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Skeletal Isomerization of Hydrocarbons on Molybdenum Catalysts

II. Catalytic Study of Unsupported Catalysts: Film and Powder

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Mechanisms of skeletal isomerization of hydrocarbons were studied on unsupported molybdenum catalysts, both powder and film, by ^{13}C labeling techniques and gas-phase chromatography. Catalytic results are very different on film and on powder. On film very fast extensive cracking was obtained, whereas on powder isomerization largely predominated. The most likely interpretation of the catalytic results on molybdenum powder is that isomerization occurs on metallic sites. The cyclic mechanism which has been observed on platinum, palladium, and iridium is not observed on molybdenum. All isomerization proceeds by the bond shift mechanism through $\alpha\gamma$-diadsorbed species of metallacyclobutane-type structure. This mechanism is close to that of olefin metathesis. Complete isomerization diagrams are proposed for several labeled hydrocarbons.

INTRODUCTION

Molybdenum is currently the subject of much research in the field of catalysis, where it finds several applications.

Molybdenum is thought to be one of the best elements in homogenous catalysis for olefin metathesis, with rhenium and tungsten (*1*). The reaction mechanism, initially suggested by Herisson and Chauvin (*2*) and now commonly accepted (*1, 3*), involves a carbene–metal complex and a π-adsorbed olefin leading reversibly to a metallacyclobutane intermediate (Fig. 1).

There are two processes which utilize molybdenum in heterogeneous catalysis, namely, the selective oxidation (or ammoxidation) of olefins and the desulfurization and denitrogenation reactions of hydrocarbons. Molybdenum also shows some activity in hydrocarbon skeletal isomerization. In its oxidized form and supported on alumina, it is a classical reforming catalyst. The first industrial catalytic reforming installation was put into operation in 1940 in the United States. It used a MoO_3/Al_2O_3 catalyst which was active, selective, and sensitive to coke deposits, but was easily regenerated and resisted sulfur contamination. Following Komarewsky's work on platinum (*4*), molybdenum was progressively replaced by the more active platinum catalyst.

Recently some authors have tried to relaunch the interest of the scientific community in molybdenum as a reforming catalyst (*5*). The question of the mechanism in molybdenum-catalyzed hydrocarbon isomerization has been studied very little. Several reaction mechanisms are possible, such as a bifunctional mechanism, a metallic mechanism, or the coexistence of several mechanisms. Among these, it would be interesting to know which ones best fit the experimental data.

In this work, hydrocarbon skeletal rear-

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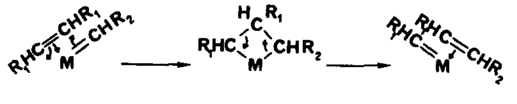


FIG. 1. Scheme of the olefin metathesis mechanism.

rangement mechanisms are studied using ^{13}C labeling techniques on unsupported molybdenum catalysts, both molybdenum powder and film.

EXPERIMENTAL

Molybdenum powder. The molybdenum powder was from Goodfellow Metals and is 99.9% pure (unknown impurities). The average grain diameter was 2 μm. The surface area was not exactly known but it should be low, only a few square meters per gram. The powder catalysts were studied in a all-glass flow system equipped with grease-free taps. The hydrogen pressure was 755 Torr and the hydrocarbon pressure was 5 Torr (1 Torr = 133.3 N m^{-2}). A double-catharometer system allowed one to observe the passage of the hydrocarbon to the catalyst. It could also show eventual adsorption or diffusion effects. Generally the reaction products were directly hydrogenated at the end of the reactor over Adams platinum heated to 140°C. Inactivity of Adams platinum in skeletal rearrangement of hydrocarbons has been verified. In consequence only saturated hydrocarbons were analyzed by FID. The mass of the catalyst varied from 0.8 to 1 g. The reaction temperature was 350°C. Before all catalytic experiments, the powder was treated under hydrogen flow at atmospheric pressure and 500°C for 15 h to reduce surface oxides.

Molybdenum films. Film samples, weighing about 15 mg, were produced by vacuum (10^{-6} Torr) evaporation of a molybdenum wire (Goodfellow Metals, 99.9% purity) onto a glass surface kept at 0°C. The catalytic experiments took place in the static mode. The hydrogen (755 Torr)–hydrocarbon (5 Torr) reaction mixture was brought into contact with the film for 10 min at 350°C. Then it was pumped off to be analyzed by gas-phase chromatography after hydrogenation of the formed olefins. Several experiments could be done successively using the same film. The hydrocarbons used were Fluka purissimum grade products.

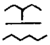
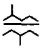
Isotope tracing experiments. ^{13}C-labeled products were used in this work largely to establish reaction mechanisms. The position of the labeled atom in the isomeric molecules was determined by mass spectrometry with a Varian CH7 spectrometer. The mass spectrometer was connected to a chromatographic column to separate the different isomers in the reaction products.

Presentation of the catalytic results. The catalytic results are shown in tables of reaction product distributions (see, for example, Table 4 below). The total conversion, denoted α_T, represents the percentage of the reactants transformed on the catalyst. This conversion is generally kept at a low level to avoid, as much as possible, the readsorption of products which have already reacted. The isomer selectivity (S_i) represents the percentage of the isomers of the initial product present in the transformed products. Methylcyclopentane and cyclohexane are considered as C_6 isomers. After S_i, we show the percentages of the different products toward all the transformed molecules. This is the reaction product distribution itself. For instance, for 100 molecules of 2-methylpentane transformed over molybdenum film (see Table 4 below) 48.7 are cracked into 6 CH_4, 10.5 into butane + ethane, and 1.2 are isomerized into 3-methylpentane. At the end of the line, we show the 3-methylpentane/*n*-hexane ratio, an additional indication of selectivity. The i/n ratio in parentheses represents the isobutane (or isopentane)/*n*-butane (or *n*-pentane) ratio. To compare the total activity of several catalysts we introduce the absolute transformation rate, defined as

$$R_T = (1 - \alpha_T)\frac{F}{w}\ln\left(\frac{1}{1 - \alpha_T}\right)$$

TABLE 1

Reaction of Various Hydrocarbons on Molybdenum Powder

Reactant	$R_T \times 10^{3b}$	$\alpha_T{}^b$ (%)	$S_i{}^c$ (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[d]	$C_5 + C_1$ (i/n)										
	1.09	12.5	91	0	0	2.1	2.6 (1.8)	4.2 (1.7)	1.4	?	—	82.2	7.4	ε[e]	0	11.1	—	—
	1.27	26.3	91.9	0	0.1	1.7	2.3 (1.7)	3.9 (1.7)	1.6	?	—	81	8.9	0.4	0	9.1	—	—
	1.31	16.4	92.8	0	0.2	1.1	2.2 (0.5)	3.7 (2.4)	0.6	1.4	84.9	—	4.7	1.3	ε	—	18.1	—
	0.33	7	39.6	0	2.8	16.5	19.5 (ε)	21.6 (0.1)	ε	0.2	21.7	17.2	—	0.5	ε	—	—	1.3
	0.16	3.3	49.4	0	0	5.7	15.6 (0.9)	29.3 (4.2)	ε	ε	8.6	3.9	4.6	—	32.3	0.9	1.9	2.2

Note. Flow reactor. Mass of catalyst = 1 g. Reaction temperature = 350°C. P_{H_2} = 755 Torr, P_{HC} = 5 Torr. Pretreatment: 15 h at 500°C under hydrogen flow (760 Torr).

[a] Total rate (see text).

[b] Total conversion in mole percentage.

[c] Isomer selectivity.

[d] Isobutane (or isopentane)/*n*-butane (or *n*-pentane) ratio.

[e] ε represents a very small amount of product.

where α_T = total conversion, F = hydrocarbon flow in microliters per second, and w = catalyst mass in grams.

RESULTS AND DISCUSSION

I. Molybdenum Powder

A. Results

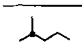
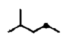
Catalytic results obtained with various nonlabeled hydrocarbons (2-methylpentane, 3-methylpentane, 2-methyl-2-pentene, *n*-hexane, and methylcyclopentane) are shown in Table 1. We observe similar activities and selectivities for 2-methylpentane, 3-methylpentane, and 2-methyl-2-pentene. Selectivities are very high, between 91 and 93%. One should note that 2-methyl-2-pentene reacts almost as fast as 2-methylpentane and that it leads to an identical distribution of reaction products. The *n*-hexane reacts three times slower than 2-methylpentane with a selectivity of only 40%. The methylcyclopentane is the least reactive; it reacts seven times slower than 2-methylpentane and has a strong tendency toward cracking (selectivity of 50%), a secondary reaction in this case.

^{13}C labeling experiments on Mo powder have been done with the following labeled molecules: 2-methyl [2-^{13}-C]pentane,2-methyl[4-^{13}-C]pentane and 3-methyl[3-^{13}C]pentane. The distribution of reaction products obtained from these molecules is identical to those in Table 1. The table of percentages of the isotopic varieties (Table 2) shows that there are no repetitive processes, measured by the amounts of 2-methyl[1-^{13}C]pentane and 3-methyl[6-^{13}C]pentane. These labeling experiments will be used to establish reaction mechanisms on molybdenum powder.

Reduction at a very high temperature. After a standard pretreatment (15 h at 500°C in hydrogen) the Mo powder was submitted to an additional reduction for 4 h at 950°C under hydrogen. The corresponding results are compared with the standard results in Table 3. The first line of the table shows the average over eight experiments done on catalysts reduced for 15 h at 500°C. The high-temperature reduction markedly

TABLE 2

^{13}C Labeling Experiments on Metallic Molybdenum[a]

	Isomer									
Reactant										
	0	100	0	98	2	0	17	83	81	19
	11	89	0	4	96	0	12	88	90	10
	53	47	0	83	17	0	91	9	37	63

[a] Percentages of isotopic varieties.

lowers the total conversion. Cracking is more affected than isomerization, which increases the selectivity. Nevertheless, the distributions of reaction products are very similar.

Influence of oxygen and water. After standard treatment of the catalyst at 500°C for 15 h under hydrogen, the temperature was reduced to 350°C and the following injections were made:

(1) a 15-μl 2-methylpentane (2-MP) injection, nonanalyzed, followed by an injection of 3 μl 2-methylpentane which was analyzed as a reference;

(2) a 10-μl of atmospheric air;

(3) a 15-μl injection of 2-MP (nonanalyzed) followed by a 3-μl injection of 2-MP analyzed to establish the effect of the oxygen injection;

(4) then an injection of 10 μl atmospheric air followed by 1 μl water to establish the eventual effect of water traces;

TABLE 3

Reactions of 2-Methylpentane on Molybdenum Powder at 350°C

	α_T[a] (%)	S_i[b] (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[c]	$C_5 + C_1$ (i/n)								
A1[d]	10.6	90.2	0	ε	2.1	2.7 (1.9)	4.7 (1.8)	1.3	?	—	81.7	6.1	ε[e]	0	13.4
A2	2.2	94.6	0	0	0.5	1.1 (0.9)	3.8 (1.3)	0.8	?	—	87.5	6.3	0	0	13.9
B1[f]	10.4	85.2	1	0.1	2.9	4 (1.3)	6.8 (1.7)	1.4	4.1	—	72.2	6.7	0.8	ε	10.8
B2	9.8	88.2	0.4	ε	2.3	3.3 (1.3)	5.7 (1.7)	1.4	4.2	—	74.5	7.3	0.8	ε	10.2
B3	7.7	90.4	0.3	0.1	1.9	2.6 (1.4)	4.7 (1.7)	1.4	4.3	—	76.5	7.6	0.6	ε	10.1

[a] Total conversion in mole percentage.

[b] Isomer selectivity.

[c] Isobutane (or isopentane)/*n*-butane (or *n*-pentane) ratio.

[d] (1) Standard results on catalysts treated 15 h at 500°C. (2) Results on a catalyst treated 15 h at 500°C, then 4 h at 950°C.

[e] ε represents a very small amount of product.

[f] Effect of oxygen and water on molybdenum powder. Standard pretreatment at 500°C, then 350°C. (1) After 15 μl 2-MP nonanalyzed, then 3 μl 2-MP analyzed. (2) After 10 μl air, then 15 μl 2-MP, then 3 μl 2-MP. (3) After 10 μl air and 1 μl water, then 15 μl 2-MP, then 3 μl 2-MP.

(5) a 15-μl 2-MP injection (nonanalyzed) and a 3-μl 2-MP injection (analyzed).

The 15 μl hydrocarbon was injected to eliminate the side effects of oxygen, that is, the regeneration of catalytic sites by oxidation of carbonaceous residues. The results of these catalytic experiments are presented in Table 3. There is a slight decrease in the total activity associated, as previously, with a slight increase of selectivity. Except for these differences, the distributions remained identical to those in the reference experiment.

B. Discussion

Surface of the catalyst after pretreatment. From the well-known affinity of molybdenum for oxygen, sulfur, and carbon there arises the question of the surface state of the Mo powder catalyst after the standard pretreatment (15 h under hydrogen flow at 500°C). We have no direct information about the surface composition of our molybdenum powder catalyst. We may suppose three kinds of contamination.

(i) Contamination with oxygen: The metal powder, which was kept in air, became superficially oxidized. It seems improbable that molybdenum oxides supported on metallic molybdenum can resist for 15 h a 500°C reduction followed by 4 h at 950°C under hydrogen flow. Cimino and De Angelis (*6*) almost totally reduced solid molybdenum oxide MoO_3 in 2 h under hydrogen flow at 400°C (XPS study). Massoth (*7*) observed metallic molybdenum at 650°C from MoO_3 reduced under hydrogen flow and heated at a rate of 5°C/min starting from room temperature (thermogravimetric study). Thus, oxygen is eliminated by a high-temperature reducing treatment. However, Table 3 shows that the catalytic results are identical for both the high-temperature pretreated catalyst and the catalyst pretreated in a standard way (excepted for total conversion), leading to the conclusion that in both cases, the same active sites are involved. The high-temperature treatment only lowers the number of these sites, most probably through a sintering phenomenon leading to a loss of specific area.

Let us now consider the case where oxidized sites form after reducing treatment. These occur either because of oxygen and/or water traces in the vector gas or because they are introduced with the starting hydrocarbons. The catalytic activity of molybdenum powder may be due to these oxidized sites. Before a catalytic experiment, an injection of oxygen (or oxygen and water) on the catalyst should increase the total conversion by increasing the number of oxidized sites. However, an injection of oxygen can also cause an increase in catalytic activity by eliminating carbonaceous residues and freeing metallic catalytic sites. This is the reason why we performed our experiments in the manner we described previously. Study of Table 3 shows that oxygen and water injections have no effect on catalytic properties. This leads to the conclusion that the catalyst is not sensitive to oxygen or water traces in the vector gas. The hydrogen flow at 350°C is enough to compensate for the effects of these oxygen traces.

(ii) Contamination with sulfur: Treatment of molybdenum powder in a hydrogen flow could give rise to the appearance of sulfur on the surface of the sample. This is indeed seen on samples of bulk molybdenum in ultrahigh vacuum chambers. Catalytic results on such sulfurized samples are very different from those on molybdenum powder in flow systems (*8*). Thus, it is possible to establish that sulfur does not take part in the catalytic sites on metallic molybdenum grains.

This result is not surprising in consideration of the surface/volume ratio of the two samples: in one case, there are 2-μm grains and in the other, a 50 × 50 × 0.5-mm foil. The surface/volume ratio is 10^3 times higher for the powder than for the foil. Thus the decontamination possibility at the surface toward the contaminant storage capacity in the bulk is 10^3 times more important for the grains than for the foil. Oudar has shown (*9*) that it is easy to eliminate sulfur under hydrogen flow at high temperature.

(iii) Contamination with carbon: Molybdenum is known to carburize easily. What is the effect of a superficial carbide on the catalytic properties of molybdenum powder? We have no clear answer, but we did observe that the catalyst maintained a stable selectivity after successive hydrocarbon injections, but lost activity due to poisoning with a hydrocarbon residue. This rules out the role of a molybdenum carbide. The decrease in activity at constant selectivity is correlated with a classical poisoning of the catalyst by carbonaceous residues.

Our conclusions on the facts considered above are as follows. When the contribution of a foreign element to the catalytic site is only somewhat possible, the catalytic results on molybdenum powder can most likely be attributed to metallic molybdenum. At oxidation state zero, molybdenum has isomerizing properties.

Unsupported Mo–MoO_3 systems of high specific area (120 m^2/g), prepared by reduction under hydrogen of molybdenum oxalate (*5*), have been studied to determine the isomerization properties of *n*-hexane (*10*). According to Burch and Mitchell (*10*), this catalyst has a bifunctional pattern, namely hydrogenation–dehydrogenation on metallic molybdenum and isomerization through an acidic mechanism in molybdenum oxide. Molière (*11*) arrived at identical conclusions for the association of tungsten–tungsten oxide, whether supported or not.

Bridgewater *et al.* (*12*) have also prepared an Mo/active carbon catalyst by reduction under hydrogen at 500°C for 16 h of MoO_3/active carbon (itself obtained through impregnation of the carrier with an aqueous solution of ammonium molybdate). The Mo/C system is very active in both hydrogenation and dehydrocyclization reactions.

Except for isomerizations of isobutane to *n*-butane on film (*33*), the isomerizing properties of metallic molybdenum have not been mentioned in the literature, as far as we know. However, this isomerizing property is very weak compared to that of platinum. For a total activity of 1 on metallic molybdenum at 350°C (Table 1), the activity of Pt 10%/Al_2O_3 is 60 at 300°C (*13*), and thus 1000 at 350°C if the total activation energy is 40 kcal/mol.

Isomerization mechanism on metallic molybdenum powder. The catalytic results obtained from labeled and unlabeled molecules allow us to build a mechanistic pattern of isomerization of hydrocarbons on molybdenum metal.

Does the cyclic mechanism, proved on platinum (*14, 15*) and later on other metals (Pd, Ir), act in the hydrocarbon isomerization process on metallic molybdenum? The answer can be derived from Table 1. On the one hand, methylcyclopentane (MCP) reacts seven times slower than 2-methylpentane (2-MP) as opposed to what happens on metals such as platinum. On the other hand, cyclohexane represents 65% of the C_6 products obtained from MCP; thus the cycle enlargement is highly favored compared with hydrogenolysis. 3-Methylpentane (3-MP) is produced 100 times faster from 2-MP than from MCP. Therefore, the possibility of a cyclic mechanism is so small that it can be disregarded.

Hydrocarbon isomerization on molybdenum occurs only by bond shift. There are several possibilities for a bond shift. It is possible for several groups (methyl, ethyl, isopropyl, *n*-propyl) to migrate. The shifts can be from one atom to the next one or to atom α (1,2 shift) or from one atom to atom β or γ (1,3 or 1,4 shifts). To propose an isomerization mechanism, one must first find the bond shifts and classify them by their respective rates. The idea is to fit the experimental results with the simplest mechanistic diagram. The diagrams suggested for isomerization of 2-MP and 3-MP are shown in Fig. 2 (2-methyl [2-^{13}C] pentane), Fig. 3 (2-methyl [4-^{13}C] pentane), and Fig. 4 (3-methyl[3-^{13}C]

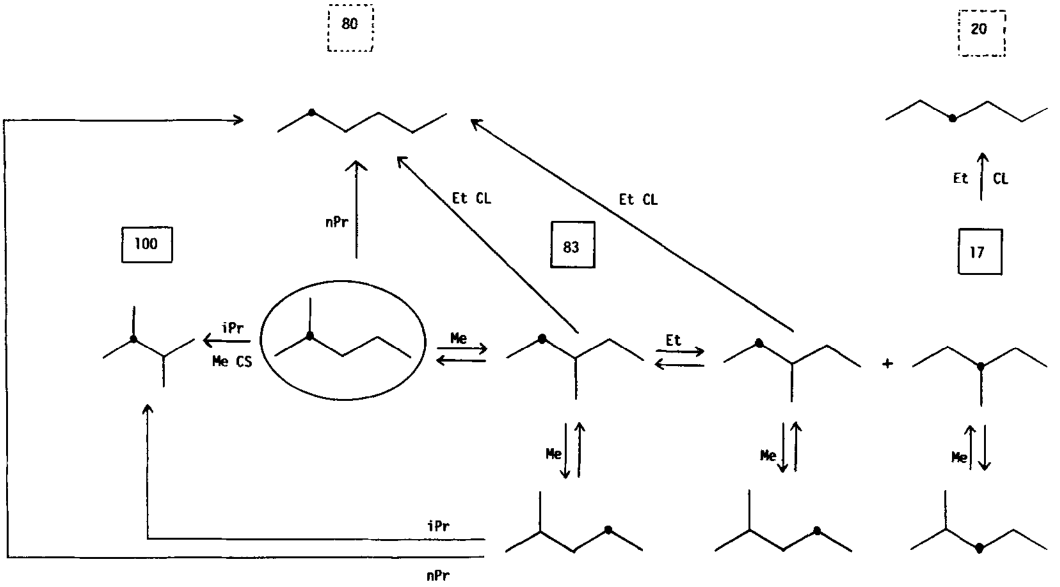


FIG. 2. Isomerization of 2-methyl[2-^{13}C]pentane on metallic molybdenum powder. The observed percentages of isotopic varieties are shown in the rectangles.

pentane). The following comments can be made:

(i) All the experimental results can be explained by 1,2 bond shifts. Successive reactions must be brought in to explain the existence of some isomers, namely, 3-methyl[3-^{13}C]pentane or *n*-[3-^{13}C]hexane obtained from 2-MP (Fig. 2 and 3). In-

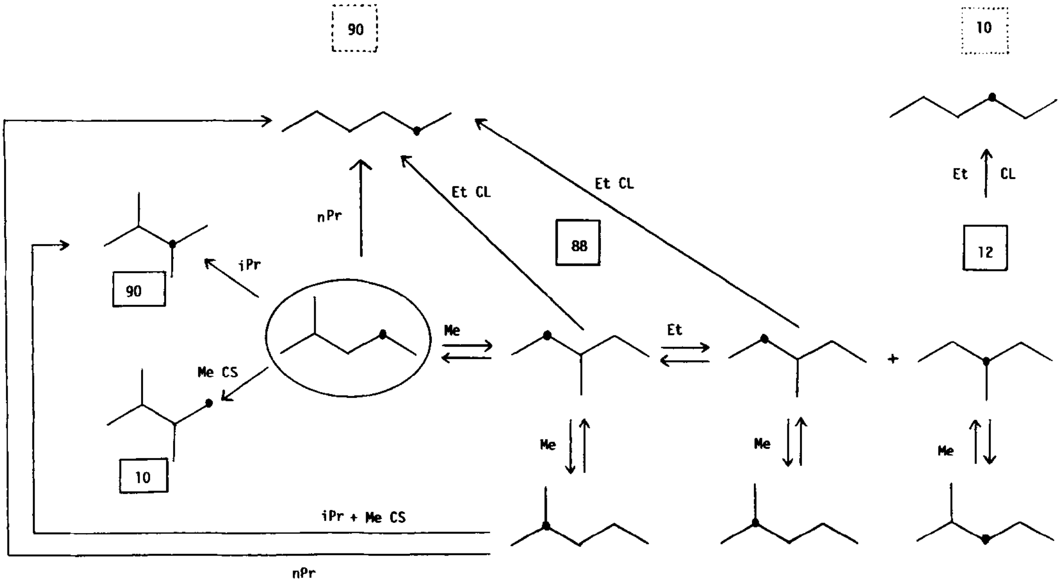


FIG. 3. Isomerization of 2-methyl[4-^{13}C]pentane on metallic molybdenum powder. The observed percentages of isotopic varieties are shown in the rectangles.

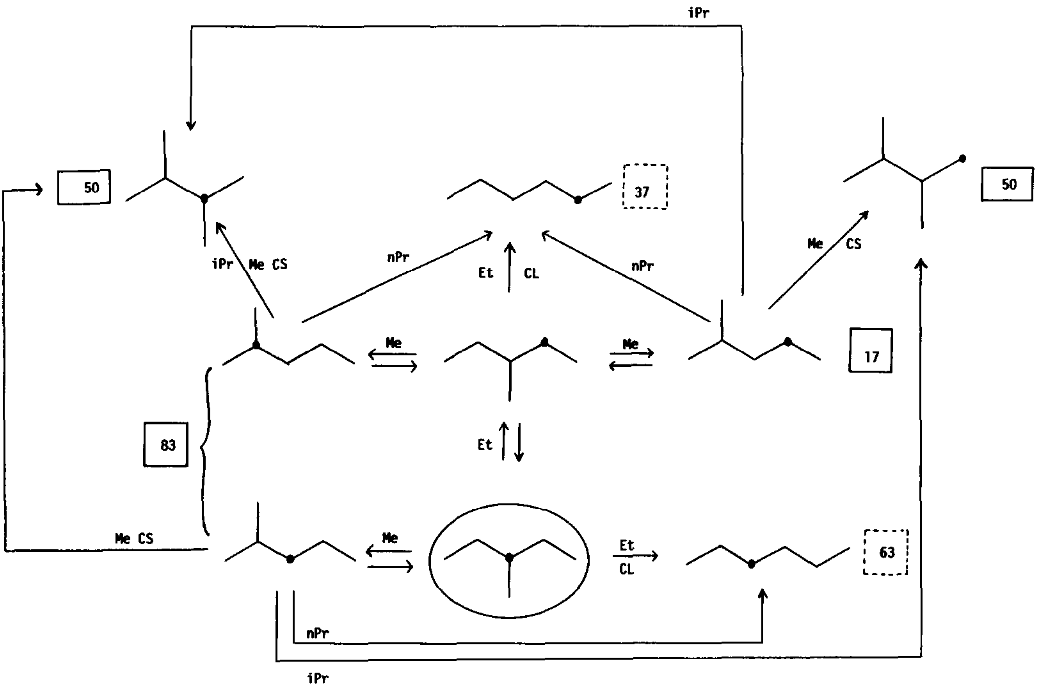


FIG. 4. Isomerization of 3-methyl[3-^{13}C]pentane on metallic molybdenum powder. The observed percentages of isotopic varieties are shown in the rectangles.

deed, it is observed that the amounts of these products decrease with the conversion. In all experiments made with 2-MP, the isobutane/*n*-butane ratio is between 1.5 and 2. The *n*-butane, obtained by a two-step reaction (two successive demethylations), is almost as important as the isobutane obtained from a simple deethylation, which proves that readsorptions after reactions are possible and quite easy.

(ii) We can suppose four possible shifts with 2-MP (Figs. 2 and 3), namely, a methyl shift, an *n*-propyl shift, an isopropyl shift, and a methyl shift which shortens the carbon chain. There are three possibilities with 3-MP (Fig. 4), viz., a methyl shift, an ethyl shift, and an ethyl shift which lengthens the carbon chain. An analysis of *n*-hexane (n-H) obtained from 2-MP shows that the chain-lengthening (CL) methyl shift does not happen. Indeed, if the CL methyl shift did happen, there would be almost no *n*-[3-^{13}C]hexane obtained from 2-methyl[4-^{13}C]pentane compared with the *n*-[3-^{13}C]hexane obtained from 2-methyl[2-^{13}C] pentane, since the direct reactions are much faster than successive reactions. Nevertheless, it is somewhat important and it can only be explained by elimination of the CL methyl shift.

(iii) Besides the shifts shown, there must also be a chain-shortening (CS) ethyl shift on 2-MP and a CS methyl shift on 3-MP leading to neohexane, which is always found in small amounts in the distributions of reaction products. Since neohexane cannot be analyzed by mass spectrometry, these two shifts cannot be proven.

(iv) The reactions leading to 2,3-dimethylbutane and to *n*-hexane are not written as equilibrated. Nevertheless, they may be equilibrated, in some cases at least, but the reactions of these two products are not studied in detail.

Classification of the shift rates. To treat this question with great precision, we must study the distribution of isomeric products as a function of conversion, which has not been done on metallic molybdenum [see Part III (*16*) for such a study on a supported catalyst]. However, it is obvious that the methyl and ethyl shifts producing 3-MP from 2-MP (or 2-MP from 3-MP) are much faster than the others. A more precise quantitative study of the tracing experiments described above is impossible.

Reactive intermediates. Among the proposed bond shift mechanisms, there are two reactive sequences, involving either α-adsorbed or αγ-diadsorbed species on metallacyclobutane-type structure. The latter one seems to be the more probable:

(a) According to Clarke and Rooney (*34*), loss of one hydrogen from the molecule, giving a surface alkyl, is sufficient for rearrangement. The transient chemisorbed species has partial double-bond character with the shifting alkyl group symmetrically bridged. The organic part of the complex can be considered as a three-center free radical.

(b) According to Gault and co-workers (*23*), the metallacyclobutane rearrangement creates a metallacarbene and a π-olefin species. Rotation of this species around the organometallic bond and a carbene addition leads to the isomeric molecule (Fig. 5). The alkylidene can be rearranged into π-olefin and desorbed. As opposed to the mechanism of Clarke and Rooney, this mechanism also explains the cracking.

In their analysis of the catalytic results obtained on Pt/Al_2O_3 from C_5 hydrocarbons (*17, 18*), Garin and Gault show that the Clarke–Rooney mechanism could very well explain the chain-lengthening and -shortening reactions whereas the mechanism of Gault and co-workers accounts well for bond shift without main chain length modification.

Rooney (*19*) is an ardent supporter of organic complexes bonded to one individual metal atom. For him, a good catalyst for homologation is a poor one for bond shift (*20*). Therefore the olefin metathesis mechanism involving metallacyclobutane species will not be correct for bond shift. Looking at the catalytic behavior of molybdenum, we note that

(i) Mo is very active in hydrocracking reactions;

(ii) multiple exchange occurs with Mo (*21*);

(iii) some activity for homologation is also observed on Mo. Hydrogenation of ethylene over supported molybdenum catalysts was studied by Lombardo *et al.* (*22*). They suggested that formation of a carbene intermediate is responsible for the multiple exchange pattern. The mechanism proposed by Gault and co-workers (*23*) is reinforced and can explain isomerization, cracking, and homologation reactions.

We believe that Gault's mechanism is the more likely for molybdenum:

(a) The metallacyclobutane compounds have been synthesized and characterized in organometallic chemistry with many metals, e.g., platinum, iron, rhodium, tungsten, and palladium (*24*). Ephritikhine *et al.* discovered in 1976 (*25*) that metallacyclobutane based on molybdenum could be pre-

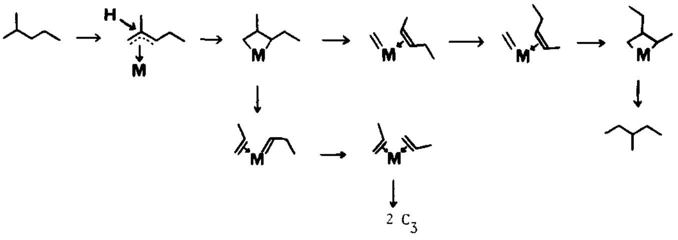


FIG. 5. Bond shift mechanism according to Gault and co-workers (*28*).

pared through nucleophilic attack of a π-allylic complex.

(b) The skeletal rearrangement through dismutation of metallacyclobutane into metallacarbene and adsorbed olefin shows a similarity to the olefin metathesis mechanism initially suggested by Herrisson and Chauvin (*2*). Molybdenum is one of the three most active metals (Mo, W, Re) for olefin metathesis (*1*).

(c) The mechanism of Gault and co-workers explains our experimental results very well. Figures 6 and 7 show the different positions in which metallacyclobutane can be situated on 2-methylpentane and 3-methylpentane. They also show the bond shifts corresponding to the formation of metallacyclobutane in these various positions. Several alkyl migrations are possible in a C_6 hydrocarbon. Their relative contributions depend mainly on the stability of the π-olefinic species [Part III (*16*) shows an important application of this] and on their ability to rotate. At a given site, the more the intermediate olefin is substituted, the more stable it is. Indeed, a reaction involving an α-olefin may need an activation energy 10 kcal/mol higher than a reaction based on a β-olefin intermediate (*26*). Otherwise, the rotation of the π-adsorbed olefin requires an activation energy of 10 to 15 kcal/mol (*27*). This energetic barrier can be increased by a few kilocalories per mole when the substituted components of the olefin involve a steric constraint. Gault and coworkers (*28*) have shown that the rotation of a symmetrical olefin seems to be favored, which can easily be explained mechanically: the rotation of a unsymmetrical, thus unbalanced, olefin would be more difficult and would more easily give rise to a desorption. When Figs. 6 and 7 are considered along with the preceding explanation, we arrive at a classification of the bond shift rates of the various groups in the order Et > Me > nPr = iPr > Et-CL > Et-CS > Me-CS > Me-CL.

At this stage, our progress in the analysis of the relative rates is limited. However, we do show that the ethyl and methyl shifts are the fastest and that the methyl shift which would lengthen the carbon chain does not occur.

II. Molybdenum Films

A. Results

Table 4 shows the catalytic results obtained from 2-methylpentane on molybdenum film. We can see a very important initial activity in extensive cracking. Molecules cracked into methane and ethane represent 60 to 80% of the transformed molecules, which correlates with a very low isomer selectivity. Successive experiments on the same film show that the extensive cracking sites are rapidly poisoned by hydrocarbon residues which cause a total activity decrease and an increase in selectivity. One should note the amount of methylcyclopentane among the C_6 products. Although the percentage fluctuates greatly, it is formed faster than *n*-hexane in all cases. The last noticeable characteristic is the considerable amount of C_7 products formed by homologation; they reach 6.1% in the second experiment.

B. Discussion

From the results it appears that the catalytic properties on molybdenum evaporated films are different from those given by the molybdenum powder. On Mo films the cracking and the homologation predominate. The question of the nature of the active sites arises.

What is the nature of these extensive cracking sites? Are they perfectly reduced sites or are they contaminated by residual gas in the reaction volume? Why is extensive cracking associated with an ability of the catalyst for 1–5 cyclization (formation of methylcyclopentane from 2-methylpentane) and for homologation? Comparison of results using films with results using supported catalysts (*29*) will partially answer these questions.

In his work at atmospheric pressure with

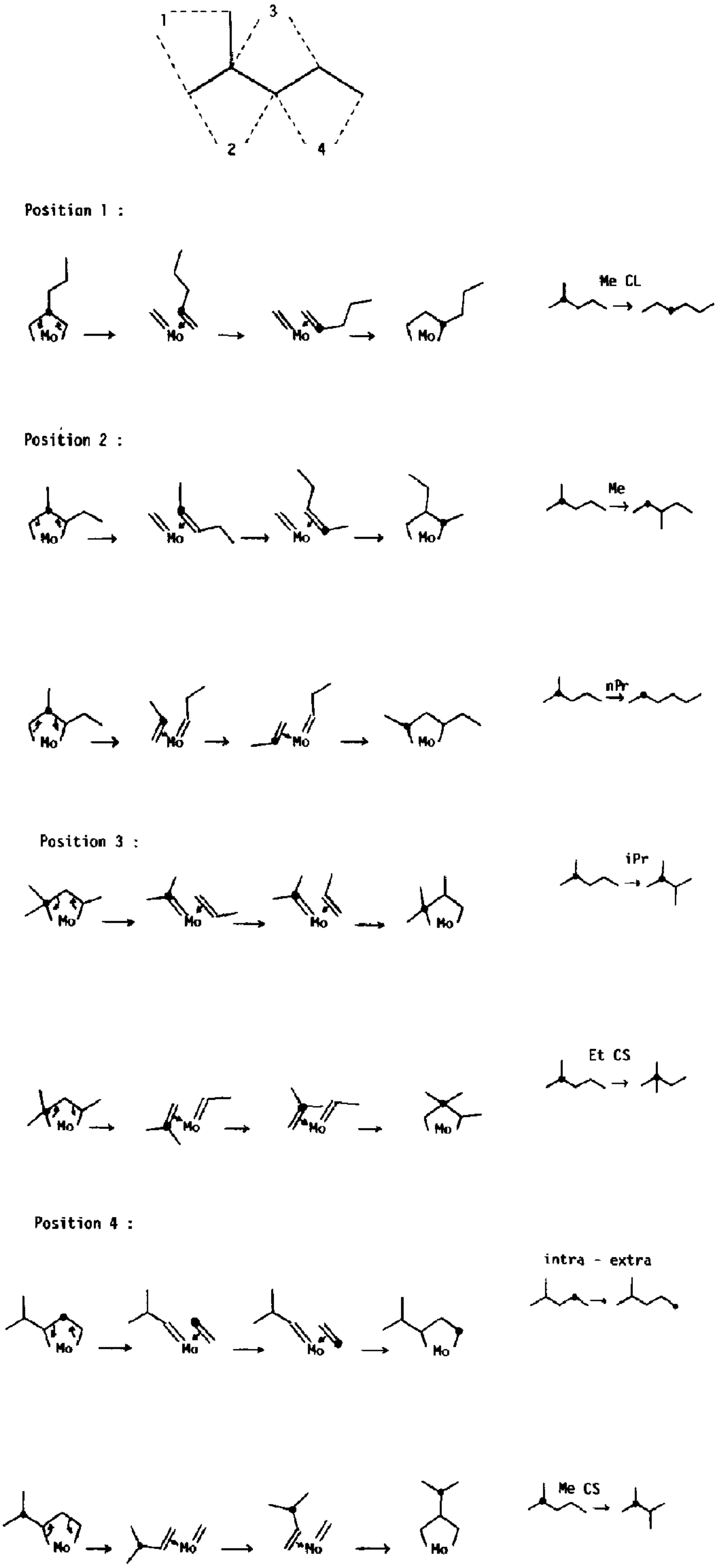


FIG. 6. Molybdenum-2-methylpentane metallacyclobutane intermediates.

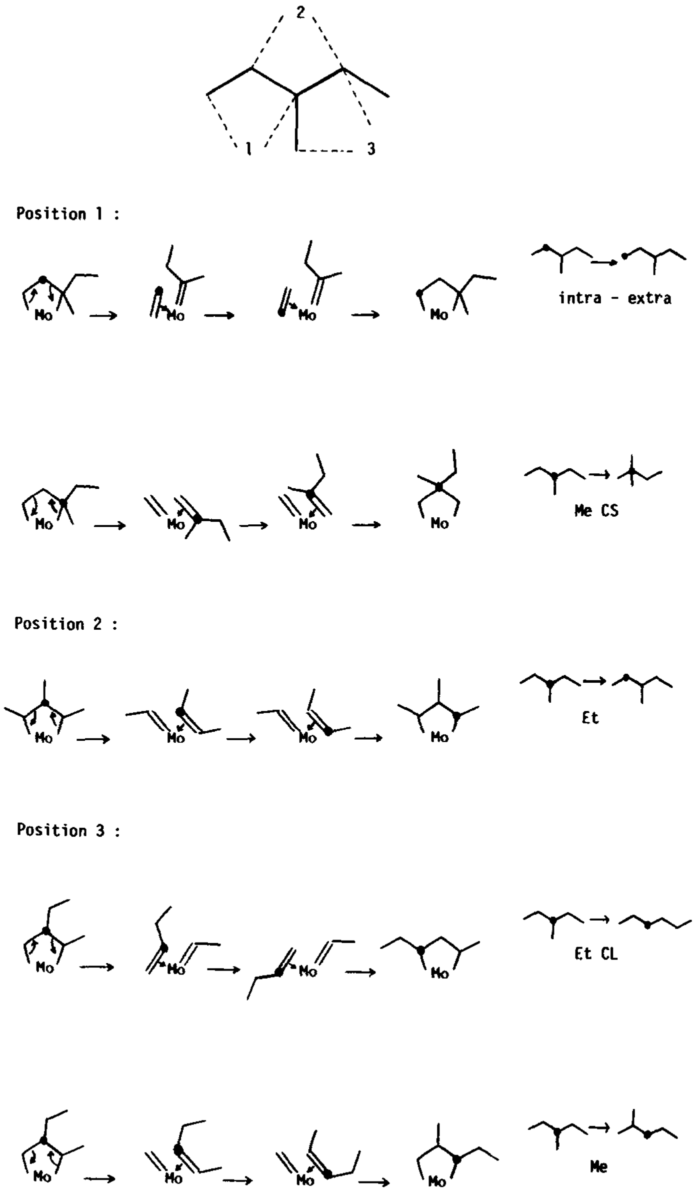


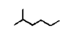
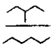
FIG. 7. Molybdenum-3-methylpentane metallacyclobutane intermediates.

tungsten films, Molière (*11*) obtained very few isomers from 2-methylpentane (less than 0.5% at 400°C), isomerization above all leading to methylcyclopentane (50% of the C_6 products). On the other hand, cracking is very different when using tungsten film rather than molybdenum film because it essentially consists of demethylation and deethylation. Extensive cracking is not observed.

In a study of the isomerization of isobutane into *n*-butane using transition metal film at 220°C ($HC/H_2 = 1/10$) ($P_{HC} = 3$ Torr), Taylor and Clarke (*33*) found that most of the metals were active (except Mn, Fe, and Co). In particular, molybdenum

TABLE 4

Product Distributions Obtained from 2-Methylpentane on Molybdenum Film

	α_T[a] (%)	S_i[b] (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[c]	$C_5 + C_1$ (i/n)									
1	52.6	6.5	48.7	13.1	11.2	10.5 (2)	9.9 (1.9)	ε	?	1.2	0.2	4.9	0.2	ε	0	6
2	4.8	56	15.7	4.6	4.3	5.6 (1.1)	10.1 (1.8)	0.2	?	6.5	1.2	37.3	8.4	ε	6.1	5.4
3	1.6	57.8	17.6	7.2	2.4	5.2 (0.8)	9.1 (1.9)	0.4	?	46.2	3.9	5.2	2.1	0	0.7	11.8
4	1.6	62.6	12.2	4.7	3.5	6 (0.9)	11 (1.8)	0.1	?	44.9	4.4	13.2	ε	0	0	10.2

Note. Reaction temperature 350°C. P_{H_2} = 755 Torr, P_{HC} = 5 Torr. Contact time = 10 min. Four successive experiments on the same film.

[a] Total conversion in mole percentage.

[b] Isomer selectivity.

[c] Isobutane (or isopentane)/*n*-butane (or *n*-pentane) ratio.

[d] ε represents a very small amount of product.

and tungsten were between 4 and 10 times more active than platinum for this reaction.

More recently, molybdenum films have been studied by O'Donohoe *et al.* (*20*). Their experimental conditions were slightly different from ours, namely, 300°C, hydrocarbon/hydrogen ratio = 1/10, initial product *n*-hexane. They obtained 63% (C_1 + C_2), 7.7% benzene, and 0.6% homologation products; essentially their results resemble ours. Molybdenum seems to favor 1–6 cyclization when possible, as opposed to 1–5 cyclization. Among our homologation products (Table 4), we observe mainly 2-methylhexane, resulting from the addition of one carbon atom at the end of the 2-methylpentane chain, and methylcyclohexane, probably resulting from a 1–6 cyclization of 2-methylhexane. O'Donohoe *et al.* (*20*) suggest a homologation mechanism very close to the olefin metathesis mechanism described previously.

The general scheme explaining isomerization, cracking, and homologation reactions on platinum catalysts proposed by Maire and Garin (*30*) can again be used to interpret our results on both Mo films and Mo powder. On powder the metallacycle adsorbed species will lead mainly to isomerization and to small amounts of cracked molecules. However, on Mo films the metallacycle adsorbed species will exclusively follow the pathways leading to cracking and homologation. It could be interpreted by an electronic or ligand effect due to the traces of impurities around the Mo aggregates. It is well known that evaporated films are very sensitive to the surface of the support (*31*). The same trends were observed by Zahraa *et al.* (*32*) on platinum catalysts where the platinum atoms were surrounded by phosphorus.

CONCLUSIONS

This study shows that catalytic results on unsupported molybdenum are very different on film and on powder. On film we observe essentially extensive cracking whereas on powder isomerization predominates. Analysis of catalytic results on molybdenum powder allows us to attribute catalytic activity to metallic molybdenum with a high level of probability. On metallic molybdenum, isomerization occurs only by bond shift. The cyclic mechanism involving a cyclopentane intermediate, which is very important on platinum, iridium, and palladium, is completely missing. It must be noted that molybdenum is about 1000 times less active than platinum at 350°C. The proposed isomerization mechanism involves a metallacyclobutane intermediate.

This mechanism is close to the olefin metathesis mechanism, making it all the more likely that molybdenum is one of the best metathesis catalysts available. Analysis of this isomerization mechanism allows us to predict the rate order of the migration of the different alkyl groups. However, the ^{13}C labeling experiments performed on unsupported molybdenum are not sufficient to confirm this in detail. The study of alumina-supported molybdenum catalysts to be reported in Part III (*16*) will go further in this direction. The proposed metallacyclobutane intermediate species can also explain the results obtained on Mo films where cracking and homologation predominate due to a kind of electronic or ligand or support effect.

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