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The Mechanisms of Hydrogenolysis and Isomerization of Hydrocarbons on Metals. VI. Isomerization of Labeled Hexanes on a 0.2% Platinum–Alumina Catalyst*

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The isomerization at low conversion of six methylpentanes (2-methyl- and 3-methyl-), labeled with carbon 13 in various positions, have been studied over a 0.2% Pt–Al_2O_3 catalyst. The nature of the carrier, an inert alumina, and the reaction temperature, 265–275°C, were such that the skeletal rearrangement proceeds only on the metallic part of the catalyst.

The position of the labeling atom in most of the isomeric reaction products, methylpentanes and *n*-hexanes, is consistent with a simple cyclic mechanism of isomerization. This mechanism consists of a dehydrocyclization to a methylcyclopentane intermediate followed by the opening of its ring.

However, ten to twenty percent of the isomers referred to as "abnormal" products, cannot be explained by this mechanism. The abnormal *n*-hexanes are formed by the succession of a dehydrocyclization–ring opening process and an exchange of the two terminal carbon atoms in the resulting adsorbed *n*-hexane. The abnormal methylpentanes may be formed either by a simple methyl or ethyl shift, or by the succession of several rearrangements in the adsorbed phase, according to a bond shift or a cyclic mechanism. The simultaneous occurrence of a single dehydrocyclization–ring opening process, the major mechanism, and of a minor process involving several successive rearrangements before desorption, suggests a heterogeneity of the 0.2% Pt–Al_2O_3 catalyst.

INTRODUCTION

It has long been known that skeletal rearrangements of hydrocarbons, such as isomerization, ring enlargement, etc., take place over *acidic catalysts*. The occurrence of these reactions over *metals* was recognized later, and their mechanism investigated only recently.

A number of skeletal rearrangements, viz., hydrogenolysis of cyclopentanes and cyclobutanes (*1–4*), dehydrocyclization to cyclopentanes (*5–10*), aromatization of trimethylpentanes (*5–7*), have been discovered by Kazanskii, Liberman, Platé and coworkers, using platinum on charcoal as a catalyst. Since the carrier in their experiments was not acidic, these reactions could be considered as occurring exclusively on the metal sites.

The mechanisms of isomerization over metals have been studied in detail by three independent groups of workers. Anderson *et al.* studied the hydrocracking and skeletal rearrangement of small hydrocarbon molecules, viz., isobutane, *n*-butane and neopentane, over a number of metal films. They observed the isomerization of isobutane to *n*-butane over palladium and platinum films, and the conversion of neopen-

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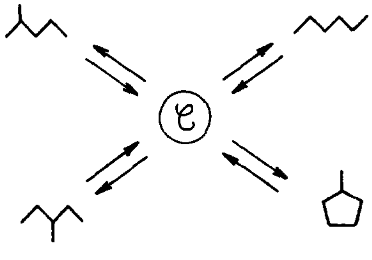
tane to isopentane over platinum; these molecules were only cracked over the other metals considered (*11–13*). The determination of the stoichiometry of the dissociatively adsorbed hydrocarbons formed at high temperature on metal and the study of the isomerization of *n*-butane-1-^{13}C led Anderson and Avery to the conclusion that the reactive species in isomerization were strongly adsorbed molecules in $\alpha\ \gamma$ position (*13*). These authors represented the determining step as the formation of a bridged intermediate from an $\alpha\ \alpha\ \gamma$ triadsorbed precursor species (*14*). With the assumption of a partial electron transfer from the hydrocarbon residue to the surface metal atom, simple molecular orbital calculations accounted for the relative reactivities of various hydrocarbons. The mechanism of rearrangement of these small molecules over platinum films will be referred to later on as a "bond shift mechanism."

Boudart *et al.* studied the isomerization and cracking of neopentane on a number of supported metal catalysts. On platinum, they showed that the selectivity for isomerization varied by a factor of one hundred for the catalysts studied and that the specific activity depended widely upon the dispersion of the metal on the carrier (*15*). They also found that not only platinum but also iridium and gold could promote the isomerization to isopentane (*16*).

The mechanisms of isomerization of larger molecules, hexanes and heptanes, have been investigated by Gault, Maire *et al.* (*17a,b*). They observed that on a 0.2% Pt–Al_2O_3 catalyst, dehydrocyclization to methylcyclopentane always accompanied the rearrangement of methylpentanes and *n*-hexane and that the initial product distributions in the isomerization of hexanes were *identical* to the initial product distribution obtained in the hydrogenolysis of methylcyclopentane: for example, the same ratios between the concentrations of 3-methylpentane and *n*-hexane were obtained initially from 2-methylpentane and from methylcyclopentane. These results suggested that the three reactions, isomerization, dehydrocyclization, and hydrogenolysis involved a common intermediate and could be represented by the following scheme:

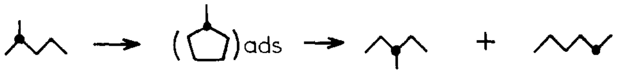


Since the isomerization of molecules like 2,3-dimethylbutane was shown to be very slow on a 0.2% Pt–Al_2O_3 catalyst, it was suggested that intermediate ($\mathcal{C}$) in the scheme represented an adsorbed species with a methylcyclopentane structure. According to this "cyclic mechanism," the isomerization of methylpentanes and *n*-hexane may then be pictured as a dehydrocyclization to an adsorbed methylcyclopentane, followed by the opening of its ring.

The cyclic mechanism of isomerization, first demonstrated in the case of hexanes over a dispersed catalyst, was extended, although not always very successfully, to explain the rearrangements of more complicated molecules, such as heptanes (*18, 19*), butylbenzene (*20*) and other alkylbenzenes (*21a,b*). In the case of hexanes themselves, the cyclic mechanism of rearrangement was shown to be very important also over platinum films and concentrated supported catalysts, although the product distributions in these cases were very different from the one obtained over dispersed catalysts. For example, on a 10% Pt–Al_2O_3 catalyst at 300°C, the initial product distributions are identical from isomerization and methylcyclopentane hydrogenolysis. However, they differ somewhat on the same catalyst at lower temperatures and on platinum films. It was then suggested that there occurs on these catalysts, and especially on platinum films, both types of skeletal rearrangement, according to a cyclic and a bond shift mechanism (*17*).

To make this point clear, the isomerization of hexanes was further investigated by using ^{13}C to label the various reactant hydrocarbons. If ($\mathcal{C}$) represents a single adsorbed methylcyclopentane intermediate, the labeling of the various isomers may be easily predicted.

For example:



On the other hand any deviation from such a simple distribution may be the clue to a more complicated process.

In the hydrogenolysis of methylcyclopentane or in the isomerization of hexanes, the various platinum catalysts, 0.2% platinum on alumina, 10% platinum on alumina and platinum films, yielded very different product distribution (*22*). We shall study in turn each of these catalysts.

The present paper will be devoted to the 0.2% Pt-Al$_2$O$_3$ catalyst, the more simple one. On this catalyst, the identity of the initial product distributions from isomerization and methylcyclopentane hydrogenolysis shows that the cyclic mechanism of rearrangement is unique or at least widely predominant (*17*). Moreover, the hydrogenolysis of cyclopentane hydrocarbons corresponds to an equal chance of breaking any cyclic bond and the distribution does not depend upon the temperature, which shows that the ring opening step is a very simple one (*22*).

EXPERIMENTAL

Apparatus

By using compounds labeled with carbon 13, we were obliged to work on a very small scale, and to limit as far as possible the loss of materials during the synthesis and the catalytic reactions. The only labeled products to be prepared and stored were therefore the labeled hexanols, and the preparation of the saturated hydrocarbons, by dehydration of the alcohols and hydrogenation of the resulting olefins, was effected in the same flow system as the skeletal rearrangement.

A pulse microreactor technique, with purified hydrogen as reactant or carrier gas, was used for the three reactions: dehydration, hydrogenation, and isomerization. The apparatus is diagrammatically represented in Fig. 1. Three microreactors *D*, *E*, *J*, are disposed in series in the flow line before the cold trap *F* and the chromatographic column *G*. Microreactor *D* containing 1.9 g of alumina effected the dehydration of the alcohol; the alumina was nonactivated γ-alumina obtained from Woelm (surface area: 100 m^2/g; particle size: 90–200 mesh; purity 99.96%); its acidic catalytic activity was extremely low: no skeletal rearrangement of 2-methylpentenes and of methylcyclopentene was observed during 1 hr at temperatures lower than 450°C. The same alumina was used as a carrier for preparing the platinum–alumina catalyst. The temperature for the dehydration in the microreactor was chosen so as to keep the extent of skeletal rearrangement during the reaction lower than 0.3% and the extent of cracking lower than 3%; it depended upon the nature of the alcohol, being 255–280°C for tertiary alcohols and 230° for secondary alcohols. Microreactor *E* containing 2 g of 10% platinum on alumina was used at 100°C

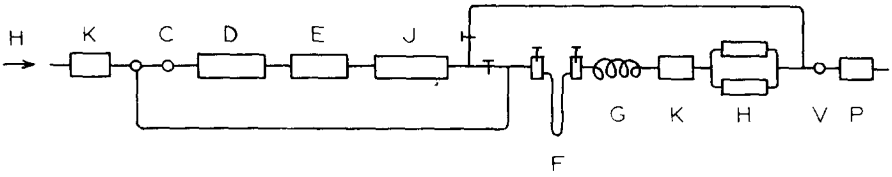


FIG. 1. Apparatus: *D*, dehydrator; *K*, katharometer; *E*, microhydrogenator; *C*, injector; *J*, microreactor; ***F***,***H***, traps; *G*, column; *P*, pump.

for the hydrogenation of the olefins which were formed on the alumina. At this temperature any possible side reaction may be excluded. Microreactor *J* contained the 0.2% platinum on alumina catalyst on which was effected the isomerization reaction. Ahead of the reactors the flow apparatus also included the injector *C* and the first branch of a katharometer K_1, and after the chromatography column it included the second branch of the katharometer K_2, several traps in parallel *H*, a needle valve *V* and a rotary pump *P*. The microreactors or the chromatography column could also be by-passed.

Procedure

Two procedures were used in the experiments. In the first, three pulses of 5 mg of alcohol were introduced every five min through the injector. The reaction products which issued from reactor *J* were condensed for 30 min in trap *F*, and then vaporized. After a small sample (0.2 mg) of these products had been removed for a separate gas chromatographic analysis, the remainder was introduced on the chromatography column *G* to separate the various C_6 molecules: 2-methylpentane, 3-methylpentane, *n*-hexane and methylcyclopentane; during this operation the by-passes were used to disconnect the microreactor section *D–J* from the chromatographic section *F–H*. Each of the separated molecules was then analyzed by chromatography to check its purity and by mass spectrometry to determine its isotopic content.

A second procedure was used whenever the purity of the saturated hydrocarbons which issued from microreactors *D* and *E* was considered insufficient. In this case, the preparation of the saturated hydrocarbons was effected in a first run by using exactly the same procedure as above except for the temperature of microreactor *J*, kept at 100°C, and the much larger amount of alcohol treated (30–50 mg). The purified saturated hydrocarbon collected in trap *H* was then reinjected through *C* over microreactor *J* to be isomerized at the required temperature. Since it eliminates any isomerization or cracking products resulting from the dehydration process, this second procedure was considered much safer than the first one and was used in most cases.

Materials

The preparation of 2-methylpentanols, 3-methylpentanols, and *n*-hexanols labeled in various positions by carbon 13 has been extensively described (*23*); these compounds were obtained by reacting ketones, aldehydes or esters with the appropriate Grignard reagents. The following labeled materials were used: acetone-2-^{13}C, ethyl bromide-1-^{13}C, methyl-(^{13}C) iodide and ethyl acetate-1-^{13}C; they were obtained from Merck and Dohme, Canada, with an isotopic purity of 53–58%.

The light compounds, alkyl halides, ketones, or aldehydes, were obtained from Fluka; their purity was higher than 99.9%, except for the 3-methylbutanal which contained about 30% of 2-methylbutanal. Cylinder hydrogen from Air Liquide Co. used as a reactant was purified by passing over a 10% Pt–Al_2O_3 catalyst and through a liquid-nitrogen trap.

Preparation of the C_6 Saturated Hydrocarbons

Almost all the possible methylpentanes and *n*-hexanes labeled with carbon 13 in the various positions were prepared, purified, and their mass spectra recorded (*23*). For this purpose the same apparatus and procedure were used as for the catalytic experiments. The purity before chromatography of some of these hydrocarbons is reported in Table 1; those selected were the ones whose skeletal rearrangement will be examined in this paper.

In this way were prepared the four 3-methylpentanes: 3-^{13}C (III–*Y*), 2-^{13}C (III–*Z*), 1-^{13}C (III–*T*) and methyl-(^{13}C) (III–*X*). Four of the five possible 2-methylpentanes: 1-^{13}C (II–*X*), 2-^{13}C (II–*Y*), 4-^{13}C (II–*Z*), 5-^{13}C (II–*T*); and two of the three possible *n*-hexanes 1-^{13}C (I–*X*) and 2-^{13}C (I–*Y*); *n*-hexane 3-^{13}C (I–*Z*) was prepared by a synthesis in seven steps from carbon dioxide ^{13}C (*24*).

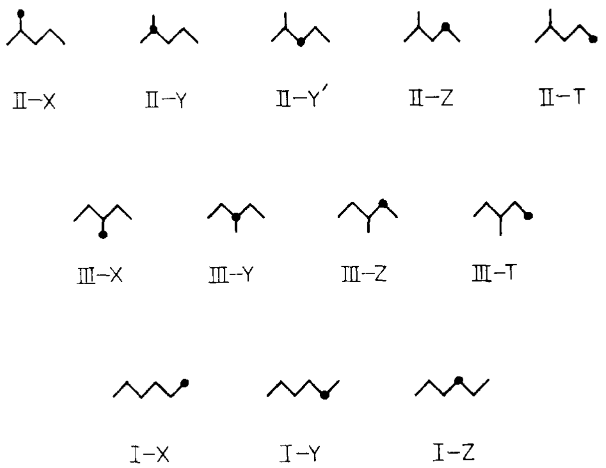


FIG. 2. Labeled hexanes.

It was further checked that no skeletal rearrangement had occurred during the dehydration, by preparing some of these hydrocarbons, viz., I–*X*, I–*Y*, III–*X*, III–*Z*, in an entirely different way, i.e., by reaction of a alkylmagnesium halide with an allylic halide and hydrogenation of the resulting olefins. The mass spectra of the saturated hydrocarbons obtained from the alcohol and from the allylic halides were identical.

Catalysts

The 0.2% and 10% platinum on alumina catalysts were prepared in the usual way by an impregnation method (*25*).

A study of the chemisorption of hydrogen at 20°C on the 0.2% $Pt–Al_2O_3$ catalyst gave the ratio of number of adsorbed hydrogen atoms over number of platinum atoms equal to 0.90. Moreover the platinum could not be detected by the classical X-ray diffraction methods. Both re-

TABLE 1

PREPARATION OF LABELED HEXANES BY CATALYTIC DEHYDRATION OF ALCOHOL

Prepared hydrocarbon	Starting material	Temperature of dehydration	Impurities (in %)			
			n-hexane	2-methylpentane	3-methylpentane	C_5
II–*X*	2 methyl-2 pentanol-1-^{13}C	286	0	—	0.1	1.
II–*Y*	2 methyl-2 pentanol-2-^{13}C	289	0	—	0.5	3.5
II–*T*	4 methyl-2 pentanol-1-^{13}C	247	0	—	21.9	17.3
III–*X*	3(methyl-^{13}C) 3 pentanol	276	0	0	—	1
III–*Y*	3 methyl-3 pentanol-3-^{13}C	278	0	0.3	—	1.9
III–*Z*	3 methyl-3 pentanol-2-^{13}C	259	0	0.2	—	
III–*T*	3 methyl-2 pentanol-1-^{13}C	251	0	0.75	—	2.7

sults are consistent with a size of the metal crystallites in the range of 15–20 Å.

Gas Chromatography

The separation of the various isomers was effected in 4 hr at 13°C on a 10 m column. This column of ¼″ was filled with 40–50 mesh fire-brick impregnated by 25% in weight of SE-30 silicone. The analyses of the reaction mixture and of the separated isomers were carried out at 25°C on a 5 m column constructed in the same way as the separative column.

Mass Spectra of the Reference Hydrocarbons

For each of the reference hydrocarbons, the peak groups in C_6, C_5, and C_4 were recorded. After correction for the naturally occurring ^{13}C and deuterium and for the fragmentation, described elsewhere (*23*), the abundances of the main ions, $C_6H_{14}^+$ and $C_5{}^{13}CH_{14}^+$, $C_5H_{11}^+$ and $C_4{}^{13}CH_{11}^+$, $C_4H_9^+$ and $C_3{}^{13}CH_9^+$ were determined in each group of peaks.

$$\text{The ratios } R_6 = \frac{^{13}CC_5H_{14}^+}{C_6H_{14}^+};\ R_5 = \frac{^{13}CC_4H_{11}^+}{C_5H_{11}^+}\ \text{and } R_4 = \frac{^{13}CC_3H_9^+}{C_4H_9^+}$$

were then calculated. From them were deduced the relative abundances a_5 and a_4 which would have been obtained for $C_4{}^{13}CH_{11}^+$ and $C_3{}^{13}CH_9^+$ if the labeled saturated hydrocarbons had been 100% pure isotopically: $a_n = R_n(1 + R_6)/R_6(1 + R_n)$. In Table 2 are reported the values of a_5 and a_4 found for the various reference hydrocarbons. While the classical rule of fragmentation at the tertiary carbon atom may be used in a very good approximation to calculate a_5 and a_4 for the methylpentanes, this is not at all the case for the *n*-hexanes; for these hydrocarbons a rearrangement of the molecule occurs in the source of the mass spectrometer during or before the fragmentation to the demethylated ion. Therefore to make the analysis more accurate, the a_5 and a_4 values found for the reference hydrocarbons were used in any case to determine the concentration of the various isotopic varieties in each isomer.

Mass Spectra of the Various Reaction Products and Location of the ^{13}C Atom in the Molecules

Each isomer, after separation, contained small amounts of the other hydrocarbons which were determined by gas chromatography. The spectra of the "pure" isomers were then deduced from the rough spectra by taking these impurities into account. The corrections were easily made by using the additive rules generally assumed in mass spectrometry (*26*). In addition, it was assumed for the calculations that the sensitivity and the fragmentation C–C or C–H for a labeled compound were the same as for the unlabeled compound. After the usual corrections for the naturally occurring isotopes and the fragmentation, the ratios R_6, R_5, R_4, and hence a_5 and a_4 were then determined for each of the three pure acyclic C_6 hydrocarbons.

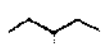
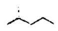
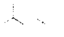
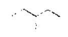
The location of the carbon 13 in the isomers was then effected by comparing these relative abundances a_5 and a_4 with the relative abundances of the reference hydrocarbons. Additive rules were assumed and computer techniques used. In the case of *n*-hexanes, a_5 and a_4 are sufficient to determine the concentrations x, y, z, of all three isotopic varieties I–*X*, I–*Y*, I–*Z*. In the case of 2-methyl and 3-methylpentanes, the mass spectra of II–*Z* and II–*T* (or of III–*Z* and III–*T*) are very similar in the C_5 and C_4 regions. So are most probably the values of a_5 and a_4 for 2-methylpentane-2-^{13}C (II–*Y*) and for 2-methylpentane-3-^{13}C (II–*Y′*). On account of these similarities, the determination of the concentrations x, y, $z + t$ in 3-methylpentanes, x, $y + y'$, $z + t$ for 2-methylpentanes can be effected within very narrow limits with the sole knowledge of a_5 and a_4. The slight variations of a_5 and a_4 on account of source conditions and other factors in the mass spectrometer (see Table 2) were also taken into account. As a result of the above calculations, the concentrations of the various isotopic species (or sum of isotopic species),

TABLE 2

Mass Spectra of Hexanes Labeled with ^{13}C; Relative Abundances a_5 and a_4

Hydrocarbon	a_5	a_4	Hydrocarbon	a_5	a_4
 I-*X*	0.682 ± 0.012	0.531 ± 0.016	 II-*X*	0.5	0.975
 I-*Y*	1.000 ± 0.001	0.519 ± 0.015	 II-*Y*	0.997 ± 0.003	0.970 ± 0.012
 I-*Z*	0.806	0.976	 II-*Z*	0.99	0.08
 III-*X*	0.152 ± 0.017	0.977 ± 0.023	 II-*T*	0.99	0.115
 III-*Y*	0.999	0.977			
 III-*Z*	0.997 ± 0.003	0.540 ± 0.003			
 III-*T*	0.918 ± 0.012	0.532 ± 0.008			

TABLE 3
Reactions of Methylpentanes on 0.2% Pt–Al_2O_3: Isomer Distributions

Exp. no.	Reacting hydrocarbon	Reaction temp. (°C)	Distribution of the C_6 hydrocarbons in %				Isomeriz. convers. α%	Cracking convers. α'%	r_p	r'_2	
										exper.	(16)
II 1		266	0.58	5.0	4.8	89.6	9.8	6.5	2.7	0.97	0.86
2		265	0.61	5.3	5.0	89.1	10.3	6.8	3.4	0.94	0.87
3		273	0.73	1.72	1.69	95.9	3.4	2.5	6.3	0.98	0.65
4		275	0.42	4.8	3.7	91.1	8.5	1.8	1.7	0.77	0.80
										r'_3	
III 5		277	0.61	4.3	88.3	6.9	11.2	3.4	0.30	1.61	1.32
6		276	0.56	3.9	89.3	6.3	10.2	3.1	0.32	1.61	1.30
7		277	0.57	3.7	90.1	5.6	9.3	2.6	0.30	1.51	1.28

$$\alpha = \frac{n\text{-hexane} + 3\text{-methylpentane}}{\Sigma C_6} \text{ (part II) or } \alpha = \frac{n\text{-hexane} + 2\text{-methylpentane}}{\Sigma C_6} \text{ (part III).}$$

$$\alpha' = \frac{\Sigma C_5}{\Sigma C_5 + \Sigma C_6};\ r'_2 = \frac{3\text{-methylpentane}}{n\text{-hexane}} \text{ (part II); } r'_3 = \frac{2\text{-methylpentane}}{n\text{-hexane}} \text{ (part III).}$$

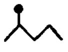
$$r_p = \frac{n\text{-pentane}}{\text{isopentane}}.$$

are given in Tables 4 and 5 with an estimation of the maximum uncertainty.

RESULTS

The isomerization of six labeled hydrocarbons was studied over the 0.2% Pt–Al_2O_3 catalyst.


(II-Y)


(II-X)


(II-T)


(III-Y)


(III-Z)


(III-T)

The temperature 265–275° and the amount of catalyst (0.65 g) were chosen so that the conversion, about 10% or lower, could be considered as very close to the initial distribution. In a tracer study, it is initial distributions which are required if valid conclusions about the reaction mechanisms are to be drawn.

Isomer Distributions

The distributions of the C_6 hydrocarbons, the conversions α and α' in isomers and demethylated products, the ratios r'_2 or r'_3 between the concentration of the two isomers and the ratio r_p between the concentrations of n-pentane and isopentane are given in Table 3 for each experiment. In order to compare the catalysts used in the present experiments and the one studied previously for the isomerization of unlabeled compound (*17*), we have also given in the two last columns of Table 3 the ratios r_2 or r_3 obtained at the same conversion in the experiments of Barron *et al.* One can see that the ratios r'_2 or r'_3 obtained in the present experiments were slightly higher than in the reference experiments, which seems to indicate that the thermal stabilization of the catalyst was not entirely achieved* (*22*).

Labeling of the Isomerization Products

The analyses of the various labeled methylpentanes and n-hexanes obtained by isomerization are reported in Tables 4 and 5. For each analysis the limits of the possible errors are also estimated. All the given values are reliable except perhaps the concentrations of the methylpentanes and particularly of the n-hexanes obtained in experiment 5, for which slightly negative values were obtained; it is possible that in this experiment the stability of the mass spectrometer filament was not perfect, resulting in an erratic change of fragmentation during the analysis.

Labeling of the Starting Hydrocarbons

The analysis of the various labeled hydrocarbons used as starting materials was also effected after their reaction on the catalyst. The results are reported in Table 6. The amounts of hydrocarbons obtained with the same skeleton as in the reacting molecule, but with a change of place of the labeling carbon atom, never exceeded 2.5%. Although it was difficult to draw any conclusion from the figures, on account of the experimental errors (in average ±1.5%), the results presented in Table 6 may be considered as a test for the stability of the ion source of the mass spectrometer and for the validity of our methods of analysis and calculations.

Labeling of the Methylcyclopentanes

The spectra of the methylcyclopentanes obtained by dehydrocyclization were also recorded and calculated. Unfortunately, since the fragmentation patterns of the methylcyclopentane in a mass spectrometer are not available in the literature, these re-

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* When a 0.2% Pt-Al_2O_3 catalyst is heated in a hydrogen flow, it is known that its catalytic properties, and especially its selectivity in isomerization and hydrogenolysis, vary continuously until a limiting value is reached. Apparently in these experiments this limit has not been yet attained.

TABLE 4

Reactions on a 0.2% Pt-Al_2O_3 Catalyst. Labeling of the Isomerization Products: Methylpentanes. Comparison between the Observed and Calculated Values.

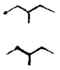
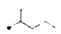
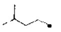
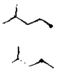
Reacting hydrocarbon		Exp. No.	α%	 x	 y	 $z + t$
	Calculated					
	According to					
	Mechanism C			0	100	0
(II-Y)	Mechanism T			0	0	100
	Observed	1	9.8	4.4 ± 1.0	77.6 ± 1.6	17.6 ± 0.5
		2	10.3	3.8 ± 1.4	68.7 ± 2.0	27.1 ± 0.1
	Calculated					
	According to					
	Mechanism C			50	0	50
(II-X)	Mechanism T			50	0	50
	Observed	3	3.4	49.4 ± 2.5	4.9 ± 4.9	45.7 ± 3.6
	Calculated					
	According to					
	Mechanism C			0	0	100
(II-T)	Mechanism T			0	0	100
	Observed	4	8.5	5.9 ± 2.2	1.4 ± 1.4	93.2 ± 2.5
				 x	 $y + y'$	 $z + t$
	Calculated					
	According to					
	Mechanism C			0	100	0
(III-Y)	Mechanism T			0	100	0
	Observed	5	11.2	1.3 ± 0.1	90.8 ± 0.15	7.95 ± 0.15
	Calculated					
	According to					
	Mechanism C			50	50	0
(III-Z)	Mechanism T			0	50	50
	Observed	6	10.2	42.7 ± 0.1	50.0 ± 0.15	7.4 ± 0.15
	Calculated					
	According to					
	Mechanism C			0	0	100
(III-T)	Mechanism T			50	0	50
	Observed	7	9.3	7.5 ± 0.1	−0.3 ± 1.8	93.1 ± 1.8

TABLE 5

REACTIONS ON A 0.2% Pt-Al_2O_3 CATALYST. LABELING OF THE ISOMERIZATION PRODUCTS: n-HEXANES. COMPARISON BETWEEN THE OBSERVED AND CALCULATED VALUES

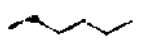
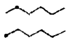
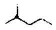
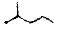
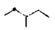
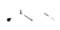
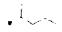
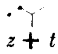
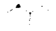
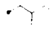
Reacting hydrocarbon		Exp. No.	α %	 x	 y	 z	 $x + y$
	Calculated						
	According to						
	Mechanism C			0	100	0	100
(II-Y)	Mechanism T			0	a	$100 - a$	a
	Observed	1	9.8	11.7 ± 2.6	89.4 ± 1.8	−1.1 ± 3.4	100.1
		2	10.3	7.9 ± 2.4	93.2 ± 1.6	−1.0 ± 3.4	101.1
	Calculated						
	According to						
	Mechanism C			75	0	25	75
(II-X)	Mechanism T			$50 + a/2$	$50 - a/2$	0	100
	Observed	3	3.4	68.6 ± 4.3	4.3 ± 3.7	27.2 ± 2.7	72.9
	Calculated						
	According to						
	Mechanism C			0	100	0	
(III-Y)	Mechanism T			0	0	100	
	Observed	5	11.2	−3.2 ± 2.1	94.8 ± 1.4	8.2 ± 3.3	
	Calculated						
	According to						
	Mechanism C			50	0	50	50
(III-Z)	Mechanism T			0	50	50	50
	Observed	6	10.2	43.8 ± 2.9	7.2 ± 2.4	49.1 ± 1.9	51

TABLE 6
Labeling of the Starting Hydrocarbons

Reacting hydrocarbon	Exp. No.	α%	 x	 $y + y'$	 $z + t$
 II-*Y*	1	9.8	0	97.6	2.4
	2	10.3	0	97.7	2.3
 II-*X*	4	3.4	97.7	1.6	0.7
			 x	 y	 $z + t$
 III-*Y*	5	11.2	0	100	0
 III-*Z*	6	10.2	0	2.5	97.5
 III-*T*	7	9.3	0.6	0.7	98.7

sults can not be used for the catalytic study.†

Discussion

Cyclic Mechanism (C)

In their main features, the distributions of the various isomers, methylpentanes and *n*-hexanes, may be explained by the simple succession of a dehydrocyclization to a cyclopentane intermediate followed by its ring opening (mechanism *C*).

In Table 4, the distributions of the *methylpentanes* obtained by isomerization are compared with the distributions provided by this mechanism. The distributions resulting from a methyl shift, as would have been expected, for example, over an acidic catalyst, were also considered (mechanism *T*); in three cases they differed from the preceding ones. It is noticeable from the Table that the observed distributions are always similar to the ones predicted by a simple cyclic mechanism. However, some discrepancies appear between the observed and calculated distributions *C*. Nine "abnormal" species are thus formed in these isomerizations.

The distributions of the *n-hexanes* obtained by isomerization are given in Table 5. They are always very similar to the distributions predicted by mechanism *C* and differ strongly in each case from the one which could have resulted from a methyl shift *T*. However, some discrepancies remain between the observed distributions and the distributions *C*.

Bond Shift Mechanism (T) *(Isomerization to n-Hexanes)*

All these discrepancies between the *n*-hexane distributions, observed and calculated according to a cyclic mechanism, are eliminated if one assumes a possible interconversion between *n*-hexane 1-^{13}C (I–*X*) and *n*-hexane 2-^{13}C (I–*Y*). In the last row of Table 5, the sums of the observed concentrations of varieties I–*X* and I–*Y* in the various experiments are compared to

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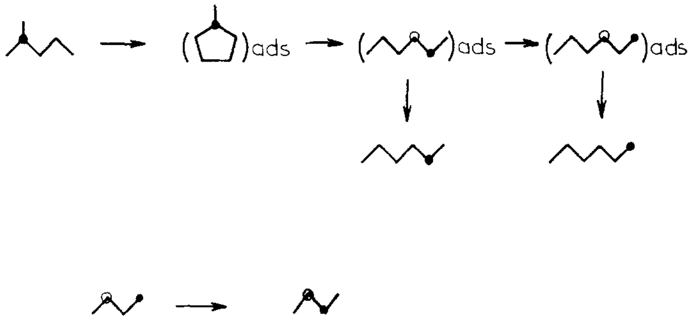
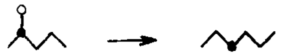
† In reverse, since a simple mechanism for the dehydrocyclization process may be deduced from the present experiments, as will be seen, the spectra of the methylcyclopentanes obtained in the various experiments will make it possible indeed to establish the fragmentation patterns of methylcyclopentane under electron impact (*27*).

the calculated values. The agreement is quite good.

This interconversion between the two varieties may easily be explained, if there takes place to a small extent in the adsorbed phase and after the hydrogenolysis of the cyclopentane intermediate, a skeletal rearrangement similar to the one described by Anderson and Avery in the case of n-butane (*13*).*

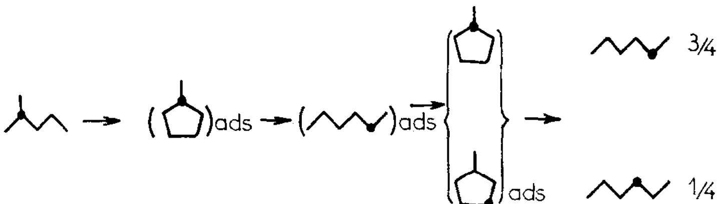


It should be pointed out at this stage that three similar reactions (according to a bond shift mechanism), could be imagined yielding n-hexane from 2-methyl or 3-methylpentanes. However, according to one of these three reactions, n-hexane-3-^{13}C should be obtained from 2-methylpentane-2-^{13}C, and this compound does not appear in the observed distribution:


[1]

For this reason, we have discarded any bond shift reaction interconverting n-hexane and methylpentanes, in order to explain the abnormal species.

Similarly, the succession in the adsorbed phase of two cyclic type rearrangements should also be discarded, whenever they involved adsorbed n-hexane. Such a process indeed would give a distribution of the hexanes different from the observed one, as can easily be seen again in the case of the isomerization of 2-methylpentane-2-^{13}C (*2*).



[2]

Bond Shift Mechanism: Isomerization to Methylpentanes

The "abnormal" methylpentane varieties may also be explained by the combination of cyclic and bond shift type reactions. For the reasons developed in the preceding section, only five bond shift rearrangements may be considered, the ones interconverting methylpentanes into each other. They include:

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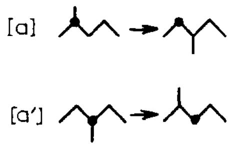
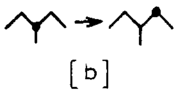
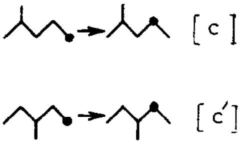
* The reaction mechanism adopted throughout this paper and the following one for the bond shift rearrangement is the one proposed by Anderson and Avery (*14*), involving an α α γ tri-adsorbed species and a bridged intermediate. In the description of the elementary steps, ○ represents the pivot carbon atom during the bond migration, ● represents a labeled carbon atom. Obviously the replacement of the bridged intermediate by an adsorbed cyclopropane (on carbon atom γ), as suggested by Muller and Gault (*28*) would lead to exactly the same conclusions.



methyl shift



ethyl shift



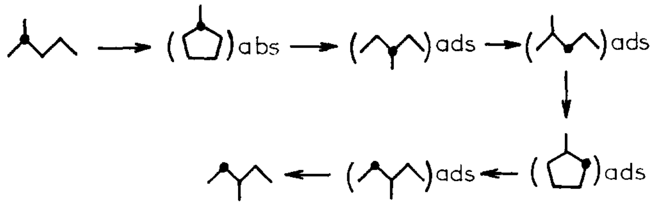
interchange of terminal carbon atoms

In fact, to explain all the isotopic varieties, it is necessary to consider not one rearrangement of type *T*, but the succession before desorption of several rearrangements according to a cyclic or a bond shift mechanism. In Fig. 3 are reported the *minimum* number of trips on the surface necessary to explain each variety. For some species at least three successive rearrangements are required, but of course the number of steps may be much larger than reported in Fig. 3. For example, the following reaction:

may be the result of one rearrangement *Ta*, but also of the succession of two rearrangements or even more:

(*C* and *Ta*, represented by the symbol *CTa*)

(or *C*, *Ta'*, and *C* represented by symbol *C Ta' C*)



The number of trips required to yield the abnormal methylpentanes species is probably rather high. This means that in this case the chance, *d*, for adsorbed molecules to be desorbed, is much smaller than unity and of the same order as the chances *t* and *c* to be rearranged by a bond shift or by a cyclic mechanism.

Heterogeneity of the Catalyst

On the contrary, when one considers the distributions of the *major* methylpentane species, it seems that the possibility of several successive cyclic type rearrangements is precluded. For example three consecutive cyclic type reactions would lead, in the case of 2-methylpentane-1-^{13}C, to a ratio of III-*Z*/III-*X* of about 2 instead of 0.9; by a similar process, 3-methylpentane-2-^{13}C would yield about 65% of 2-methylpentane-1-^{13}C instead of 43%. One has to assume here that the probability of desorption of adsorbed molecules *d* is much larger than their probability of cyclization *c* and close to unity.

It is, therefore, very difficult to relate the major methylpentane varieties, obtained by a simple cyclic type isomerization, and the "abnormal" varieties, resulting from several successive rearrangements on the surface. In fact two types of site seem to be present on the catalyst. One type of site, the more numerous, is responsible for the "normal" varieties, *n*-hexane and methylpentanes, which result from a *single* de-

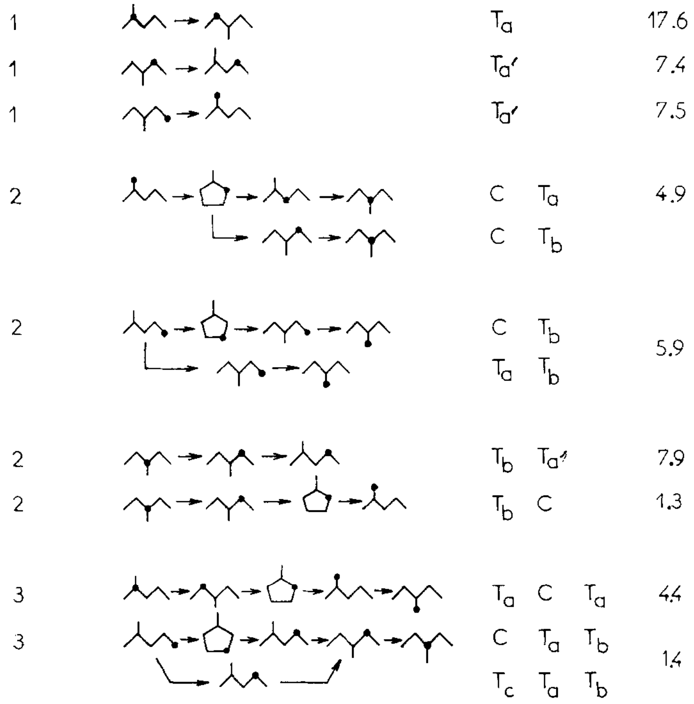


FIG. 3. Interpretation of the "abnormal" methylpentane species. *Ta*, represents a bond shift rearrangement according to reaction [*a*]; *C*, represents a cyclic type rearrangement. First row: minimum of trips required to explain the isotopic species; Last row: percent of the species in the product distribution.

hydrocyclization–ring opening process. For these sites $t = 0$ and $c \ll d$. Related to the second type of site are the "abnormal" varieties, *n*-hexane or methylpentanes, resulting from the succession of *several* rearrangements according to a cyclic or a bond shift mechanism. For these sites $d \gtrapprox c$. Excluded from the possible bond shift type rearrangements are the ones which interconvert *n*-hexanes and methylpentanes.

This last remark suggest a possible identification of the sites: it is known that over a concentrated platinum catalyst, methylpentanes isomerize mostly between each other and very little to *n*-hexane. Similarly the amounts of *n*-hexane obtained by hydrogenolysis of methylcyclopentane are very small on this concentrated catalyst (*22*). On the contrary, over a dispersed catalyst, the isomerization of *n*-hexane to methylpentanes is as easy as the isomerization between methylpentanes.

Now when a catalyst with a low content of platinum has not been thoroughly stabilized, it retains some of the properties of a concentrated catalyst (for example, the ratio of 2-methylpentane to 3-methylpentane in hydrogenolysis of methylcyclopentane is too high and the ratio of *n*-hexane to methylpentane is too low) (*22*); this is indeed the case of the catalyst used in the present work. It is, therefore, tempting to assume that, while a simple cyclic mechanism without repetition takes place over the dispersed sites of the catalyst, the second process yielding the "abnormal" methylpentane and *n*-hexane species is due to those sites characteristic of a concentrated catalyst. The study of the isomerization of various labeled methylpentanes over a 10% Pt–Al_2O_3 catalyst has confirmed this assumption (*29*).

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