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The Mechanisms of Hydrogenolysis and Isomerization of Hydrocarbons on Metals

VII. Isomerization of Labeled Hexanes and Hydrogenolysis of Methyl (^{13}C) Cyclopentane on a 10% Platinum–Alumina Catalyst

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The isomerization of 2-methyl-2-^{13}C, 3-methyl-3-^{13}C, and the hydrogenolysis of methyl-(^{13}C) cyclopentane were studied over a 10% platinum–alumina catalyst at 270°C. Methylcyclopentane hydrogenolysis yielded mainly 2-methylpentane and 3-methylpentane, and isomerization was mostly restricted to an interconversion between both methylpentanes.

The position of the carbon 13 in the various reaction products could only be explained by assuming that several successive rearrangements take place in the adsorbed phase, before desorption. A model was devised whereby acyclic adsorbed hydrocarbons may either be desorbed, or be rearranged according to a cyclic or a bond shift mechanism. The only bond shift reactions envisaged in this model were the three possible methyl- and ethyl- shifts involving a tertiary carbon atom, and the same rate was assumed for each of these three reactions.

With these assumptions, the observed initial product concentrations (ten independent values) could be reproduced with two parameters only: the probability *d* of desorption of the adsorbed species, and the probability *t* of bond shift rearrangement. The mean number of rearrangements before desorption, equal to $1/d$, was two for the experiments described, so that not less than seven trips had to be envisaged to account for all of the reaction products. The differences between these results on the 10% Pt–Al_2O_3 catalyst and the ones obtained on a highly dispersed catalyst, where most of the isotopic varieties are explained by a single dehydrocyclization–ring opening process, are interpreted in terms of metallic particle sizes. It is believed that on the dispersed catalysts, the active sites consist of a single atom, and the only possible path for isomerization is the cyclic mechanism. On catalysts with large crystallites, such as the 10% Pt-alumina catalyst, it is believed that sites involving several metal atoms are present on the surface, which allows the occurrence of bond shift reactions and of the repetitive process.

INTRODUCTION

It was shown several years ago that concentrated platinum catalysts (5–20% platinum on an inert alumina) behave very differently from the highly dispersed one used in the reforming process (*1–3*).

The hydrogenolysis of methylcyclopentane over dispersed catalysts (0.2–1.5% Pt-on-alumina) corresponds at any temperature to an equal chance of breaking of any cyclic bond and the isomerization of both methylpentanes yields *n*-hexane as one of the major reaction products.

On the contrary the concentrated catalysts act very selectively in the hydrogenolysis of methylcyclopentane and in the

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isomerization of hexanes. Methylpentanes mainly are formed by the ring opening of methylcyclopentane and the isomerization of hexanes is mostly restricted to an interconversion between both methylpentanes. Moreover, over a 10% Pt–Al_2O_3 catalyst, the product distributions in isomerization and methylcyclopentane hydrogenolysis depend very strongly upon the temperature and the reactant pressures. An increase in temperature or a decrease in hydrogen pressure result in a decrease of selectivity (*1, 2*). These changes in selectivity with the various experimental conditions indicate rather complicated mechanisms for both reactions, isomerization and methylcyclopentane hydrogenolysis.

The aim of this paper is the investigation of these mechanisms by the use of hydrocarbons labeled with carbon 13.

EXPERIMENTAL

The apparatus, the experimental procedures, the method of preparation of the hydrocarbons and the treatment of the mass spectrometric data have been described in the preceding paper (*4*). Slight modifications only will, therefore, be reported in this section.

Catalysts

Two batches of 10% Pt–Al_2O_3 catalysts were prepared by slowly reducing platinum complex salts deposited on an inert alumina: one batch (*A*) was obtained by using chloroplatinic acid, and a second one (*B*) by reducing platinous tetrammine chloride. In both cases the reduction temperature was kept below or equal to 200°C and the flow rate of hydrogen near 10 cm^3/min.

In the case of the Pt–Al_2O_3 catalyst prepared from platinous tetrammine chloride, the ammonium chloride formed during the reduction was subsequently desorbed by passing over the catalyst, in the microreactor flow system, several doses of hydrocarbons at 350°C.

A study of the chemisorption of hydrogen at 20° on the 10% Pt–Al_2O_3 catalyst *A* gave a ratio of number of adsorbed hydrogen atoms to number of platinum atoms equal to 0.045 (instead of 0.90 for the 0.2% Pt–Al_2O_3 catalyst used in the previous study (*4*)). This ratio 0.045 corresponds to a mean size of 185 Å for the crystallites in excellent agreement with the X-ray line broadening measurements: values of 180 and 200 Å were found for catalyst *A* and *B*, respectively.

Apparatus and Procedure

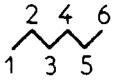
Three hydrocarbons were reacted over the catalysts: 3-methylpentane-3-^{13}C, 2-methylpentane-2-^{13}C, and methyl (^{13}C) cyclopentane. The preparation of these hydrocarbons from the corresponding tertiary alcohols was effected in the same flow line as their isomerization or hydrogenolysis. Two microreactors containing 2 g of Al_2O_3 at 245° and 2 g of Pt–Al_2O_3 at 100°C, respectively, were arranged in the flow line ahead of the main reactor itself. This reactor consisted of five glass tubes in parallel containing various amounts of catalyst (0.10–0.70 g); the tubes, isolated from each other, were used in turn so that the isomerization of hydrocarbons could be studied at various conversions.

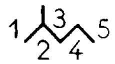
The temperature chosen for the dehydration of the acyclic alcohols over alumina (245°) was low enough to keep the extent of rearrangement during the preparation below 0.3%. The resulting error for the analysis of the isotopic species was then smaller than 2%. It was checked that the cyclic alcohol did not yield any acyclic hydrocarbons during the dehydration over alumina.

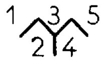
Materials

The syntheses of 3-methyl-3-pentanol-3-^{13}C and of 2-methyl-2-pentanol-2-^{13}C have been described (*5*). Methyl (^{13}C) cyclopentanol was prepared from methyl (^{13}C) magnesium iodide and cyclopentanone.

As in the preceding paper (*4*), I–*X*, I–*Y*, I–*Z* represent the *n*-hexanes-1-^{13}C, 2-^{13}C, and 3-^{13}C. The 2-methylpentanes labeled on carbon 1, 2, 3, 4, and 5 are referred to as II–*X*, II–*Y*, II–*Y′*, II–*Z*, and II–*T*, respectively. Lastly, III–*X*, III–*Y*, III–*Z*, and III–*T* represent the 3-methyl (^{13}C) pentane, the 3-methylpentane-3-^{13}C, 2-^{13}C and 1-^{13}C.







RESULTS

(*A*) *Isomerization of Methylpentanes*

Isomerization of 2-methylpentane-2-^{13}C and 3-methylpentane-3-^{13}C at 270° was studied at various conversions, in order to determine the initial distributions of the reaction products. The same batch *A* of a 10% Pt–Al_2O_3 catalyst prepared from chloroplatinic acid was used in all the experiments except one which was performed over a catalyst *B* prepared from platinous tetrammine chloride.

Isomer distributions. Typical distributions are given in Table 1. Each methylpentane yielded the other methylpentane and *n*-hexane as the two main isomeric products. In Table 1 conversions α and α' are thus expressed as a function of concentrations x_2, x_3, x_1 of 2-methylpentane, 3-methylpentane, and *n*-hexane, respectively, as follows:

$$\alpha = \frac{x_1 + x_3}{x_1 + x_2 + x_3} \qquad \alpha' = \frac{x_2 + x_1}{x_1 + x_2 + x_3}$$

The ratios r_2 and r_3 between the concentrations of the two main hexane isomers obtained from 2-methylpentane and 3-methylpentane, $r_2 = x_3/x_1$; $r_3 = x_2/x_1$, are plotted vs. conversion α or α' in Fig. 1. Most of the plots lay on the same curve whatever the method of preparation of the catalysts. It was then possible, by extrapolation, to obtain the initial values for r_2 and r_3; they were found to be equal to 4.5 and 16, respectively. In the same figure are given the values obtained for r_2 and r_3 at 300°C over the same 10% Pt–Al_2O_3 catalyst (Barron, Maire *et al.* (*2*)). As expected from the known variations of the ratios with temperature (1c), the values given by these authors are lower than the ones here.

Several abnormal plots with very low values of r_2 and r_3 were obtained, however. They all correspond to experiments with a very small amount of catalyst (less than 150 mg).

Methylcyclopentane was found in each experiment and in larger amounts from 2-methylpentane (3–10% of the reaction products) than from 3-methylpentane (1–2%). Traces of neohexane and 2,3-dimethylbutane were also obtained from both hydrocarbons. Besides these C_6 hydrocar-

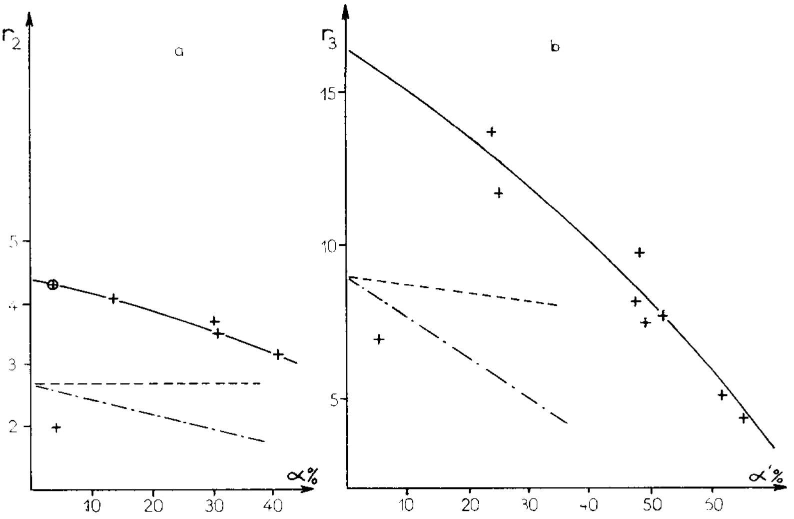
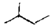
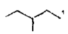
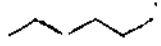
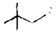
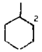
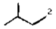


FIG. 1a. Isomerization of 2-methylpentane: r_2 (α) plots.

FIG. 1b. Isomerization of 3-methylpentane: r_3 (α') plots: —, isomerization at 272°C; +, on a catalyst prepared from $PtCl_6H_2$; ⊕, on a catalyst prepared from $Pt(NH_3)_4Cl_2$; – – –, hydrogenolysis of methylcyclopentane at 300°C; –.–.–., isomerization of methylpentanes at 300°C.

TABLE 1

Isomerization of Methylpentanes over 10% Pt on Al_2O_3. Distributions of the Reaction Products

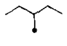
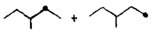
	Run	T(°C)	α or α'	[1]	[1]	[1]	[1]	[2]	[2]	[2]	[2]	[2]	[2]	C_2H_6[2]
3 methylpentane	8	270	24.5	93.1	—	6.9	3.6	1.9	10.1	23.5	36.2	15.1	—	—
	12	271	25.8	92.1	—	7.9	3.3	—	10.0	22.6	27.4	18.7	44.7	—
	9	270	52.3	88.5	—	11.5	3.4	0.9	9.0	18.8	29.1	12.0	41.5	11.8
	7	273	5.4	87.5	—	12.5	9.0	1.2	39.2	81.6	114.7	34.1	262	54.1
2 methylpentane	2	272	13.7	—	80.3	19.7	1.5	7.1	35.0	18.4	26.6	44.8	—	—
	3	271	30.5	—	77.9	22.1	1.9	3.0	21.4	13.2	—	—	—	—
	1	271	4.1	—	66.3	33.7	4.9	12.6	85.9	39.7	42.2	84.4	—	—

[1] Expressed as percent of the two main hexane isomers.

[2] Amounts (in weight) of the minor C_6 hydrocarbons and of the cracking products; they are related to the amounts of the two main hexane isomers, taken as 100.

TABLE 2

Isomerization of 2-Methylpentane 2 ^{13}C. Labeling of the 3-Methylpentane Isomers

Run	T(°C)	Weight of catalyst (mg)	α	 III-X	 III-Y	 III-Z + III-T
1	271	120	4.1	14.8 ± 3	28 ± 4.5	56.8 ± 2.3
2	272	210	13.7	2 ± 2	31.5 ± 3.5	66.3 ± 1.5
3	271	330	30.5	2.2 ± 2	27.6 ± 3.8	70.2 ± 1.7
4	272	410	29.8	1.5 ± 2	30.8 ± 3	68.1 ± 1.8
5	273	700	40.8	2.5 ± 2	29.7 ± 4.0	67.8 ± 1.8
6	269	230	4.0	0.8 ± 2	27.8 ± 3	71.3 ± 1
0.2% $Pt-Al_2O_3$	266	650	9.8	4.4 ± 1	77.6 ± 1.6	17.6 ± 0.5

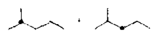
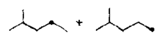
bons, appreciable amounts of molecules with a lower molecular weight were formed (mostly pentanes, butanes, and propane) and the ratio n-pentane over isopentane corresponded very closely to the one provided by an equal break of the various $C-CH_3$ bonds: 2 from 2-methylpentane and 0.5 from 3-methylpentane. In the abnormal experiments (runs 1 and 7), the neohexane and the cracking products were in much larger amounts than in the other experiments.

Labeling of the isomerization products. Since n-hexane was always obtained in very small amounts, only the methylpentane isomer was analyzed by mass spectrometry to determine the position of the labeling atom. In Tables 2 and 3 are given for different conversions, together with the limits of the possible errors, the distributions of the various labeled methylpentanes obtained from 2-methylpentane-2-^{13}C and 3-methylpentane-3-^{13}C. In the same table are also reported the distributions obtained from the same two hydrocarbons over a 0.2% $Pt-Al_2O_3$ catalyst. Striking differences appear: over a 10% $Pt-Al_2O_3$ catalyst the species resulting from a simple cyclic mechanism (III-Y and II-Y in isomerization of II-Y and III-Y, respectively) are no longer largely predominant as they were over 0.2% Pt on Al_2O_3. Conversely, the species which were considered as minor over the dispersed catalyst appear in appreciable if not predominant amounts. No noticeable differences are observed between run 6, performed with a catalyst (B) prepared from $Pt(NH_3)_4Cl_2$, and runs 2–5 where the catalyst is prepared from $PtCl_6H_2$ (A).

Runs 1 and 7 are associated with experiments done with a very small amount of catalyst (abnormal plots in Fig. 1). They also correspond to abnormal distributions of the isotopic species: for example, in isomerization of 2-methylpentane-2-^{13}C much more 3-methyl (^{13}C)-pentane and less 3-methylpentane-2-^{13}C are obtained in run 1 than in runs 2–6.

TABLE 3

Isomerization of 3-Methylpentane 3 ^{13}C. Labeling of the 2-Methylpentane Isomers

Run	T(°C)	Weight of catalyst (mg)	α'	 II-X	 II-Y + II-Y'	 II-Z + II-T
7	273	120	5.4	17.6	60.7	21.9
8	270	210	24.5	16.1	72.2	11.7
9	270	330	52.3	22.8	60.8	16.4
10	271	410	48.7	14.2	69.5	16.2
11	273	700	65.1	30.8	38.6	30.4
Equilibrium			70	33	33	33
0.2% $Pt-Al_2O_3$	277	650	11.2	1.3	90.8	7.95

In run 11 the conversion α (equal to 65.1%) is very close to the limit conversion (70%). Similarly the distribution of the isotopic isomers is very close to the statistical one.

Initial distribution. The initial distributions over the 10% Pt–Al_2O_3 catalyst (*A*) were deduced from the data reported in Tables 2 and 3. The following figures are retained: For the isomerization of II–*Y*: III–*X* $= 2 \pm 2$; III–*Y* $= 31 \pm 2$; III–*Z* + *T* $= 67 \pm 2$. For the isomerization of III–*Y*: II–*X* $= 7 \pm 2$; II–*Y* $= 81 \pm 2$; II–*Z* $= 12 \pm 2$. In the isomerization of II–*Y*, the distributions do not change much with the conversions and the extrapolated figures coincide in fact with the one obtained for the lowest conversion. In the isomerization of III–*Y*, however, the extrapolation is useful, since the distributions are much more conversion dependent.

Labeling of the reacting hydrocarbons. The rearrangement of a labeled methylpentane to its isomer is generally accompanied by a rearrangement to the same methylpentane labeled in a different way. Such a rearrangement, referred to as a "change in labeling of the starting hydrocarbons," may be the result either of an initial process, or of a readsorption process. In Table 4 are reported the distributions at various conversions of the isotopic 3-methylpentanes and 2-methylpentanes obtained from III–*Y* and II–*Y*, respectively. II–*Z* or II–*T* and II–*X* are both formed in the isomerization of II–*Y*. The ratio $\rho = (z + t)/x$ extrapolated at small conversion was found to be equal to 1.1. Isomerization of 3-methylpentane-3-^{13}C yielded III–*Z* or III–*T* as initial products. III–*X* was only the result of a readsorption process.

(*B*) *Hydrogenolysis of Methyl (^{13}C)-cyclopentane*

The hydrogenolysis of methyl (^{13}C) cyclopentane was studied over 10% Pt-on-Al_2O_3 at 270 and 230°C. Since the hydrogenolysis of methylcyclopentane is much faster than the isomerization of the resulting hexanes, the product distribution in this reaction does not change much with the conversion, provided it is not complete (*3*). Therefore, only one experiment was performed at each temperature, and the observed distribution of the isotopic species was considered as an initial distribution.

Product distributions. The 2-methylpentane, 3-methylpentane, and *n*-hexane were the main reaction products, the latter in smaller amounts. Initial ratios r_1 (2-methylpentane/3-methylpentane), r_2 (3-methyl-

TABLE 4

Isomerization of Labeled Methylpentanes. Labeling of the React'ng Hydrocarbons

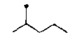
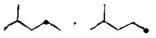
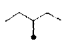
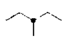
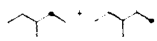
Isomerization of 2-methylpentane 2 ^{13}C				
Run	α	II–*X*	II–*Z* + II–*T*	ρ
1	4.1	4.0	4.1	0.975
2	13.7	5.0	4.5	1.1
3	30.5	7.85	5.3	1.48
4	29.8	7.15	4.0	1.80
5	40.8	16.0	9.6	1.66
Isomerization of 3-methylpentane 3 ^{13}C				
Run	α'	III–*X*	III–*Y*	III–*Z* + III–*T*
7	5.4	0 ± 0.5	97.6 ± 0.5	2.3 ± 0.5
8	24.5	0 ± 0.5	83.7 ± 1	16.3 ± 0.5
9	52.3	2 ± 2	54.9 ± 2	42.6 ± 0.5
10	48.7	0.5 ± 0.5	58.5 ± 2	41 ± 0.5
11	65.1	10.6 ± 3	18.3 ± 4.2	70.8 ± 1
Equilibrium	70	16.6	16.6	66.6

TABLE 5

Hydrogenolysis of Methylcyclopentane and Isomerization of Hexane over 10% $Pt\text{-}Al_2O_3$ Isomer Distributions

Reacting hydrocarbon	MCP	*n*-H	MCP	2-MP	MCP	2-MP
Temperature (°C)	$r_1 = x_2/x_3$		$r_2 = x_3/x_1$		$r_3 = x_2/x_1$	
298	3.5	3.5	2.8	2.8	9	9
270	3.3	—	3.1	4.5	10.3	16
(270)	—	—	—	1.9	—	6
230	4.4	—	4.05	—	17.8	—

x_1, x_2, x_3 are the concentrations of *n*-hexane (*n*-H), 2-methylpentane (2-MP), 3-methylpentane (3-MP), respectively.

Between parentheses, the abnormal experiment of isomerization (run 1).

pentane/*n*-hexane) and r_3(2-methylpentane/*n*-hexane) obtained in both experiments are reported in Table 5 and compared to the initial ratios obtained in the isomerization of hexanes under the same conditions. The data obtained by Maire *et al.* (*2*) are also reported in the first line of the table. Obviously at 270°C, ratios r_1, r_2, r_3 are different in hydrogenolysis and isomerization, while they are identical in the experiments at 298°C.

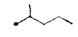
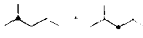
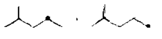
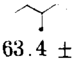
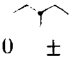
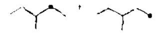
Labeling of the hydrogenolysis products. The position in the various molecules of the labeling atom was determined by mass spectrometry. In Table 6 are reported the analyses of the various acyclic hydrocarbons. At 230°C, methyl (^{13}C)-cyclopentane yields simply labeled hydrocarbons, the ones which are expected with a simple ring opening. At 270°C, more complicated distributions are obtained. The hydrogenolysis of methylcyclopentane at this temperature does not consist any more of the breaking of the cyclic bonds, but in a combination of the ring opening and the skeletal rearrangements of the resulting adsorbed hydrocarbons.

Discussion

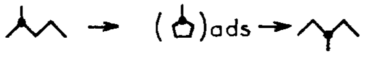
In contrast to the situation over a dispersed catalyst, the distributions of the isotopic species obtained in the isomerization

TABLE 6

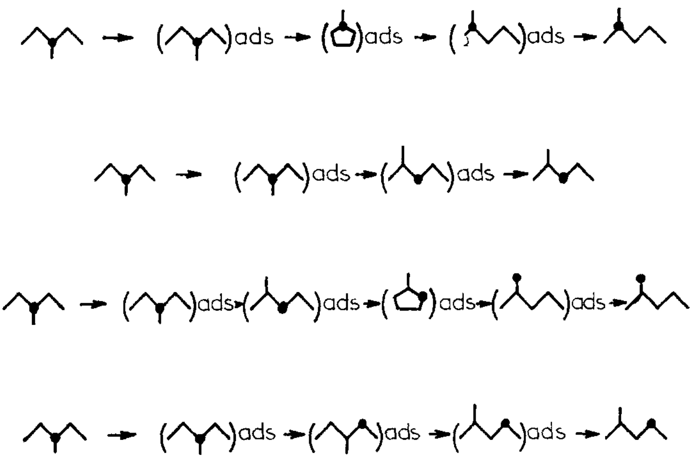
Hydrogenolysis of Methyl (^{13}C) Cyclopentane over 10% Pt-on-Al_2O_3. Labeling of the Reaction Products

Product		II-*X* 	II-*Y* + *Y′* 	II-*Z* + *T* 
2-methylpentane	270°	87.0 ± 1	8.0 ± 1	5.0 ± 1
	230°	100 ± 1	0 ± 0.5	0 ± 0.5
		III-*X* 	III-*Y* 	III-*Z* + *T* 
3-methylpentane	270°	63.4 ± 1	0 ± 1	36.8 ± 1
	230°	100 ± 1	0 ± 0.5	0 ± 0.5
		I-*X* 	I-*Y* 	I-*Z* 
n-hexane	270°	89.2 ± 1	1.1 ± 1	9.7 ± 0.5
	230°	100 ± 1	−0.5 ± 0.5	0.2 ± 0.5

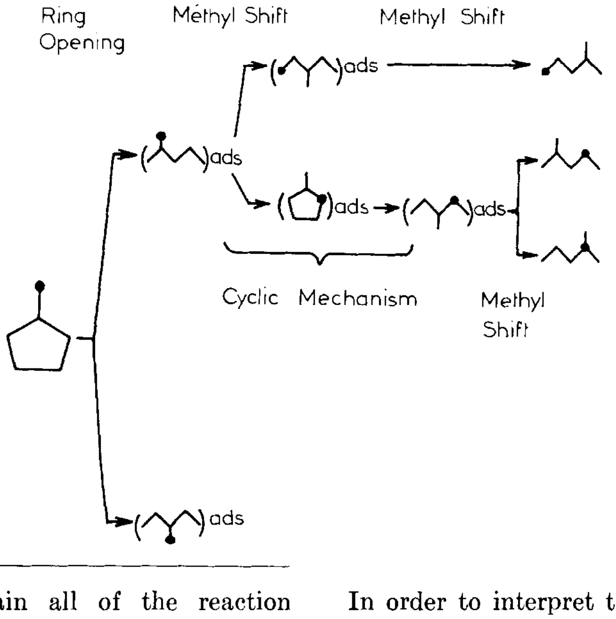
of the methylpentanes over 10% Pt–Al_2O_3 cannot be explained by a simple dehydrocyclization–ring opening process. For example, 3-methylpentane-3-^{13}C, which would result from 2-methylpentane-2-^{13}C through this cyclic mechanism, represents only a little more than one third of all the isotopic varieties.



Nor is a simple bond shift mechanism sufficient to explain all of the reaction products: 2-methylpentane-1-^{13}C and 2-methylpentane 4- or 5-^{13}C are obtained in the isomerization of 3-methylpentane-3-^{13}C; they can only be explained if one assumes at least two successive rearrangements in the adsorbed phase, by a bond shift or a cyclic mechanism:



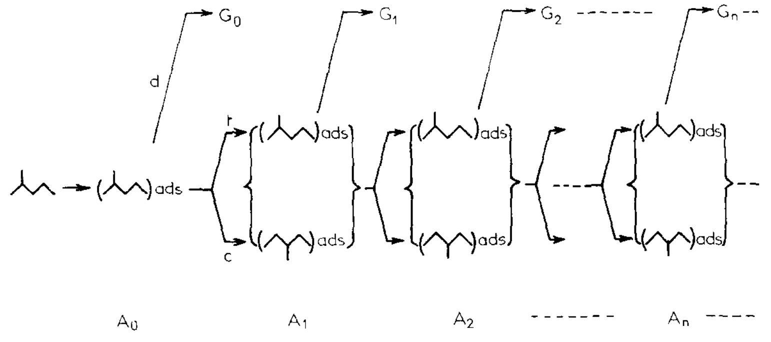
Similarly the hydrogenolysis of methyl (^{13}C) cyclopentane yields hydrocarbons which may only be obtained by at least one or two rearrangements, after the opening of the cyclopentane ring:



In order to interpret the results *qualitatively*, one has then to assume that the isomerization of hexanes or the hydrogenolysis of methylcyclopentane consists of a succession of skeletal rearrangements in the adsorbed phase. A *quantitative* interpretation of the initial distributions of products would reinforce this proposed reaction mechanism.

General Schemes

The initial distributions obtained from both methylpentanes may be interpreted by examining carefully the fates of the adsorbed species. Let us call d, t, and c the chances for an adsorbed molecule to desorb or to rearrange according to a bond shift or a cyclic mechanism $(d + t + c = 1)$. The species adsorbed initially A_0 may then either be desorbed to yield gaseous molecules G_0 or be converted into several other adsorbed molecules A_1; species A_1 in turn may either desorb to give molecules G_1, or rearrange into adsorbed molecules A_2 and the process may be repeated indefinitely, until no adsorbed molecules remain on the surface (scheme 1).



According to such a mechanism the concentrations of the successive adsorbed species A_1 A_2 A_n and the concentrations of the successively desorbed molecules decrease to zero. The distribution of the gaseous product molecules initially formed is then obtained by adding up the desorbed molecules $G_1 + G_2 + \ldots + G_n + \ldots$ and dividing by $(1 - d)$.

A similar scheme may account for the hydrogenolysis of methylcyclopentane. In this case, however, the first step is the ring opening of the adsorbed methylcyclopentane and the first desorbed molecules, G_0, have to be considered as reaction products. The distributions of the reaction products are then obtained very simply by adding up the desorbed molecules $G_0 + G_1 + G_2 + \ldots + G_n + \ldots$.

Definition of the Various Parameters

The mechanism represented by schemes 1 and 2 is in fact oversimplified, since c or t or d represents not one but several independent parameters. The first task in order to verify the proposed mechanism is then to limit as far as possible the number of independent parameters. This limitation is possible in the case of a 10% Pt–Al_2O_3 catalyst, on account of the peculiarities of the reactions.

Rearrangement parameters. For example, twenty-two rearrangements of the various hexanes may be represented as occurring according to a bond shift mechanism (Fig. 2). *But* since 2,3-dimethylbutane and 2,2-dimethylbutane are produced only in very minor amounts in isomerization and hydrogenolysis, the ten rearrangements involving these hydrocarbons can be ignored. The six reactions involving n-hexane are ignored similarly on account of the small amounts of n-hexane formed over a concentrated catalyst. Moreover, the interchange reaction between two terminal carbon atoms is negligible in the case of n-hexane, since no n-hexane-2-^{13}C is obtained in the hydrogenolysis of methyl (^{13}C)-cyclopentane. We shall also consider as negligible the interchange reactions in the case of methylpentanes.

There remain then three possible reactions, two methyl shifts and one ethyl shift.

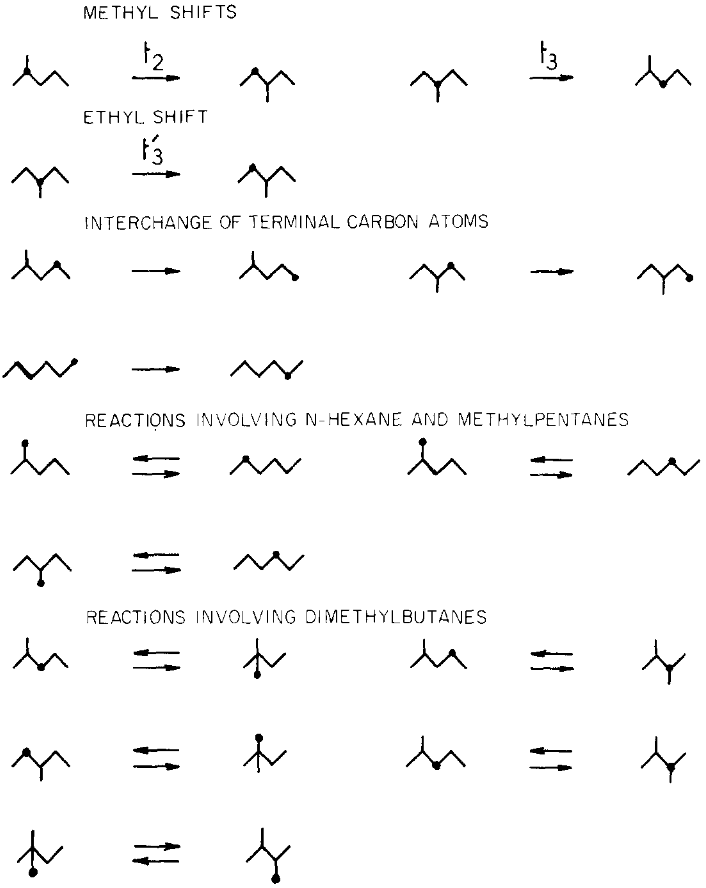
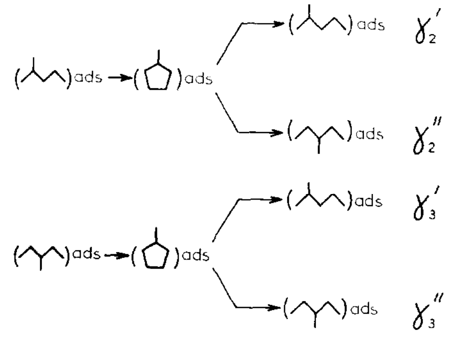


Fig. 2. Possible rearrangements according to a bond shift mechanism.

We shall define for these three reactions the probability parameters t_2, t_3, and t'_3, respectively.

Cyclization and desorption parameters. Only the interconversions between the methylpentanes will be considered in the cyclization–ring opening process. Four parameters may then be defined: γ'_2 γ''_2 γ'_3 γ''_3, three of which are independent since: $\gamma'_2/\gamma''_2 = \gamma'_3/\gamma''_3 = \beta$ (scheme 2).



Similarly, two desorption parameters d_2 and d_3 should also be introduced for 2-methylpentane and 3-methylpentane.

In conclusion. Eight parameters in total must be considered: γ'_2, γ'_3, β, t_2, t_3, t'_3, d_2, d_3. But three relationships exist between them:

Two normalization relationships

$$d_2 + t_2 + \gamma'_2(1 + 1/\beta) = 1, \quad [1]$$

$$d_3 + t_3 + t'_3 + \gamma'_3(1 + 1/\beta) = 1, \quad [2]$$

and one equation resulting from equilibrium conditions:

$$\frac{(\text{2-methylpentane})_\infty}{(\text{3-methylpentane})_\infty} = \frac{t_3}{t_2} = \frac{\gamma'_3}{\gamma''_2}$$

Five independent parameters remain then to interpret the experimental results. Later on, it will be assumed that there is an equal chance for desorbing 2-methylpentane and 3-methylpentane ($d_2 = d_3$) and an equal probability for any bond shift rearrangement ($t_2 = t_3 = t'_3$); two independent parameters will then be left.

Method for Calculating the Product Distributions

The rearrangements of species A_0 to species A_1, from A_1 to A_2, ... from A_p to A_{p+1}, etc., may be simulated by a linear operator involving the probability parameters which have just been defined above. Let us call x'_p, y'_p, z'_p, t'_p, u'_p the concentrations of the various isotopic 2-methylpentanes in A_p (II–X, II–Y, II–Z, II–T, II–Y'); x''_p, y''_p, z''_p, t''_p the concentrations of the isotopic 3 methylpentanes (III–X, III–Y, III–Z, III–T). Call x'_{p+1}, y'_{p+1}, etc., the corresponding concentration in A_{p+1}. By using the various rearrangement, cyclization, and desorption parameters the (x'_{p+1}; y'_{p+1}; . . . x''_{p+1}; . . .) may be expressed as linear functions of the (x'_p, y'_p, . . . x''_p . . .) (Table 7).

It is possible, by using a medium-sized computer, to calculate successively the concentrations of the adsorbed species x'_p, y'_1 . . . x''_1 . . .; x'_2, y'_2 . . . x''_2 . . .; . . .; x'_n, y'_n . . . x''_n . . .; . . .; until negligible values, and to add up simultaneously the concentrations of all the gaseous molecules. If the sum of the concentrations of the first adsorbed species A_0 is taken as unity, the distributions of the various gaseous isomers x', y' . . . x'', y'' . . . may be expressed

in isomerization as and in hydrogenolysis as

$$x' = \sum_1^\infty x'_p \frac{d}{1-d} \qquad x' = \sum_0^\infty x'_p d$$

$$y' = \sum_1^\infty y'_p \frac{d}{1-d} \qquad y' = \sum_0^\infty y'_p d$$

$$x'' = \sum_1^\infty x''_p \frac{d}{1-d} \qquad x'' = \sum_0^\infty x''_p d$$

with $x' + y' + \ldots x'' + \ldots = 1$.

The normalized values

$$X' = \frac{x'}{x' + y' + z' + t' + u'} \cdots X'' = \frac{x''}{x'' + y'' + z'' + t''},$$

etc., will be used in this paper.

The variations of the product distributions will then be studied when changing the various parameters and the best values of the parameters determined to fit the experimental data.

Dependency of the Calculated Distributions upon the Various Parameters

Isomerization of 2-methylpentane-2-^{13}C. The X'', Y'', Z'', T'', concentrations of the 3-methylpentane products are almost independent of t_3, t'_3 and β, but depend very strongly upon t_2 and d. A relationship may be found between t_2 and d so that the calculated ratio $Z'' + T''/Y''$ equals the observed one: 2.15 (Fig. 3). On the other hand X'' is strongly dependent upon d, and only d; from the observed value $0 \leqslant X'' \leqslant 0.04$, it follows that d is larger than 0.35.

Isomerization of 3-methylpentane-3-^{13}C. The observed distribution of the 2 methylpentanes can be reproduced only if parameter t'_3 is used with a value of between 0.10 and 0.20. For each value of t'_3, t_2, t_3, and d are included within strictly limited values.

Hydrogenolysis of methylcyclopentane. The calculated product distributions vary sharply with d, but rather little with t_2, t_3, t'_3, and β, as can be seen in Table 8. The observed distributions are best reproduced with a desorption parameter d very near to 0.5.

Comparison between the Observed and Calculated Distributions

Since the isomerizations of 2-methylpentane-2-^{13}C, 3-methylpentane-3-^{13}C and the hydrogenolysis of methyl (^{13}C)-cyclopentane were performed under exactly the same experimental conditions, an attempt was made to account for all the observed initial distributions with the same set of parameters. The experimental data consisted of eight independent values of the concentrations for the methylpentane isomers and of two concentration ratios for the reacting hydrocarbons. To limit the number of the parameters it was assumed that the transposition parameters were the same ($t_2 = t_3 = t'_3 = t$) and the desorption probabilities identical ($d_2 = d_3 = d$). The product distributions of the three reactions were

TABLE 7
RECURRENT RELATIONSHIP BETWEEN THE CONCENTRATIONS OF THE ADSORBED SPECIES

$$\begin{aligned}
x'_{p+1} &= \tfrac{3}{4}\gamma'_2x'_p + \tfrac{1}{2}\gamma'_2u'_p + t_3x''_p + \gamma'_3x''_p + \tfrac{1}{2}\gamma'_3z''_p + \tfrac{1}{2}t_3t''_p \\
y'_{p+1} &= \gamma'_2y'_p + \gamma'_3y''_p + \tfrac{1}{2}t_3z''_p \\
z'_{p+1} &= \tfrac{1}{2}\gamma'_2z'_p + \tfrac{1}{2}\gamma'_2t'_p + \tfrac{1}{2}t_3z''_p + \tfrac{1}{2}\gamma'_3t''_p \\
t'_{p+1} &= \tfrac{1}{2}\gamma'_2t'_p + \tfrac{1}{2}\gamma'_2z'_p + \tfrac{1}{2}t_3t''_p + \tfrac{1}{2}\gamma'_3t''_p \\
u'_{p+1} &= \tfrac{1}{4}\gamma'_2x'_p + \tfrac{1}{2}\gamma'_2u'_p + t_3y''_p + \tfrac{1}{2}\gamma'_3z''_p \\
x''_{p+1} &= \tfrac{1}{2}\gamma''_2x'_p + \tfrac{1}{2}t_2x'_p + \gamma''_3x''_p + \tfrac{1}{2}t'_3t''_p \\
y''_{p+1} &= \gamma''_2y'_p + t_2u'_p + \gamma''_3y''_p + \tfrac{1}{2}t'_3z''_p \\
z''_{p+1} &= \tfrac{1}{2}\gamma''_2x'_p + t_2y'_p + t_2z'_p + \gamma''_2u'_p + \tfrac{1}{2}t'_3z''_p + t'_3y''_p + \gamma''_3z''_p \\
t''_{p+1} &= \tfrac{1}{2}t_2x'_p + \gamma''_2z'_p + t_2t'_p + \gamma''_2t'_p + t'_3x'_p + \tfrac{1}{2}t'_3t''_p + \gamma''_3t''_p
\end{aligned}$$

TABLE 8
HYDROGENOLYSIS OF METHYL (^{13}C) CYCLOPENTANE CALCULATED DISTRIBUTIONS

			2-methylpentane			3-methylpentane		
d	$t_2 = t_3$	t'_3	X'	$Y' + U'$	$Z' + T'$	X''	Y''	$Z'' + T''$
0.7	0.15	0	95.4	3.1	1.4	79.6	0.4	20.0
0.5	0.15	0.1	87.1	8.4	4.5	61.9	3.2	34.9
0.45	0.15	0.1	84.5	10.0	5.6	59.2	3.8	36.9
0.40	0.15	0.1	81.5	11.7	6.7	56.2	4.6	39.1
0.35	0.15	0.1	78.5	13.5	8.0	53.2	5.4	41.4
0.35	0.10	0.1	78.8	14.6	6.6	54.5	5.0	40.5
0.35	0.20	0.1	78.6	12.3	9.1	52.3	5.4	42.2
0.35	0.15	0.2	78.4	13.2	8.5	49.2	5.5	45.2

then calculated as a function of d and t with three different values of β (2, 3.3, and 5).

For each value of β the calculated distributions which best fitted the observed data were chosen. They are reported in Table 9. In each case, the agreement between the observed and calculated values of the isomer concentrations is really excellent and it is interesting to note that the

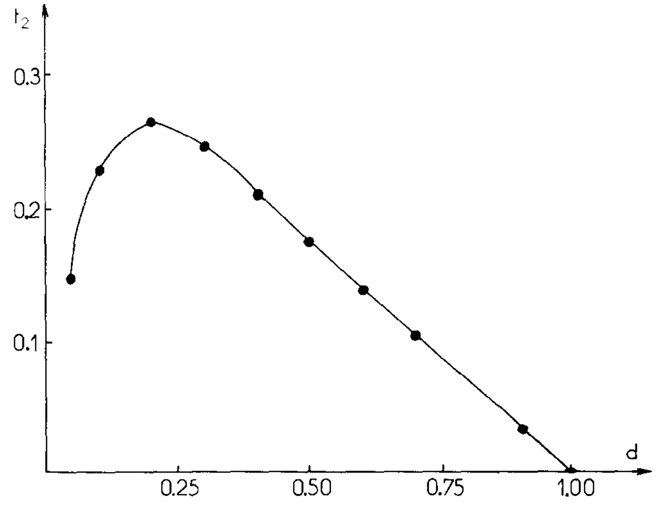
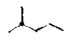
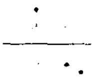
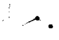
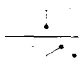


FIG. 3. Isomerization of 2-methylpentane 2-^{13}C. Relationship between parameters t_2 and d in order to reproduce the observed $Z'' + T''/Y$ ratio: β equals 3.3.

TABLE 9

HYDROGENOLYSIS OF METHYLCYCLOPENTANE AND ISOMERIZATION OF HEXANE. COMPARISON BETWEEN THE CALCULATED AND OBSERVED DISTRIBUTIONS

Reacting hydrocarbon	Reaction products	Observed distribution	β:3.3 d:0.52 t:0.17	2.0 0.52 0.20	5.0 0.52 0.14
	 X''	2.2	0.9	0.6	1.05
	 Y''	30.0	30.5	31.9	29.6
	 $Z'' + T''$	68.0	68.6	67.4	69.3
	 $\frac{X'}{Y' + T'}$	1.10	1.23	2.45	0.7
	 X'	12.0	10.8	9.1	11.2
	 $Y' + U'$	81.0	82.7	81.9	84.4
	 $Z' + T'$	7.0	6.5	9.0	4.4
	 $\frac{X''}{Z'' + T''}$	0.0	0.02	0.02	0.02
	 X'	87	88.4	89.2	87.7
	 $Y' + U'$	8	7.3	6.0	8.4
	 $Z' + T'$	5	4.3	4.8	3.8
	 X''	63	59.1	61.0	58.0
	 Y''	0	3.0	2.2	3.7
	 $Z'' + T''$	37	38.6	36.7	38.3
		μ	1.26	0.70	1.92
		$10^3\Delta$	3.55	3.87	6.4

best value for d, viz. 0.52, is independent of β. The $(Z' + T')/X'$ ratio obtained in the isomerization of 2-methylpentane-2-^{13}C (2-methylpentane-4- and -5-^{13}C over 2-methylpentane-1-^{13}C) allows one to select for β the intermediate value of 3.3. This value corresponds approximately to the ratio 2-methylpentane/3-methylpentane obtained in the hydrogenolysis of methylcyclopentane, when no rearrangement of the acyclic hydrocarbons takes place.

To fit the fourteen observed data (of which ten are independent), three parameters are then introduced:

$$\beta = 3.3 \qquad t = 0.17 \pm 0.01 \qquad d = 0.52$$

These three parameters are not independent, but should be related by Eqs. [1] and

[2]. Since it was supposed that t_2 equals t_3, $\gamma''_2 = \gamma'_3$ and Eqs. [1] and [2] yields by eliminating γ''_2:

$$(1 - d - t)/t = \beta/(\beta - 1). \qquad [3]$$

The ratio $\mu = \frac{1 - d - t}{t} \Big/ \frac{\beta}{\beta - 1}$ is reported in Table 9. Again μ is very close to the predicted value of unity for the intermediate value of β (3.3).

Abnormal Reactions

Very different values of the various parameters and especially of the desorption probability are found when an attempt is made to reproduce the product concentrations in runs 1 and 7. The observed distribution in run 1 is in excellent agreement with the calculated distribution corresponding to $d = 0.04$; $t_2 = t_3 = 0.14$; $t'_3 = 0$; $\beta = 3.3$. The same values of the parameters in the isomerization of 3-methylpentane-3-^{13}C explain the occurrence of II–X and II–Z or –T, in run 7, but not quantitatively. Obviously, with the above values of the parameters, relation [3] does not hold any more, which seems to signify that the simplifications $d_2 = d_3$ and $t_2 = t_3$ cannot be made in this case.

However, it remains that for some reason connected with the experimental conditions (association of a pulse injection of the hydrocarbon with a very small amount of catalyst), the probability of desorption d is very low.

Skeletal Rearrangement as a Chain Reaction

The main evidence afforded by this work is that, over a concentrated Pt–Al$_2$O$_3$ catalyst, the isomerization cannot be taken any longer as a simple reaction step, but as the succession of several rearrangements on the surface. A value of 0.5 for the desorption probability means that four steps in the adsorbed phase are necessary to account for 90% of the reaction products and seven to account for 99%. In the abnormal experiments, as much as fifty-seven and one hundred and ten steps, respectively, have to be envisaged.

The isomerization of a hydrocarbon on a metal surface is then in a formal way very similar to a chain reaction. It would be useful therefore, to define a mean number of rearrangements before desorption λ, equivalent to the chain length which was introduced in the classical chain reactions. According to scheme 1, for one molecule adsorbed, d are desorbed as unmodified molecules, $(1 - d)d$ are desorbed after having reacted once on the surface; $(1 - d)^2d$ have reacted twice and $(1 - d)^nd$ have been submitted to n superficial rearrangements before desorption. The mean number of rearrangements per reacted molecule may then be expressed as:

$$\begin{aligned}\lambda &= [(1 - d)d + 2(1 - d)^2d + 3(1 - d)^3d \\ &\quad + \cdots + n(1 - d)^nd + \cdots] [d/(1 - d)] \\ &= d[1 + 2(1 - d) + 3(1 - d)^2 \\ &\quad + \cdots + n(1 - d)^{n-1} + \cdots] = (1/d)\end{aligned}$$

The probability of desorption d then has just the same mathematical significance as the probability of chain termination in a nonbranched chain reaction (*6*).

Comparison between the Initial Product Distributions in Isomerization and Methylcyclopentane Hydrogenolysis

It has been shown several times that the initial distribution of the hexane isomers was the same in the isomerization of a methylpentane or n-hexane and in the hydrogenolysis of methylcyclopentane. This was in fact the case over a very dispersed Pt–Al$_2$O$_3$ catalyst (0.2%) and over a 10% Pt on Al$_2$O$_3$ at high temperature (300°C) (*3*, *7*). In our experiments over 10% Pt–Al$_2$O$_3$ at 270°C, however, as can be seen from Table 5, the initial distributions are no longer the same in both reactions.

It is possible from the values of the parameters d, t, and γ to explain this fact and to foresee in which conditions the initial distributions may be identical. For one molecule adsorbed, and $(1 - d)$ molecule reacted, the probability for a desorbed molecule not to have been submitted to a cyclic type rearrangement is $(t + t^2 + t^3 + \ldots + t^n + \ldots)\ d = (td)/(1 - t)$. The fraction of the reacted molecules which has escaped a cyclic mechanism is then

$p = [t/(1-t)][d/1-d)]$. The condition for a similarity of the hexane distributions in hydrogenolysis and isomerization is that p be as small as possible, which means that either t or d is very small. It was shown in a preceding paper (*4*) that over the dispersed sites of a 0.2% Pt–Al_2O_3 catalyst, the probability of rearrangement according to a bond shift mechanism was very small indeed. For this reason the identity of both distributions could be observed on this catalyst (*7*). Over a concentrated Pt–Al_2O_3 catalyst, on the other hand, t is significant and p depends upon the value of d. In the present experiments, d is not small and p equals 0.20. The isomer distributions of isomerization and methylcyclopentane hydrogenolysis are no longer similar. At a higher temperature (300°C), in Maire's experiment, the distributions are identical, which seems to indicate a rather low value for d (*3*).

More generally the various parameters introduced in this work and especially d should depend upon the experimental conditions: temperature, hydrogen, and hydrocarbon pressures. A systematic study of the variations of d and t with these conditions would be most valuable and is now being undertaken in this laboratory.

Dispersed and Concentrated Catalysts

It was previously suggested that the differences between the dispersed and the concentrated Pt–Al_2O_3 catalysts were due to a particle size effect and that two different types of sites were present on a platinum surface, the concentrations of which were determined by the size of the metal crystallites (*1c, 2*).

However, it has recently been claimed that the difference between the dispersed and concentrated catalysts was due to some contamination of the concentrated catalysts by chlorine during their preparation (*8*). This interpretation has to be rejected, since the product distributions in hydrogenolysis and isomerization are independent of the salt used for the impregnation (H_2PtCl_6, $Pt(NH_3)_4Cl_2$, and $Pt(NH_3)_4(OH)_2$) and of the carrier (alumina, pumice, silica) (*9*); moreover, the platinum films prepared by evaporation of a Specpure wire are very close in their behavior to the concentrated supported catalysts (*3, 10*).

Once the simplest explanations such as the acidic property of the carrier or a chlorine effect have been ruled out, one cannot escape the earlier conclusion that two different types of sites are responsible for the bond shift and the cyclic mechanism, respectively. The very sites which seem to be linked to a cyclic type mechanism, are present predominantly over the extremely dispersed catalysts such as the 0.2% Pt on Al_2O_3. We believe that these sites consist of a single atom or a very small number of metal atoms (presumably 2 or 3) and that the cyclization process also require a single metal atom. The study of the mechanism of dehydrocyclization of various substituted pentanes thoroughly confirms this view (*11*).

Conversely, the bond shift rearrangement involves an $\alpha\ \alpha\ \gamma$-triadsorbed species (*12–16*) and obviously requires several metal atoms not necessarily contiguous. Such defects, consisting of a group of several platinum atoms, would be more frequently found on a concentrated supported catalyst than on a dispersed catalyst; this could explain the ability of the concentrated catalysts to promote the bond shift rearrangement.

An excellent confirmation of these proposals is given in a study of the isomerization of hexanes on polycrystalline and ultrathin films, recently published by Anderson *et al.* (*17*). These authors observed that the most dispersed catalysts, ultrathin films with an average crystal size of 20 Å, gave rise to a concentration of methylcyclopentane in the reaction products much higher than on the polycrystalline films. This seems to indicate that in the case of films as in the case of supported catalysts, the dehydrocyclization process is more favored on small particles than on large crystallites.

Within the framework of the above theory, two points deserve some further comments: In the isomerization of labeled hexanes on 0.2% platinum–alumina (*4*), some abnormal varieties, amounting to 10–20% of the reaction products, could not be accounted for by a simple dehydrocyclization–ring opening process; these varieties were assumed to be due to the existence on the dispersed catalyst, in a very small amount indeed, of these particular multiatomic sites characteristic of the large crystallites. This interpretation is now strongly supported by the present results, and by the physicochemical studies, which showed a rather wide range of crystallite sizes even in the highly dispersed supported catalysts (*18*).

The second point concerns the exact nature of the sites. We believe that the sites responsible for the bond shift mechanism cannot be identified at all with the atoms regularly disposed in the crystal lattice, for the following reason: The sintering of a dispersed catalyst, which results in a growth of the crystallites, is accompanied by a decrease in activity but not by a change in the selectivity of the catalyst; indeed, the only reaction mechanism for isomerization of hexanes over a sintered dispersed catalyst is not the bond shift mechanism, but the cyclic mechanism (*19*).

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