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LETTER TO THE EDITORS

The Mechanism of Isomerization of Hexanes on Platinum Catalysts

We wish to report some preliminary results about a comparative study of the hydrogenolysis of methylcyclopentane and isomerization of hexane isomers on platinum catalysts.

Hydrogenolysis of methylcyclopentane on platinum catalysts (*1, 2*) gives mainly *n*-hexane (I), 2-methylpentane (II), and 3-methylpentane (III) (Fig. 1).

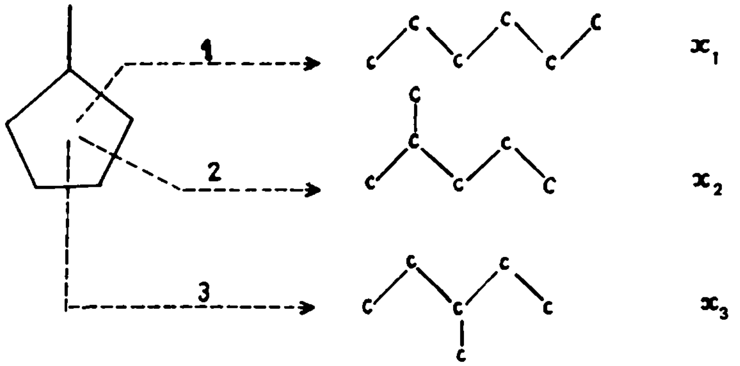

FIG. 1. Diagrammatic representation of the hydrogenolysis of methylcyclopentane.

The isomerization of any of these three hexane isomers (I, II, III) on the same catalysts gives the other two with a much smaller rate than the rate of hydrogenolysis.

We believe that a careful comparison of the product distributions of both reactions may help to elucidate their mechanisms.

EXPERIMENTAL

Although this study includes reactions on different bulk catalysts and on evaporated films, we report here mainly the results obtained on a 0.2% platinum catalyst supported on alumina; the temperature range was 270–330°C. A microcatalytic reactor was employed in conjunction with a gas-liquid chromatograph using hydrogen as a carrier gas.

RESULTS

The relative abundance of the main products from each of the four reactants was expressed as the ratios x_1/x_2, x_3/x_1, and x_2/x_3, where x_1, x_2, and x_3 are the concentrations of I, II, and III as products, respectively. These ratios were plotted as a function of conversion to hexane isomers and the curves extrapolated to zero conversion in order to ascertain the initial ratios.

Thus in Fig. 2, the values of x_3/x_1 from the hydrogenolysis of methylcyclopentane and from the isomerization of II at 300°C are compared at similar conversions. It can be seen from the plots that the initial ratios for both reactions are identical.

At higher degrees of conversion, these ratios diverge strongly: Since the rate of hydrogenolysis of methylcyclopentane is

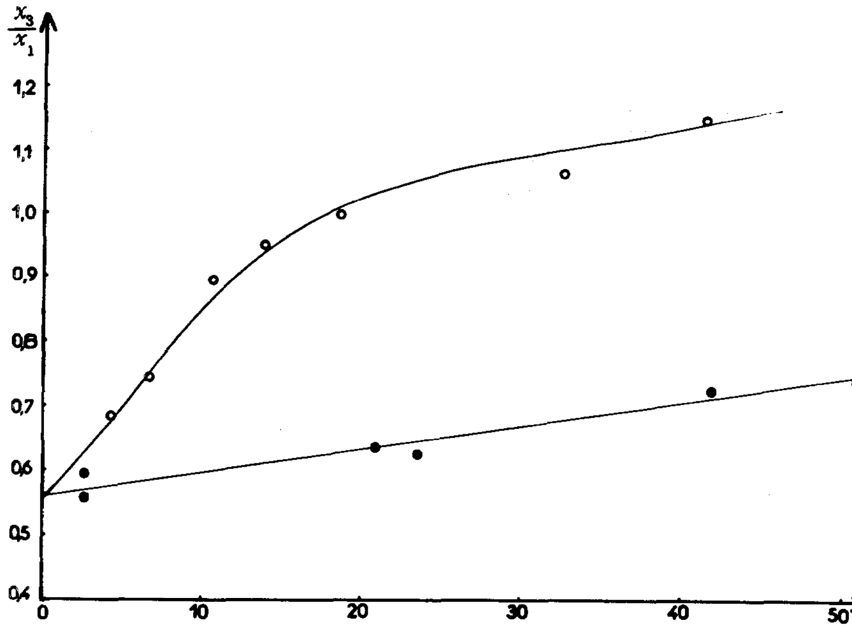

FIG. 2. Comparison of the product ratio x_3/x_1 from the hydrogenolysis of methylcyclopentane and from isomerization of 2-methylpentane at 300°C: α is the conversion to hexane isomers expressed in %; ●, hydrogenolysis; ○, isomerization.

much larger than the rate of a subsequent isomerization of the hexanes products, the x_3/x_1 ratio for hydrogenolysis varies less with the conversion than the corresponding ratio for the isomerization of II, as can be seen from the plots.

The appropriate initial ratios from the isomerization of I, II, and III, respectively, together with the corresponding values from the hydrogenolysis of methylcyclopentane are given in the table; both sets of initial ratios are identical in each case and differ widely from the equilibrium values; the latter were determined experimentally and are in good agreement with those obtained elsewhere (*3*).

TABLE 1

INITIAL RATIOS OF HEXANE ISOMERS FROM REACTIONS OF METHYLCYCLOPENTANE, I, II, AND III ON PLATINUM-ALUMINA AT 300°C

Ratios	x_1/x_2	x_2/x_3	x_3/x_1
Hydrogenolysis	0.9	2.15	0.55
Isomerization of I	—	2.2	—
Isomerization of II	—	—	0.55
Isomerization of III	0.9	—	—
Equilibrium	0.55	1.65	1.1

The initial distribution of products also corresponds closely to an equal chance of breaking any of the five carbon–carbon bonds in the methylcyclopentane ring.

Simultaneous dehydrocyclization to methylcyclopentane was also noted during isomerization, and its concentration varied with the extent of reaction, passing through a maximum (ca. 6%) at an intermediate conversion.

As previously reported for hydrogenolysis (*1*, *2*), n-hexane (I) and methylpentanes (II, III) are the main reaction products together with methylcyclopentane in isomerization. The amount of 2,3-dimethylbutane formed in isomerization was less than 2% of the total hexanes.

Cracking to hydrocarbons of lower molecular weight and dehydrocyclization to benzene are also occurring, especially at higher temperature.

DISCUSSION

The identity of the product distributions from hydrogenolysis and isomerization, the almost complete absence of 2,3-dimethylbutane and the formation of methylcyclopentane during isomerization strongly suggest that a common intermediate with a five-membered ring structure is responsible for these reactions. The maximum in methylcyclopentane formation during isomerization is consistent with this mechanism, shown in Fig. 3, provided that hydrogenolysis is more rapid than isomerization, and this has been verified; the intermediate cyclic complex must also have a higher chance of desorbing as methylcyclopentane than of cracking.

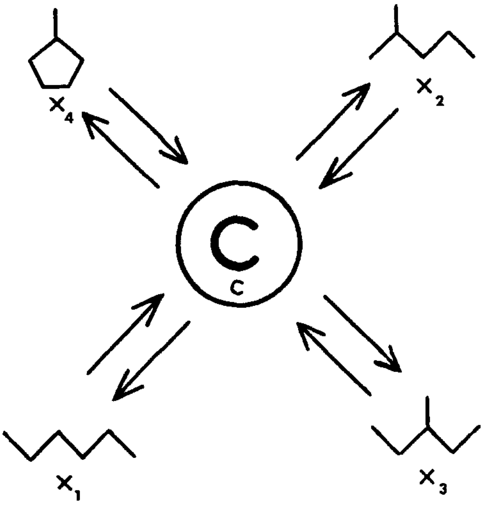

FIG. 3. Diagrammatic representation of the common mechanism of isomerization, dehydrocyclization, and hydrogenolysis of the hexane isomers and methylcyclopentane, respectively.

These results therefore support the view that the same sites in platinum-alumina catalysts can also promote isomerization in addition to dehydrocyclization and hydrogenolysis, and that a common intermediate is involved.

Recently the concept of π-bonded intermediates in reactions of hydrocarbons on metals has been introduced (*4*), the role of these species in exchange of cycloalkanes with deuterium on films of several metals has been investigated (*5*), and their role in catalysis more generally discussed (*6*). It is tempting to suggest that the cyclic intermediate C in Fig. 3 is a π-bonded complex and that intermediates of this nature play an important part on the supported catalysts (bifunctional catalysts) in such reactions of hydrocarbons as isomerization and hydrogenolysis.

The conclusion that isomerization of hexanes is *not* due to the rearrangement of carbonium ions following the adsorption of intermediate olefins at acidic sites of the support (*7*) is also substantiated by the following observations:

(1) Only double bond shift in methylcyclopentene took place on alumina alone at temperatures up to 450°C. No cracking products could be detected under these conditions.

(2) Similar distributions of the hexane isomers were observed in hydrogenolysis and isomerization with platinum supported on alumina, pumice, or charcoal, and in hydrogenolysis on evaporated films of "spectroscopically pure" platinum.

(3) The observed initial distributions were quite different from those due to the isomerization on acidic catalysts (*8*), where the carbonium ion mechanism is known to be responsible.

(4) Isomerization of 2,3-dimethylbutane is extremely slow in comparison with isomerization of I, II, and III. In this case, a four-membered cyclic complex may be necessary, and because of the strain involved in its formation, isomerization is largely prevented.

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