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Conversion of Methylcyclopentane and Acyclic Hexanes over Supported Platinum Catalysts

I. Isomerization Kinetics and Hydrogenolysis Selectivities

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In studies of the conversion of methylcyclopentane (MCP), *n*-hexane (nC_6), 2-methylpentane (2MP), and 3-methylpentane (3MP) over a Pt/SiO$_2$ catalyst with an average Pt particle size less than 20 Å, it is found that MCP formation from acyclic hexanes is independent of residence time. Since a cyclic mechanism via a five-membered ring intermediate is the predominant hexane isomerization route, this observation suggests that isomerization is best approximated by a sequential reaction, (nC_6, 2MP, or 3MP) $\rightarrow^{k_1}$ MCP $\rightarrow^{k_2}$ (nC_6, 2MP, and 3MP), in which the quasi-steady-state approximation, $d[\mathrm{MCP}]/dt = 0$, is applicable. The quasi-steady-state approximation requires that $k_2 \gg k_1$; viz., the five-ring closure of hexane to MCP is rate-controlling. k_1 is established to be rate-controlling by experiments with mixed hexane and MCP feeds. Also, the formation of MCP from the acyclic hexanes is found to be independent of time on stream while the generation of isomerized products decreases by 30–40% with time. Based on a hydrodynamic analog of a sequential reaction, this observation indicates that k_1 and k_2 deactivate at the same rate thereby maintaining k_1/k_2 constant with time on stream. This argument implies that the ring closure of hexane to MCP and the ring opening of MCP occur on the same site and is consistent with microscopic reversibility which requires a common intermediate. Kinetic parameters calculated from the sequential reaction model using the quasi-steady-state approximation show that five-ring closure between two primary carbon atoms (2MP and 3MP) is about three times faster than that between a primary and a secondary carbon atom (nC_6). For ring opening of five-ring intermediates, the reaction order in MCP concentration is higher with acyclic hexane feeds than with MCP feed due to a lower surface hydrocarbon coverage with the former feedstocks. During isomerization of the acyclic hexanes, hydrogenolysis to smaller molecules is a competing reaction pathway. For 2MP and 3MP, the rupture of the C–C bond in β-position to the tertiary carbon atom is preferred and with the β bond in 3MP being more reactive than that in 2MP. In the case of nC_6, the center C–C bond ruptures three times faster than the other C–C bonds. These observations are in good agreement with literature data.

INTRODUCTION

In metal-catalyzed skeletal isomerization of hydrocarbons it has been observed that essentially identical "initial" ratios of hexane isomers are formed from the ring opening of methylcyclopentane (MCP) and the isomerization of *n*-hexane (nC_6), 2-methylpentane (2MP), and 3-methylpentane (3MP) over platinum on nonacidic alumina catalysts (*1*). This consistency led Gault and co-workers (*1, 2*) to propose that the isomerization of the three acyclic hexanes and the ring opening of MCP involved a common five-membered ring intermediate—the so-called cyclic mechanism (*3*). The possible existence of this cyclic mechanism via five-ring intermediates was strengthened by subsequent studies using ^{13}C-labeled 2MP (*3, 4*). To isomerize to the other two acyclic isomers, each hexane must first form a five-ring intermediate via five-ring closure which subsequently ring-opens, yielding an isomeric mixture of hexanes. MCP is also

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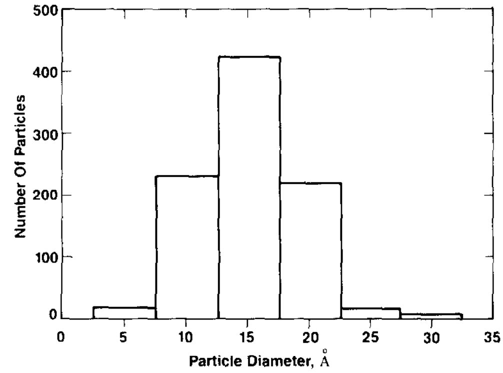
produced by desorption of the five-ring intermediate. If adsorption–desorption is fast, the former step may be viewed as ring closure of hexane to MCP and the latter step as ring opening of MCP. The slower step of the two then controls the overall reaction rate. The three acyclic hexanes may differ in their rates of ring closure, but the kinetic parameters for ring opening of the five-ring intermediates are assumed to be the same for all four hydrocarbons. In this study a kinetic model is used to analyze the above two steps separately. Such analysis allows us to gain a better understanding about the isomerization of acyclic hexanes.

EXPERIMENTAL

Catalyst

The Pt/SiO_2 catalyst was prepared by ion exchange of 80- to 100-mesh Davison Grade 62 silica gel with a 0.01 *M* $Pt(NH_3)_4(NO_3)_2$ solution at room temperature. Procedures for cleaning the gel prior to ion exchange followed those of Uchijima *et al.* (*5*). Ion exchange was carried out by first adding silica gel to distilled water and adjusting the pH to 10 with 0.1 *M* aqueous ammonia solution. A known amount of 0.01 *M* $Pt(NH_3)_4(NO_3)_2$ solution was then added dropwise to the mixture over a period of 2 hr with rapid agitation. After complete addition of the $Pt(NH_3)_4(NO_3)_2$ solution, the pH of the mixture was again adjusted to 10 with aqueous ammonia and the mixture was stirred for an additional 4 hr. The mixture was then filtered and the Pt-loaded gel was repeatedly washed with distilled water. Finally, the Pt-loaded gel was dried at 100°C overnight. After drying, the catalyst was reduced under a 50/50 H_2/He gas mixture (80 $cm^3/min/g$ catalyst) in a fused-silica tube furnace. During reduction the temperature was increased at a rate of 1°C/min to 300°C and held there for 2 hr. The reduced catalyst contained 0.83 wt% Pt.



$$\text{Volume Average Diameter} = \frac{\Sigma n_i d_i^4}{\Sigma n_i d_i^3} = 18.4\ \text{Å}$$

FIG. 1. Platinum particle size distribution.

Platinum Particle Size by Transmission Electron Microscopy

The average platinum particle size of the Pt/SiO_2 catalyst was determined by transmission electron microscopy (TEM). The instrument employed was a Philips 400T transmission electron microscope equipped with a field emission gun, which has been described elsewhere (*6*). The Pt/SiO_2 catalyst was prepared for TEM measurement by grinding and then ultrasonically dispersing the powdered material in ethanol. A drop of the ethanol suspension was introduced onto a holey carbon film mounted on a conventional microscope grid. Specimens were dried in air prior to insertion into the microscope. The microscope was operated at a magnification of 220,000 and the micrographs were enhanced to a magnification of 530,000 by photographic enlargement. The Pt particle size distribution shown in Fig. 1 was obtained by counting over 900 Pt particles on 11 different micrographs. The Pt particles exhibit a volume average diameter of 18.4 Å.

Reaction Study

Conversion reactions of MCP, nC_6, 2MP, and 3MP and mixed hexane and MCP feedstocks were carried out at 277°C in a stainless-steel, fixed-bed reactor under hydrogen at 1 atm total pressure. The H_2/hydrocarbon(s) reaction mixtures were generated by bubbling H_2 through a saturator maintained at 0°C. The H_2/hydrocarbon molar ratios for MCP, nC_6, 2MP, and 3MP were near 18, 16, 10, and 12, respectively. Gas-phase compositions of the mixed hexane and MCP feedstocks were analyzed both before and after reaction runs and were found to remain essentially constant. During reaction the flow rate of the H_2/hydrocarbon(s) reaction mixtures was maintained near 100 cm^3/min. The amount of Pt/SiO_2 catalyst used was varied from 0.44 to 3.0 g to obtain a total conversion at the first sampling (10 min on stream) with pure hydrocarbons of about 10–16%. The Pt/SiO_2 catalyst was diluted with 40- to 80-mesh fused silica to make a total bed volume of 8 cm^3. Prior to each run, the catalyst was dried under He (400 cm^3/min) at 300°C for 1 hr and then re-reduced *in situ* under H_2 (500 cm^3/min) at 300°C for 1 hr. Blank tests, using fused silica, gave no conversion under standard reaction conditions. Reaction products and the gas-phase compositions of mixed hexane and MCP feeds were analyzed on line with a Varian 3700 gas chromatograph equipped with a 50-m SP-2100 coated fused-silica capillary column and flame ionization detector.

Reagents

The four hydrocarbons, MCP (Fluka, purum, >99%), nC_6 (Aldrich, 99+%), 2MP (Alfa, 99%), and 3MP (Aldrich, 99+%), were dried over 4A molecular sieves (Baker) prior to use. GC analysis showed nC_6 (0.75%) to be the major impurity in MCP, MCP (0.61%) to be the major impurity in nC_6. The 3MP (0.06%) and 2,3-dimethylbutane (0.06%) were the major impurities in 2MP, while 2MP (0.24%) and 2,3-dimethylbutane (0.04%) were the major impurities in 3MP. 2-Methyl-2-pentene was obtained from Aldrich. GC analysis showed 2-methyl-1-pentene (0.1%), 2-ethyl-1-butene (0.1%), and *trans*-3-methyl-2-pentene (0.2%) as the major impurities in this olefin. Hydrogen and helium were both of 99.995% purity. For bulk catalyst reductions, hydrogen was purified by passing it through a Deoxo unit (Engelhard), a gas purifier (Matheson), and a liquid nitrogen trap. Helium was purified by passing it through a gas drier (Ultra Scientific), a gas purifier (Matheson), and a liquid nitrogen trap. For reaction studies, both hydrogen and helium were purified by passage through a gas drier (Ultra Scientific). Fused silica was obtained from Thermal American. Before use the fused silica was washed with 0.1 *M* HNO_3 and NH_4OH solutions and distilled water, and then calcined at 500°C overnight. $Pt(NH_3)_4(NO_3)_2$ was obtained from Alfa.

RESULTS AND DISCUSSION

Hexane Isomerization Occurs Predominantly via Five-Ring Intermediates

Table 1 summarizes the total conversions, reaction rates, and product distributions at 10 and 210 min on stream with MCP, nC_6, 2MP, and 3MP feedstocks. The products obtained from the three hexanes can be conveniently divided into three groups: (a) cracking products, C_1 to C_5, (b) hexane isomers, and (c) MCP. As shown in Table 2, the conversion of each of the three acyclic hexanes gives the other two isomers in the same statistical ratio as that found from the ring opening of MCP. This observation confirms the results reported by Barron *et al.* (*1*) with a 0.2% platinum on nonacidic alumina catalyst using a pulse microreactor, which led Gault and coworkers to propose the cyclic mechanism for hexane isomerization over highly dispersed platinum particles.

MCP Formation from the Three Acyclic Hexanes Is Independent of Residence Time

An important observation resulted from a residence time study using an nC_6 feedstock. In Fig. 2 the product composition from the conversion of nC_6 is plotted as a function of the residence time where cracking products (C_1 to C_5) are lumped into one group. Figure 2, as expected, shows that with increasing residence time

TABLE 1

Total Conversion, Rate, and Product Distribution at 10 and 210 min on Stream with Pure Hydrocarbon Feeds

Feed:	MCP[a]		nC_6[b]		2MP[a]		3MP[a]	
Time on stream (min):	10	210	10	210	10	210	10	210
Amount of Pt/SiO_2 (g)	0.44		3.00		1.27		1.44	
Total conversion (%)	15.98	10.96	9.25	7.29	9.44	6.55	12.69	9.03
Rate (mole/g-cat · hr) × 10^4	51.2	35.1	4.9	3.8	18.1	12.6	18.2	12.9
Product distribution[c]								
Methane	2.1	2.2	12.5	13.5	16.1	18.0	23.7	26.7
Ethane	—	—	12.9	14.1	8.0	9.1	8.9	10.0
Propane	0.2	0.2	38.1	42.5	12.1	14.5	1.6	1.1
i-Butane	—	—	0.2	—	7.4	8.6	0.3	0.3
n-Butane	—	0.1	12.5	13.7	0.6	0.4	8.7	9.7
i-Pentane	—	—	0.2	0.2	4.4	4.7	19.3	22.1
n-Pentane	0.1	—	11.3	12.4	11.7	13.1	5.2	5.5
Cyclopentane	1.8	2.1	0.7	0.7	0.4	0.6	0.2	0.3
2,2-Dimethylbutane	—	—	—	—	—	0.1	0.3	0.3
2,3-Dimethylbutane	—	—	—	—	0.2	0.3	—	0.1
2-Methylpentane	40.3	41.6	31.5	28.0			31.3	29.1
3-Methylpentane	19.1	20.3	13.9	12.3	19.6	18.4		
n-Hexane	38.1	35.1			41.0	33.8	29.7	25.6
Methylcyclopentane			14.6	16.9	8.7	12.8	4.5	6.7
Benzene	0.4	0.7	1.4	1.6	—	—	—	—
Cyclohexane	—	—	1.0	1.1	—	—	—	—

[a] Impurities have been deducted from GC data.

[b] Without deduction of impurity of MCP. Total conversion is calculated by assuming an nC_6 purity of 99.4 mole%.

[c] Moles per 100 moles feed converted. Where dashes represent no detectable amount by GC and blank spaces the feed.

nC_6 concentration decreases and the concentrations of C_1–C_5, 2MP, and 3MP increase. Unexpectedly, however, the concentration of MCP remains near 1.3 mole% over the entire range of residence times (conversions).

Hexane isomerization may be viewed as hexane molecules first forming five-membered ring intermediates which subsequently ring-open to give 2MP, 3MP, and nC_6. MCP is produced by the direct desorption of the intermediate. The observation

TABLE 2

Ratios of Hexane Isomers from Conversion of MCP, nC_6, 2MP, and 3MP on Pt/SiO_2 at 277°C

Feed:	MCP		nC_6		2MP		3MP	
Time on stream (min):	10	210	10	210	10	210	10	210
Relative amount[a]								
2-Methylpentane	2.1	2.1	2.3	2.3			2.0	2.0
3-Methylpentane	1.0	1.0	1.0	1.0	1.0	1.0		
n-Hexane	2.0	1.7			2.1	1.8	1.9	1.8

[a] Equilibrium ratio at 277°C is 2-methylpentane : 3-methylpentane : *n*-hexane = 2.0 : 1.0 : 1.1 calculated from the thermodynamic data in Ref. (*18*).

TABLE 3

Product Composition at 10 and 210 min on Stream with Feed of nC_6 or nC_6 Mixed with Different Amounts of MCP

Feed:	nC_6		5% MCP + 95% nC_6		10% MCP + 90% nC_6		25% MCP + 75% nC_6	
Time on stream (min):	10	210	10	210	10	210	10	210
Amount of Pt/SiO_2 (g)	3.00		3.00		3.00		3.01	
Product composition[a] (mole%)								
Methane	1.1	1.0	1.3	1.2	1.2	1.1	1.4	1.2
Ethane	1.2	1.0	1.3	1.1	1.1	0.9	1.0	0.8
Propane	3.4	3.0	3.7	3.3	3.2	2.7	2.7	2.3
i-Butane	tr.	—	tr.	tr.	tr.	tr.	0.1	0.1
n-Butane	1.1	1.0	1.2	1.1	1.1	0.9	0.9	0.8
i-Pentene	tr.	tr.	tr.	tr.	0.1	tr.	0.1	0.1
n-Pentane	1.0	0.9	1.2	1.0	1.0	0.9	1.0	0.9
Cyclopentane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
2,2-Dimethylbutane	—	—	—	—	—	—	—	—
2,3-Dimethylbutane	—	—	—	—	—	—	—	—
2-Methylpentane	2.8	2.0	4.9	4.1	6.2	5.5	11.2	10.6
3-Methylpentane	1.2	0.9	2.1	1.7	2.6	2.3	4.8	4.6
n-Hexane	86.6	89.0	82.4	84.8	81.9	84.0	75.2	76.9
Methylcyclopentane	1.3	1.2	1.4	1.3	1.3	1.3	1.3	1.7
Benzene	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.1
Cyclohexane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

[a] Where tr. represents the amount present is less than 0.05 mole% and dashes represent no detectable amount by GC.

that the formation of MCP is independent of residence time strongly suggests that the overall reaction can be approximated by a sequential reaction, (nC_6, 2MP, or 3MP) $\rightarrow^{k_1}$ MCP $\rightarrow^{k_2}$ (nC_6, 2MP, and 3MP), in which the quasi-steady-state approximation, $d[\mathrm{MCP}]/dt = 0$, is applicable. k_1 is the rate constant for the formation of the five-ring intermediate and k_2 is the rate constant for the subsequent ring opening of the five-ring intermediate. The above analysis is applicable provided adsorption–desorption processes are fast.

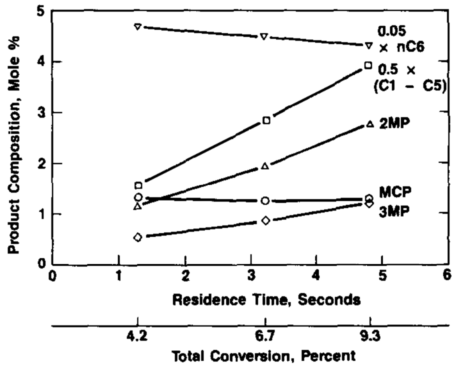


FIG. 2. Product composition from the conversion of nC_6 as a function of residence time. Data at 10 min on stream.

Five-Ring Closure of Hexane to MCP Is Rate-Controlling

The applicability of the quasi-steady-state approximation implies that $k_2 \gg k_1$; viz., the ring closure of hexane molecules to five-ring intermediates is the rate-controlling step in the overall reaction. This assumption is strengthened by studies using mixed hexane and MCP feeds. Table 3 gives the product compositions at 10 and 210 min on stream with various mixed nC_6/MCP feedstocks. Remarkably a 75% nC_6/25% MCP feed yields the same amount

TABLE 4

Product Composition at 10 and 210 min on Stream with Feed of 2MP or 2MP Mixed with MCP

Feed:	2MP[a]		9% MCP + 91% 2MP[a]	
Time on stream (min):	10	210	10	210
Amount of Pt/SiO$_2$ (g)	1.27		1.30	
Product composition[b] (mole%)				
Methane	1.5	1.2	1.1	0.7
Ethane	0.7	0.6	0.6	0.4
Propane	1.1	0.9	0.9	0.6
i-Butane	0.7	0.6	0.5	0.3
n-Butane	0.1	tr.	0.1	tr.
i-Pentane	0.4	0.3	0.3	0.2
n-Pentane	1.1	0.8	0.8	0.5
Cyclopentane	tr.	tr.	0.1	0.1
2,2-Dimethylbutane	—	tr.	—	—
2,3-Dimethylbutane	tr.	tr.	tr.	tr.
2-Methylpentane	88.1	91.4	87.1	90.3
3-Methylpentane	1.8	1.2	2.5	2.1
n-Hexane	3.8	2.2	5.4	3.9
Methylcyclopentane	0.8	0.8	0.8	1.0
Benzene	—	—	—	—
Cyclohexane	—	—	—	—

[a] Impurities have been deducted from GC data.

[b] Where tr. represents the amount present is less than 0.05 mole% and dashes represent no detectable amount by GC.

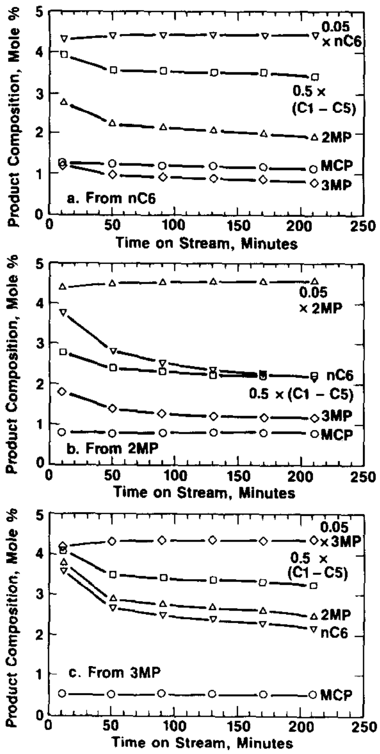


FIG. 3. Product composition as a function of time on stream in the conversion of the three hexanes.

TABLE 5

Product Composition at 10 and 210 min on Stream with Feed of 3MP or 3MP Mixed with MCP

Feed:	3MP[a]		12% MCP + 88% 3MP[a]	
Time on stream (min):	10	210	10	210
Amount of Pt/SiO$_2$ (g)	1.44		1.51	
Product composition[b] (mole%)				
Methane	2.9	2.3	1.7	1.2
Ethane	1.1	0.9	0.6	0.4
Propane	0.2	0.1	0.2	0.2
i-Butane	tr.	tr.	tr.	tr.
n-Butane	1.1	0.8	0.6	0.4
i-Pentane	2.3	1.9	1.2	0.9
n-Pentane	0.6	0.5	0.4	0.3
Cyclopentane	tr.	tr.	tr.	0.1
2,2-Dimethylbutane	tr.	tr.	tr.	tr.
2,3-Dimethylbutane	tr.	tr.	tr.	tr.
2-Methylpentane	3.8	2.5	6.0	5.4
3-Methylpentane	83.6	88.0	83.0	85.7
n-Hexane	3.6	2.3	5.7	4.8
Methylcyclopentane	0.5	0.6	0.5	0.6
Benzene	—	—	—	—
Cyclohexane	—	—	—	—

[a] Impurities have been deducted from GC data.

[b] Where tr. represents the amount present is less than 0.05 mole% and dashes represent no detectable amount by GC.

of MCP, 1.3 mole%, in the product as the neat nC_6. As summarized in Tables 4 and 5, respectively, 0.8 mole% MCP is obtained from both pure 2MP and 91% 2MP/9% MCP feeds, while 0.5 mole% MCP results from both pure 3MP and 88% 3MP/12% MCP feeds. These findings strongly indicate that the MCP ring opening is a rapid reaction, yielding only a steady-state MCP concentration in the product.

MCP Formation from the Three Acyclic Hexanes Is Independent of Time on Stream

During the conversion of the three acyclic hexanes, the change in product composition with time on stream is also consistent with the proposed sequential reaction model. Figures 3a, 3b, and 3c show the change of product composition with time on stream for nC_6, 2MP, and 3MP feeds, respectively. As the catalyst deactivates with time on stream, total conversion decreases. However, while the rate of formation of C_1–C_5 crackate and hexane

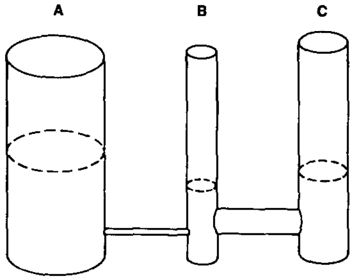


FIG. 4. Hydrodynamic analog of a sequential reaction $A \rightarrow^{k_1} B \rightarrow^{k_2} C$ with $k_2 \gg k_1$.

isomers decreases 30–40% after 210 min on stream, the rate of formation of MCP remains constant over this time period for all three hexanes.

It is easier to understand this change in product composition with time on stream due to catalyst deactivation by looking at the hydrodynamic analog of a sequential reaction $A \rightarrow^{k_1} B \rightarrow^{k_2} C$ with $k_2 \gg k_1$ (see Fig. 4). Catalyst deactivation can be thought of as a process in which k_1 and k_2, the flows into cylinders B and C, respectively, both decrease with time on stream. To maintain a constant level in cylinder B with decreasing level in cylinder C with time requires that k_1 and k_2 decrease at the same rate. The k_1/k_2 ratio thereby remains constant with time. This analysis suggests that five-ring closure of hexane to MCP and subsequent ring opening of five-ring intermediates occur on the same sites.

The active sites for both MCP ring opening and hexane isomerization have attracted considerable attention in recent years. Gault and co-workers have extensively studied the effect of Pt particle size on the product selectivity of MCP ring opening. Based on these studies, Gault and co-workers proposed that the cyclic mechanism actually involved two different mechanisms (*3*). A nonselective mechanism, which offers an equal chance of rupturing the five-ring C–C bonds in a MCP molecule and gives a statistical ratio of the three hexane isomers, is proposed to occur on a single Pt atom (dicarbene surface intermediate). The second mechanism, a selective one which ruptures C–C bonds between two secondary carbon atoms and yields only 2MP and 3MP, is assumed to require an active site of two contiguous Pt atoms (dicarbyne surface intermediate). Due to a difference in the Pt ensemble size requirement, the nonselective mechanism is thought to be predominant with small Pt particles. Kramer and Zuegg (*7*), although accepting the existence of the selective and nonselective mechanisms, have suggested the existence of different active sites. They proposed that the nonselective mechanism occurs on the phase boundary between Pt particles and the support, while the selective mechanism takes place on the Pt surface.

By application of Gault's model, only the nonselective mechanism appears to occur on the Pt/SiO_2 catalyst employed in this study. It is difficult, however, to imagine that the present catalyst, which has an average Pt particle size of 18.4 Å, gives no products from the selective mechanism since the Pt ensemble size requirement for the selective mechanism is only twice that of the nonselective mechanism. It is also difficult to accept, according to Kramer and Zuegg's model, that the MCP ring opening and the isomerization of the three hexanes in this study occur solely on the phase boundary between Pt particles and the silica support.

Constant MCP formation rates with residence time and with time on stream from the three acyclic hexanes could potentially arise from the equilibrium being established between the reactant hexane and MCP under the conditions studied. The observed MCP concentrations are, however, larger than the equilibrium values, calculated from the Gibbs energy data in Ref. (*18*), by a factor of 2 with nC_6 and 2MP feeds. For 3MP feed, the observed MCP concentration is six times higher than the equilibrium value. Although the differences may be within the probable accuracy of the thermodynamic data employed, the postulation of equilibrium between the reactant hexane and MCP requires that all four molecules are in equilibrium with each other, a situation which does not happen under the conditions studied. Therefore, we interpret the constant MCP concentrations from the three hexanes as a steady-state phenomenon, and not one of equilibrium.

Kinetic Parameters for the Ring Closure and Ring Opening Reactions

Kinetic parameters for the ring closure and ring opening reactions can be calculated by considering the following overall reaction scheme in the case of $n\mathrm{C}_6$ feed,

$$\mathrm{C}_1\text{–}\mathrm{C}_5 \xleftarrow{k_3^{n\mathrm{C}_6}} n\mathrm{C}_6 \underset{\frac{2}{5}k_2^{n\mathrm{C}_6}}{\overset{k_1^{n\mathrm{C}_6}}{\rightleftarrows}}$$

$$\mathrm{MCP} + \mathrm{H}_2 \begin{array}{l} \xrightarrow{\frac{2}{5}k_2^{n\mathrm{C}_6}} \mathrm{2MP} \\ \xrightarrow[\frac{1}{5}k_2^{n\mathrm{C}_6}]{} \mathrm{3MP} \end{array}$$

in which the ring closure rate constant k_1, the ring opening rate constant k_2, and the lumped cracking rate constant k_3 are superscript with $n\mathrm{C}_6$ to distinguish them from the rate constants obtained from 2MP, 3MP, and MCP feeds. The assumptions that MCP ring opening gives the ratio of 2MP : 3MP : $n\mathrm{C}_6$ = 2 : 1 : 2 (see Table 2) and cracking products come mainly from the reactant $n\mathrm{C}_6$ (see Table 1 and the text below) in the scheme are experimentally well justified. Representation of cracking reactions by one rate constant is for the purpose of simplicity and does not affect the conclusions to be reached below.

Assuming all reactions are first order, the following differential equations describe the concentration change of each compound with residence time:

$$\frac{d[n\mathrm{C}_6]}{dt} = -\left(k_1^{n\mathrm{C}_6} + k_3^{n\mathrm{C}_6}\right)[n\mathrm{C}_6] + \frac{2}{5}k_2^{n\mathrm{C}_6}[\mathrm{MCP}][\mathrm{H}_2] \quad (1)$$

$$\frac{d[\mathrm{MCP}]}{dt} = k_1^{n\mathrm{C}_6}[n\mathrm{C}_6] - k_2^{n\mathrm{C}_6}[\mathrm{MCP}][\mathrm{H}_2] \quad (2)$$

$$\frac{d[\mathrm{2MP}]}{dt} = \frac{2}{5}k_2^{n\mathrm{C}_6}[\mathrm{MCP}][\mathrm{H}_2] \quad (3)$$

$$\frac{d[\mathrm{3MP}]}{dt} = \frac{1}{5}k_2^{n\mathrm{C}_6}[\mathrm{MCP}][\mathrm{H}_2] \quad (4)$$

$$\frac{d[\mathrm{C}_1 - \mathrm{C}_5]}{dt} = k_3^{n\mathrm{C}_6}[n\mathrm{C}_6]. \quad (5)$$

Since hydrogen concentration remains essentially constant during the reaction, the hydrogen concentration term can be combined with $k_2^{n\mathrm{C}_6}$ to define a new ring opening rate constant $k_2^{n\mathrm{C}_6 *} = k_2^{n\mathrm{C}_6}[\mathrm{H}_2]$.

The above differential equations can be solved to obtain expressions for the concentration of each compound in terms of residence time. Similar equations can be obtained for the 2MP, 3MP, and MCP feeds. With a residence time corresponding to the amount of catalyst used for each feed, the product composition data after 10 min on stream are fitted by these expressions to obtain k_1 and k_2^* for $n\mathrm{C}_6$, 2MP, 3MP, and MCP feedstocks (see Table 6). The k_1 rate constants for 2MP and 3MP are about threefold higher than that for $n\mathrm{C}_6$. These results suggest that the rate of five-ring closure between two primary carbon atoms is three times faster than that between a primary and a secondary carbon atom. This rate difference does not result from a higher activation energy for five-ring closure between a primary and a secondary carbon atom, as the opposite has been observed (*8*). It is likely that this rate difference is simply due to a surface concentration effect. It seems that surface precursors leading to five-ring closure between two

TABLE 6

First-Order Ring Closure and Ring Opening Rate Constants

Feed	$n\mathrm{C}_6$	2MP	3MP	MCP
Rate constant[a] (sec^{-1})				
$k_1 \times 10^2$	1.65	5.57	4.20	
k_2^*	1.17	6.30	7.00	0.24

[a] Data at 10 min on stream. $k_2^* = k_2[\mathrm{H}_2]$.

primary carbon atoms are more abundant than surface precursors leading to five-ring closure between a primary and a secondary carbon atom.

Surprisingly, k_2^* for $n\mathrm{C}_6$ is about five times and k_2^*'s for 2MP and 3MP are about 30 times higher than that for MCP. Since a common five-ring intermediate is involved in MCP ring opening and isomerization of the three acyclic hexanes, the surface ring opening rate constant must be the same no matter from what molecule it is formed. Since in our study adsorption–desorption is not rate-controlling, it is reasonable to assume that the differences in the k_2^* ring opening rate constants result from their changes in MCP concentration reaction orders for the ring opening reaction.

To extract relative MCP concentration reaction orders for the ring opening reaction, Eq. (2) is modified for an $n\mathrm{C}_6$ feed to be

$$\frac{d[\mathrm{MCP}]}{dt} = k_1^{n\mathrm{C}_6}[n\mathrm{C}_6] - k_2^{\mathrm{MCP}*}[\mathrm{MCP}]^n,$$

where $k_2^{\mathrm{MCP}*} = 0.24$. Similar equations can be written for 2MP and 3MP feeds. By applying the quasi-steady-state approximation, $d[\mathrm{MCP}]/dt = 0$, and the k_1 values in Table 6, n, the reaction order in MCP concentration for the ring opening reaction relative to the assumed first-order dependency for MCP, can be calculated for $n\mathrm{C}_6$, 2MP, and 3MP feeds (see Table 7). It is remarkable that a modest 45% increase in the reaction order in the case of 3MP can account for a 30-fold larger apparent ring opening rate constant.

TABLE 7

Relative Reaction Order in MCP Concentration for the Ring Opening Reaction

Feed	$n\mathrm{C}_6$	2MP	3MP	MCP
Relative reaction order in MCP concentration[a]	1.2	1.4	1.45	1

[a] Data at 10 min on stream. Calculated directly from GC data.

The higher reaction orders in MCP concentration for $n\mathrm{C}_6$, 2MP, and 3MP feeds require elucidation. It may be argued that the higher reaction orders in MCP concentration with acyclic hexane feeds are simply due to their much lower MCP partial pressure, only about 1% of that with MCP feed. The situation, however, is complicated by the presence of hexanes in the cases with acyclic hexane feeds.

It is helpful to consider the reactions occurring on the Pt surface. Assume that the rate-controlling step in MCP ring opening is the C–C bond rupture of a dehydrogenated surface species with a five-membered ring structure. This dehydrogenated surface species may be formed by a series of consecutive dehydrogenation steps, unimolecular or bimolecular, all equilibrated (*9*). The rate equation can be written as

$$r = k_{2\mathrm{s}}\bar{K}\,\frac{P_{\mathrm{MCP}}}{P_{\mathrm{H}_2}^{m/2}}\,\theta_{\mathrm{s}}^{e},$$

where $k_{2\mathrm{s}}$ is the surface ring opening rate constant, P_{MCP} is the partial pressure of MCP, P_{H_2} is the partial pressure of hydrogen, m is the number of consecutive dehydrogenation steps, θ_{s} is the surface coverage of empty sites, and e is the number of contiguous surface Pt atoms required to accommodate the dehydrogenated surface species. $\bar{K}$ includes the site density of the Pt surface, the equilibrium constant of each dehydrogenation step and the equilibrium constant for the dissociative adsorption of hydrogen which is considered to be a constant at a fixed temperature. In our study at the same total pressure and with a large excess of hydrogen, the hydrogen partial pressure dependence term is essentially constant for all four feeds. Thus, the only term that may affect the reaction order in MCP partial pressure is θ_{s}, the surface coverage of empty sites. In general, we may say that θ_{s} is a function of the kind of hydrocarbon present in the system and has a negative hydrocarbon pressure dependence. The negative hydrocarbon pressure dependence of θ_s results in a reduction in the MCP reaction order. MCP feed has the lowest hydrocarbon pressure but shows the largest reduction in the reaction order (MCP feed has the lowest reaction order in MCP partial pressure, as shown in Table 7). This indicates that the dependence of θ_s on hydrocarbon pressure is more negative with MCP than with $n\text{C}_6$, 2MP, and 3MP feedstocks. In other words, MCP will give higher surface coverage of hydrocarbon than $n\text{C}_6$, 2MP, and 3MP feeds. The higher reaction order in MCP concentration for the ring opening reaction with the acyclic hexane feeds results from a lower surface hydrocarbon coverage.

Hydrogenolysis Selectivities

As shown in Table 1, hydrogenolysis to smaller molecules is another major reaction during the conversion of the three hexanes. The observations that only small amounts of i-butane and i-pentane from $n\text{C}_6$, *n*-butane from 2MP, and propane and i-butane from 3MP indicate that under the conditions studied secondary reactions, occurring via either the readsorption of primary products from gas phase or multiple reactions during one sojourn of molecules on the Pt surface, are minimal. In a recent paper (*10*) assessing the diffusional inhibition via primary and secondary cracking analysis, a parameter μ was defined as the size of the average C_1–C_5 molecules, i.e.,

$$\mu = \sum_{i=1}^{5} i n_{\text{C}_i} \Big/ \sum_{i=1}^{5} n_{\text{C}_i},$$

where n_{C_i} is the number of moles of C_i. For purely primary cracking, $\mu = 3$. The μ values calculated from data in Table 1 for the three hexanes are within 1% of 3. This consistency demonstrates the absence of both secondary cracking and diffusional inhibition in the present study.

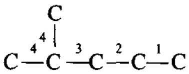
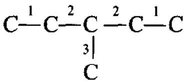
Since secondary hydrogenolysis reactions are minimal, it is possible to calculate from the product distributions the relative rates of rupturing different C–C bonds in the $n\text{C}_6$, 2MP, and 3MP molecules. The cracking patterns for $n\text{C}_6$, 2MP, and 3MP are discussed below.

a. $n\text{C}_6$. Cracking products from $n\text{C}_6$ are mainly methane, ethane, propane, *n*-butane, and *n*-pentane. The relative bond rupture reactivities of the five C–C bonds in an $n\text{C}_6$ molecule are calculated in terms of the "reactivity factor" defined by Leclercq *et al.* (*11*) which ratios the actual rupture rate of the bond under consideration to its statistical rupture rate. The relative statistical rupture rate of a bond corresponds to the number of bonds identical to the one being considered and it is the relative rate that would be expected if all the C–C bonds exhibit the same reactivity toward rupture. Table 8a summarizes these calculations. The center C–C bond is three times more reactive with respect to bond rupture than the adjacent and the terminal bonds. The observed high rupture rate for the center C–C bond of $n\text{C}_6$ is in good agreement with studies on ultrathin Pt films (*12*) and Pt/silica catalysts (*13*). Lankhorst *et al.* (*14*) also observed a similar preference for internal fission in their study of $n\text{C}_6$ conversion over a Pt/silica catalyst and attributed it to the center bond being the weakest bond in an $n\text{C}_6$ molecule. The bond energies for the five C–C bonds in $n\text{C}_6$, however, indicate that the C–C bonds next to the center bond have the same bond energy as the center one (*15*).

b. 2MP. The relative bond rupture activities of the five C–C bonds in a 2MP molecule are presented in Table 8b. The number of moles of methane formed from the conversion of 100 moles of 2MP is calculated from the relative reactivity factors to be $4.4 \times (1 + 2 \times 1.35) = 16.3$, which is close to the observed amount of 16.1 (see Table 1). The bond in the β-position to the tertiary carbon atom exhibits the highest reactivity, followed by the bond in the α-position to the tertiary carbon atom and the two bonds between the tertiary and the two primary carbon atoms. The bond between the primary and the secondary carbon atoms is the least reactive.

TABLE 8

Relative Rate in Rupturing C–C Bonds in Hexane Molecules

1. C–C bond	2. Number of identical bonds in the molecule	3. Relative statistical rupture rate	4. Relative actual rupture rate[b]	5. Relative reactivity factor (4)/(3)
a. nC_6, $C\overset{1}{-}C\overset{2}{-}C\overset{3}{-}C\overset{2}{-}C\overset{1}{-}C$				
1[a]	2	2	1	0.5
2[a]	2	2	1.1	0.55
3[a]	1	1	3.4/2[c]	1.7
b. 2MP, 				
1[d]	1	1	1	1
2[d]	1	1	1.7	1.7
3[d]	1	1	2.8/2[c]	1.4
4[d]	2	2	2.7	1.35
c. 3MP, 				
1[e]	2	2	3.7	1.85
2[e]	2	2	1.7	0.85
3[e]	1	1	1	1

[a] Rupture of bond 1 gives methane and *n*-pentane. Rupture of bond 2 gives ethane and *n*-butane. Rupture of bond 3 gives two propane molecules.

[b] Calculated from the data at 10 min on stream in Table 1.

[c] Since rupture of one bond 3 gives two propanes, the rate of rupturing bond 3 is one-half of the rate of formation of propane.

[d] Rupture of bond 1 gives methane and i-pentane. Rupture of bond 2 gives ethane and i-butane. Rupture of bond 3 gives two propanes. Rupture of bond 4 gives methane and *n*-pentane.

[e] Rupture of bond 1 gives methane and i-pentane. Rupture of bond 2 gives ethane and *n*-butane. Rupture of bond 3 gives methane and *n*-pentane.

c. 3MP. The reactivity order for the rupture of the five C–C bonds in a 3MP molecule is shown in Table 8c. The number of moles of methane formed from the conversion of 100 moles of 3MP is calculated from the relative reactivity factors to be 5.2 × (1 + 2 × 1.85) = 24.4, which agrees well with the observed amount of 23.7 (see Table 1). Similar to 2MP, the bond in the β-position to the tertiary carbon atom has the highest reactivity, followed by the bond in the α-position to the tertiary carbon atom and the bond between the tertiary and the primary carbon atoms.

For 2MP and 3MP, the general observation is that the C–C bond in the β-position to the tertiary carbon atom is the easiest ruptured. Leclercq *et al.* (*11*) reported similar results and gave a mechanistic interpretation for this observation which was based on the 1,1,3-triadsorbed 3C surface species postulated by Anderson (*12*). It was argued that in the 1,1,3-triadsorbed species the C–C bond contiguous to the carbon atom doubly bonded to platinum is most easily broken. Comparing 3MP with 2MP, it appears that the reactivity difference between the β bond and the α bond is larger when the β bond involves a primary carbon atom. The β bond between primary and secondary carbon atoms (e.g., the β bond in 3MP) is more reactive than the β bond between

TABLE 9

Conversion of 2-Methyl-2-pentene over Fused Silica and Pt/SiO_2 under He at Atmospheric Pressure and 277°C

Catalyst:	Fused silica			Pt/SiO_2		
Time on stream (min):	10	50	210	10	50	210
Amount of Pt/SiO_2 (g)		—			1.27	
Total conversion (%)	30	29	27	36	32	30
Selectivity (%)						
Cracking	—	—	—	0.2	0.1	—
Double-bond shift[a]	98.1	98.1	98.1	93.8	96.1	97.9
Isomerization[b]	1.9	1.9	1.9	6.1	3.8	2.1

[a] Mainly 2-methyl-1-pentene.

[b] Mainly 3-methyl-2-pentene with fused silica. Pt/SiO_2 gives about the same amount of 3-methyl-2-pentene and also 2,3-dimethyl-2-butene. The latter accounts for the slightly higher selectivity for isomerization with Pt/SiO_2.

two secondary carbon atoms (e.g., the β bond in 2MP). The rate differences in rupturing the various C–C bonds in the three hexane molecules may reflect the existence of different 3C surface intermediates.

The preferential rupture of the C–C bond in β-position to the tertiary carbon atom in 2MP and 3MP and the formation of large amounts of propane in the case with nC_6 question whether an additional acid-catalyzed route is involved in the cracking of the three hexanes. The involvement of acid cracking, however, is rejected on the grounds that only trace amounts of cyclohexane and benzene are observed with MCP feed (see Table 1). Previous studies (*16, 17*) showed that if acidic sites were present ring enlargement of MCP to cyclohexane and subsequent dehydrogenation to benzene occurred more readily than β scission. Additional experiments with 2-methyl-2-pentene further demonstrate that little acid cracking activity is involved in the conversion of the three acyclic hexanes over the Pt/SiO_2 catalyst. These experiments were carried out at atmospheric pressure and 277°C by flowing 100 cm^3/min of a reaction mixture of 2-methyl-2-pentene in He (He/2-methyl-2-pentene molar ratio ≃15) over either "inert" fused silica or the Pt/SiO_2 catalyst. The results are presented in Table 9. Pt/SiO_2 and fused silica exhibit similar selectivity patterns with over 90% selectivity for the double-bond shifts yielding 2-methyl-1-pentene, 4-methyl-1-pentene, and 4-methyl-2-pentene. Pt/SiO_2 and fused silica give about the same amount of 3-methyl-2-pentene, while only Pt/SiO_2 gives 2,3-dimethyl-2-butene which accounts for the slightly higher isomerization selectivity found for Pt/SiO_2.

CONCLUSIONS

An important conclusion which emerged from this study is that hexane isomerization via five-ring intermediates is best approximated by a sequential reaction, (nC_6, 2MP, or 3MP) $\rightarrow^{k_1}$ MCP $\rightarrow^{k_2}$ (nC_6, 2MP, and 3MP) in which the quasi-steady-state approximation, $d[\mathrm{MCP}]/dt = 0$, is applicable and $k_2 \gg k_1$; viz., the five-ring closure of hexane to MCP is rate-controlling in the overall reaction. The constant MCP formations from the three hexanes with residence time and with time on stream are consistent with the model. The kinetic parameters for the ring closure and the ring opening steps can be calculated from the model which offers a more detailed understanding of hexane isomerization via five-ring intermediates. The model may be applied equally well to the isomerization of other hydrocarbons via five-ring intermediates.

It is also observed that the five C–C bonds in acyclic hexane molecules rupture at different rates. For a molecule with a tertiary carbon atom (2MP or 3MP), the C–C bond in the β-position to the tertiary carbon atom is preferentially ruptured. Further, the β bond between a primary and a secondary carbon atom is more reactive than the β bond between two secondary carbon atoms. Internal fission in $n\mathrm{C}_6$ is preferred. These differences may reflect the existence of different 3C surface intermediates which in turn are dependent upon the particular acyclic hexane molecule undergoing hydrogenolysis.

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