in CO insertion rate for organometallic compounds when a Lewis acid interacts with the O atom of the carbonyl ligand.

## Conclusions

The reaction network of growing chains on the surface of Fischer-Tropsch catalysts, which fascinated Emmett, can now be visualized as a chain growth initiated by dissociation of adsorbed CO. The sites where this occurs have to be large ensembles. This dissociation rate is enhanced by oxophilic metal ions or oxides. In combination with Rh they induce a CO adsorption mode with C and O bonding, which is an obvious precursor to CO dissociation. Three termination steps enable the alkyl groups to leave the catalyst surface. Two of them result in the formation of hydrocarbons, viz., H addition and  $\beta$ -H abstraction. The third termination "step" is initiated by CO insertion in the metal-alkyl bond resulting in the formation of an acyl group. Subsequently, hydrogen atoms are added to this acyl group, resulting in higher oxygenates (aldehydes and primary alcohols). This third termination mode is identical with the hydroformylation of olefins, once the adsorbed olefin has added one hydrogen atom. This CO insertion is favored by isolated metal atoms, e.g., Rh. Base metal additives such as Fe and Zn ions on the surface of Rh effectively

block the large Rh ensembles required for CO dissociation and possibly H<sub>2</sub> dissociation. Their presence, therefore, results in a depression of methanation and of the simple olefin hydrogenation. A site isolation of surface Rh is also indicated by IR data which show that bridging CO chemisorption is completely suppressed when the catalyst contains Fe and Zn. Increased hydroformylation in the presence of Zn might be attributed to Zn ions, which induce a Lewis acid promoted CO insertion. Along with this, the addition of base metals such as Fe and Zn to Rh improves the methanol synthesis, possibly due to the same Lewis acid promotion favoring CO insertion into M-H bonds. In this case, formyl is an intermediate of methanol formation.

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Registry No. CO, 630-08-0; Rh, 7440-16-6; Zn, 7440-66-6; Fe, 7439-89-6; Mn, 7439-96-5; ZnO, 1314-13-2; MgO, 1309-48-4; CaO, 1305-78-8; La<sub>2</sub>O<sub>3</sub>, 1312-81-8; Nd<sub>2</sub>O<sub>3</sub>, 1313-97-9; ZrO<sub>2</sub>, 1314-23-4; TiO<sub>2</sub>, 13463-67-7; Nb<sub>2</sub>O<sub>5</sub>, 1313-96-8; MnO<sub>2</sub>, 1313-13-9; SiO<sub>2</sub>, 7631-86-9; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; Zr, 7440-67-7; Ti, 7440-32-6; V, 7440-62-2; Nb, 7440-03-1; ethylene, 74-85-1.

# Hydrogen Control of Platinum-Catalyzed Skeletal Reactions of Alkanes: Selectivities and Surface Species

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Conversions of *n*-pentane, *n*-hexane, 3-methylpentane, *n*-heptane, 2-methylhexane, 3-methylpentane, 2,3dimethylpentane, 2,4-dimethylpentane, 2,2-dimethylpentane, 3,3-dimethylpentane, n-octane, and 2-methylheptane to aromatics, skeletal isomers, C5-cyclic products, and fragments were studied on Pt black catalysts and compared to each other. Yields of these skeletal reactions show maxima as a function of the hydrogen pressure between 5 and 60 kPa (35 and 450 Torr) hydrogen pressure. Low hydrogen pressures favor highly dehydrogenated surface intermediates leading to aromatization and/or hydrogenolysis. Under higher hydrogen pressures,  $C_5$ -cyclic intermediates prevail: these give cyclopentane and/or skeletal isomers. Radiotracer studies confirm that the main route of skeletal isomerization involves C<sub>5</sub>-cyclic intermediates. A new type of hydrogenolysis, "C<sub>5</sub>-unit splitting", is reported. Comparison of the present results with single-crystal data by Somorjai et al. permits us to suggest that the hydrogen control of the selectivities by controlling the surface intermediates may be valid for both types of catalysts.

## Introduction

The mechanisms of skeletal reactions-formation and rupture of C<sub>5</sub>-ring, aromatization, isomerization, and hydrogenolysis---over dispersed and single-crystal Pt catalysts have been discussed extensively during recent years; still, there is no consensus on this question.<sup>1</sup> Hydrogenolysis likely involves multidissociated intermediates attached to the catalysts via more than one C atom of the alkane.<sup>2</sup> Two of the present authors reported evidence that-at least over monofunctional Pt catalysts-aromatization involves dehydrogenation into di- or trienes followed by ring closure.<sup>3,4</sup> Gault and his school postulated at least four different surface intermediates for C5-cyclization and the related isomerization, all of them being greatly dehydrogenated.<sup>1b,5</sup> This concept was seriously criticized; instead, the loss of one H atom from each

carbon atom to form a C<sub>5</sub>-ring was suggested to be sufficient.<sup>6</sup> The role of surface hydrogen for such "associative" surface species was first stressed by Liberman.<sup>7</sup> We also suggested earlier<sup>8,9</sup> a less dehydrogenated, flat surface intermediate for the C5-cyclic reaction. The presence of a tertiary C atom in the molecule would facilitate the formation of the necessary surface species; this route was also supported by the predominance of cis-dimethylcyclopentanes among the products of cyclization.9 The occurrence of a parallel C<sub>5</sub>-cyclization via more dehydrogenated intermediates at lower hydrogen pressure has also been pointed out.<sup>1a,d,6,8</sup> All these experiments were carried out in a large excess of hydrogen (1:5 to 1:200) and with total pressures up to 1 bar.

The other mechanism of isomerization, the so-called bond shift<sup>10</sup> or C<sub>3</sub>-cyclic route,<sup>11</sup> has also been disputed. Our previous results are in agreement with the intermediate proposed by McKervey

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et al.,<sup>12</sup> at least over Pt. Another reaction involving more dehydrogenated intermediates<sup>13</sup> may also take place; this should be responsible, e.g., for the formation of aromatics under low hydrogen pressures from substituted pentanes.<sup>14</sup> Of course, the importance of various routes is strongly catalyst dependent. The excellence of platinum in C5-cyclic reactions has been interpreted in terms of its atomic geometry.<sup>15</sup> The same metal may also give different product compositions as a function of, e.g., dispersion.<sup>1b,16</sup> One of the reasons that dispersion effects arise may be that active sites at the borderline of the metal and the support may possess peculiar catalytic properties.<sup>17</sup> Earlier works of the authors have stressed, in addition, the regulating effects of hydrogen. Yields of individual products have, as a rule, maxima as a function of hydrogen pressure.<sup>1a,d,18,19</sup> These hydrogen effects can be superimposed by dispersion effects and can be separated from them by careful analysis.<sup>18</sup> Their neglect may lead to serious inaccuracies.

Recently, an excellent single-crystal study has been reported where alkane reactions were compared with results obtained over dispersed catalysts, indicating that well-defined surfaces may, indeed, serve as models of real catalysts.<sup>20</sup>

We report in the present work various "skeletal" transformations of alkanes: *n*-pentane, hexane, heptane, and octane isomers. Their behavior will be classified according to reaction types: aromatization, C<sub>5</sub>-cyclization, skeletal isomerization, and hydrogenolysis. The regulating effect of hydrogen on each reaction will be demonstrated and it will be shown that this is similar for analogous reactions of alkanes of different structures. Structural effects are also detectable, and wherever important they will also be pointed out. Surface intermediates are suggested for the above reactions and the slight variation of their structure as a function of the reactant structure is discussed. The response of isomer yields to hydrogen pressure will permit us to distinguish between the two ( $C_5$ - and  $C_3$ -cyclic) routes of isomerization. The role of the C<sub>5</sub>-cyclic surface intermediate in skeletal isomerization is confirmed by <sup>14</sup>C radiotracer studies. Finally, some analogies with single crystals will be pointed out.

#### **Experimental Section**

Most experiments were carried out in a static-circulation apparatus<sup>21</sup> connected to a Chrom 31 type gas chromatograph with a 50-m squalane coated steel capillary column. The reaction mixture contained 1.23 kPa (0.133 kPa = 1 Torr) hydrocarbon and 4-60 kPa hydrogen. Radiotracer studies—and a few inactive experiments-were performed in a pulse-microcatalytic system<sup>22</sup> attached upflow to a Packard 419 gas chromatograph with a 2-m packed column of 18% squalane on Chromosorb P. The stream was split after the column, one part going to the FID and the other part passing through a proportional counter that monitored radioactivity after mixing methane quenching gas to the flow.

Platinum black catalyst was reduced in aqueous medium with HCHO in concentrated KOH.<sup>23</sup> Its specific surface after standard thermal pretreatment (as described in ref 19) was 1.8 m<sup>2</sup> g<sup>-1</sup>

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Figure 1. Rates of individual reactions of 3-methylpentane. T = 603 K, p(HC) = 1.23 kPa, t = 5 min. Catalyst: 0.1 g of Pt black.

(determined by nitrogen adsorption according to the Brunauer-Emmett-Teller (BET) method<sup>24</sup>). The mean crystallite size was about 30 nm (X-ray diffraction agreeing well with electron microscopy<sup>25a</sup>). The catalysts were partially covered by oxygen and carbon;<sup>25b</sup> additional carbonaceous residues were accumulated during reaction. However, with a sufficiently large hydrogen excess (which was always fulfilled), product accumulation curves were straight lines up to 40 min. Deactivation could not be appreciable in our case, with sampling 5 min after the start of the run. Any precursor of carbonaceous residues was removed by regeneration with air at the reaction temperature (2 kPa, 2 min) followed by hydrogen circulation (8 kPa, 3 min). In pulse experiments air and subsequent hydrogen slugs introduced into the He carrier gas were used for regeneration. Previous experience showed several times<sup>3,8,18,19</sup> that this treatment restores initial activity and can be repeated several hundred times without appreciable irreversible deactivation or surface loss.

The hydrocarbons, n-pentane, n-hexane, 3-methylpentane, n-heptane, 2- and 3-methylhexanes, 3-ethylpentane, 2,3-, 2,4-, 2,2-, and 3,3-dimethylpentanes, n-octane, and 2-methylheptane, were Merck or Fluka products, GC grade, with purities always better than 99.5%. Radioactive [methyl-14C]-3-methylpentane was synthesized at our institute (purity: 99.8%, radiochemical purity: 99.3%). The radioactive impurities isopentane and 2-methylpentane (0.3 and 0.4%, respectively) were taken into correction during calculation. Relative molar radioactivity (rmr) values were calculated by dividing the percent radioactivity (r) in each fraction by the corresponding mole percent (m) of the fraction.<sup>26</sup>

Due to the unknown amounts of surface deposits, it is impossible to determine true turnover numbers (TON). We used, instead, rates of product formation related to the BET surface. If we assume that the surface is clean (which is certainly not true), with a value of  $10^{19}$  atom Pt per squared meter,  $1 \times 10^{-8}$  mol m<sup>-2</sup> s<sup>-1</sup> would correspond to a TON of  $6 \times 10^{-4}$  molecule per Pt atom per second. The TON values presented in our work are between  $10^{-4}$  and  $10^{-2}$  s<sup>-1</sup>; however, if we try to take into account that 10-20% of the BET surface consists of uncovered Pt atoms,<sup>25b</sup> these values can be multiplied by 5-10. This is a fair agreement with the single-crystal work,<sup>20</sup> where values between  $10^{-3}$  and 7  $\times$  10<sup>-2</sup> were reported at  $T \approx 600$  K.

## Results

Hydrogen Regulation of Yields and Selectivities. Yields of individual product types have maxima as a function of hydrogen

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Figure 3. Rates of formation of  $C_5$ -cycloalkanes from heptane isomers as a function of the hydrogen pressure.

pressure. This is illustrated in Figure 1 for the example of 3methylpentane. The figure also shows yields of olefins (3methyl-2-pentene isomers); their formation will not be tackled hereafter.

The optimum hydrogen pressure for aromatization is almost the same for *n*-hexane, methylhexanes, and *n*-heptane (about 15 kPa).<sup>19</sup> It may be somewhat lower for alkanes where skeletal rearrangement is also necessary for aromatic ring formation (as in Figure 1). Aromatization *selectivity* also has its highest values in the low hydrogen pressure range, as shown in Figure 2.

The position of the maxima is enormously influenced by the structure of the reacting hydrocarbons in the  $C_5$ -ring formation (Figure 3). The increase of the size of the molecule shifts the maxima toward higher  $p(H_2)$  values—for example, *n*-pentane has its maximum cyclization rate at 10 kPa (where most heptane isomers just start to cyclize).

As a consequence of strong hydrogen and structure dependences of the yields, selectivities measured at different hydrogen pressures will be different for various alkanes, Table I. Very high  $C_5$ cyclization selectivities are found with branched-chain heptane isomers at higher hydrogen pressures. These values compare well with *n*-alkane data obtained over single-crystal Pt surfaces.<sup>20</sup> The

	% selectivity for						
	hydrogen-	aromat-	C5-	isomer-	olefin		
alkane	olysis	ization	cyclization	ization	formation		
	A.	$p(H_2) = 1$	6 kPa				
n-pentane	60		22	18			
n-hexane	35	45	9	11			
3-methylpentane	27		39	24	10		
n-heptane	59	14	18	8	1		
2-methylhexane	35	34	19	9	3		
3-methylhexane	50	22	19	2	7		
3-ethylpentane	44	5	32	7	12		
2,3-dimethyl- pentane	55	11	17	2	15		
2,4-dimethyl- pentane	27	6	44	3	20		
2,2-dimethyl- pentane	32	3	60	4	1		
3,3-dimethyl- pentane	49	5	37	5	4		
	B. 1	$p(H_{2}) = 4$	0 kPa				
n-pentane <sup>b</sup>	52	× 27	17	31			
<i>n</i> -hexane	51	7	23	19			
3-methylpentane <sup>c</sup>	14		25	48	13		
n-heptane	42	6	35	17			
2-methylhexane	36	16	34	11	3		
3-methylhexane	46	16	27	4	7		
3-ethylpentane	24	1	58	14	3		
2,3-dimethyl- pentane	26	4	61	6	3		
2,4-dimethyl- pentane	11	1	84	4			
2,2-dimethyl- pentane	19		76	4	1		
3,3-dimethyl- pentane	28		64	. 8			

 ${}^{a}T = 603 \text{ K}; p \text{ (hydrocarbon)} = 1.23 \text{ kPa. } {}^{b}p(\text{H}_2) = 33 \text{ kPa. At } 40 \text{ kPa}$ no reaction was observed.  ${}^{c}p(\text{H}_2) = 48 \text{ kPa. Catalyst: } 0.1 \text{ g of Pt black.}$ 

TABLE II: Overall Selectivities (in mol %) of *n*-Hexane Reactions over Pt Black and Various Pt Faces

catalyst	$p(H_2), kPa$	$S_{ m hydr}$	$S_{\rm arom}$	$S_{C_{5}-cycl}$	$S_{\rm isom}$
Pt(100) <sup>a</sup>	27	24	6	41	29
Pt(13,1,1) <sup>a</sup>	27	31	7	43	19
["stepped"(100)]					
Pt(111) <sup>a</sup>	27	26	15	35	24
	80	25	7	26	42
	27 <sup>b</sup>	43	32	11	14
$Pt(332)^{a}$	27	30	17	41	12
["stepped"(111)]					
$Pt(10,8,7)^a$	27	21	19	40	20
["kinked"(111)]					
Pt black <sup>c</sup>	6	46	43	5	6
	15	35	45	9	11
	32	56	15	16	13
	40	51	7	23	19
	64	54	6	13	17
	92 <sup>d</sup>	58	28	4	10

<sup>a</sup> T = 573 K; static system; p(hexane) = 2.2 kPa; ref 20. <sup>b</sup> T = 693 K. <sup>c</sup> T = 603 K; static-circulation system; p(hexane) = 1.23 kPa. <sup>d</sup> T = 663 K. Pulse system: 0.15 g Pt and 1  $\mu$ L of hexane pulsed into H<sub>2</sub>.

regulating effect of hydrogen is illustrated by selectivity values for n-hexane (Table II); Pt black produced more fragments.

The possible cyclopentane structures determine the structure of the isomers to be formed via the  $C_5$ -cyclic route.<sup>27-29</sup> Scheme I summarizes this for  $C_7$ -alkanes and cycloalkanes. Maximum yields of isomers are obtained at  $p(H_2)$  values where the yield of the structurally corresponding cyclopentanes also has a maximum (Figures 3 and 4a). The shape of the curves is also similar. Isomer formation is also possible via a bond shift mechanism. The distinction of parallel routes is possible with excellent but laborious <sup>13</sup>C tracer studies.<sup>1b,27</sup> Instead, we selected two isomers that could

TABLE III: Composition and Radioactivity Data of the Effluent of the Reaction of Labeled 3-Methylpentane plus Unlabeled Methylcyclopentane over Platinum Black<sup>a</sup>

carrier		type	% composition <sup>c</sup>									
gas	Т, К	compn <sup>b</sup>	<c4< th=""><th>iC5</th><th>nC<sub>5</sub></th><th>2MP</th><th>3MP</th><th>nH</th><th>t-3M2P=</th><th>МСР</th><th>Bz</th><th>1-MCP=</th></c4<>	iC5	nC <sub>5</sub>	2MP	3MP	nH	t-3M2P=	МСР	Bz	1-MCP=
H <sub>2</sub>	603	т	0.37	0.17	0.06	6.77	76.58	0.58	0.05	15.26		
-	2	r	0.16	0.19		1.34	96.54			1.77		
		r/m	0.40	1.12		0.20	1.261			0.116		
	663	m	8.25	1.04	0.89	11.07	61.98	2.30	0.71	13.00	0.15	0.35
		r	5.68	1.64	0.49	7.02	74.66	2.79	1.01	5.38	0.6	3
		r/m	0.69	1.58	0.55	0.63	1.205	1.21	1.42	0.414	1.2	5
5% H,	603	m	2.18	0.33	0.38	2.85	72.27	0.85	0.62	19.68	0.21	0.59
-		r	1.81	0.41		1.23	93.04		0.79	2.47	0.2	2
		r/m	0.83	1.33		0.43	1.287		1.27	0.125	0.2	3
starting mixture <sup>d</sup>		m					76.20			23.80		
e		r					100			0		
		r/m					1.314			0		

<sup>a</sup>Catalyst, 0.4 g Pt black, presintered at 473 K. Pulse system, 3  $\mu$ L pulses into 60 mL/min carrier gas. <sup>b</sup>m is the mole percent composition, r is the percent composition of radioactive material. <sup>c</sup>MP, methylpentane; MCP, methylcyclopentane; Bz, benzene; nH, n-hexane. The superscript symbol (=) means olefin. <sup>d</sup> The radiochemical impurities were subtracted from the starting mixture as well as from all effluent analyses.

#### SCHEME I



be produced by a bond shift route only and plotted their yields as a function of hydrogen pressure. Figure 4b shows a completely different hydrogen response for these isomers. We believe that this provides an additional method for distinguishing isomerization routes. The formation of 2-methylhexane from 3-methylhexane follows the bond shift type hydrogen response pattern; thus we propose that in this case this mechanism prevails. It was reported that under different conditions, on Pt/Al<sub>2</sub>O<sub>3</sub> (hydrocarbon pressure: 5 Torr, hydrogen pressure: 755 Torr), 18-22% 2methylhexane was formed via bond shift from 3-methylhexane.<sup>13</sup> In our case, the prevailing bond shift may be due to our lower  $p(H_2)$  values and to the different catalyst.

The optimum  $p(H_2)$  for the C<sub>5</sub>-cyclization of gem-dimethylpentanes was lower than that of other substituted pentanes (Figure 3). The same is true for their isomerization (Figure 5, cf.  $p(H_2)$ ) values for maximum yields with those in Figure 4a). 3,3-Dimethylpentane produced 2,2-dimethylpentane as the only isomer; 2,2-dimethylpentane gave two isomers: 2-methylhexane was formed with much lower yields than 3,3-dimethylpentane.

Radiotracer Studies of Isomerization Pathways. We also studied the isomerization pathway by means of radioactive tracers, following earlier studies in this field.<sup>1a,3,30-32</sup>

In the present study, a mixture of [methyl-14C]-3-methylpentane and inactive methylcyclopentane was used. Relative molar radioactivities (rmr) of individual hydrocarbons before and after reaction have been monitored. An unchanged rmr value would mean that the components of the mixture reacted totally inde-



Figure 4. Rate of isomer formation from heptanes as a function of the hydrogen pressure: (a) isomers likely formed via C<sub>5</sub>-cyclic route; (b) isomers likely formed via bond-shift route.



Figure 5. Rate of isomer formation from gem-dimethylpentanes as a function of hydrogen pressure.

pendently of each other and their interconversion would be nil. On the other hand, completely identical rmr values after reaction would mean that all molecule types had equilibrated with each other.26

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TABLE IV: Radioactivity Data of Various Components as a Function of Experimental Conditions

carrier				rel	rmr <sup>b</sup>			
gas	<i>T</i> , K	2MP	3MP	МСР	2MP/MCP	2MP	MCP	
H <sub>2</sub>	573		1.284	0.012	0	0	0.93	
	603	0.20	1.261	0.12	1.70	15.7	9.2	
	618	0.29	1.265	0.22	1.33	22.9	17.3	
	633	0.44	1.280	0.31	1.43	34.3	23.9	
	648	0.51	1.238	0.36	1.40	41.2	29.4	
	663	0.63	1.205	0.414	1.53	52.3	34.1	
5% H <sub>2</sub>	573	0.18	1.294	0.084	2.14	13.9	6.5	
-	603	0.43	1.287	0.125	3.44	33.4	9.7	
	633	0.38	1.282	0.100	3.80	29.6	7.8	

<sup>a</sup> The starting mixture was 3MP with a rmr of 1.314. <sup>b</sup> Relative rmr of 3MP is 100.

Data obtained at two hydrogen pressures are shown in Table III. The initial rmr of 3-methylpentane decreases somewhat, due to its dilution with the ring-opening product of inactive methylcyclopentane. On the other hand, radioactivity appears in methylcyclopentane and its rmr increases as temperature (and total conversion) increases. However, the value of the rmr did not reach that of 3-methylpentane after reaction (Table IV). This increase was much more marked under higher hydrogen pressures. The rmr of 2-methylpentane was always higher than that of methylcyclopentane but never reached that of 3-methylpentane.

For products of lower concentration, the rmr of smaller fragments,  $<C_4$ , was about half of that of 3-methylpentane, indicating the statistical rupture of the molecule into two parts.<sup>10</sup> Isopentane preserves the <sup>14</sup>C atom in its methyl label whereas *n*-pentane should be inactive. The rmr values of pentanes in Table III support this argument, except for the experiment at 390 °C, where secondary scrambling of C atoms may have occurred. 3-Methylpent-2-ene is a product of 3-methylpentane, as judged from their rmr. Benzene and methylcyclopentene are formed mainly from radioactive 3-methylpentane in 100% hydrogen and from unlabeled methylcyclopentane in 5% hydrogen. This is in agreement with previous results demonstrating that ring expansion of methylcyclopentane into benzene is largely suppressed by hydrogen.<sup>1a,d,14</sup>

Hydrogenolysis: Yields and Selectivities. Hydrogenolysis may even prevail in some cases (Table I). Hydrogenolysis yields show maxima as a function of  $p(H_2)$ ; there is a tendency to shift these maxima toward higher  $p(H_2)$  values with larger reactant molecules, as discussed elsewhere.<sup>33</sup> Much more interesting information can be obtained from the study of the hydrogenolysis "pattern". The probability of chain rupture in individual positions is not equal. The "reactivity factor"  $\omega$  defined by Leclercq et al.<sup>34</sup>  $[\omega]$  is the actual rate of rupture divided by the rate of rupture for random hydrogenolysis] represents a quantative measure of the favored or hindered rupture of individual bonds. The  $\omega$  values are largely influenced by the molecular structure of the feed.<sup>34,35</sup> Hydrogen effects are illustrated by Table V for the example of n-hexane. End methyl group loss predominates under low hydrogen pressures and the predominant reaction direction is shifted toward the middle of the molecule as the hydrogen pressure increases. Differences are much less sharp between  $\omega$  values measured over single crystals, although the hydrogen pressure range covered is less wide here.

The variation of  $\omega$  values with  $p(H_2)$  depends strongly on the structure of the reactant alkane. For example,  $\omega_1$  increases with increasing  $p(H_2)$  with *n*-heptane feed. We found that the elimination of a *pentyl unit* (producing *n*-pentane plus another fragment from *n*-hexane, heptane, and octane isomers) follows a similar hydrogen dependence. The corresponding  $\omega$  values of *n*-alkanes fall on a single curve and decrease as hydrogen pressure increases. If the C<sub>5</sub>-unit split off from the molecule has a methyl substituent (e.g., in the case of methylhexanes and 2-methyl-

TABLE V: Selectivities of C-C Bond Rupture of *n*-Hexane in Terms of  $\omega$  over Various Pt Catalysts<sup>*a*</sup>

catalyst	$p(H_2),$ kPa	$C_1 - C_2$	$C_2 - C_3$	$C_3 - C_4$	
$Pt(100)^{b}$	27	0.40	1.0	2.20	
$Pt(13,1,1)^{b}$	27	0.35	0.85	1.95	
$Pt(111)^{b}$	27	0.90	0.40	1.90	
	80	0.80	0.60	1.75	
Pt(332) <sup>b</sup>	27	0.65	0.50	1.00	
$Pt(10,8,7)^{b}$	11	0.50	0.55	1.40	
	27	0.60	0.60	1.35	
	80	0.70	0.70	1.20	
Pt black <sup>c</sup>	6	2.09	0.23	0.35	
	16	2.02	0.25	0.47	
	32	1.03	0.61	1.73	
	40	0.92	0.71	1.75	
	64	0.87	0.44	2.39	
Pt black <sup>d</sup>	92	1.03	0.80	1.60	

<sup>a</sup>Calculated on the basis of the amount of the larger fragment (*n*-pentane, *n*-butane, and propane). Methane excess appears in most cases for both single crystals and Pt black. <sup>b</sup>T = 573 K, ref 20. <sup>c</sup>Static-circulation system, p(hexane) = 1.23 kPa, T = 603 K. <sup>d</sup>Pulse system, hydrogen carrier gas, T = 603 K, ref 35.



**Figure 6.** Selectivities (expressed as  $\omega$  values, see text) of C<sub>5</sub>-unit splitting from various alkanes as a function of hydrogen pressure. Feed: (O) *n*-hexane; ( $\times$ ) *n*-heptane; ( $\Delta$ ) *n*-octane; ( $\oplus$ )  $\omega_1$  from 3-methylhexane; (+)  $\omega_6$  from 3-methylhexane; ( $\diamond$ )  $\omega_1$  from 2-methylhexane; ( $\Psi$ )  $\omega_6$  from 2-methylheptane.

heptane, Figure 6), the drop of  $\omega$  at higher hydrogen pressures is less abrupt.

The hydrogenolysis fragments also contain cyclopentane and methylcyclopentane. Their yields as a function of  $p(H_2)$  give plots that are different from both those that are characteristic of the cyclization of the parent alkane itself and direct cyclization of *n*-pentane. This is depicted in Figure 7, with *n*-octane reactant as an example. Here the reaction *n*-octane  $\rightarrow C_8$ -cycloalkane requires the highest  $p(H_2)$  for optimum yield and the reaction *n*-pentane  $\rightarrow$  cyclopentane the lowest one. The formation of cyclopentane from *n*-octane follows the plot for the *n*-octane  $\rightarrow$ *n*-pentane reaction, indicating that cyclopentane should be regarded as a product of the subsequent cyclization of an *n*-pentane

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Figure 7. Yields of C5-cyclic products from various alkanes as a function of hydrogen pressure. (X) formation of trans-1-methyl-2-ethylcyclopentane from *n*-octane; ( $\Delta$ ) formation of cyclopentane from *n*-octane; (O) formation of cyclopentane from *n*-pentane feed;  $(\bullet)$  formation of *n*pentane fragment from n-octane.

fragment rather than as a result of the dealkylation of ethylmethylcyclopentane. Also a n-pentane fragment formed on the catalyst surface behaves differently from *n*-pentane introduced in the gas phase.

#### Discussion

Comparing the present results with previous studies,<sup>8,19,29</sup> we obtain increases in the hydrogen pressures giving maximum yields for different reactions in the following order: aromatization < hydrogenolysis < C<sub>5</sub>-cyclization and C<sub>5</sub>-cyclic isomerization < bond-shift isomerization. This does not correspond to the overall hydrogen stoichiometry of the reactions; we believe that this reflects the degree of dehydrogenation of the surface intermediates.

Aromatization rates and selectivities show maxima at lowest hydrogen pressures, Figures 1 and 2 and Table I, confirming the low hydrogen content of the reaction intermediate. Apparently, the hydrogen pressure at which these greatly dehydrogenated surface intermediates become unfavorable is independent of their molecular structure. Maybe surface platinum-carbon ensembles are active in this reaction.<sup>36</sup> However, the aromatic selectivity, i.e. which fraction of adsorbed molecules form aromatic precursors, is strongly influenced by the alkane structure: the extra methyl groups of heptane isomers seems to hinder aromatization although thermodynamical aromatization of heptanes is more favorable than that of hexanes.

Aromatization of hexanes likely starts by their dehydrogenation to hexenes, which is a fast process over single-crystal<sup>20</sup> and dispersed<sup>37</sup> Pt catalysts. *cis*-Hexatriene is the direct precursor of ring closure. The "triangular" accommodation of an ethylene molecule on a fcc plane of hexagonal symmetry<sup>38,39</sup> has been adopted to interpret the possible surface geometry of polyenes prior to cyclization.<sup>1a,40</sup> This would involve one  $\pi$ - and two  $\sigma$ -bonds between a C=C unit and two Pt atoms; another Pt site would then catalyze ring closure (Figure 8). Such an intermediate could explain why hexane aromatization proceeds 3-4 times more rapidly on (111) and (10,8,7) planes than on planes with tetragonal symmetry like (100).<sup>20</sup> The growth of carbon deposits verified on single crystals<sup>41</sup> could be attributed to polymerization of trans-polyenes.1a,42

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Figure 8. Proposed surface species responsible for aromatization and C5-cyclic reactions. "Hexylidyne" has been postulated for some types of hydrogenolysis after analogous species reported by Somorjai et al.<sup>20,46</sup>



Figure 9. Possible surface species for  $C_5$ -cyclization of *n*-pentane (a) and 3,3-dimethylpentane (b).

Both methylcyclopentane and 3-methylpentane need skeletal rearrangement to form a C<sub>6</sub>-ring. The  $C_5 \rightarrow C_6$  ring expansion probably involves a bond-shift type mechanism. The cyclic structure obviously facilitates this reaction as opposed to openchain alkanes.<sup>43</sup> Dehydrogenation is necessary in both cases; for methylcyclopentane, Kane and Clarke<sup>44</sup> suggested that it occurs prior to ring enlargement.

 $C_5$ -cyclic reactions require still higher hydrogen pressures (Figure 1 and Table I). Such an effect may arise if the surface intermediate for the C5-cyclic reactions is less dehydrogenated than that for aromatization. An important parameter for  $C_5$ -cyclic reactions is the spacing between active sites (metal atom geometry).<sup>15</sup> Therefore the plane symmetry should not be very important in it and, indeed, this was reported on single-crystal surfaces.<sup>20</sup> A proposed C<sub>5</sub>-cyclic intermediate is also depicted in Figure 8. These data are in agreement with earlier suggestions that tertiary C atoms in the reactant facilitate C5-cyclization: the maximum yields of these alkanes are higher. Here the surface intermediate may, indeed, be attached by two of its atoms to the surface like in Figure 8. n-Pentane, in turn, may interact with the surface via a "metalacyclohexane"-like intermediate<sup>6</sup> (Figure 9a). While hydrogen is necessary to block threefold interstices lest they form multiple carbon-metal bonds unfavorable for C<sub>5</sub>-cyclization in the former case, this is not so important for *n*-pentane: its optimum  $p(H_2)$  is lower. This metalacyclohexane with an apparently lower adsorption energy<sup>34</sup> cannot displace efficiently adsorbed hydrogen; at slightly higher  $p(H_2)$  values all reactions cease (Figure 7). One of the methyl groups of gemdimethylpentanes, in turn, may also interact with the surface (Figure 9b); apparently, this may also lead to preferential  $C_5$ cyclization (Figure 3) and  $C_5$ -cyclic isomerization (Figure 5). The

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<sup>(42)</sup> Sárkány, A.; Lieske, H.; Szilágyi, T.; Tóth, L. Proc. Int. Congr. Catal., 8th 1984. 2. 613.

<sup>(43) (</sup>a) Davis, B. H. Proc. Int. Congr. Catal., 8th 1984, 2, 479. (b) Amir-Ebrahimi, V.; Gault, F. G. J. Chem. Soc., Faraday Trans. 1 1981, 77, 1813

<sup>(44)</sup> Kane, A. F.; Clarke, J. K. A. J. Chem. Soc., Faraday Trans. 1 1980, 76. 1640.

# SCHEME II



lower optimum  $p(H_2)$  values for such intermediates point to their relative low adsorption energies. Still, their formation is predominant, as shown by the high C<sub>5</sub>-cyclization selectivities of *gem*-dimethylpentanes (Table I).

The two mechanisms able to form saturated skeletal isomers can be clearly distinguished on the basis of their hydrogen dependence (Figures 3-5).  $C_5$ -cyclization and  $C_5$ -cyclic isomerization have a "C" common surface species:<sup>28</sup> the product will appear as an isomer or as an (alkyl-) cyclopentane depending on the conditions. Table I indicates that our conditions favor the desorption of the  $C_5$ -cyclic surface species as cyclopentanes. This is strongly catalyst dependent; on Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>, for example, isomer formation predominates, especially at higher hydrogen pressures.<sup>29</sup> Also, the structure of the reactant is important here (cf. Table I and ref 13 and 27).

Direct evidence for the role of  $C_5$ -cyclic intermediates is also supplied by our radiotracer experiments.

The rmr values of methylcyclopentane and 2-methylpentane gradually approach that of 3-methylpentane as conversion increases (Table IV). According to Scheme II, in the case of a total equilibration between surface species, the rmr values should be equal also in the gas phase: this state is approached but not reached. Again,  $p(H_2)$  influences the extent of equilibration. Apart from the diluting effect of inactive methylcyclopentane in the feed, the contribution of bond shift (BS in Scheme II) also increases the rmr of 2-methylpentane. The monotonic increase of bond shift isomer yields (Figure 4b) with  $p(H_2)$  point to its less dehydrogenated intermediates.<sup>12</sup>

Hydrogenolysis has been attributed to multiply adsorbed species attached to the metal by at least two C atoms.<sup>2,10,33,34</sup> Clarke and Rooney<sup>45</sup> proposed end adsorption on carbonized surfaces (i.e., at lower hydrogen pressures). One of the possible surface species would be here an "-ylidyne" adsorption.<sup>46</sup> A hexylidyne species is also shown in Figure 8: If another C atom of such an adspecies interacts with the metal, C–C bond rupture can occur. However tempting it would be to attribute end demethylation to a preferential "-ylidyne" attachment on (111) type planes (Table V),





this idea should be rejected. Free rotation could not bring  $C_3$  of a hexylidyne close to another metal site; i.e., such sorption cannot cause  $C_1-C_2$  rupture. (1,4-Interaction would lead to  $C_2-C_3$  breaking.<sup>33b</sup>) Another argument is that  $\omega_1$  values of, e.g., *n*-pentane and *n*-heptane are low at low  $p(H_2)$  and increase parallel with hydrogen pressure.<sup>33a</sup>

Instead, on the basis of the data in Figure 6 a new type of hydrogenolysis reaction is suggested involving the adsorption of a  $C_5$ -unit to the surface. This species can be related to the "C" common intermediate as shown in Scheme II; under hydrogen-deficient conditions, however, it undergoes fragmentation instead of cyclization/isomerization. Some of its fragments can never-theless appear as  $C_5$ -rings (Figure 7); that is why it is likely that its adsorption occurs in a cyclopentane-like form (Chart I).

The presence of a tertiary C atom in methylhexanes (Chart Ib) does not increase their  $C_5$ -cyclization yield but increases the selectivity of  $C_5$ -unit splitting at hydrogen pressures near the maximum yields of cyclization (cf. Figures 3 and 7). This enhancement is more marked at the chain end farther from the methyl group. It has to be noted that the concept that definite structural parts of "archetypal" molecules may react as "units" more or less independently of their substituents has been first proposed by Foger and Anderson.<sup>47</sup>

Finally if we compare our disperse Pt black with single-crystal faces, a surprising degree of agreement can be observed, especially if temperature differences are also considered.<sup>48</sup> The analogous regulating effect of hydrogen points to similar surface intermediates and their identical response to  $p(H_2)$  changes. Pt black resembled more closely planes with (111) symmetry than other single-crystal faces. This indicates that relating the activity of our catalyst to its (111) plane as a rough, first approximation is justified even in view of up-to-date results of single-crystal studies. The obvious differences are due either to structures not present in well-defined faces or to the different importance of carbonization.

**Registry No.** *n*-Pentane, 109-66-0; *n*-hexane, 110-54-3; 3-methylpentane, 96-14-0; *n*-heptane, 142-82-5; 2-methylhexane, 591-76-4; 3-methylhexane, 589-34-4; 3-ethylpentane, 617-78-7; 2,3-dimethylpentane, 565-59-3; 2,4-dimethylpentane, 108-08-7; 2,2-dimethylpentane, 590-35-2; 3,3-dimethylpentane, 562-49-2; *n*-octane, 111-65-9; 2-methylheptane, 592-27-8.

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<sup>(46)</sup> Gavezotti, A.; Simonetta, M.; Van Hove, M. A.; Somorjai, G. A. Surf. Sci. 1982, 122, 292.

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