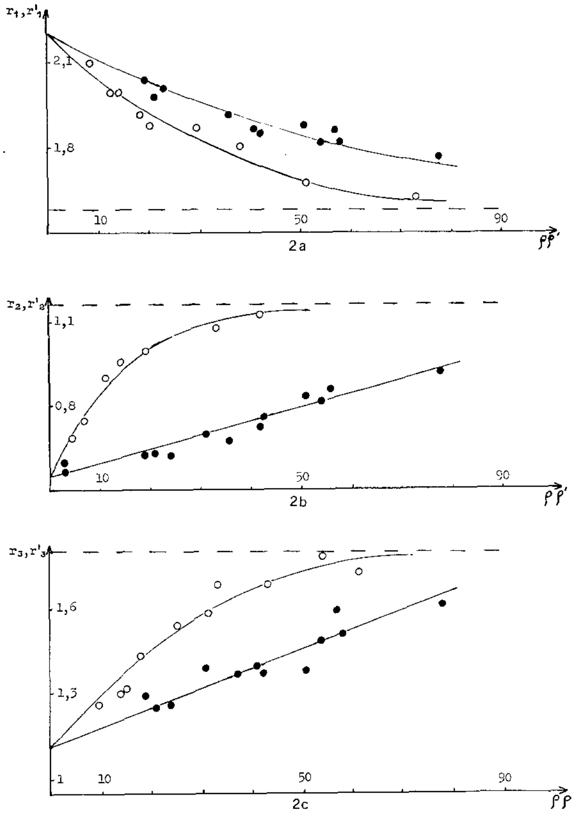


FIG. 2. Variations of the ratios $r$ and $r'$ with the conversions; 0.2% platinum on alumina at 300°C. (2a), ○, $r'_1 = f(\rho')$ isom. of *n*-hexane; ●, $r_1 = f(\rho)$ hydrog. (2b), ○, $r'_2 = f(\rho')$ isom. of II; ●, $r_2 = f(\rho)$ hydrog. (2c), ○, $r'_3 = f(\rho')$ isom. of III; ●, $r_3 = f(\rho)$ hydrog.

ratios are obtained by extrapolation of the curves $r = f(\rho)$ and $r' = f(\rho')$. It is quite clear that the initial distribution in any isomerization reaction is the same as the corresponding initial distribution obtained in hydrogenolysis, though the initial slopes of the curves are very different for both reactions.

This initial distribution of hydrogenolysis approximately corresponds to an equal chance for breaking the five cyclic bonds: $r_1 = 2.15$; $r_2 = 0.55$; $r_3 = 1.1$.

The dashed lines in the figures represent the equilibrium values for $r_1$, $r_2$, $r_3$ determined experimentally (*10*). It must be noticed that the initial ratios are very different from the equilibrium ones.

Methylcyclopentane was formed during the isomerization of all three hexanes. Figure 3 represents the variations of the mole fractions $\alpha = x_4/\Sigma x_i$ of methylcyclopentane with the conversions. Though the experimental errors were large, because of the small size of the peaks of methylcyclopentane in the chromatograms, it is clear that methylcyclopentane goes through a maximum when the conversion is increased. Apparently the plots $\alpha = g(\rho')$ corresponding to the isomerization of the three hexanes are grouped on the same curve.

The initial distributions for hydrogenolysis and sometimes for isomerization were determined at different temperatures. They are reported in Table 1: It can be seen that the

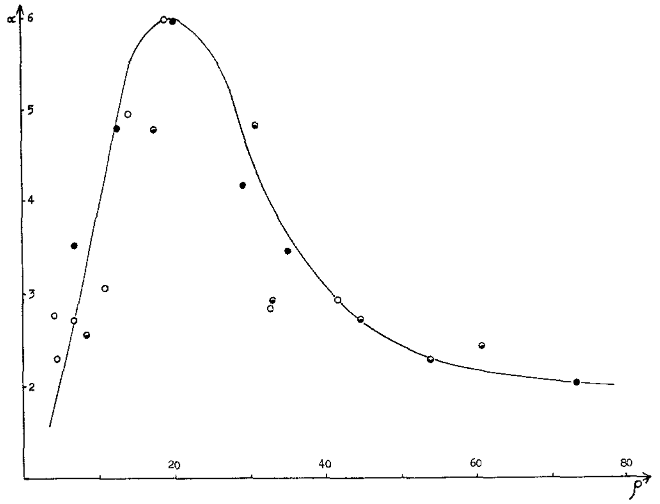


FIG. 3. Dehydrocyclization of the hexanes on 0.2% platinum on alumina at 300°C; $\alpha = g(\rho')$ plots: ○, 2-methylpentane; ●, *n*-hexane; ◒, 3-methylpentane.

TABLE 1

INITIAL DISTRIBUTIONS OF HEXANES ISOMERS ON A 0.2% PLATINUM-ALUMINA CATALYST AT VARIOUS TEMPERATURES

*Slopes of the $r = f(\rho)$ Plots*

| Temperature (°C) | $r_1, r'_1$ | $r_2, r'_2$ | $r_3, r'_3$ | Slope |
|---|---|---|---|---|
| 320° | $r_1 = 2.17$ | $r_2 = r'_2 = 0.60$ | $r_3 = 1.14$ | $0.75\ 10^{-2}$ |
| 300° | $r_1 = r'_1 = 2.20$ | $r_2 = r'_2 = 0.55$ | $r_3 = r'_3 = 1.10$ | $0.60\ 10^{-2}$ |
| 280° | $r'_1 = 2.20$ | — | — | — |
| 260° | $r_1 = 2.15$ | $r_2 = 0.60$ | $r_3 = 1.25$<br>$r'_3 = 1.28$ | $0.3\ 10^{-2}$ |
| 240° | $r_1 = 1.96$ | $r_2 = 0.68$ | $r_3 = 1.28$ | — |
| 230° | $r_1 = 1.83$ | $r_2 = 0.74$ | $r_3 = 1.25$ | $0.05\ 10^{-2}$ |
| 220° | $r_1 = 1.74$ | $r_2 = 0.74$ | $r_3 = 1.29$ | — |

product distribution does not vary much with temperature in the hydrogenolysis of methylcyclopentane, and this confirms a similar result obtained in the hydrogenolysis of methylcyclobutane on the same catalyst (*4*). On the other hand, the distributions in hydrogenolysis and isomerization, when determined, were identical.

The initial slope of the curve $r_1 = f(\rho)$ (hydrogenolysis) is also reported in the table, for various temperatures. It increases with temperature.

**b. 10% Platinum on alumina.** It seemed of interest to repeat the preceding experiments on another supported catalyst; the 10% platinum-on-alumina catalyst was then chosen because the product distributions of hydrogenolysis (and of isomerization) obtained on this catalyst were very different from these obtained on a 0.2% platinum-alumina catalyst.

The variations with conversions of the different ratios $r_i$ and $r'_i$ are represented in Figs. 4a to 4c. Here again the initial distributions in isomerization and hydrogenolysis are identical. The initial distribution of hydrogenolysis is substantially different from the distribution obtained on a 0.2% platinum-alumina catalyst: $r_1 = 3.5$; $r_2 = 2.8$; $r_3 = 9$.

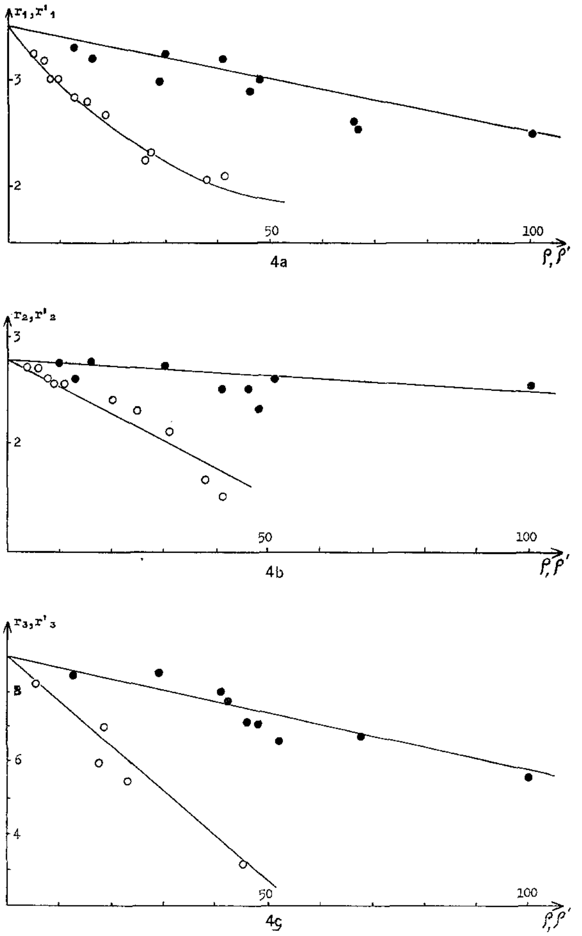


FIG. 4. Variations of the ratios $r$ and $r'$ with the conversions; 10% platinum on alumina at 298°C: ○, isomerization, $r' = f(\rho')$; ●, hydrogenolysis, $r = f(\rho)$. (4a), ○, $r' = f(\rho')$ isom. of $n$-hexane; ●, $r_1 = f(\rho)$ hydrog. (4b), ○, $r'_2 = f(\rho')$ isom. of II; ●, $r_2 = f(\rho)$ hydrog. (4c), ○, $r'_3 = f(\rho')$ isom. of III; ●, $r_3 = f(\rho)$ hydrog.

On 10% platinum-alumina, methylcyclopentane was formed only in a very small amount (less than 1%) and could not be accurately determined.

### 3. *Side Reactions: Isomerization to 2,3-Dimethylbutane and Extensive Cracking*

Very small amounts of 2,3 dimethylbutane, 1% to 2% of the total reaction products, were formed during hydrogenolysis and isomerization on any supported catalysts. These amounts do not seem to vary much with temperature and conversion.

Cracking to hydrocarbons of lower molecular weight occurs on any catalyst; for example, on a 0.2% platinum-alumina catalyst, at the lower reaction temperatures, less than 1% of the total reaction products from isohexanes was present as hydrocarbons in the $C_1$–$C_5$ range; their amounts increased with temperature and reached 40% at 340°C. Among these products, *n*-pentane and isopentane were the major ones, but *n*- and isobutanes, propane, ethane, and methane were also present.

In Figs. 5a and 5b, *n*-pentane and isopentane, expressed as per cent of the total products, are plotted versus conversion to hexanes in hydrogenolysis and isomerization on a 0.2% platinum-alumina catalyst. The upward curvatures of these plots express the fact that isomerization is a reversible process, while extensive cracking is irreversible.

From the figures it seems that *n*-pentane and isopentane are not initially formed in hydrogenolysis, but in a secondary reaction, presumably the cracking of the hexanes. On the contrary, both pentanes are formed initially from 2-methyl- and 3-methylpentanes. Similarly, *n*-pentane is the major cracking product from *n*-hexane; but Fig. 5b shows that isopentane is also formed initially to a smaller extent. The initial ratio *n*-pentane over isopentane ($s$) was determined by extrapolation in the cracking of *n*-hexane and was equal to 5 ± 0.5. The same ratio was 1.2 and 0.3 in the cracking of, respectively, 2-methyl- and 3-methylpentanes.

The two latter figures can be interpreted by supposing that the rates of cracking of a secondary–primary $CH_2$–$CH_3$ bond, $v_1$, and of a tertiary–primary bond, $v_2$, are in the ratios 1:0.6. In the cracking of 2-methylpentane indeed, $s = 2\ v_2/v_1$, while in the cracking of 3-methylpentane, $s = v_2/2\ v_1$.

### 4. *Isomerization of 2,3-Dimethylbutane*

Since a mechanism was suggested for the isomerization of hexanes, involving a cyclopentane intermediate (*3*), it was of interest to compare the isomerization of 2,3-dimethylbutane (V) and of 3-methylpentane on platinum catalysts. Both hydrocarbons were passed over the same catalyst, under the same conditions of temperature and flow rate. On a 0.2% platinum-alumina catalyst, the isomerization of 2,3-dimethylbutane was studied between 294° and 370°C; it was

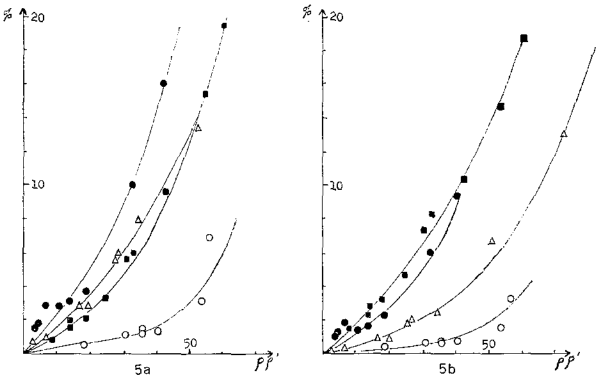


FIG. 5. *n*-Pentane (5a) and isopentane (5b) formed on 0.2% platinum on alumina at 300°C; per cent of pentanes formed during the hydrogenolysis of methylcyclopentane, ○; the isomerizations of 3-methylpentane, ■; 2-methylpentane, ● and *n*-hexane, △.

noticeable at 330° only (about 0.5%) and was never higher than 2%. The main isomerization product was 2-methylpentane. An extensive cracking to $C_1$–$C_5$ hydrocarbons, especially to isopentane, was the main observed reaction.

On the contrary, isomerization of 3-methylpentane was noticeable even at 277°C and at temperatures higher than 340°C the hexane distributions were very close to the equilibrium distribution among (I), (II), and (III). The extent of cracking was somewhat smaller for 3-methylpentane than for 2,3-dimethylbutane, on platinum catalysts.

TABLE 2

ISOMERIZATION AND CRACKING OF 2,3-DIMETHYLBUTANE (V) AND OF 3-METHYLPENTANE (III) ON PLATINUM-ALUMINA CATALYSTS

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *0.2% Platinum on Alumina* | | | | | | | | | |
| Temperature (°C) | 277 | | 292 | | 332 | | 347 | | 366 | |
| Starting material | V | III | V | III | V | III | V | III | V | III |
| Isomerization (%) | 0 | 11.2 | 0 | 16.4 | I | 56 | 2 | equil | 3 | equil |
| Pentane (%) | — | 0.45 | 0.1 | 1.1 | — | 6.5 | 1.3 | — | 7 | — |
| Isopentane (%) | — | 1.30 | 7.7 | 2.5 | — | 6.6 | 23 | — | 79 | — |
| | *10% Platinum on Alumina* | | | | | | | | | |
| Temperature (°C) | 300 | | 350 | | | | | | | |
| Starting material | V | III | V | III | | | | | | |
| Isomerization (%) | 4.5 | 45 | 12 | Equilibrium | | | | | | |
| $n$-Pentane (%) | 0.4 | 1.6 | 3 | — | | | | | | |
| Isopentane (%) | 3.4 | 2.15 | 14 | — | | | | | | |

[a] Isomerization of 3-methylpentane is expressed in per cent as $100[(x_1 + x_2)/(x_1 + x_2 + x_3)]$. Isomerization of 2,3-dimethylbutane is expressed as $\left[\sum_1^3 x_i/(x_1 + x_2 + x_3 + x_5)\right]100$, $x_1$, $x_2$, $x_3$, $x_5$ being the concentrations of $n$-hexane, 2-methylpentane, 3-methylpentane, 2,3 dimethylbutane; cracking is expressed as per cent of pentane or isopentane in the $C_5 + C_6$ hydrocarbon mixture.

Table 2 summarizes the results of these experiments.

On a 10% platinum-on-alumina catalyst, similar results were obtained. The isomerization of 2,3-dimethylbutane, mainly to 2-methylpentane, was very small, when compared to the isomerization of 3-methylpentane. However, for the same temperature, the extent of isomerization of 2,3-dimethylbutane was smaller on a 0.2% platinum-alumina catalyst than on a 10% platinum-alumina catalyst.

### 5. *Isomerization on Alumina*

The activity of the carrier was tested for the isomerization of methylcyclopentene and 3-methylpent-2 ene. Platinum-on-alumina catalysts were replaced in the microreactor by the alumina. Flow rates and hydrogen pressure were unchanged. In some experiments, a microhydrogenator (10% platinum-alumina at 100°C) was inserted in the flow line between the reactor and the chromatography column to check a possible skeletal rearrangement of the olefins.

**a. Methylcyclopent-1-ene.** Up to 200°C, methylcyclopent-1-ene did not react on alumina; between 200° and 350°C double-bond shift was observed. A cracking to lower molecular weight hydrocarbons could only be detected at 350°C (1.5%) and was smaller than 3% at 400°C; cracking to hexenes and isomerization to cyclohexenes were not observed up to 450°C.

**b. Isohexenes.** Only double-bond shifts took place, when 2-methylpent-1-ene and 3-methylpent-2-ene were passed over alumina up to 380°C. At 390°C, less than 2% of skeletal rearrangement occurred, and 14–16% at 450°C; on the other hand, isomerization on alumina appeared to be more selective on alumina than on platinum-alumina, under these conditions: for example, mainly 2-methylpentenes were obtained from 3-methylpent-2-ene.

## B. *Isomerization, Hydrogenolysis, and Aromatization on Platinum Films*

### 1. *Isomerization of Hexanes*

The isomerization of 2-methylpentane and 3-methylpentane were studied at 270°C, the isomerization of *n*-hexane at 270°C and 330°C. The five hexane isomers, methylcyclopentane, and benzene were obtained in any experiment. The amounts reported in Table 3 of these hydrocarbons were obtained after 4 hr of reaction. After such a reaction time, the platinum films were entirely deactivated. The extent of deactivation depended widely upon the starting material, and that explains the large range in the conversions obtained with the different hydrocarbons.

Very large amounts of 2,3-dimethylbutane were formed on platinum films. The presence of 2,2-dimethylbutane was ascertained by the retention time in chromatography on a silicone oil column, correct within 0.5%, and by the mass spectra, after gas chromatographic separation.

The kinetics of the formation of methylcyclopentane and benzene were followed in every run. The ratios $r'$ of the initial rates for the formation of benzene and methylcyclopentane is much larger in the reactions of *n*-hexane (0.22) than in those of 2-methyl- and 3 methylpentanes ($0.7 \times 10^{-2}$); it does not seem to depend upon temperature.

The kinetics of isomerization was only followed in the case of 3-methylpentane. In Fig. 6 the per cent of hexane isomers, methylcyclopentane, and benzene obtained from 3-methylpentane are plotted versus time, together with the per cent of 3 methylpentane. All three of these products are formed initially. The strong downwards curvature of the plots was probably due to the fast deactivation of the platinum film.

Apparently the film is not so poisoned for the aromatization as for the dehydrocyclization to methylcyclopentane.

TABLE 3

Reaction Products Obtained on Platinum Films from Various Hydrocarbons[a]

| Starting material | 3-Methyl pentane | *n*-Hexane | *n*-Hexane | Methylcyclopentane | |
|---|---|---|---|---|---|
| $T$(°C) | 275 | 270 | 330 | 327 | 272 |
| 2-Methylpentane | 35.5 | 32.4 | 9.6 | 33.9 | 51.7 |
| 3-Methylpentane | — | 13.45 | 6.4 | 19.6 | 27.0 |
| *n*-Hexane | 5.8 | — | — | 12.7 | 10.3 |
| 2,3-Dimethylbutane | 36.6 | 24.45 | 36.8 | 7.5 | 6.2 |
| 2,2-Dimethylbutane | 0.95 | 2.5 | 5.0 | 0.0 | 0.0 |
| Methylcyclopentane | 20.9 | 19.75 | 30.2 | — | — |
| Benzene | 0.2 | 7.45 | 12.05 | 26.3 | 4.8 |
| Conversion | 49.6 | 6.6 | 1.7 | 19.7 | 17.5 |

[a] The product distributions are expressed as per cent of the total $C_6$ reaction products.

### 2. *Hydrogenolysis of Methylcyclopentane*

The contact reactions of methylcyclopentane on platinum films were studied at 272° and 327°C; the opening of the cyclopentane ring mainly gives 2-methylpentane, 3-methylpentane, and *n*-hexane; 2,3-dimethylbutane and benzene were also present in the reaction products.

In the last two columns of Table 3, the gas chromatographic analysis at 272° and 327° of the $C_6$ reaction products (hexanes and benzene) is given; the amounts of various hydrocarbons are expressed as the per cent of the total $C_6$ reaction products.

In Figs. 7a and 7b, the per cent of hexane isomers and benzene are plotted versus time. From these plots it can be seen that benzene is always obtained as an initial reaction product; the higher the temperature, the higher is the rate of formation of benzene. These plots show a strong downwards curvature, and that is a consequence of the very fast loss of activity of the catalyst during the reaction (*2*).

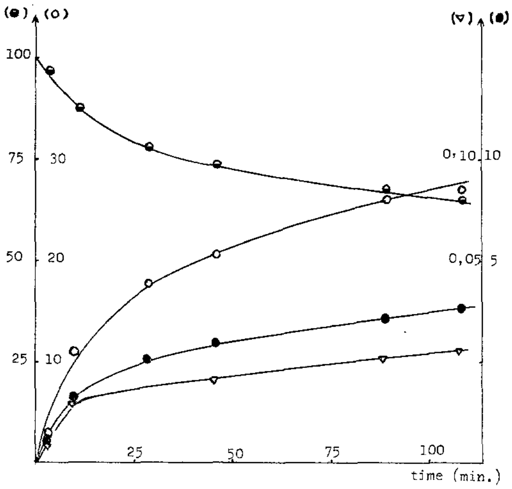


FIG. 6. Reaction products obtained on platinum film from 3-methylpentane at 270°C: ◒, 3 methylpentane; ○, hexane isomers; △, benzene; ●, methylcyclopentane.

However, it is noticeable that at 330° the ratio of benzene to total hexanes in the final analysis (0.35) is higher than the initial ratio (0.15). So the deactivation of the catalyst is faster for hydrogenolysis than for aromatization. This also explains the differences between the curvatures of the hexane and benzene plots in Fig. 7b; the comparison between the rates of aromatization of *n*-hexane and methylcyclopentane excluded the explanation of this effect by a reaction of the *n*-hexane formed in hydrogenolysis.

The amounts of 2,3-dimethylbutane obtained on platinum films, although small, were four to six times bigger than the amounts obtained on supported catalysts; that could be due to a further isomerization of the reaction products, since the analysis was done at 20% conversion.

The distributions in 2-methylpentane, 3-methylpentane, and *n*-hexane related in Table 3 were similar, but not exactly identical in hydrogenolysis and isomerization. Thus the ratio $x_2/x_3$ was 2.41 and 1.51 in the isomerization of hexanes at 270° and 330°, 1.92 and 1.72 in the hydrogenolysis of methylcyclopentane at the same temperatures. The agreement is better for the ratio $x_2/x_1$ obtained from 3-methylpentane (6.15) and from methylcyclopentane (4.98). However, it must be kept in mind that the initial distributions could not be obtained, for the mass spectrometrical analysis of the five hexane isomers was not possible.

### 3. *Aromatization of 1,1,3-Trimethylcyclopentane*

The contact reactions of 1,1,3-trimethylcyclopentane (VI) were studied on platinum film at 300° and 330°C. The course of the reaction was continuously followed using the mass spectrometer. A fast equilibration of (VI) and the corresponding cyclic olefins was reached within the first 2 min of reaction. Less than 1% of saturated acyclic hydrocarbons were formed throughout the reaction.

On the contrary xylenes appeared right at the very beginning of the runs, and were the main reaction products; small amounts of toluene were also formed, as initial reaction product.

According to the gas chromatographic analysis, the aromatics present in the final reaction mixture at 18% conversion, consisted of toluene (19%), *meta*-xylene (53%), and *para*-xylene (28%); no *ortho*-xylene could be detected.

## DISCUSSION

### A. *Isomerization on Supported Platinum Catalysts*

The first question which arises is whether isomerization takes place on the metal sites of the supported catalysts, or on the acidic sites of the carrier, via a carbonium ion mechanism.

It has already been shown that the hydrogenolysis of cyclic hydrocarbons takes place on metal and not on acidic sites in supported platinum catalysts (*4*). Since isomerization and hydrogenolysis are connected, for example, in the reaction products on various catalysts, apparently isomerization also takes place on metal sites.

The following observations substantiate this statement:

(1) The initial product distributions of isomerization of methylpentanes and *n*-hexane on platinum-alumina catalysts are very different from the distributions

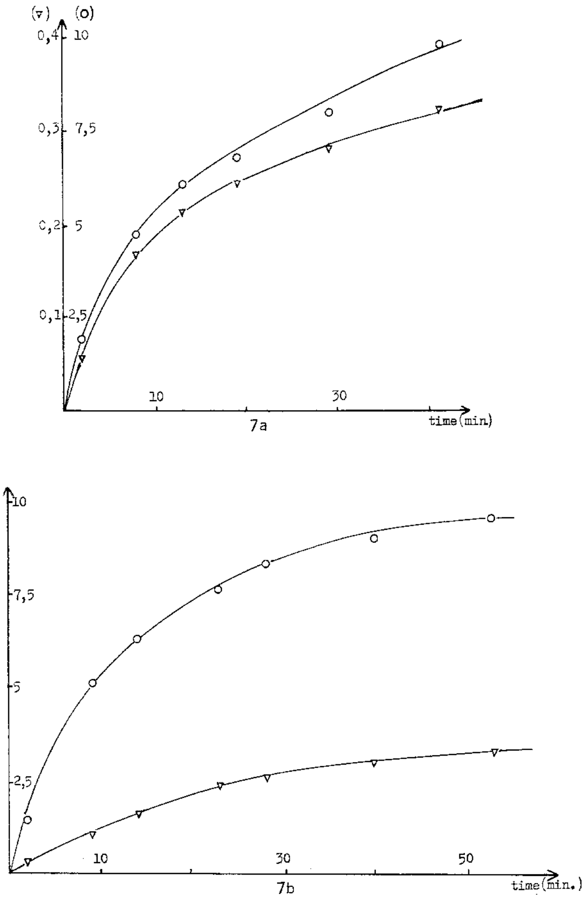


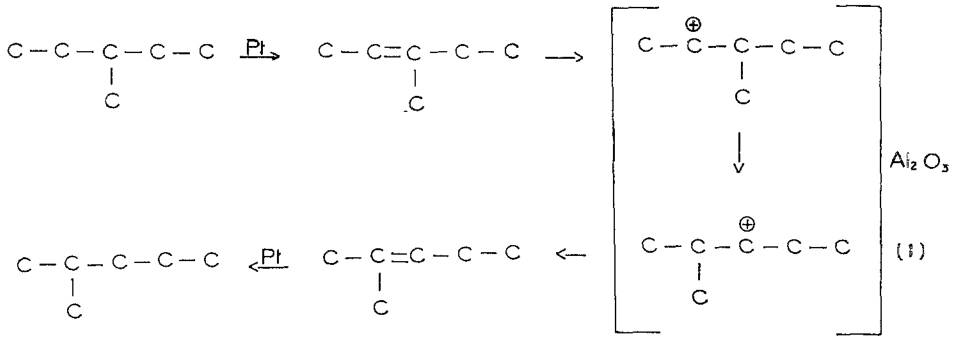
FIG. 7. Hydrogenolysis and aromatization of methylcyclopentane on platinum films at 272°C (Fig. 7a) and 327°C (Fig. 7b): ○, hexanes; △, benzene.

obtained on acidic catalysts; for example, the primary products of isomerization of 2-methylpentane or 3-methylpentane on aluminum chloride are only the other methylpentane and 2,3-dimethylbutane; on the other hand, the primary products from *n*-hexane are 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane in nearly the same proportions as found in equilibrium (*12, 13*). The initial product distributions obtained on the various platinum-alumina catalysts from methylpentanes and *n*-hexane were very different from these distributions and from the equilibrium one; *n*-hexane was always found as a primary product from any hydrocarbon, and 2,3-dimethylbutane was never formed in appreciable amount.

(2) The rates of isomerization of methylpentanes and *n*-hexane on platinum-alumina are very similar and much larger than the rate of isomerization of 2,3-dimethylbutane; on the contrary, on an acidic catalyst the rate of isomerization of this latter hydrocarbon to 2-methylpentane is larger than the rate of isomerization of 2-methylpentane to *n*-hexane (*12*).

(3) The acidity of the carrier in supported platinum catalysts does not seem to be essential for isomerization, in our experiments. When the differences of adsorptive properties are taken into account, isomerization takes place in the same range of temperature on platinum-charcoal, platinum-pumice, and platinum-alumina; it is also noticeable that similar distributions were obtained on these three catalysts.

(4) If platinum-alumina, under our conditions, was operating as a dual-function catalyst, reaction (1) should be proposed for isomerization, e.g., of 3-methylpentane. Such a scheme is ruled out by the fact that alumina does not catalyze the isomerization of acyclic olefins below 400°C, while isomerization on platinum-alumina takes place at 280°C. Therefore, for all these reasons, we believe that isomerization takes place on the metal sites of platinum-alumina and other supported platinum catalysts.

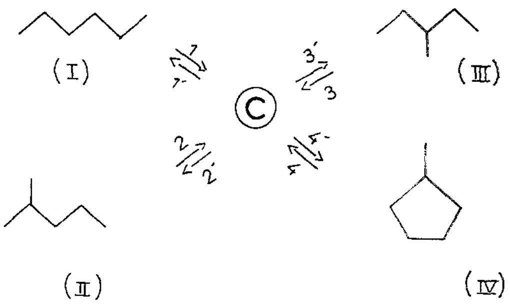


A second question which arises is the nature of the intermediate species in isomerization. On platinum-alumina catalysts, the product distributions in hydrogenolysis of methylcyclopentane and in isomerization of hexanes widely varied with the concentration of the metal on the carrier. These variations were the same in both reactions. Furthermore, the initial distributions in isomerization and in hydrogenolysis were identical. This identity clearly shows that a common intermediate is involved in both reactions, on supported platinum catalysts.

That is confirmed by the fact that dehydrocylization to methylcyclopentane accompanies the isomerization of hexanes. Scheme 1 summarizes the relationships between isomerization, hydrogenolysis, and dehydrocyclization. Isomerization of *n*-hexane, for instance, is represented by the consecutive elementary steps 1–3′ or 1–2′; its dehydrocyclization by the reactions 1–4′; hydrogenolysis of methylcyclopentane by any of the steps 4–1′, 4–2′, 4–3′. The maximum in methylcyclopentane formation during isomerization is consistent with this mechanism provided that hydrogenolysis is faster than isomerization, which has been verified.

The intermediate C in this scheme represents a number of adsorbed species in interconversion. One or more of these species necessarily has a cyclopentane structure; that is proved by the absence of 2,3-dimethylbutane in the isomerization products and by the fact that it is difficult to isomerize this hydrocarbon on platinum-alumina catalysts under the same conditions. 2,3-Dimethylbutane can be dehydrocyclized only via a cyclobutane intermediate, which is not likely to occur under these conditions.

The intermediate species in the dehydrocyclization of hexanes are also intermediates in the reverse reaction, i.e., in the hydrogenolysis of methylcyclopentane. The mechanisms of hydrogenolysis of methylcyclopentane on platinum catalysts have been studied in a previous paper (*4*). According to the concentration of platinum on the carrier and the experimental conditions, three mechanisms had to be considered.



Scheme 1

Among these mechanisms, one corresponded to an equal chance of rupturing the five cyclic bonds of methylcyclopentane. Since ditertiary CH—CH bonds were opened according to this mechanism, and since cis–trans equilibrium of disubstituted cyclopentanes was reached during hydrogenolysis, it was suggested that $\alpha,\beta,\gamma$ triadsorbed species were responsible for this type of cracking; these species were shown to be $\pi$-bonded to the metal and to cause inversion of the carbon atom (*14*, *15*).

It is noticeable that isomerization takes place under the experimental conditions where the nonselective mechanism of hydrogenolysis is significant, i.e., on a 0.2% platinum-alumina catalyst, where this mechanism is the only one operating, and on a 10% platinum-alumina catalyst at the temperatures where it is becoming important (above 290°C) (*4*).

So it is tempting to assume that the species responsible for isomerization and dehydrocyclization of hexanes are also the $\alpha,\beta,\gamma$ triadsorbed species responsible for this type of hydrogenolysis. The first elementary step of isomerization could thus be described by reaction (2).

energy associated with isomerization is higher than the activation energy of hydrogenolysis, and that explains the increase of the slope $r = f(\rho)$ with temperature (Table 1).

The fact that the distributions in isomerization and in hydrogenolysis were very close at the same contact times may be the result of a coincidence, since the initial distributions and, of course, the equilibrium distributions are identical for both reactions. A possible explanation could be that the concentration of the intermediate remains almost constant throughout the course of the reaction.

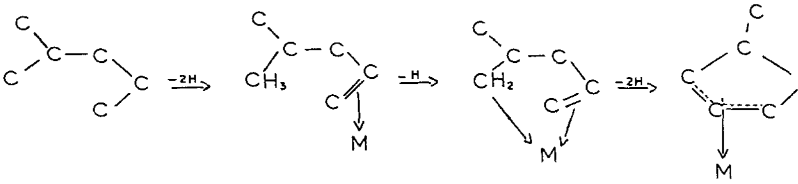
If the reactions are assumed to be first order versus hydrocarbon, which is strictly true in the case of hydrogenolysis (*4*), the following equations can be written:

$$dx_i/dt = -k_i x_i + k_{-i}c$$

$c$ being the concentration of the intermediate. Supposing $c$ constant, the integration gives, when $i$ is the starting material,

$$x_i = (ck_{-i}/k_i) + [1 - (ck_{-i}/k_i)]e^{-k_i t}$$

$$x_j = (ck_{-j}/k_j)(1 - e^{-k_j t}) \qquad (j \neq i)$$



(2)

Such a scheme is similar to that proposed by Sheppard and Rooney to explain the dehydrocyclization of *o*-methylethylbenzene to indane, and it should be outlined that the results obtained by these authors were a very good confirmation for the proposed cyclic mechanism of isomerization (*16*).

The variations of the product distributions with conversions correspond to the readsorption and further isomerization of the primary reaction products. These variations were much larger in isomerization than in hydrogenolysis, since the rate of hydrogenolysis is eight to ten times larger than the rate of isomerization, under the experimental conditions considered. Similarly, the activation

When isomerization of (I) and hydrogenolysis of (IV), for example, are considered, it can be easily checked that $r_1/r'_1$ equals 1. These equations also show that the same amounts of methylcyclopentane, $x_4$, should be obtained from any of the three hexanes and this has been verified.

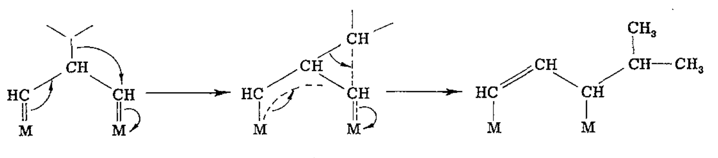
### *B. Isomerization on Platinum Films*

The isomerization of hexanes on platinum films is a further proof that this reaction does take place on metals. The distributions in methylpentanes and *n*-hexane can be compared in hydrogenolysis and in isomerization on platinum films and that shows that the mechanism shown in Scheme 1, important on supported catalysts, also occurs on platinum films.

However, these distributions are not strictly identical and it is therefore necessary to introduce another mechanism of isomerization. Some other facts are in favor of such a mechanism: The large amounts of 2,3-dimethylbutane in the product distributions of isomerization cannot be explained by the cyclic mechanism. On the other hand, Anderson and Baker have shown that isobutane and neopentane can be isomerized on platinum films (*1*, *2*); the reverse reaction of isomerization at a quaternary carbon atom also occurs on platinum films: small amounts of 2,2-dimethylbutane are formed from hexanes. In all these reactions, cyclopentane intermediates cannot be formed and another mechanism should be considered.

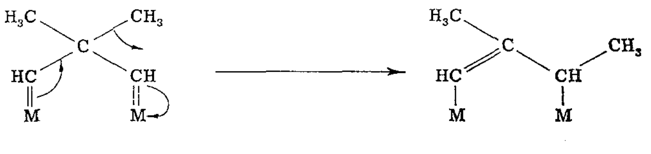
The species associated with this mechanism could be strongly adsorbed on two carbon atoms in the $\alpha,\gamma$ positions. That is suggested by the fact that gem-disubstituted alkanes are isomerized by this mechanism.

It was recently suggested that $\alpha,\alpha,\gamma$ triadsorbed species were involved in the demethylation of polymethylcyclopentanes on cobalt films, for, when the reaction was studied in presence of deuterium, four deuterium atoms were present in the demethylated molecule (*17*). On the other hand $\alpha,\alpha,\gamma,\gamma$ tetraadsorbed species can be formed on platinum, and their existence was shown in the hydrogenolysis of substituted cyclopropane hydrocarbons (*18*). If similar species do intervene Scheme 2 can be proposed for the second type of isomerization:



Scheme 2

and for the isomerization or formation of gem-disubstituted hydrocarbons



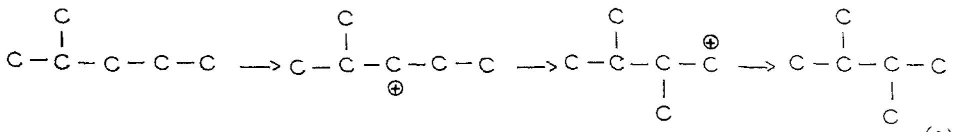
The $\alpha,\alpha,\gamma,\gamma$ species described in these schemes are believed to be (*d-p*) $\pi$-bonded to the metal atoms (*17*).

A strong electron donation to the metal in these species would explain an electron deficiency in the molecule and a weakening of the bonds similar to that determining the skeletal rearrangement in carbonium ions. In fact, such a mechanism is, at least in its effects, very similar to a carbonium ion mechanism [reaction (3), top of next page]. However, this mechanism is not truly a carbonium ion mechanism, since it occurs on platinum films and not on platinum-alumina catalysts, where carbonium ions are more likely to be formed.

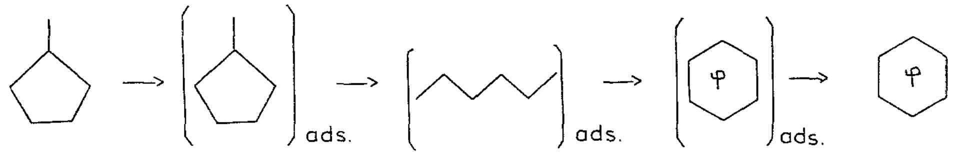
On the other hand, the proposed mechanism in Scheme 2 is very similar to the one proposed by Csicsery and Pines to explain the aromatization on $Cr_2O_3$–$Al_2O_3$ of labeled 2,2,3- and 2,3,4-trimethylpentanes (*19*, *20*). These authors explain their results by the consecutive formation and hydrogenolysis of a cyclopropane intermediate. The proposed mechanism involves the same kind of concept, but has the advantage of not introducing an adsorbed cyclopropane species, which cannot be formed on metal surfaces.

## *C. Aromatization*

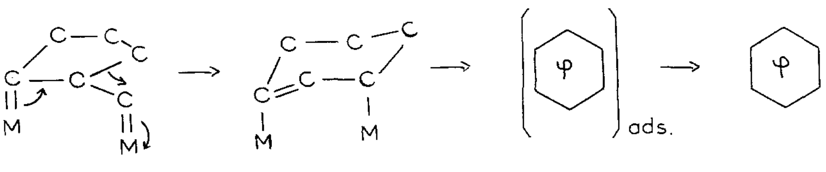
The formation of benzene from methylcyclopentane and from 3-methylpentane may occur according to one of the mechanisms given in Schemes 1′ and 2′, which closely correspond to the two mechanisms of isomerization. According to the first mechanism (Scheme 1′), the adsorbed methylcyclopentane intermediate would be opened to



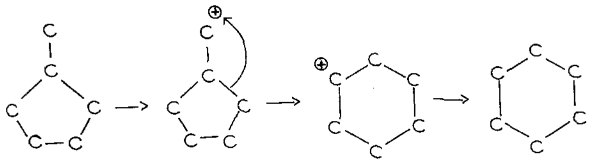
(3)



Scheme 1'



Scheme 2'



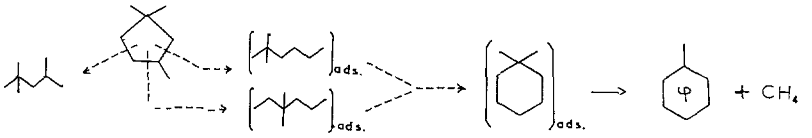
(4)

adsorbed *n*-hexane, which would be dehydrocyclized to benzene without leaving the surface. Such a mechanism would explain the initial formation of benzene from isohexanes and methylcyclopentane. According to a second mechanism (Scheme 2'), a direct enlargement of the cyclopentane ring would occur on the metal surface. This mechanism involves the same adsorbed species than the isomerization to 2,3-dimethylbutane. It is very close to the mechanism of isomerization of methylcyclopentane on acidic catalysts [reactiun (4), above], but involves polyadsorbed species, and not carbonium ions.

To chose between these two proposed mechanisms, 1' and 2', is difficult indeed, but the fact that the extent of aromatization is larger on platinum films, where 2,3-dimethylbutane is formed in isomerization, than on platinum-alumina catalysts, seems to be in favor of the second mechanism, i.e., the enlargement of the methylcyclopentane ring.

On the other hand a third mechanism has to be introduced to explain the very large amounts of benzene formed from normal hexane. This mechanism of aromatization involves probably a 1–6 ring closure, and was introduced by Herrington and Rideal (*21*), to explain the aromatization of larger paraffins.

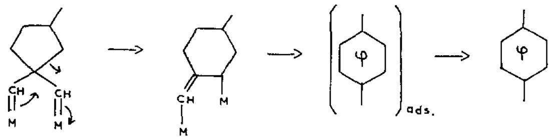
Only toluene and not xylenes should be obtained in the aromatization of 1,1,3-trimethylcyclopentane by the mechanism involving the opening of the ring (1'), since the hydrogenolysis of gem-disubstituted cyclopentanes only affects the bonds between secondary and tertiary carbon atoms (*22*, *23*).



Mechanism 1'

Moreover, the hydrogenolysis of 1,1,3 trimethylcyclopentane is very slight on platinum films; that excludes the possibility of mechanism 1', even for the formation of toluene. Thus the aromatization of the trimethylcyclopentane may occur only through a ring enlargement, and that is a definite proof of the existence of this mechanism (2').

The complete absence of *ortho*-xylene excludes a carbonium ion mechanism and shows that platinum cannot be considered as an acidic catalyst; if such was the case, *ortho*-xylene would accompany toluene in the reaction products (*24*).



Mechanism 2'

### D. Extensive Cracking

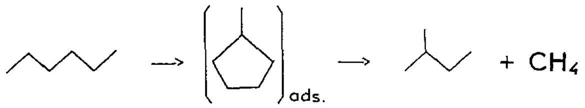
The mechanism of cracking of hexanes to hydrocarbons of lower molecular weight mostly involves species adsorbed on two adjacent carbon atoms. It was therefore possible to compare the rates of cracking of tertiary–primary and secondary–primary bonds in two different isohexanes. But the direct formation of isopentane from *n*-hexane on this catalyst involves a more complicated mechanism of reaction. Here again, two different mechanisms could be considered: either an extensive cracking after dehydrocyclization to a cyclopentane intermediate (5), or an extensive cracking after isomerization according to the second mechanism of isomerization (6).

Since isopentane was not initially formed from methylcyclopentane, we prefer the second scheme to explain this type of extensive cracking.

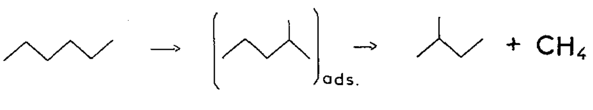
## CONCLUSION

In conclusion, there are at least two different mechanisms of isomerization operating on platinum catalysts. One of these involves a cyclic intermediate; the other one, involving a alkyl shift, is very similar to an acidic-type mechanism. Aromatization also occurs in the same conditions and probably through a ring enlargement.

These reactions occur on both supported



(5)



(6)

platinum catalysts and platinum films; in fact, platinum films seem to favor aromatization and alkyl shift resulting in the formation of 2,3-dimethylbutane from hexanes. Since these latter reactions are also occurring on acidic catalysts, via a carbonium ion mechanism, we believe that one should be very careful about the role of the metal in dual-function catalysts. There is no doubt that the carrier plays an important part in isomerization and ring enlargement on platforming catalysts, under operating conditions, i.e., at temperatures much higher than those used in our experiments. But, even under these conditions, the platinum certainly catalyzes by itself for a large part isomerization and aromatization, and cannot be considered as a simple hydrogenating–dehydrogenating agent.

Since the metal appears to play such an important part in hydrocarbon reactions on platinum catalysts at high temperatures, it would now be interesting to compare the catalytic activity of this metal with the activity of the other Group VIII metals; some work is in progress in this direction.

## REFERENCES

*1.* ANDERSON, J. R., AND BAKER, B. G., *Nature* **187**, 937 (1960).

*2.* ANDERSON, J. R., AND BAKER, B. G., *Proc. Roy. Soc.* (*London*) **A271**, 402 (1963).

*3.* BARRON, Y., MAIRE, G., CORNET, D., AND GAULT, F. G., *J. Catalysis* **2**, 152 (1963).

*4.* MAIRE, G., PLOUÏDY, G., PRUD'HOMME, J. C., AND GAULT, F. G., *J. Catalysis* **4**, 556 (1965).

*5.* KEMBALL, C., *Proc. Roy. Soc.* (*London*) **A207**, 539 (1951).

*6.* PINES, H., OLBERG, R., AND IPATIEFF, V., *J. Am. Chem. Soc.* **68**, 2513 (1946).

*7.* HUANG-MINLON, *J. Am. Chem. Soc.* **68**, 2847 (1946).

*8.* GAULT, F. G., AND GERMAIN, J. E., *Bull. Soc. Chim. France,* p. 1365 (1959).

*9.* MORTIMER, J. V., AND GENT, P. L., *Nature* **197**, 789 (1963).

*10.* CONDON, F. E., *Catalysis* **6**, 158 (Reinhold, New York, 1958).

*11.* MCKENNA, T. A., AND IDLEMAN, J. A., *Anal. Chem.* **31**, 2000 (1959).

*12.* EVERING, B. L., AND WAUGH, R. C., *Ind. Eng. Chem.* **43**, 1820 (1951).

*13.* CONDON, F. E., *Catalysis* **6**, 141 (Reinhold, New York, 1958).

*14.* ROONEY, J. J., GAULT, F. G., AND KEMBALL, C., *Proc. Chem. Soc.,* p. 407 (1960).

*15.* GAULT, F. G., ROONEY, J. J., AND KEMBALL, C., *J. Catalysis* **1**, 255 (1962).

*16.* SHEPPARD, F. E., AND ROONEY, J. J., *J. Catalysis* **3**, 129 (1964).

*17.* ROONEY, J. J., AND GAULT, F. G., unpublished work.

*18.* PRUD'HOMME, J. C., AND GAULT, F. G., *Bull. Soc. Chim. France* (1966), in press.

*19.* CSICSERY, S. M., AND PINES, H., *J. Am. Chem. Soc.,* 3939 (1962).

*20.* PINES, H., AND CSICSERY, S. M., *J. Org. Chem.* **29**, 399 (1964).

*21.* HERINGTON, E. F. G., AND RIDEAL, E. R., *Proc. Roy. Soc.* (*London*) **A184**, 434, 447 (1945).

*22.* KAZANSKII, B. A., RUMIANTSEVA, Z. A., AND BATUEV, M. I., *Izv. Akad. Nauk SSSR Otd. Khim. Nauk* **84**, 483 (1947).

*23.* GAULT, F. G., *Annal. Chim.,* p. 647 (1960).

*24.* PINES, H., AND GREENLEE, T. W., *J. Org. Chem.* **26**, 1052 (1961).