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Conversion of Methylcyclopentane and Acyclic Hexanes over Supported Platinum Catalysts

II. Partial Pressure and Temperature Effects on the Formation of Methylcyclopentane from the Three Acyclic Hexanes

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The sequential reaction model proposed in Part I (*J. Catal.* **112,** 290 (1988)) of this series for the isomerization of acyclic hexanes via five-ring intermediates is supported by studies of the partial pressure and reaction temperature effects on methylcyclopentane (MCP) formation from *n*-hexane (nC_6), 2-methylpentane (2MP), and 3-methylpentane (3MP). MCP concentration is found to increase linearly with increasing $P_{\text{hexane}}/P_{H_2}$ ratio as predicted by the model. Enhanced MCP formation with increasing hexane partial pressure and with decreasing hydrogen partial pressure results from an increase in the surface concentration of the five-ring intermediates. Enhanced surface coverage by five-ring intermediates is accompanied by a decrease in hydrogenolysis presumably by reducing the surface coverage of the 3C intermediates. The sequential reaction model for the acyclic hexanes also predicts a linear relationship between ln[MCP] and $1/T$ with the slope of the line giving the activation energy difference between ring closure and ring opening reactions. Experimental results are in excellent agreement with this prediction. Activation energy differences between ring closure and ring opening reactions indicate that the five-ring closure between two primary carbon atoms (2MP and 3MP) has a somewhat higher activation energy than five-ring closure between a primary and a secondary carbon atom (nC_6). Differences between five-ring closures of 2MP and 3MP and nC_6 are also evidenced by changes in reaction rates with decreasing hydrogen partial pressure and increasing reaction temperature. The relative nC_6 concentration from either MCP ring opening or 2MP and 3MP isomerization decreases with time on stream and with decreasing hydrogen partial pressure. These observations, together with results of MCP ring opening over Pt/TiO_2 catalysts, suggest that a carbonaceous layer deposited on the Pt surface during reaction sterically hinders the formation of MCP-like five-ring intermediates having tertiary–secondary C–C bonds bound to the Pt surface. © 1988 Academic Press, Inc.

INTRODUCTION

In Part I (*1*) of this series the conversion reactions of methylcyclopentane (MCP), *n*-hexane(nC_6), 2-methylpentane, (2MP), and 3-methylpentane (3MP) over a Pt/SiO_2 catalyst at 277°C and under fixed hydrocarbon and hydrogen partial pressures were reported. Constant MCP formation from the three acyclic hexanes with residence time and time on stream strongly suggested that hexane isomerization occurs via five-ring intermediates, as concluded from the isotopic data by Gault and his co-workers (*2*), and is best approximated by a sequential reaction, (nC_6, 2MP, or 3MP) $\xrightarrow{k_1}$ MCP $\xrightarrow{k_2}$ (nC_6, 2MP, and 3MP), in which the quasi-steady-state approximation, $d[\text{MCP}]/dt = 0$, is applicable. In follow-up studies we have investigated the effects of partial pressure and reaction temperature on the formation of MCP from the three acyclic hexanes and have compared the experimental results with those predicted by the sequential reaction model. The findings of the present study are in good agreement with the model developed in Part I.

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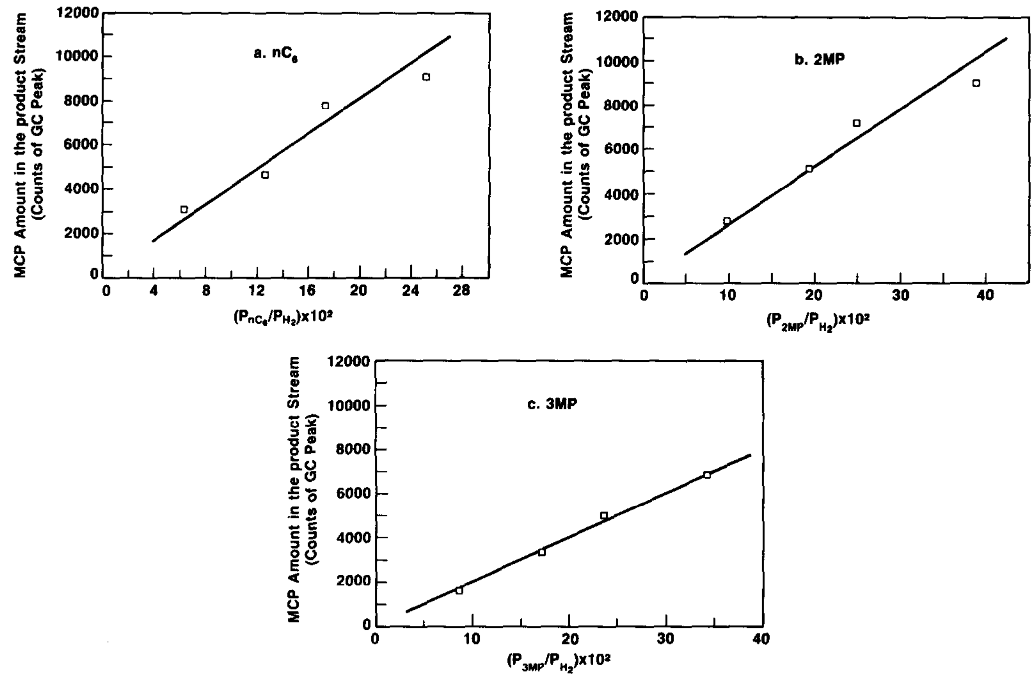


FIG. 1. MCP formation from the three hexanes as a function of $P_{\text{hexane}}/P_{H_2}$ ratio. Reaction temperature, 277°C. Data at 10 min on stream.

EXPERIMENTAL

MCP, nC_6, 2MP, and 3MP conversions at different hydrocarbon pressures were accomplished by passage of hydrogen through a saturator maintained at 18°C. This procedure gave a 2.4-fold higher hydrocarbon partial pressure than that employed in Part I where a saturator temperature of 0°C was used. Hydrogen partial pressures were changed by diluting hydrogen with helium yielding H_2/He ratios of 3/1, 1/1, and 1/3. Conversions at temperatures up to 357°C were carried out under the same hydrocarbon and hydrogen partial pressures used in Part I. Total pressure was maintained at 1 atm and the same Pt/SiO_2 catalyst as that in Part I was used. The reactor system, procedures, and reagents were the same as those employed in the earlier study.

A Pt/TiO_2 catalyst was prepared by an ion exchange technique, the same as that used in preparing Pt/SiO_2. Precalcined Degussa P-25 TiO_2 (70% rutile, 30% anatase, 35 m^2/g) was used as support. After ion exchange, the Pt-loaded TiO_2 was washed, dried at 120°C overnight, and sieved to 80- to 100-mesh size. It was then calcined in flowing oxygen at 350°C for 2 hr and reduced in flowing hydrogen at 200°C for 2 hr in a fused-silica tube furnace. The reduced catalyst contained 0.61 wt% Pt. MCP conversion reactions over Pt/TiO_2 were conducted in the same flow reactor at 200°C, 1 atm total pressure, and a H_2/MCP molar ratio of 18. The flow rate of the H_2/MCP reaction mixture was kept at 10 cm^3/min to obtain the total conversions given in Table 7.

RESULTS AND DISCUSSION

MCP Formation from the Three Acyclic Hexanes Increases Linearly with Increasing $P_{\text{hexane}}/P_{H_2}$ Ratio

As shown in Figs. 1a, 1b, and 1c, MCP concentration increases linearly with increasing $P_{\text{hexane}}/P_{H_2}$ ratio. This linear increase in the rate of MCP formation from the three acyclic hexanes with increasing hexane partial pressure and with decreasing hydrogen partial pressure can be predicted by the sequential reaction model, ($n\mathrm{C}_6$, 2MP, or 3MP) $\xrightarrow{k_1}$ MCP + H_2 $\xrightarrow{k_2}$ ($n\mathrm{C}_6$, 2MP, and 3MP) proposed in Part I for hexane isomerization via five-ring intermediates. Consider the following differential equation which describes the change in MCP concentration with residence time for an $n\mathrm{C}_6$ feed:

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

Similar differential equations can be written for 2MP and 3MP feeds. Applying the quasi-steady-state approximation, $d[\mathrm{MCP}]/dt = 0$, we have

$$\frac{[\mathrm{MCP}][\mathrm{H}_2]}{[n\mathrm{C}_6]} = \frac{k_1^{n\mathrm{C}_6}}{k_2^{n\mathrm{C}_6}} = \text{a constant}$$

or

$$\frac{[\mathrm{MCP}]}{P_{n\mathrm{C}_6}/P_{\mathrm{H}_2}} = \frac{k_1^{n\mathrm{C}_6}}{k_2^{n\mathrm{C}_6}}.$$

Thus, a plot of [MCP] vs $P_{n\mathrm{C}_6}/P_{\mathrm{H}_2}$ should give a straight line with slope of $k_1^{n\mathrm{C}_6}/k_2^{n\mathrm{C}_6}$. A similar linear relationship should exist between [MCP] and $P_{2\mathrm{MP}}/P_{\mathrm{H}_2}$ and between [MCP] and $P_{3\mathrm{MP}}/P_{\mathrm{H}_2}$. The linear relationships shown in Figs. 1a–1c, therefore, strongly support the proposed sequential reaction model.

The linear relationship between [MCP] and $P_{\mathrm{hexane}}/P_{\mathrm{H}_2}$ can assist one in understanding the factors affecting the catalytic behavior of other supported platinum catalysts, e.g., Pt/NaY where one is concerned whether the $P_{\mathrm{hydrocarbon}}/P_{\mathrm{H}_2}$ ratio in the pores of the NaY zeolite support is the same as that of the surrounding gas phase since NaY is known to enhance the hydrocarbon concentration within its pores (*3*). Preliminary studies in this laboratory, however, indicate that the $P_{\mathrm{hexane}}/P_{\mathrm{H}_2}$ ratio in the zeolite pores of a Pt/NaY catalyst is about the same as that in the pores of the Pt/SiO_2 catalyst.

The above dependence of the MCP concentration in the product upon the relative hexane and hydrogen partial pressures is analogous to paraffin dehydrogenation. Consider the equilibrium

$$\text{paraffin} \underset{k'}{\overset{k}{\rightleftarrows}} \text{olefin} + \mathrm{H}_2,$$

where k is the dehydrogenation rate constant of the paraffin and k' is the hydrogenation rate constant of the olefin. At equilibrium

$$k[\text{paraffin}] = k'[\text{olefin}][\mathrm{H}_2].$$

So

$$\frac{[\text{olefin}][\mathrm{H}_2]}{[\text{paraffin}]} = \frac{k}{k'}$$
$$= K \text{ (the equilibrium constant)}$$

or

$$\frac{[\text{olefin}]}{P_{\text{paraffin}}/P_{\mathrm{H}_2}} = K.$$

Thus, the equilibrium olefin concentration in the product increases linearly with the $P_{\text{paraffin}}/P_{\mathrm{H}_2}$ ratio, which is the same linear relationship found between [MCP] and $P_{\mathrm{hexane}}/P_{\mathrm{H}_2}$. Paraffin dehydrogenation at equilibrium can therefore be applied to understand the formation of MCP by isomerization of hexane via five-ring intermediates.

Before a dehydrogenation reaction reaches equilibrium, the olefin concentration in the product depends upon the dehydrogenation rate constant k. When the equilibrium is reached, however, the olefin concentration is limited by the equilibrium. Three reaction variables can shift the equilibrium point: reaction temperature, paraffin partial pressure, and hydrogen partial pressure. At a given reaction temperature, the equilibrium olefin concentration in the product increases with increasing paraffin partial pressure and with decreasing hydrogen partial pressure, or with increasing $P_{\text{paraffin}}/P_{\mathrm{H}_2}$ ratio as concluded above. When the paraffin and/or hydrogen partial pressures are changed to obtain a different equi-

TABLE 1

Effect of Hexane and Hydrogen Partial Pressures on the Hydrogenolysis Selectivity and Yield in the Conversion of the Three Hexanes[a]

Feed	nC_6				2MP				3MP			
Hexane partial pressure (mm Hg)	45	112	45	45	67	151	67	67	60	145	60	60
Hydrogen partial pressure (mm Hg)	715	648	358[b]	179[b]	693	609	347[b]	173[b]	700	615	350[b]	175[b]
$(P_{\mathrm{hexane}}/P_{\mathrm{H_2}}) \times 10^2$	6.3	17.3	12.6	25.1	9.7	24.8	19.3	38.7	8.6	23.6	17.1	34.3
Amount of Pt/SiO_2 (g)	3.00	3.01	2.99	3.01	1.27	1.27	1.27	1.27	1.44	1.44	1.44	1.44
Total conversion (%)	9.25	5.36	11.0	16.5	9.44	5.05	8.75	6.98	12.7	7.05	12.2	10.4
Overall rate (mole/g-cat · hr) × 10^4	4.9	6.8	5.8	8.8	18.1	21.3	16.8	13.4	18.2	26.2	17.4	14.8
Hydrogenolysis Selectivity (%)	44	37	31	18	31	23	18	13	34	28	22	15
Yield (%)	4.07	1.98	3.41	2.97	2.93	1.16	1.58	0.91	4.32	1.97	2.68	1.55

[a] Reaction temperature, 277°C. Data at 10 min on stream.

[b] Total pressure is 760 mm Hg. The balance is helium, 1 mm Hg = 133.3 N m^{-2}.

librium olefin concentration, the equilibrium constant is unchanged, since it is a function of temperature only. The dehydrogenation and hydrogenation rate constants also remain constant. Thus the surface concentration of the intermediate species must have changed to accommodate the different olefin concentrations in the product. A similar argument can be applied to the formation of MCP during hexane isomerization via five-ring intermediates. When the $P_{\mathrm{hexane}}/P_{\mathrm{H_2}}$ ratio is increased, the surface coverage of the five-ring intermediates increases and their desorption results in an increase in the MCP concentration in the product. Although increasing the surface coverage of the five-ring intermediates is beneficial to MCP formation, the formation of other products, e.g., small hydrogenolysis products with less than six carbon atoms, may decrease.

As shown in Table 1, in the conversion of the three acyclic hexanes the selectivity and yield of hydrogenolysis products (C_1 to C_5) both decrease as $P_{\mathrm{hexane}}/P_{\mathrm{H_2}}$ ratio increases. Since a higher $P_{\mathrm{hexane}}/P_{\mathrm{H_2}}$ ratio gives a higher surface coverage of the five-ring intermediates, as concluded above, it seems reasonable to suspect that this increase in the surface coverage of the five-ring intermediates is at the expense of the surface coverage of the 3C intermediates which lead to hydrogenolysis. An increase in the surface coverage of the five-ring intermediates appears to do more than just decrease the surface coverage of 3C intermediates. As shown in Table 2, the preference in rupturing the center C–C bond in nC_6 and the β bond in 3MP also decreases as $P_{\mathrm{hexane}}/P_{\mathrm{H_2}}$ increases. This observation again indicates the possible existence of different 3C surface intermediates for rupturing different C–C bonds in a hexane molecule, as concluded from the cracking patterns in Part I. An increase in the surface coverage of five-ring intermediates seems to have different effects on the various 3C intermediates.

MCP Formation from the Three Acyclic Hexanes as a Function of the Reaction Temperature

The sequential reaction model is able to predict the change in MCP formation from the three hexanes with reaction temperature. As derived above, the following equation, in the case of an nC_6 feed, can be obtained from the sequential reaction model using the quasi-steady-state approximation:

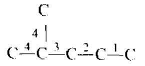
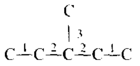
$$\frac{[\mathrm{MCP}]}{P_{n\mathrm{C}_6}/P_{\mathrm{H}_2}} = \frac{k_1^{n\mathrm{C}_6}}{k_2^{n\mathrm{C}_6}}.$$

Expressing the two rate constants in Arrhenius form, we have

$$\frac{[\mathrm{MCP}]}{P_{n\mathrm{C}_6}/P_{\mathrm{H}_2}} = \frac{A_1 e^{-E_1/RT}}{A_2 e^{-E_2/RT}} = \frac{A_1}{A_2} e^{-(E_1-E_2)/RT} = \frac{A_1}{A_2} e^{-\Delta E/RT},$$

TABLE 2

Effect of Hexane and Hydrogen Partial Pressures on the Relative Reactivity Factor in Rupturing C–C Bonds in the Three Hexane Molecules[a]

Feed	$C\overset{1}{-}C\overset{2}{-}C\overset{3}{-}C\overset{2}{-}C\overset{1}{-}C$				 $C\overset{4}{-}\overset{\overset{C}{4\vert}}{C}\overset{3}{-}C\overset{2}{-}C\overset{1}{-}C$				 $C\overset{1}{-}C\overset{2}{-}\overset{\overset{C}{\vert 3}}{C}\overset{2}{-}C\overset{1}{-}C$			
Hexane partial pressure (mm Hg)	45	112	45	45	67	151	67	67	60	145	60	60
Hydrogen partial pressure (mm Hg)	715	648	358[b]	179[b]	693	609	347[b]	173[b]	700	615	350[b]	175[b]
$(P_{\text{hexane}}/P_{H_2}) \times 10^2$	6.3	17.3	12.6	25.1	9.7	24.8	19.3	38.7	8.6	23.6	17.1	34.3
Relative reactivity factor[c]												
Bond 1	0.5	0.5	0.5	0.5	1	1	1	1	1.85	1.9	1.7	1.45
Bond 2	0.55	0.6	0.6	0.6	1.7	1.6	1.7	1.9	0.85	0.85	0.85	0.8
Bond 3	1.7	1.65	1.6	1.2	1.4	1.45	1.5	1.75	1	1	1	1
Bond 4					1.35	1.25	1.3	1.3				

[a] Reaction temperature, 277°C. Data at 10 min on stream.

[b] Total pressure is 760 mm Hg. The balance is helium.

[c] See Part I for the details in calculating the relative reactivity factors.

where $\Delta E = E_1 - E_2$. E_1 and E_2 are the activation energies for ring closure and ring opening reactions, respectively, and A_1 and A_2 are the respective preexponential factors. Superscripts denoting $n\mathrm{C}_6$ are omitted for simplicity. Taking logarithms of both sides, we have

$$\ln[\mathrm{MCP}] = \ln(P_{n\mathrm{C}_6}/P_{\mathrm{H}_2}) + \ln(A_1/A_2) - (\Delta E/R)(1/T)$$

which upon plotting ln[MCP] vs $1/T$ should yield a straight line with slop $-(\Delta E/R)$. The same relationship holds for 2MP and 3MP feeds. As shown in Fig. 2, the experimental results are in good agreement with this prediction.

The data after 10 min on stream at 357°C with $n\mathrm{C}_6$ and 2MP feeds show slight deviations from the straight lines. However, the MCP concentration measured at 1 min on stream with $n\mathrm{C}_6$ falls right on the line (see the solid circle in Fig. 2). The decrease in MCP concentration with time on stream at higher reaction temperatures as the result of catalyst deactivation can be rationalized using the hydrodynamic analog of a sequential reaction developed in Part I. It can be argued that at the reaction temperature of 357°C the catalyst after 10 min on stream has deactivated to a point where the amount of water flowing from cylinder A into cylinder B and cylinder C is not enough to maintain the constant level in cylinder B.

The difference in activation energy between ring closure and ring opening reactions, ΔE, for the three hexanes is obtained from the slope of the straight lines, as given in Table 3. If we assume that the activation energy for ring opening reaction, E_2, is the same for all three hexanes, it can be concluded that five-ring closure between two primary carbon atoms (2MP and 3MP) has a somewhat higher activation energy than five-ring closure between a primary and a secondary carbon atom ($n\mathrm{C}_6$). We reported

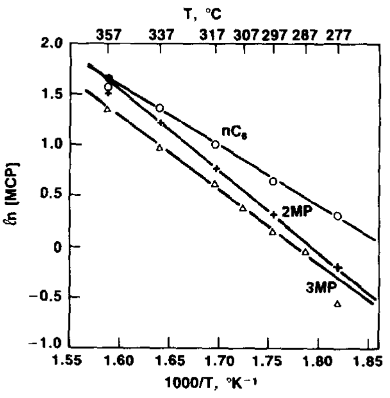


FIG. 2 MCP formation from the three hexanes as a function of reaction temperature. Data at 10 min on stream, except for the solid circle at 357°C with $n\mathrm{C}_6$ feed (1 min on stream).

TABLE 3

Activation Energy Difference between Ring Closure and Ring Opening Reactions

Feed	ΔE (kcal/g-mole)
nC_6	12
2MP	16
3MP	14

in Part I that at 277°C 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 cannot be rationalized by the difference in activation energies. It is likely that this rate difference is due to surface species concentration effects. Surface precursors leading to five-ring closure between two primary carbon atoms may be more abundant, per gram of catalyst, than surface precursors leading to five-ring closure between a primary and a secondary carbon atom.

Differences between five-ring closure of 2MP and 3MP and five-ring closure of nC_6 are also evidenced by the change in their reaction rates with decreasing hydrogen pressure and with increasing reaction temperature. As shown in Table 4, the rate of formation of hexane isomers plus MCP increases by about 10% for both 2MP and 3MP feeds when the hydrogen partial pressure is reduced to one-half. Further decreases in hydrogen partial pressure do not change this rate significantly. For nC_6 feed, however, the increase in the rate of formation of hexane isomers plus MCP with decreasing hydrogen partial pressure is more pronounced. This rate increases by a factor of 1.4 when the hydrogen partial pressure is halved and increases further by a factor of 2.5 when the hydrogen partial pressure is reduced to one-quarter. The change in the rate of formation of hexane isomers plus MCP with reaction temperature is significantly different between nC_6 and 2MP or 3MP. At 297°C, nC_6 exhibits a rate one-third of those given by 2MP and 3MP (see Table 5), while at 357°C the rate for nC_6 feed is about 1.7 times larger than those for 2MP and 3MP feeds. As it has been concluded in Part I that the rate-controlling step in the formation of hexane isomers plus MCP is the five-ring closure of hexane molecules, the above data clearly indicate the difference in five-ring closure between two primary carbon atoms and between a primary and a secondary carbon atom. It seems that the concentration of the surface precursors leading to five-ring closure between a primary and a secondary carbon atom increases faster with decreasing hydrogen partial pressure and with increasing reaction temperature than the concentration of the surface precursors leading to

TABLE 4

Effect of Hydrogen Partial Pressure on the Rate of Formation of Hexane Isomers Plus MCP in the Conversion of the Three Hexanes[a]

Feed	nC_6			2MP			3MP		
Hydrogen partial pressure (mm Hg)	715	358[b]	179[b]	693	347[b]	173[b]	700	350[b]	175[b]
Hexane partial pressure (mm Hg)	45	45	45	67	67	67	60	60	60
Total conversion (%)	9.25	11.0	16.5	9.44	8.75	6.98	12.7	12.2	10.4
Overall rate (mole/g-cat · hr) × 10^4	4.9	5.8	8.8	18.1	16.8	13.4	18.2	17.4	14.8
Selectivity for hexane isomers plus MCP (%)	54	65	73	69	82	87	66	77	84
Rate for hexane isomers plus MCP (mole/g-cat · hr) × 10^4	2.7	3.8	6.4	12.5	13.8	11.7	12.0	13.4	12.4

[a] Reaction temperature, 277°C. Data at 10 min on stream.

[b] Total pressure is 760 mm Hg. The balance is helium.

TABLE 5

Effect of Reaction Temperature on the Rate of Formation of Hexane Isomers plus MCP in the Conversion of the Three Hexanes[a]

Feed	nC_6				2MP				3MP			
Reaction temperature (°C)	297	317	337	357	297	317	337	357	297	317	337	357
Amount of Pt/SiO_2 (g)	1.80	0.60	0.20	0.08	0.80	0.50	0.25	0.15	0.70	0.40	0.20	0.13
Total conversion (%)	12.0	13.3	13.4	13.6	13.4	15.8	15.4	16.6	16.5	16.0	12.5	16.9
Overall rate (mole/g-cat · hr) × 10^4	21.1	70.5	212	540	39.4	74.2	145	259	48.9	82.9	130	271
Selectivity for hexane isomers plus MCP (%)	51	59	63	65	64	71	74	76	64	72	78	77
Rate for hexane isomers plus MCP (mole/g-cat · hr) × 10^4	10.8	41.6	134	351	25.2	52.7	107	197	31.3	59.7	101	209

[a] Total pressure is 760 mm Hg. H_2/nC_6 molar ratio = 16, $H_2/2MP$ = 10, and $H_2/3MP$ = 12. Data at 10 min on stream.

five-ring closure between two primary carbon atoms.

Steric Factor Affecting the Selectivity in Opening the Five-Ring Intermediates

It has been shown in Part I that the same statistical ratio among 2-methylpentane, 3-methylpentane, and *n*-hexane (2 : 1 : 2, respectively) is obtained from MCP ring opening and hexane isomerization. The 2MP/3MP ratio remains near 2 with time on stream and with decreasing hydrogen partial pressure, as shown in Table 6; however, the relative amount of nC_6 decreases significantly with time on stream and with decreasing hydrogen partial pressure. As lower hydrogen partial pressures generally result in faster catalyst deactivation, this shift from a statistical selectivity to a selectivity which disfavors the opening of the five-ring intermediates at the C–C bond nearest to the substituted methyl group with catalyst deactivation may be caused by the carbonaceous layer deposited on the Pt surface.

Ponec and his co-workers have argued in several papers (*4–6*) that the carbonaceous layer deposited on a metal surface during reaction can cause significant changes in the selectivity of the hydrocarbon conversion reactions. In their discussion of this effect, the carbonaceous layer is thought of as an inert blocking material and its influence on the selectivity is considered only in geometrical terms. Two possible explanations for the decrease in the relative amount

TABLE 6

Ratios of Hexane Isomers as functions of Hydrogen Partial Pressure and Time on Stream[a]

Feed	MCP			nC_6			2MP			3MP		
Hydrogen partial pressure (mm Hg)	719	360[b]	180[b]	715	358[b]	179[b]	693	347[b]	173[b]	700	350[b]	175[b]
Hydrocarbon partial pressure (mm Hg)	41	41	41	45	45	45	67	67	67	60	60	60
Relative amount at 10 min on stream												
2-Methylpentane	2.1	2.1	2.1	2.3	2.3	2.2				2.0	2.0	2.0
3-Methylpentane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0			
n-Hexane	2.0	1.7	1.6				2.1	2.0	1.7	1.9	1.8	1.6
Relative amount at 210 min on stream												
2-Methylpentane	2.1	2.1	2.1	2.3	2.4	2.3				2.0	2.0	2.0
3-Methylpentane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0			
n-Hexane	1.7	1.6	1.5				1.8	1.6	1.2	1.8	1.6	1.5

[a] Reaction temperature, 277°C.

[b] Total pressure is 760 mm Hg. The balance is helium.

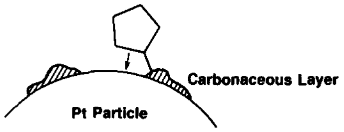


FIG. 3. Steric hindrance due to the carbonaceous layer.

of $n\mathrm{C}_6$ by carbonaceous layer are considered:

(a) As argued by Ponec, two types of five-ring intermediates, single-site and multisite, are operating and the carbonaceous layer, acting like sulfur poisoning or alloying with an inert metal, causes a shift from the multisite to the single-site intermediates by eliminating large Pt ensembles;

(b) The formation of the five-ring intermediates having tertiary–secondary C–C bonds bound to the Pt surface (their rupture gives $n\mathrm{C}_6$) is sterically hindered by the presence of the carbonaceous layer.

(a) is not applicable as it has been shown in Part I that a single type of active sites is involved in MCP ring opening and hexane isomerization. The second explanation is favored and the steric hindrance is considered to result from the interaction of the carbonaceous layer with the substituted methyl group, as illustrated in Fig. 3.

TABLE 7

MCP Ring Opening over Pt/TiO$_2$ at 200°C[a]

Catalyst	Pt/TiO$_2$[b]	Pt/TiO$_2$[b]	Pt/TiO$_2$[c]	Pt/TiO$_2$[d]
Amount of catalyst (g)	1.50	1.00	1.55	1.55
Total conversion (%)	13.91	9.23	11.24	6.69
Overall rate (mole/g-cat · hr) × 10^4	13.1	13.0	10.2	6.1
Product distribution[e]				
Methane	17.5	16.7	13.7	12.5
Ethane	—	—	—	—
Propane	0.2	0.2	0.1	—
i-Butane	0.1	—	—	—
n-Butane	0.1	—	—	—
i-Pentane	0.3	0.3	0.3	0.2
n-Pentane	0.9	0.6	0.7	0.4
Cyclopentane	18.3	17.9	14.2	13.7
2,2-Dimethylbutane	—	—	—	—
2,3-Dimethylbutane	—	—	—	—
2-Methylpentane	40.2	40.7	47.0	48.3
3-Methylpentane	23.3	23.8	26.6	27.4
n-Hexane	17.0	16.7	11.3	10.0
Methylcyclopentane				
Benzene	0.2	0.2	0.2	0.3
Cyclohexane	0.1	0.1	—	—
Relative amount of hexane isomers				
2-Methylpentane	1.73	1.71	1.77	1.76
3-Methylpentane	1.0	1.0	1.0	1.0
n-Hexane	0.73	0.70	0.43	0.37

[a] H_2/MCP molar ratio = 18. Data at 30 min on stream.

[b] Prior to reaction, the catalyst was dried in flowing He at 200°C for 1 hr and then re-reduced in flowing H_2 at 200°C for 1 hr *in situ* in the reactor.

[c] Same as [b], except that the re-reduction temperature was 350°C.

[d] Same as [b], except that the re-reduction temperature was 400°C.

[e] Moles per 100 moles MCP converted. Dashes represent no detectable amount by GC and blank space the feed. Impurity has been deducted from GC data.

MCP ring opening over a Pt/TiO_2 catalyst reduced at different temperatures supports the above argument. The experiments were designed based on the general observation that the reduction by hydrogen of a Pt/TiO_2 catalyst at high temperatures results in a suboxide overlayer of TiO_2 on the surface of the Pt particles (*7, 8*). As shown in Table 7, with increasing reduction temperatures, lesser relative amounts of nC_6 are formed. The 2MP/3MP ratio of about 1.7 is, however, independent of the reduction temperature. These results indicate that the suboxide overlayer in Pt/TiO_2 causes the same effect as the carbonaceous layer in Pt/SiO_2, viz., steric hindrance of the formation of the five-ring intermediates having tertiary–secondary C–C bonds bound to the Pt surface.

CONCLUSIONS

Support of the sequential reaction model proposed in Part I for hexane isomerization via five-ring intermediates has been obtained by studying the partial pressure and reaction temperature effects on the rate of formation of MCP from the three acyclic hexanes. The rate of MCP formation from the three hexanes increases linearly with increasing hexane partial pressure and with decreasing hydrogen partial pressure as predicted by the sequential reaction model. This linear increase in MCP formation rate with $P_{\text{hexane}}/P_{H_2}$ ratio is consistent with an increase in the surface coverage of five-ring intermediates. The higher surface coverage of five-ring intermediates causes a decrease in the surface coverage of the 3C intermediates which in turn reduces hydrogenolysis. A linear relationship between ln[MCP] and $1/T$ was found for the conversion of the three acyclic hexanes. This observation is in agreement with that predicted by the sequential reaction model. The slope of the line gives the activation energy difference between ring closure and ring opening reactions. The five-ring closure between two primary carbon atoms (2MP and 3MP) has a somewhat higher activation energy than the five-ring closure between a primary and a secondary carbon atom (nC_6). The difference between five-ring closure of 2MP and 3MP and five-ring closure of nC_6 is also evidenced by the faster increase in the concentration of the surface species leading to five-ring closure of nC_6 with decreasing hydrogen partial pressure and with increasing reaction temperature.

The carbonaceous layer deposited on the Pt surface during reaction sterically hinders the formation of five-ring intermediates having tertiary–secondary C–C bonds bound to the Pt surface. The suboxide overlayer of TiO_2 formed on the surface of the Pt particles in a Pt/TiO_2 catalyst reduced at high temperatures causes the same effect as the carbonaceous layer.

Note added in proof. One referee of this manuscript expressed concern about the constancy of MCP formation from the three acyclic hexanes. To support our experimental observation, we report the results of a mathematical modeling study of the time-on-stream behavior of a sequential reaction.

For a sequential reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, the change in the concentrations of A, B, and C with residence time can be described by the following differential equations, assuming both reactions are first order:

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[C]}{dt} = k_2[B].$$

In the case that there is no B or C in feed A, the above differential equations can be solved to give

$$[A] = [A]_0 e^{-k_1 t} \qquad (1)$$

$$[B] = \frac{k_1}{k_2 - k_1}[A]_0(e^{-k_1 t} - e^{-k_2 t}) \qquad (2)$$

$$[C] = [A]_0 + \frac{[A]_0}{k_2 - k_1}(k_1 e^{-k_2 t} - k_2 e^{-k_1 t}), \qquad (3)$$

where $[A]_0$ is the initial concentration of A.

For a flow reactor loaded with a fixed amount of catalyst and operated under constant flow rate of feed, the catalyst deactivation with time on stream can be simulated by assuming that the residence time stays unchanged while the two rate constants decrease with

TABLE 8

τ	[A]	[B]	[C]	x^a (%)
1	875.4650	17.84022	106.6946	12.45349
2	883.2973	17.98525	98.71739	11.67026
3	887.6635	18.06283	94.27360	11.23364
4	890.6682	18.11444	91.21727	10.93317
5	892.9468	18.15243	88.90070	10.70531
10	899.7434	18.25842	81.99816	10.02565
50	913.9856	18.42537	67.58893	8.601430
100	919.5072	18.45815	62.03457	8.049272
150	922.5784	18.46507	58.95643	7.742151
200	924.6891	18.46420	56.84662	7.531083
1000	935.5151	18.36378	46.12102	6.448481
10000	948.4290	17.91009	33.66081	5.157091

Note. Parameters: $[A]_0 = 1000$, $a_1 = 0.133$, $b = 0.1$, $c = 50$, $t = 1$.

[a] x is the conversion of A, $([A]_0 - [A]) \times 100/[A]_0$.

time on stream following the Voorhies power relationship,

$$k_1 = a_1\tau^{-b},$$

where τ represents the time on stream and a_1 and b are empirical constants. If we limit our discussion to the case in which k_1/k_2 remains constant with time on stream, as in this case of hexane isomerization via five-ring intermediates, the same power relationship applies to k_2, i.e.,

$$k_2 = a_2\tau^{-b},$$

where a_2 is another empirical constant. As $k_1/k_2 = a_1/a_2$ = a constant $(1/c)$, so $a_2 = ca_1$. By selecting values for $[A]_0$, a_1, b, c, and t, the change in the concentrations of A, B, and C with time on stream (τ) can be calculated using Eqs. (1), (2), and (3) above. Table 8 gives the numerical results.

The table clearly shows that, as the catalyst deactivates with time on stream (τ), the conversion (x) decreases and thus [A] increases with time on stream. As expected, [C] decreases with time on stream. From $\tau = 1$ to $\tau = 10{,}000$, [C] drops by two-thirds and x decreases from 12.5 to 5.2%; however, over this entire period of time on stream [B], the intermediate concentration, is essentially a constant. This result simulates well the experimental data of constant MCP concentration in the conversion of the three acyclic hexanes reported in Part I. A full account of the above mathematical modeling will be submitted for publication at a later date.

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