

## Isomerization and Dehydrocyclization of Hexanes over Monofunctional Supported Platinum Catalysts

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This paper deals with a study of the isomerization and dehydrocyclization reactions of hexanes in the presence of inert-alumina-supported platinum catalysts.

The activities for these reactions per exposed metal atom were found to be independent of the metal crystallite size, at least in the range of from 15 to 50 Å. It was also shown that five-membered ring structures, which are intermediates in the monofunctional platinum isomerization, are not involved in the conversion of *n*-hexane into benzene. Five-membered and six-membered ring closure of *n*-hexane are parallel reactions.

The dehydrocyclization of *n*-hexane to benzene proceeds along two different routes: (i) by a platinum-catalyzed six-ring closure; (ii) by a thermal six-ring closure of hexatrienes formed by dehydrogenation of *n*-hexane over the platinum function.

### INTRODUCTION

Skeletal isomerization and cyclization reactions of saturated hydrocarbons are not restricted to dual-function catalysts containing both a platinum and an acid function. In experiments over evaporated platinum films Anderson and Avery (1) found that the platinum function itself is capable of catalyzing skeletal isomerization of butanes and pentanes. Similar results were obtained by Barron *et al.* (2, 3) with hexanes over platinum films and over platinum-on-an-inert-support catalysts. These authors (3) and Maire *et al.* (4) also studied the hydrogenolysis of methylcyclopentane over the same catalysts and concluded that the isomerization of the hexanes and the hydrogenolysis of methylcyclopentane involve a common intermediate.

Similar results were found in the isomerization of *n*-heptane over platinum-on-neutral silica gel (5). Apparently, the platinum-type isomerization of hexanes and heptanes proceeds through intermediate

five-ring structures. The most remarkable observation made by Barron *et al.* (3, 4) was that the product distributions in hydrogenolysis of methylcyclopentane and in isomerization of the hexanes varied with the concentration of the metal on the platinum-alumina catalysts. It was suggested (4) that the different behavior of the platinum-on-alumina catalysts with a high platinum content was due to a larger size of the crystallites. According to this view the intrinsic activity of platinum for these reactions would be highly dependent on the platinum particle size. This is in striking contrast with, for instance, the hydrogenation of benzene over supported platinum catalysts, where no effect whatsoever of crystallite size could be detected (6). Since, generally speaking, the existence of a possible particle-size effect on platinum-catalyzed reactions is still a controversial subject in the literature, it seemed of interest to publish the results of a study of hexane isomerization and methylcyclopentane hydrogenolysis over essentially

monofunctional supported platinum catalysts.

Monofunctional supported platinum catalysts also catalyze the conversion of hexanes and higher saturates into aromatics. Aromatics are formed both from paraffins which can undergo direct 1-6-ring closure and from paraffins which possess only five carbon atoms in a row. In the former case aromatization proceeds with a substantially higher selectivity and produces virtually only those aromatics which can be formed by direct six-ring closure (7). In the latter case the paraffin is believed (3, 8) to undergo five-ring closure, followed by ring expansion on the metal sites. It is still possible, however, for the five-ring formed to undergo ring opening to form a hydrocarbon with six carbon atoms in a straight chain, which subsequently could close directly to a six-ring. This possibility was mentioned by Barron *et al.* (3), but was rejected for reasons not well understood.

This paper presents evidence in favor of the latter view, i.e., six-ring closure preceded by five-ring opening rather than ring expansion.

Finally, a study was undertaken to gain a better understanding of the effect of platinum dispersion and hydrogen pressure on six-ring closure. The results should help in explaining the effect of the platinum content on the dehydrocyclization of *n*-heptane over supported platinum catalysts (9). For this investigation we chose the dehydrocyclization of *n*-hexane to benzene over catalysts consisting of platinum-on-inert-alumina support.

#### EXPERIMENTAL METHODS

**a. Apparatus.** The experiments with *n*-hexane, 2-methylpentane, and methylocyclopentane were conducted in a flow system using 0.5 to 2.0 ml of catalyst of 0.125- to 0.250-mm particle size. Those with 2,5-dimethylhexane, 2,2,4-trimethylpentane, 1,1,3-trimethylcyclopentane, 1,1-dimethylcyclohexane, and isopropylcyclopentane were carried out in a micropulse reactor-chromatographic analyzer setup. This

arrangement was similar to the one reported by Kokes *et al.* (11).

**b. Materials.** *n*-Hexane, 1-hexene, 2-methylpentane, and methylocyclopentane (pure grade) were obtained from Phillips Petroleum Co. The other hydrocarbons used in the pulse experiments were all from the American Petroleum Institute. Gas chromatographic analyses confirmed the high purities of these samples.

**c. Catalysts.** Pechiney alumina, type A was used as catalyst support. This material was chosen after it had been verified that, following a calcination treatment in air at 500°C for 3 hr, it was essentially inert for skeletal isomerization and cyclization of hexenes as well as for ring opening of methylocyclopentane at temperatures up to 500°C.

In order not to impart any acidity to the carrier the catalysts were prepared by impregnation of the support with  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$  in aqueous solution. They were then dried at 120°C for 3 hr and subsequently calcined at 500°C in air for 3 hr. By subjecting these catalysts to a reduction treatment in hydrogen at various severities (500-650°C), samples were obtained in which platinum particles were sintered to various degrees.

The degree of dispersion (av particle size) of platinum was determined by hydrogen chemisorption. The measurements were carried out in a conventional static sorption apparatus (12). Prior to the adsorption proper the samples were reduced in hydrogen at 400°C and atmospheric pressure for 1 hr and then heated under vacuum ( $10^{-6}$  Torr) at 400°C for 16 hr. The samples were subsequently cooled down to -78°C and the amount of hydrogen was determined which adsorbed at -78°C and 10 Torr pressure (13).

**d. Analysis.** A column (4 m  $\times$  4 mm) filled with squalane on chromosorb-P (20:100 pbw) at 50°C was used to analyze the reactor effluent samples from the flow experiments. A precolumn hydrogenation section, containing Pt/inert alumina (2:100 pbw) was applied at 85°C.

The products from the pulse reactor experiments were analyzed on a 6 m  $\times$  4

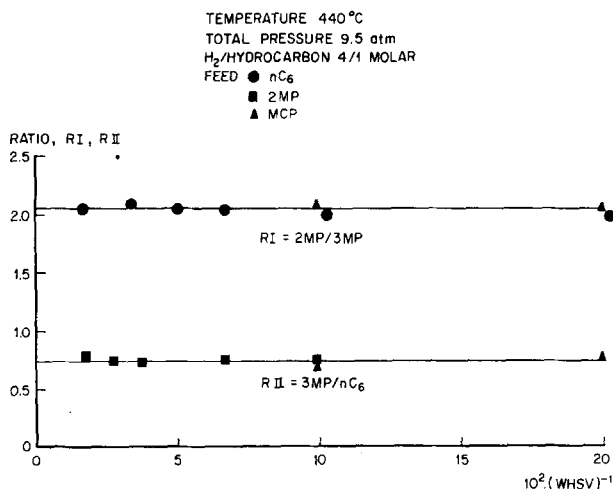


Fig. 1. Ratio of hexane isomers formed as a function of space velocity.

mm Bentone/diisodecylphthalate on Kammagkieselguhr column (12:100 pbw) at 100°C.

In order to determine *n*-hexane/linear hexenes ratios the liquid samples from the flow experiments were analyzed on a 4 m × 4 mm column, filled with a mixture of phenoxathiine and isoquinoline on chromosorb-P (10:100 pbw) at 10°C. We applied a post-column splitter leading to (a) a dummy absorber connected with a flame-ionization detector to determine saturates plus olefins, and (b) a Hg(ClO<sub>4</sub>)<sub>2</sub> absorber connected with a flame-ionization detector to find the amount of saturates. Both chromatograms were correlated via the methylcyclopentane peak.

## RESULTS

**a. Isomerization of hexanes.** *n*-Hexane, 2-methylpentane and methylcyclopentane were charged separately over 0.5% Pt-on-inert-alumina in a continuous flow system at various space velocities. Although at each condition the catalyst activity suffered from a rather heavy decline, the ratios of the hexane isomers formed in the effluent turned out to be totally independent of catalyst age. This observation is in line with the monofunctional character of the catalyst. The results in Fig. 1 show that at rather high space velocities the ratios of the hexane isomers formed are constant, as

could be expected from the above observation. In agreement with Barron *et al.* (3) and Maire *et al.* (4), it is found that the hydrogenolysis of methylcyclopentane and the isomerization of the hexanes involve a common intermediate. The ratios found for the relative formation of the isomers are in close agreement with those observed by Barron *et al.* (3) and Maire *et al.* (4), at 300°C for their 0.2% Pt-on-alumina catalyst (2-methylpentane/3-methylpentane = 2.2; and 3-methylpentane/*n*-hexane = 0.55), but are in striking contrast with the values given by these authors for their 10 wt % Pt-on-alumina catalyst (i.e., 2-methylpentane/3-methylpentane = 3.5; and 3-methylpentane/*n*-hexane = 2.8).

In another series of experiments we determined the initial rates of formation of 2-methylpentane and 3-methylpentane from *n*-hexane under differential conditions in the continuous flow system. In order to take catalyst activity decline into account, the initial rates were determined by extrapolating the rates observed at various catalyst ages to catalyst age zero.

Figure 2 shows the rates of formation of 2-methylpentane and 3-methylpentane in millimoles per gram atom platinum as a function of the hydrogen/platinum atomic ratio. Since one hydrogen atom is adsorbed per one exposed platinum atom it follows that the rate of "platinum-type" isomeriza-

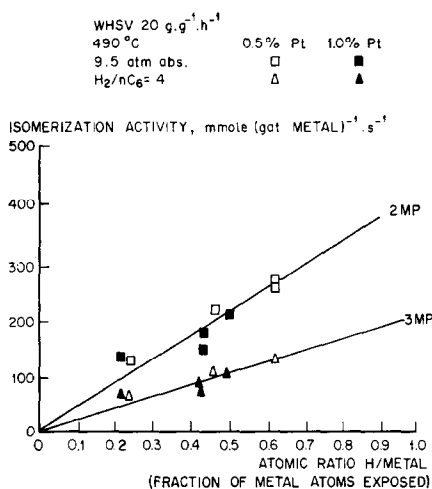


FIG. 2. Relation between metal dispersion and isomerization activity.

tion per exposed platinum atom is independent of the platinum particle size in the range 15–45 Å.

**b. Aromatization of hexanes.** *n*-Hexane and 2-methylpentane were charged over

0.5 wt % Pt-on-inert alumina in the continuous flow system at various space velocities. Product compositions at each space velocity were obtained by extrapolation to zero catalyst life.

The results are shown by Figs. 3 and 4. As shown (cf. Fig. 3), the curves representing the formation of methylcyclopentane and benzene from *n*-hexane have nonzero slopes as 1/WHSV approaches zero. With 2-methylpentane as a feed the curve representing the methylcyclopentane production is very similar to the previous one. However, the curve of benzene formation runs tangentially to the space velocity axis (cf. Fig. 4). This indicates that the intermediate five-ring structure in the "platinum-type" isomerization of hexanes is not involved in the conversion of *n*-hexane into benzene. Apparently, the five-membered and six-membered ring closure reactions of *n*-hexane are parallel reactions.

It is strongly suggested that aromatization of paraffins with five carbon atoms in

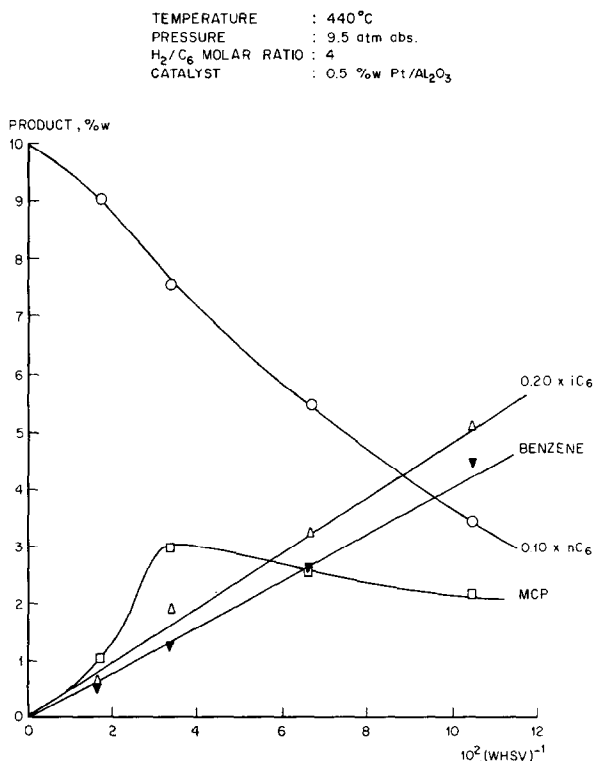


FIG. 3. Product composition from *n*-hexane as a function of space velocity.

TEMPERATURE : 440°C  
 PRESSURE : 9.5 atm abs.  
 H<sub>2</sub>/2MP MOLAR RATIO: 4  
 CATALYST : 0.5 %w Pt/Al<sub>2</sub>O<sub>3</sub>

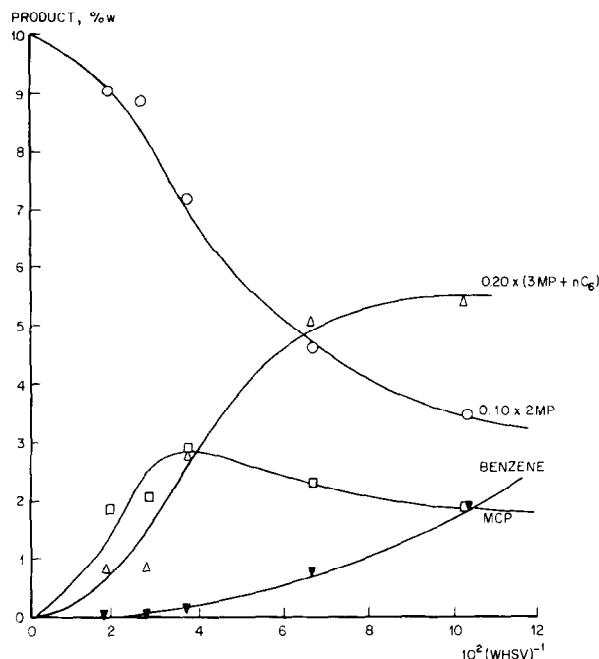


Fig. 4. Product composition from 2-methylpentane as a function of space velocity.

a straight chain is preceded by an isomerization (via intermediate five-membered rings) to structures containing six carbon atoms in a straight chain.

Additional information was obtained in the micropulse reactor connected with the chromatographic analyzer (Table 1).

**c. Six-membered ring closure.** In Fig. 5 we plotted the initial rate of formation of

benzene from *n*-hexane under differential conditions in the continuous flow system. It is shown also that the rate of aromatization of *n*-hexane per exposed platinum atom is independent of the platinum particle size in the range 15–45 Å. These experiments were repeated at three different lower hydrogen partial pressures (cf. Fig. 6), i.e., at  $p_{\text{H}_2} = 2, 2.5,$  and 4 atm. Again

TABLE 1  
MICROPULSE REACTOR EXPERIMENTS

Injection: 2  $\mu$ l; carrier gas: hydrogen at 1.2 atm and 4.5 liters/hr; temp: 480°C; and catalyst: 500 mg 1.0%w Pt-on-inert-alumina.

Compound	Conversion into toluene (mole %)	Conversion into C <sub>8</sub> aromatics (mole %)	C <sub>8</sub> -aromatics distribution (%)			
			Ethylbenzene	<i>p</i> -Xylene	<i>m</i> -Xylene	<i>o</i> -Xylene
2,5-Dimethylhexane	—	60	0.6	87.0	10.8	1.6
2,2,4-Trimethylpentane	—	20	1.6	41.6	49.7	7.1
1,1,3-Trimethylcyclopentane	—	25	1.8	36.1	55.7	6.4
Isopropylcyclopentane	7	10	27	7	24	42
1,1-Dimethylcyclohexane	53	8	2	10	28	60

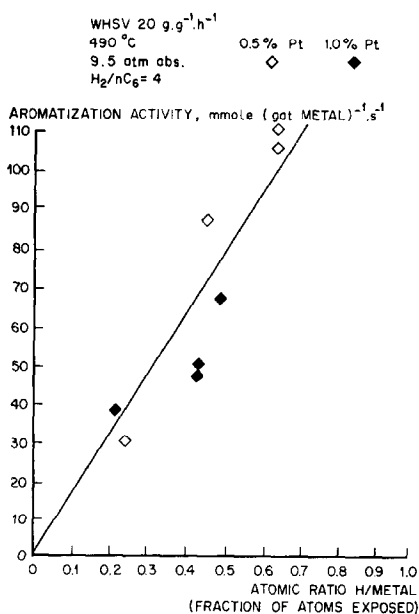


FIG. 5. Relation between metal dispersion and aromatization activity.

a linear relation was found between the rate of benzene formation and the H/Pt atomic ratios. It is noteworthy that these linear relations when extrapolated to H/Pt  $\rightarrow$  0 give rise to positive intercepts on the rate axis. The value of the intercept depends on the hydrogen partial pressure applied.

Table 2 summarizes the results obtained by passing *n*-hexane and *n*-hexane + 30% hexene-1 over these catalysts with three different H/Pt ratios at the conditions given in Fig. 6 at  $p_{H_2} = 2$  atm. Apparently, the equilibrium between hexane and the linear hexenes has been established. Hence one would expect that also the equilibrium

TABLE 2  
EQUILIBRIUM RATIO *n*-HEXANE/ $\Sigma$  LINEAR  
HEXENES<sup>a</sup>

H/Pt	<i>n</i> -Hexane	<i>n</i> -Hexane + 30 wt % 1-hexene
0.24	3.4	3.4
0.46	3.8	3.7
0.64	3.9	3.8

<sup>a</sup>  $n\text{-C}_6/\Sigma \text{ linear C}_6 = 3.7$  calculated value Rossini, F. D., et al., *J. Res. Nat. Bur. Stand.* **36**, 559 (1946).

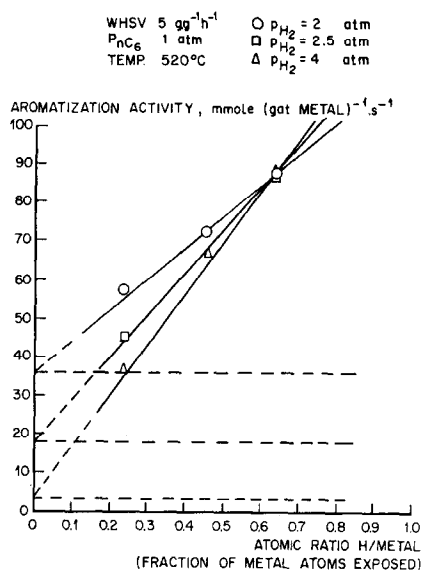


FIG. 6. Relation between metal dispersion and aromatization activity at low hydrogen partial pressures.

between hexane and the hexatrienes will prevail. Since hexatrienes once formed over platinum can easily undergo six-ring closure by a thermal reaction at temperatures around 500 °C (14) it is suggested that the intercepts in Fig. 6 relate to the contribution of thermal cyclization of the intermediate hexatrienes to the total cyclization.

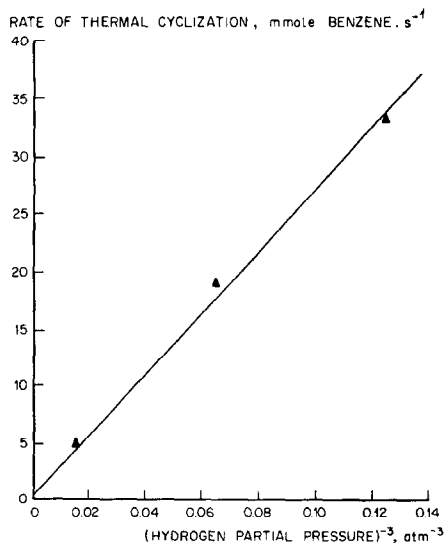


FIG. 7. Effect of hydrogen pressure on the contribution of thermal cyclization of hexatrienes.

That these hexatrienes are in equilibrium with the *n*-hexane feed is consistent with the observation that the intercepts are inversely proportional to the third power of the hydrogen partial pressure (cf. Fig. 7).

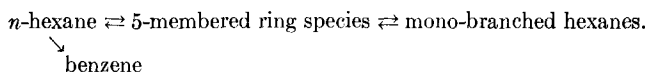
#### DISCUSSION

It was found that the rate of "platinum-type" isomerization per exposed platinum atom is independent of the platinum particle size. Hence it is *not* expected that the product distributions in hydrogenolysis of methylcyclopentane and in isomerization of the hexanes will depend on the concentration of the metal on the carrier in monofunctional catalysts. The large discrepancy reported by Barron *et al.* (3, 4) between the performance of alumina-supported 0.2 and 10 wt % Pt catalysts is probably due to the mode of preparation. Platinum was applied in the form of chloroplatinic acid (10). Although the alumina used by these authors was probably sufficiently inert, this no longer holds after the addition of chloride (ex  $H_2PtCl_6$ ). Hence the catalysts

hydrocarbon one would expect the same product composition of the  $C_8$ -aromatics formed from 2,5-dimethyl hexane, 2,2,4-trimethylpentane, and 1,1,3-trimethylcyclopentane. While it is true that 2,2,4-trimethylpentane and 1,1,3-trimethylcyclopentane yield very similar distributions of xylenes (8) this does not hold for 2,5-dimethylhexane. In the latter case *p*-xylene is the predominant product, which points to a direct 1-6-ring closure (7).

Ring expansion of isopropylcyclopentane would have led to a 1,1-dimethylcyclohexyl species which subsequently would have been converted mainly into toluene, some *o*- and *m*-xylene, and even less *p*-xylene and ethylbenzene (see Table 1). The actual results obtained with isopropylcyclopentane and 1,1-DMCH suggest at least a significant contribution of ring opening followed by a 1-6-ring closure and, in fact, a very minor role of ring expansion.

We now arrive at the following scheme for the reactions of hexanes over monofunctional supported platinum catalysts.



became more bifunctional as more platinum and consequently as more chloride was used.

Our results strongly suggest that the aromatization of branched paraffins which contain five carbon atoms in their main chain is preceded by an isomerization via intermediate five-ring structures to hydrocarbons which can undergo direct 1-6-ring closure.

Additional information has been obtained from the pulse experiments mentioned in Table 1.

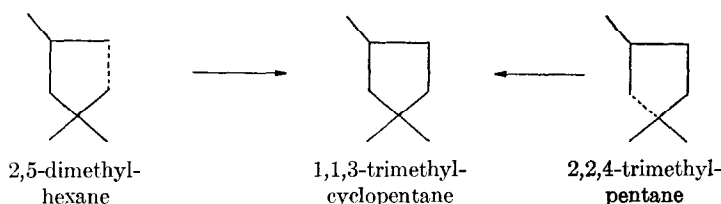
For instance, if the aromatization were to proceed through a five-membered ring

The dehydrocyclization of *n*-hexane to benzene proceeds along two different reaction paths:

(a) platinum-catalyzed ring closure whose contribution to total rate of aromatization is (under differential conditions) proportional to total platinum surface area regardless of metal particle size;

(b) thermal six-ring closure of hexatrienes formed by dehydrogenation from *n*-hexane over the platinum function.

The contribution via the latter route becomes apparent only at low hydrogen partial pressures. The former route also explains why the rate of dehydrocyclization



of *n*-heptane over alumina-supported platinum increases with platinum content (9).

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