

Transformations of 3-Methylpentane and 3-Methylpentenes over Platinum Black Catalyst

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Reactions of 3-methylpentane, 3-methyl-1-pentene, *cis*- and *trans*-3-methyl-2-pentenes have been studied over a platinum black catalyst, in a pulse-microcatalytic system, in the presence of carrier gases with different hydrogen contents. The yields of dehydrogenation of 3-methylpentane, C₅-cyclization, skeletal isomerization, and benzene formation are discussed in detail as a function of hydrogen pressure. An enhanced reactivity of the terminal olefinic double bond has been observed under hydrogen-deficient conditions: this manifested itself as benzene formation (presumably in bond-shift type dehydro-isomerization reaction) as well as in "non-hydrogenative" C₅-cyclization resulting in 1-methylcyclopentene. On the other hand, "hydrogenative" mechanisms of C₅-cyclization and C₅-cyclic isomerization have been found to prevail in the presence of more hydrogen; a common half-hydrogenated intermediate for both saturated and unsaturated hydrocarbons and a "dual-site" mechanism has been proposed for this process.

INTRODUCTION

Two mechanisms have been proposed for metal catalyzed skeletal isomerization of saturated hydrocarbons. A "bond-shift" mechanism has been proposed as entirely responsible for isomerization of hydrocarbons having five or less carbon atoms (1). With hydrocarbons containing six or more carbon atoms, an additional mechanism involving C₅-cyclic intermediates can also be effective (2). These two mechanisms can and do occur simultaneously (3) but factors such as catalyst dispersion (3-5) or the amount of hydrogen present during reaction (6) may decide which of them will predominate.

Both mechanisms of isomerization have been suggested to have multiple-bonded adsorbed species as surface intermediates. Anderson and Avery (1) proposed α, α, γ -adsorption for bond-shift isomerization. More recently, McKerverey *et al.* (7) proposed a π -complex-like surface species in-

stead. The C₅-cyclic mechanism should consist of a ring closure and a ring opening step even though not all cyclic intermediate can appear in the gas phase as a cyclopentane homologue. For ring closure α, α, ω - or α, ω -intermediates have been proposed involving either two (2) or a single surface metal atom (5), whereas π -allylic or $\alpha, \alpha, \beta, \beta$ -tetraadsorbed species have been suggested for ring hydrogenolysis (8). Liberman (9), on the other hand, developed a mechanism involving associative adsorption of the hydrocarbon in a way similar for both ring closure and opening.

It would be logical to expect that the desorption of more or less dissociated surface species would result in the appearance of unsaturated intermediates in the gas phase. In fact, such compounds have actually been observed in metal catalyzed skeletal rearrangement reactions (10). Three of the four possible olefins from 2-methylpentane were formed in its re-

action on Pt (11). No evidence has been obtained so far about the actual role (intermediate or by-product) of unsaturated compounds in C_5 -cyclization and C_5 -cyclic isomerization. Of the very few data available about the ability of unsaturated compounds to form five-membered rings, the Pt-catalyzed transformation of hexenes, hexadienes and hexatriene (12, 13) into methylcyclopentene can be mentioned.

The present work approaches the problem of the role of olefins by comparing the transformations of 3-methylpentane and three 3-methylpentene isomers on a platinum black catalyst, under identical conditions. This was done by studying their reactions in the presence of hydrogen at various partial pressures. By doing so we expected to obtain more information about the nature of surface intermediates and, further, it was hoped that the results will help to interpret the strong influence of hydrogen on the isomerizing and C_5 -cyclizing selectivity of platinum black catalyst shown previously by the authors (6, 14).

EXPERIMENTAL METHODS

Apparatus and Catalyst

The experiments were carried out in a pulse-type microreactor (15) using hydrogen, helium and hydrogen-helium mixtures as carrier gases (16). The carrier-free platinum black catalyst was prepared from H_2PtCl_6 by reducing it with HCHO in KOH (17). Its specific surface was about $2 \text{ m}^2 \text{ g}^{-1}$, and crystallite size (as concluded from the pretreatment at 360°C) about $400\text{--}500 \text{ \AA}$ (18). Catalyst activity was adjusted before experiments by pulse-like injections of air; this was followed by hydrogen pulses when the carrier gas was helium (16).

The analyses were carried out by using a column packed with Chromosorb P coated with 18% of squalane; other details have been described earlier (16).

Hydrocarbons

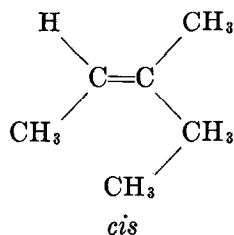
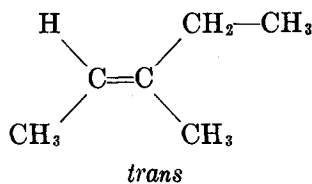
3-Methylpentane: Merck "Reference for gas chromatography" containing 99.40% 3-methylpentane and 0.60% 2-methylpentane.

3-Methyl-1-pentene was supplied by EGA Chemie. Prior to use, it was shaken several times with $FeSO_4$ solution and distilled after drying. No impurity was found by gas chromatography.

cis-3-Methyl-2-pentene was supplied by Fluka and treated as described previously. Impurity: 0.54% of 3-methylpentane.

trans-3-Methyl-2-pentene was purified by preparative gas chromatography on a squalane column from a commercial preparation (EGA-Chemie) containing about 11% *cis*- and 89% *trans*-isomer. Impurities after purification: 0.07% 3-methylpentane and 0.32% *cis*-3-methyl-2-pentene.

In order to avoid confusion in the nomenclature, the structure of these hydrocarbons has been checked by NMR spectroscopy.¹ The *cis* and *trans* denotations are applied to the longest chain:



RESULTS

Table 1 contains data on the product composition obtained from 3-methylpentane and 3-methylpentenes in the presence of hydrogen at different partial pressure,

¹ The authors gratefully thank Dr. P. Sohár for kindly performing the NMR measurement.

TABLE 1
Transformation of 3-Methylpentane and Methylpentenes over Pt Black^a

Starting hydrocarbon	Carrier gas	Effluent composition (mole%) ^b								
		<C ₅	3MP	Sat. skeletal isomer ^c	3M1P=	2E1B=	c-3M2P=	t-3M2P=	C ₅ -cyclic ^d	Benzene
3-Methylpentane	He	0.67	97.32	0.03	0.13	—	0.33	0.51	0.33	0.09
3-Methyl-1-pentene		0.69	7.14	0.03	74.15	1.07	5.11	8.01	1.63 ^e	2.15 ^e
<i>cis</i> -3-Methyl-2-pentene		0.42	1.42	—	1.28	1.73	90.39	2.63	1.01	0.53
<i>trans</i> -3-Methyl-2-pentene		0.44	2.02	—	1.14	2.37	2.31	90.06	0.65	0.65
3-Methylpentane	5% H ₂	0.73	96.05	0.46	0.14	—	0.46	0.70	0.81	0.04
3-Methyl-1-pentene	95% He	0.78	15.02	0.20	60.45	1.95	7.46	11.95	1.62	0.52
<i>cis</i> -3-Methyl-2-pentene		0.57	8.38	0.24	1.38	1.99	76.34	9.20	1.27	0.11
<i>trans</i> -3-Methyl-2-pentene		0.48	8.25	0.09	1.41	2.60	5.63	79.68	1.38	0.07
3-Methylpentane	20% H ₂	1.19	92.74	1.68	0.11	—	0.56	0.83	2.19	—
3-Methyl-1-pentene	80% He	0.92	43.96	0.73	32.16	1.24	6.69	11.67	2.51	0.11
<i>cis</i> -3-Methyl-2-pentene		0.88	39.69	0.99	1.10	0.97	44.22	8.79	2.75	0.03
<i>trans</i> -3-Methyl-2-pentene		0.81	42.51	0.87	1.08	1.42	5.19	44.61	3.07	0.04
3-Methylpentane	35% H ₂	2.15	89.55	4.00	0.08	—	0.40	0.59	2.56	0.04
3-Methyl-1-pentene	65% He	1.36	56.38	1.27	26.87	—	4.28	6.91	2.90	0.06
<i>cis</i> -3-Methyl-2-pentene		1.28	55.36	1.79	0.63	—	33.26	4.21	2.91	0.03
<i>trans</i> -3-Methyl-2-pentene		1.40	55.72	1.77	0.61	1.01	2.59	33.60	2.89	0.04
3-Methylpentane	H ₂	1.04	94.50	2.26	0.04	—	0.22	0.33	1.02	—
3-Methyl-1-pentene		1.07	63.27	1.92	27.63	—	1.73	2.74	1.64	—
<i>cis</i> -3-Methyl-2-pentene		0.87	62.10	2.38	0.31	—	30.65	1.84	1.34	—
<i>trans</i> -3-Methyl-2-pentene		0.67	62.37	1.98	0.35	—	1.33	31.70	1.24	—

^a $t = 360^{\circ}\text{C}$, catalyst: 0.4 g Pt; carrier gas: 60 cm³ min⁻¹; 3 μ l pulses each.

^b Compositions are corrected for initial impurities, and therefore the sum is sometimes less than 100%.

^c 2-Methylpentane + *n*-hexane + 2,2-dimethylbutane for 3-methylpentane (2MP:nH 8-10), 2-methylpentane + 2,2-dimethylbutane for methylpentenes; 2,2-DMB up to 0.1%, in the presence of hydrogen only.

^d Methylcyclopentane + 1-methylcyclopentene.

^e Possibly with 3-methyl-1,3-pentadiene.

at a typical experimental temperatures of 360°C. Whereas dehydrogenation reactions (including dehydro-isomerization into benzene) prevail in helium, a wider spectrum of products and higher conversion can be observed in the presence of hydrogen of even low partial pressure.

Although hydrogenation and double bond isomerization give most of the products from methylpentenes, hereafter we shall confine ourselves to the study of cyclization, isomerization and aromatization.

Benzene yields decrease drastically with increasing hydrogen content, approaching zero in 20% H₂ throughout the whole temperature range. Different starting hydrocarbons produce various amounts of benzene: 3-methyl-1-pentene gives by far the highest and 3-methylpentane the lowest

yields, 3-methyl-2-pentene isomers being in an intermediate position (cf. Table 1).

Plotting the values of isomer and C₅-cyclic yields as a function of the hydrogen content of the carrier gas, curves with a maximum are obtained. The maxima are shifted towards higher hydrogen pressures with increasing temperature.

The yields of C₅-cyclic products (methylcyclopentane and 1-methylcyclopentene) are shown in Fig. 1. Whereas the shape of the curves was essentially the same with all starting hydrocarbons, actual yield values were identical only with higher hydrogen pressures. At lower hydrogen pressures, the structure of the starting hydrocarbon was the main factor determining total C₅-cyclic yield. 3-Methylpentane underwent practically no cyclization in the absence of hydrogen, but this

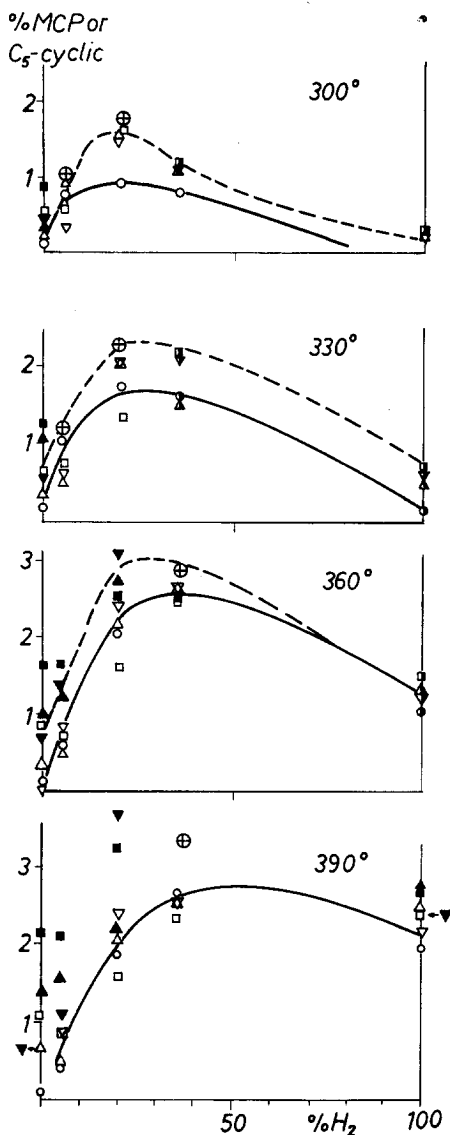


FIG. 1. Yields of C_5 -cyclic products (solid symbols) and methylcyclopentane (open symbols) from 3-methylpentane and 3-methylpentenes, as a function of the hydrogen content of the carrier gas. Symbols of different shape denote various starting hydrocarbons as follows: (○) 3-methylpentane; (□) 3-methyl-1-pentene; (△) *cis*-3-methyl-2-pentene; (▽) *trans*-3-methyl-2-pentene; (⊕) means coinciding (■, ▲, ▼). The solid line has been fitted to the open circle points, the broken line (where possible) to △ and ▽.

was not the situation with olefins (especially 3-methyl-1-pentene) which gave mainly 1-methylcyclopentene.

3-Methylpentenes, similarly to 3-methylpentane, gave also the saturated skeletal isomer 2-methylpentane (Fig. 2), with maxima at higher hydrogen pressures (at 390°C, above atom of hydrogen, the figure thus displaying only the ascending part of the curve). 3-Methyl-1-pentene produced here somewhat less skeletal isomer than other methylpentenes, whereas saturated 2-methylpentane produced more (Fig. 3).

Figure 3 also contains data on the dehydrogenation of 3-methylpentane (almost entirely into 3-methyl-2-pentene isomers): the maxima here are at much lower hydrogen pressures ("below zero" at 300°C which obviously means that even the amount of hydrogen retained in helium after regeneration (19) gives higher coverages than optimum for this process).

It has been found earlier that benzene yields decreased considerably when the platinum catalyst was deactivated by subsequent pulses of *n*-hexane in helium; with hydrogen-containing carrier gases the deactivation was slowed down considerably (20). Essentially the same was true with unsaturated starting *n*-hydrocarbons (16). Although the selective deactivation and regeneration phenomena are to be dis-

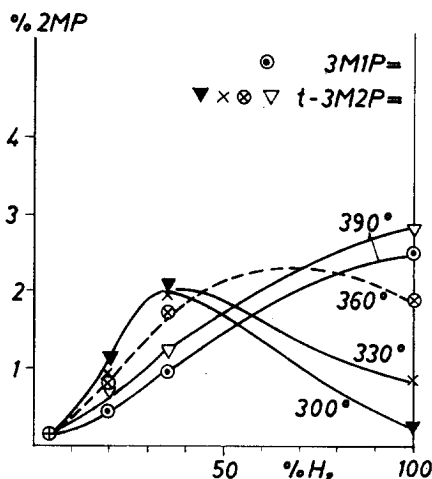


FIG. 2. Yields of 2-methylpentane from 3-methylpentene isomers. Symbols as shown; data for *cis*-3-methyl-2-pentene generally coincide to those for the *trans*-isomer.

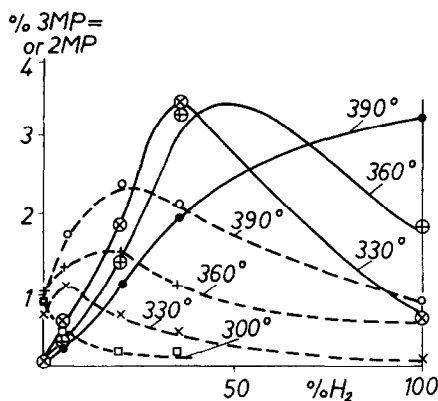


Fig. 3. Yields of 3-methylpentenes and 2-methylpentane from 3-methylpentane. (\otimes , \oplus , \bullet) and solid lines denote 2-methylpentane yields; (\square , \times , $+$, \circ) and broken lines 3-methylpentene yields at temperatures shown.

cussed in a separate paper (21) it is worthwhile to check the possible effects of catalyst deactivation under our conditions.

Table 2 contains data on 3-methylpentene isomers having reacted in carrier gases with different compositions. Deactivation in helium is significant, but much slower in the presence of hydrogen. The relative extent of catalyst deactivation is different for various reactions; even so, it is obvious that eventual deactivation during the first pulse could not possibly change dramatically the shape of the curves depicted in Figs. 1-3.

With 3-methylpentane, the extent of deactivation was much smaller. A peculiar feature should be mentioned here: in the course of catalyst deactivation in helium, the amount of 3-methyl-2-pentenes decreased and that of the thermodynamically less stable 3-methyl-1-pentene even increased (Fig. 4). Partial reactivation of a deactivated catalyst increased somewhat the 3-methyl-2-pentene formation (without a similar increase of cyclization and skeletal isomerization).

DISCUSSION

If we consider the three types of reactions, two factors can be found determining

the yields: these are the hydrogen partial pressure and the structure of the starting hydrocarbon. Curves in Fig. 1 show convincingly that the latter factor is important only with lower hydrogen pressures: at higher hydrogen concentrations the various hydrocarbons react similarly.

The only skeletal rearrangement reaction taking place even in the absence of hydrogen is benzene formation which has been shown earlier to have a bond-shift character (6). Olefins, especially 3-methyl-1-pentene, tend to be more ready to undergo aromatization than 3-methylpentane. The fact has to be pointed out that the formation of 3-methyl-1-pentene from 3-methylpentane is higher under hydrogen-deficient conditions, similar to those favorable for benzene formation. It is possible that terminal dissociatively adsorbed species may play a role in both cases, the formation and further reaction of which is facilitated by the presence of a terminal double bond in the initial molecule.

The appearance of minor amounts of 2,2-dimethylbutane in the presence of hydrogen indicates that bond shift isomerization takes place in the presence of hydrogen, too, but its extent may not be considerable.

It has been suggested previously that isomerization in hydrogen proceeds mainly via C_5 -cyclic intermediates (6, 14). The appearance of methylcyclopentane in the gas phase is less convincing evidence (22) than the 3-methylpentane/*n*-hexane ratio being close to that observed in ring opening of methylcyclopentane (14a).

Let us concentrate now on the ring closure step. 3-Methylpentane gives methylcyclopentane only in the presence of hydrogen. This fact or the existence of maximum yields as a function of hydrogen pressure does not, however, mean that dissociatively adsorbed species may not take part in cyclization and isomerization reactions, since similar curves were observed also for aromatization of *n*-hexane (14b). In the case of aromatization, how-

TABLE 2
Transformation of 3-Methylpentenes over Deactivating Pt Black^a

Carrier gas	Starting hydrocarbon	Pulse No.	Effluent composition (mole%) ^b					
			<C ₈	3MP	2MP	3MP=	C ₅ -cyclic ^c	Benzene
He	3M1P=	I	1.74	14.81	0.06	79.46	3.34	0.52
		III	0.29	0.03	—	99.23	0.38	0.08
	<i>c</i> -3M2P=	I	1.27	3.49	0.09	92.49	1.51	0.61
		III	0.06	—	—	99.57	—	0.36
	<i>t</i> -3M2P=	I	0.97	2.08	0.08	99.23	1.00	0.44
		III	0.09	—	—	99.13	0.37	0.07
5% H ₂ + 95% He	3M1P=	I	1.81	31.93	0.18	62.05	3.49	0.55
		III	0.62	21.32	0.02	74.32	3.25	0.46
	<i>c</i> -3M2P=	I	1.34	11.89	0.20	83.64	2.27	0.33
		III	0.51	6.84	0.07	89.88	1.87	0.24
	<i>t</i> -3M2P=	I	1.11	12.51	0.17	83.40	2.28	0.14
		III	0.42	7.30	0.06	90.20	1.48	0.14
35% H ₂ + 65% He	3M1P=	I	5.51	64.92	2.02	22.37	4.06	0.12
		III	4.19	67.40	1.54	22.87	3.90	0.08
	<i>c</i> -3M2P=	I	4.32	56.77	2.52	32.05	3.77	0.02
		III	3.62	56.81	2.34	32.66	4.03	0.04
	<i>t</i> -3M2P=	I	3.60	57.59	2.19	32.89	3.27	0.01
		III	2.78	57.00	1.78	34.50	3.46	—

^a Catalyst: 0.4 g Pt, treated with 10 ml air + 10 ml H₂ prior to Pulse I; carrier gas: 60 cm³ min⁻¹, 3 μ pulses each.

^b See footnote *b* to Table 1.

^c Methylcyclopentane + 1-methylcyclopentene.

ever, hexenes—being intermediates of hexane aromatization—turned out to be much more reactive than *n*-hexane (11, 20). This is analogous to the higher reactivity of 3-methyl-1-pentene in benzene formation.

Methylpentenes react similarly to 3-methylpentane in the presence of more hydrogen; with carrier gases of low hydrogen pressures, however, they give more C₅-cyclic products, consisting of mainly 1-methylcyclopentene. Under such conditions, the amount of the latter depends mainly on the structure of the initial hydrocarbon, 3-methyl-1-pentene being most reactive. The same can be observed

with deactivating catalysts: Figure 5 shows that whereas the C₅-cyclizing activity is nearly proportional to the hydrogenating activity of the catalyst in the medium range of conversion (at higher hydrogenation yields, a saturation value is achieved), the plot has an intersection with the ordinate at a positive value. The product obtained at zero (or very low) hydrogenation activity consists completely of 1-methylcyclopentene.

Thus, it can be concluded that, in principle, two ways of C₅-cyclization can be distinguished. One way is the formation of 1-methylcyclopentene from methylpen-

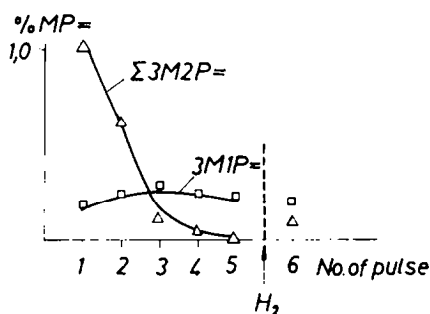
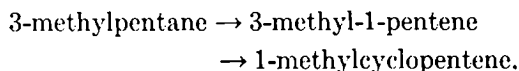


FIG. 4. Yields of various 3-methylpentenes from 3-methylpentane, from subsequent pulses introduced into helium without regeneration: $t = 360^\circ\text{C}$. The arrow denotes a 30 min hydrogen flow at 360°C . (Δ) 3-methyl-2-pentenes; (\square) 3-methyl-1-pentene.

tenes; this way manifests itself (although with lower conversions) with not too much hydrogen present and is not correlated with the hydrogenating activity of the catalyst. This, "non-hydrogenative" C_5 -cyclization may be similar to that reported for n -hexenes and hexadienes (12, 13), and since 3-methyl-1-pentene gives most C_5 -cyclic unsaturated product, this route can

be regarded as identical to that suggested in the literature involving terminally adsorbed species (2). The formation of 1-methylcyclopentene may be due to the much higher thermodynamic stability of this isomer. Naturally it cannot be excluded that, to a lesser extent, also 3-methylpentane may react this way:



The nature of the other, "hydrogenative" route of C_5 -cyclization can be judged from the fact that both *cis*- and *trans*-isomers produce nearly the same amounts of C_5 -cyclic products although the stereochemistry of only the *cis*-isomer is favorable for cyclization (cf. Figs. 1 and 5). (It has to be noted that *cis-trans* isomerization has been found to be among the rate determining steps for benzene formation from unsaturated $n\text{-C}_6$ species. It is not justified, therefore, in gases with low hydrogen concentrations (16), to regard it as a very

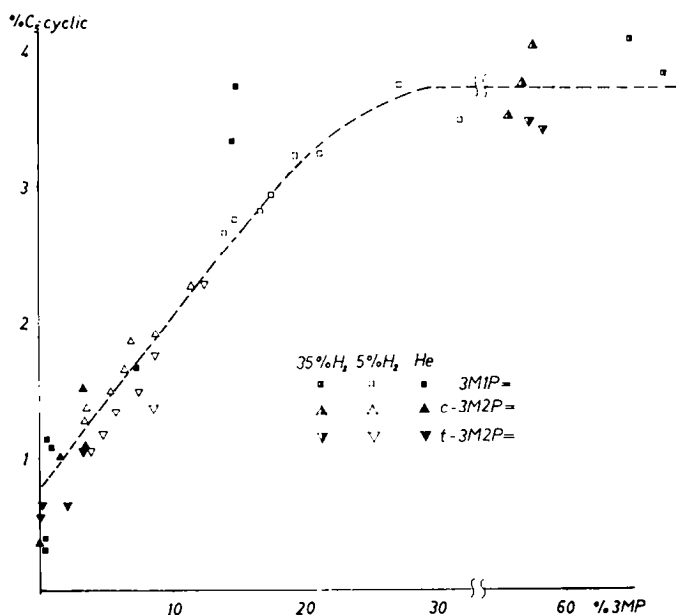
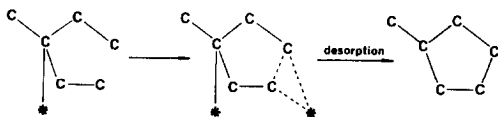


FIG. 5. Yields of C_5 -cyclic products as a function of the yields of 3-methylpentane from various 3-methylpentenes at $t = 360^\circ\text{C}$. Symbols with different shapes denote various starting hydrocarbons; open, half-filled and filled symbols denote different carrier gases as shown.

fast process; see Table 2 where differences due to the original structure are noticeable over deactivating catalysts.)

Summing up the facts it may be concluded that (i) the main pathway of isomerization must involve a common intermediate for both 3-methylpentane and 3-methylpentenes; (ii) the probability of its formation is nearly proportional to the hydrogenation activity of the catalyst; and (iii) it does not preserve the *cis-trans* isomerism of the starting hydrocarbon.

It is not probable that some allylic species would be active in cyclization since these are formed more readily from olefins than from an alkane and would conserve the original geometry of the molecule; it is more logical to assume that the surface species in question is a *half-hydrogenated adsorbed state*. Since a tertiary carbon atom has the lowest C-H bond energy (23), adsorption via this carbon atom can be regarded as preferential. The half-hydrogenated intermediate of "hydrogenative" C₅-cyclization is presumably "weakly" adsorbed on a platinum site [in terms of the suggestions in (24)], whereas, another site may interact with the two ends of the chain and bring about a new carbon-carbon bond. The participation of surface hydrogen atoms in cyclization may be similar to that suggested by Liberman (9). Olefins are side products formed via loss of a second hydrogen atom from the carbon atom next to the primary adsorption, giving, consequently, mostly 3-methyl-2-pentenes. It cannot be decided so far whether the cyclizing site involves a flat plane atom or one at an edge or corner (25); our suggestion may be valid in either case.



The resulting C₅-cyclic surface product may desorb as such or may suffer ring opening before desorption. The ring open-

ing mechanisms will be discussed in another paper. Since the latter process requires stoichiometric hydrogen, it is not surprising that methylpentenes consuming surface hydrogen in hydrogenation give less skeletal isomer.

These facts can be interpreted in terms of various chemisorbed intermediates the formation of which is governed by the hydrogen coverage (not defined under our conditions but obviously being in correlation with hydrogen pressure). Under hydrogen-deficient conditions, "strong" hydrocarbon-metal interactions prevail (24), involving presumably multiple carbon metal bonds, with secondary and primary carbon atoms only. Such interactions lead to the formation of thermodynamically less favored 3-methyl-1-pentene from 3-methyl-pentane, to its "non-hydrogenative" cyclization, and to the accumulation of carbonaceous deposits on the surface.

With more hydrogen, single ("weak") interactions (which are preferential with the tertiary carbon atom) become predominating; the lifetime of the half-hydrogenated surface species is prolonged, and thus its characteristic reactions including dehydrogenation into 3-methyl-2-pentene, cyclization and ring opening take place. That is why the yields of all these products increase with increasing hydrogen pressure. The maximum yield of 3-methyl-2-pentenes can be interpreted in terms of facilitated desorption of these products as a more favorable reaction as compared with further dehydrogenation giving carbonaceous species.

With still more hydrogen present, a competition occurs between hydrogen and hydrocarbons for active sites; thus, after a maximum catalyst activity, the well-known negative hydrogen order can be observed.

The shift of the maxima towards higher hydrogen pressures with increasing temperatures (Figs. 1-3) can be explained by

the fact that at higher temperatures more hydrogen is necessary to maintain the same equilibrium hydrogen coverage. Although "hydrogen coverage" cannot be defined quantitatively under our conditions, this fact is in favor of our above explanation in terms of the existence of an optimum amount of hydrogen for different reactions.

Data on deactivation are in agreement with our "dual-site" concept for cyclization and C₅-cyclic isomerization processes: a partial reactivation by hydrogen allows some 3-methyl-2-pentene to form at the primary adsorption sites but the other sites for ring closure remain still blocked (cf. Fig. 4). We feel that this interpretation does not contradict the statement that "surface carbiding (interstitial atoms and/or carbonaceous residues) is a principal influence in regulating cyclization route" (26) but we stress the role of hydrogen, too, in preventing formation of carbon residues and thereby generating surface sites for C₅-cyclization.

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