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Selectivity of Iridium Catalysts in Reactions of C_6 Hydrocarbons: The Role of Surface Carbonaceous Layers and Metal Particle Size

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Skeletal reactions of methylcyclopentane and hexane have been studied on Ir and the results are compared with earlier data on neohexane reactions. The conclusions are as follows: (1) Ir can catalyze the isomerization of hydrocarbons; (2) only under certain experimental conditions is the methylcyclopentane ring opening selective ("no" hexane); when covered by carbonaceous layers, Ir shows also a less selective ring opening. (3) the particle size dependence of the catalytic properties of Ir, as well as its sensitivity for self-poisoning, are much less pronounced than with Pt.

INTRODUCTION

It is a general and very interesting problem to understand how to relate the catalytic properties of metals to their position in the Periodic Table. This problem is also a complicated one since one cannot ignore that the catalytic performance is usually determined by various side processes, such as self-poisoning by the reaction mixture. In the case of hydrocarbon reactions, one is concerned with deposition on the surface of carbonaceous fragments of molecules, or finally carbon. This has been recognized long ago by Beeck (*1*) who argued that the order of activities of metals in ethylene hydrogenation is actually given by the extent of an unreactive carbonaceous layer which leaves only a small fraction of the active sites as the "working surface." In recent times the problem of carbon(aceous) layers has been studied in many details by Somorjai and his associates (*2, 3*) and studies have been extended also to the selectivity in the hydrocarbon reactions (*3–5*). Moreover, several interesting and practically important phenomena like particle size effects in the hydrocarbon reactions on Pt are to a great extent, if not entirely, caused by the particle-size-sensitive formation of the carbon(aceous) layers (*4*). In this respect the information available on iridium is still far from complete (*5*).

There are also some more specific problems regarding iridium as a catalyst of skeletal reactions of hydrocarbons. Some authors have reported that iridium is a good catalyst for non-destructive reactions (isomerization, dehydrocylization, aromatization) (*6–8*) while others observed only hydrogenolysis (hydrocracking) (*9–12*). An open question is whether this is because different temperatures were applied, or different forms of catalysts (bulk metals, supported catalysts with different particle sizes, etc.) or because the various catalysts used were covered to a different extent by a carbon(aceous) layer.

Although the reactivity toward hydrocarbons of various crystallographic planes of Ir is different, similar to Pt (*13*), there is no clear evidence available that the particle size effects in hydrocarbon reactions on Ir are comparable with those observed with Pt. Although some effects are reported (*14, 15*), most authors claim that with iridium (*8, 10*) there is no particle size effect observable at all. Also these problems can be related to the differences in the carbon(aceous) layers on Pt on the one side and Ir on the other and differences between the carbon(aceous) layers on the surfaces of catalysts of various authors.

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Gault and co-workers (7, 8) stressed explicitly that iridium is a metal for which a particular pronounced difference exists between the isomerization selectivity of 2-methyl- and 3-methyl pentanes (2MP and 3MP) on the one hand and that of *n*-hexane (HEX) on the other. The authors speculated that this is because iridium strongly prefers the formation of carbyne-like intermediates (splitting off of all H's from the CH_3-end groups). Since a carbyne bond cannot be formed in the position 5 of *n*-hexane, the 1,5 dehydrocyclization cannot run freely on Ir. This has consequences for isomerization as well. The authors (7, 8) have proved that on Ir the prevailing isomerization intermediates each involve five of the six hexane carbon atoms (i.e., the so-called "cyclic" mechanism prevails strongly). The structure of these intermediates is supposed to be similar to that of methylcyclopentane. However, these intermediates cannot form a 1,5 dicarbyne structure which would induce isomerization from isohexanes into *n*-hexane. Therefore, Gault *et al.* conclude that 2MP $\rightleftarrows$ 3MP isomerization is possible but that isohexanes $\leftrightarrows$ *n*-hexane isomerization is not. Moreover, the authors found that methylcyclopentane ring opening did not lead to *n*-hexane formation, as one would expect for a reaction reverse to that of dehydrocyclization. However, the explanation by the authors (7, 8) is not free of problems. We have made some experiments with neohexane (2,2-dimethylbutane) and we have observed isomerization with this molecule which cannot form 1,5 dicarbyne-intermediates (5). Some preliminary experiments showed that at variance with the statements by Gault *et al.* (7, 8), some isomerization was observable also with *n*-hexane (5, 16). However, the extent of *n*-hexane isomerization was strongly dependent on the carbon(aceous) layer (5, 16). This has naturally led to the question as to the extent to which the methylcyclopentane ring opening selectivities of Ir are dependent on the carbonaceous layer. In this paper, we report results dealing with this question. The results presented concern methylcyclopentane ring opening and the skeletal reactions of *n*-hexane and they will be compared with the results available on neohexane (5).

EXPERIMENTAL

Apparatus and data evaluation. An open, plug flow, static bed reactor was used in an all-glass apparatus, operating close to 1 atm pressure (actually, pressures a few mbars higher than atmospheric were used). The apparatus and methods of analysis have been described in earlier papers (17). In standard experiments for purpose of comparison, the same flow rate (9 ml/min) has been used throughout, as well as the hydrogen/hydrocarbon ratio (H_2/hex = 16/1; H_2/MCP = 17/1).

The GLC data were converted by means of calibration factors into molar concentrations of individual species: (C_i; C_k stands for hydrocarbon in the feed) and these were used to calculate the overall conversion:

$$\alpha(\%) = 100 \frac{\sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)}}{6C_6^{(k)} + \sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)}}$$

(j = various isomers).

In the region of experimental conditions where the reactor behaves as a differential reactor the rate per unit weight (W) is

$$r_w = 10^{-2} \cdot \alpha F W^{-1}$$

where F is the feed ("k"-hydrocarbon) in required units.

The selectivity in production of $C_i^{(j)}$ has been calculated as

$$S_i^{(j)} = \frac{iC_i^{(j)}}{\sum_{i=1}^{6} \sum_{j,j\neq k} iC_i^{(j)}}$$

Selectivity in isomerization is a sum over all $S_i^{(j)}$ for all isomers, etc.

Catalyst preparation. Ir/SiO_2 catalyst has been prepared from $(NH_4)_2$ $IrCl_6$ (Drijfhout, Amsterdam). A water solution of this compound was mixed with 25% NH_4OH and heated under stirring to 70°C. A catalyst with 0.4% Ir was prepared by adsorption of the Ir complex from this solution onto Kieselgel 60 (Merck 7729); a catalyst with 1% Ir was prepared by impregnating silica by a solution of the required concentration of Ir. Catalysts were dried overnight at 100°C in air. These catalysts were also used in our earlier work (*5*, *16*). When necessary this catalyst was further diluted by mechanically admixed inert silica.

Ir/Al_2O_3 (10% wt) was the same catalyst as used in the laboratory of the late Professor F. G. Gault in their earlier work (*7*, *8*). The catalyst was kindly supplied by Professor G. Maire.

RESULTS

Methylcyclopentane

Measurements of catalytic activity and determination of selectivity parameters have been performed at various temperatures. Temperature was varied both in an increasing and decreasing order, in order to test whether the changes in the parameters monitored are reversible with temperature.

The rate data obtained at standard flow, pressure and gas composition are presented in Fig. 1.

Measurements with this sample of Ir/Al_2O_3 have been extended here up to rather high values of conversion, but the rates determined at $\alpha < 10\%$ make us confident that the lines can indeed be drawn as has been done in Fig. 1. The data corresponding to the "clean surface" (right-hand side in Fig. 1) were determined after the surface had been cleaned by oxidation in oxygen at 523 K for 5 h and reduced at 723 K for 15 h. The poisoned surface (left side in Fig. 1) has been prepared by the following treatment. The surface of the catalyst with which the measurements described on the right in Fig. 1 had been performed was treated at 673 K with a *n*-pentane/N_2 mixture (1/2) during 2 h; thereafter it was reduced again at 723 K during 15 h and used directly for measurements with MCP to give the results on the left in Fig. 1.

A catalyst which was first highly active at 474 K achieved the same activity only at temperatures about 100°C higher; evidently most of the active sites were covered by carbonaceous layers. Poisoning by MCP brought about the same effects in selectivity as the poisoning by *n*-pentane.

The most essential selectivity data are summarized in Tables 1 and 2.

A remark concerning the comparison is needed here. The selectivity for a certain

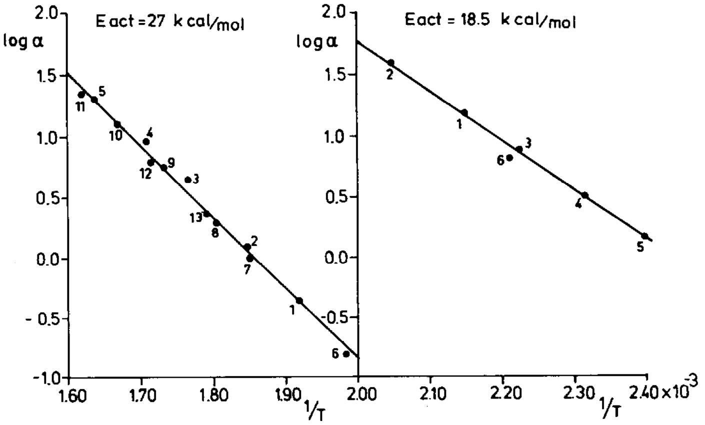


FIG. 1. Logarithm of the conversion α (~ reaction rate) as a function of the reciprocal temperature. Left—Ir/Al_2O_3 after poisoning; E_{act} = 113 kJ/mol (27 kcal/mol). Right—Ir/Al_2O_3 after cleaning by repeated oxidation reduction; E_{act} = 78 kJ/mol (18.5 kcal/mol). The numbers indicate the order in which the points were measured.

TABLE 1

Selectivity in Ring Opening of MCP as a Function of the Catalyst Treatment (as Expressed by S_i Values)

Treatment	Temp. (K)	2MP	3MP	HEX	Total conv. α	$\frac{2MP^a}{3MP}$	$\frac{HEX^b}{2MP}$
(1) Cleaned by oxidation (0.267 g catalyst) at 523 K	492	61.6	32.6	2.1	4.6	1.9	0.03
(2) Cleaned by oxidation (0.602 g catalyst)	488	60.5	30.8	2.5	38.3	1.96	0.04
(3) After deposition of carbon(aceous) layer by MCP/H_2 reaction at 673 K, ½ h	488	57.8	25.5	15.0	0.37	2.27	0.26
(4) After reactions of 2-2 dimethylbutane on the same surface	487	55.4	22.6	17.8	0.47	2.45	0.32
(5) After deposition of carbon(aceous) layer by *n*-pentane/H_2 at 573 K, ½ h	488	63	28.3	8.2	2.9	2.22	0.13

Note. In experiments 3–5, 0.6 g catalyst was used.

[a] With statistical random ring opening, this value is 2.

[b] With statistical random ring opening, this value is 1; the highest "selectivity" corresponds to 0.

reaction product or group of products is a parameter dependent in general on temperature, on the apparent contact time, and on overall conversion. To approximate to an ideal comparison, but one experimentally difficult to achieve, we make two partial comparisons. In Table 1 data are compared at (approximately) the same temperature; in some cases this was possible when using different amounts of catalysts (i.e., different apparent contact times). In Table 2, on the other hand, data are compared at varying temperature but at the same conversion.

In spite of some differences in details, the overall conclusion is in both cases the same: carbon(aceous) deposits on the surface of Ir/Al_2O_3 catalysts affect the selectivity in the ring opening. Virgin surfaces of Ir/Al_2O_3 reveal an evidently "selective" ring opening, with an almost total absence of hexane among the products. Surfaces with increasing amount of the carbon(aceous) deposits show an increasing tendency to a

TABLE 2

Selectivity in Ring Opening of MCP as a Function of the Catalyst treatment (as Expressed by the S_i Values)

Treatment	Temp. at α = 10% (K)	S_{cr}-% hydrogenolysis	2MP	3MP	HEX	E_{act} (kcal/mol)	$\frac{2MP}{3MP}$	$\frac{HEX}{2MP}$
As under code 1, in Table 1	447	3.6	63.4	31.5	1.3	18.5	2.01	0.02
Code 3	554	1.5	55.2	25.4	17.4	25	2.17	0.32
Code 4	537	1.4	58.4	25.2	14.6	28	2.32	0.25
Code 5	517	1.2	61.2	26.4	10.3	24	2.32	0.17

TABLE 3

Influence of the Particle Size on the Selectivity in Ring Opening of MCP ("Clean" Surfaces)

Catalyst	Temp. (K)	$\bar{d}$[a] (nm)	2MP	3MP	HEX	$\frac{2MP}{3MP}$	$\frac{HEX}{2MP}$	$\frac{HEX}{3MP}$[b]
Pt/Al_2O_3, type A Ref. (*20*)	510	4.4	72.0	19.2	8.8	3.8	0.12	0.46
Pt/Al_2O_3, type A Ref. (*20*)	510	1.55	44.2	16.3	39.5	2.7	0.89	2.42
2.25% Pt/Al_2O_3, Ref. (*18*)	493	17	—	—	—	—	—	0.31
2.5% Pt/Al_2O_3, Ref. (*18*)	493	1.2	—	—	—	—	—	2.5
10% Ir/Al_2O_3 (code 1, Table 1)	457	18	63.4	31.5	1.3	2.0	0.02	0.04
0.4% Ir/SiO_2	449	<1.5	62.2	32.8	1.3	1.9	0.02	0.04

[a] Average diameter of the particles.

[b] With statistical random ring opening, this value is 2.

"non-selective" ring opening, with appreciable amounts of hexane among the products. Hexane is formed in higher amounts at the cost of both isomers and due to the lower total hydrogenolytic cracking (see Table 2).

The high selectivity ("no-hexane") in the ring opening of Ir-fresh catalysts cannot be suppressed by diminishing the particle size of Ir, as a comparison of various of our catalysts has shown. With Pt catalysts, however, this is possible: the smallest particles of Pt show a non-selective, statistical distribution (2 : 2 : 1) of the three products hexane, 2-methyl, and 3-methyl pentanes (*18–20*). In contrast, the smallest particles of Ir which we were able to prepare (smaller than about 1.5 nm, according to the E.M.) still showed an almost "pure" selective ring opening (see Table 3).

However, we noticed the same resistance of smaller particles against poisoning as with Pt catalysts (*4*); when the smallest Ir particle catalyst is compared with that with large particles, the former shows a much higher resistance against self-poisoning by the carbon(aceous) deposits than the latter.

Hexane

The overall picture of hexane conversion on Ir is compared with that obtained with Pt in Figs. 2 and 3. A remark on this comparison is also needed. With Pt, it is impossible to cover the whole region of temperatures indicated in the plots by experiments with the one and the same amount of catalyst, since at high temperatures too high a conversion and too great an extent of consecutive reactions (mainly hydrogenolysis into smaller, more stable molecules) would deform the picture. However, use of different amounts of Pt catalyst (i.e., different apparent contact times) leads to variations in the isomerization/dehydrocyclization (i.e., MCP formation) ratio. For this reason there is a break in the plot for Pt (Fig. 3). Determination of S at higher temperatures is actually only possible because of progres-

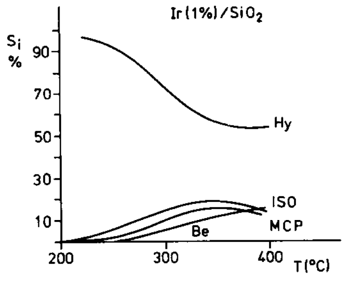


FIG. 2. Ir/SiO_2(1%) catalyst. Selectivities in various skeletal rearrangements of *n*-hexane in the indicated range of temperatures. Hy, hydrogenolysis; ISO, isomerization; MCP, dehydrocyclization into methylcyclopentane; Be, aromatization into benzene.

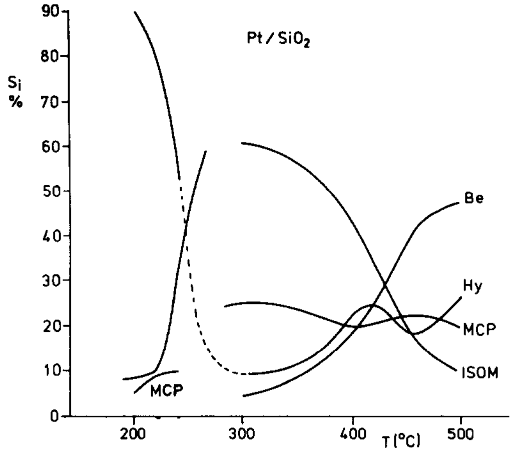


FIG. 3. Pt/SiO$_2$(5%) ("Eurocat") catalyst. Selectivities in various skeletal rearrangements, as in Fig. 2. For other details see the text.

sive self-poisoning, which keeps the total conversion low.

A qualitative conclusion from Figs. 2 and 3 is straightforward: (i) Ir is a worse catalyst for hexane isomerization than Pt, but it can catalyze isomerization; (ii) isomerization selectivity shows a maximum as a function of temperature, this maximum being at higher temperature for Ir than for Pt.

Figure 4 illustrates the influence on the product distributions of deposition of a carbon(aceous) layer on the surface of various Pt (*14, 21*) and Ir catalysts. An exact comparison is difficult since poisoned surfaces which show some difference in selectivities (as compared with virgin surfaces) also have too different activities to be measured at the same temperature as the virgin surfaces and the selectivity is in general a function of temperature. However, some cautious qualitative conclusions are nevertheless possible.

Contrary to an effect of a mere temperature increase, it is not the isomerization selectivity but mainly the dehydrocyclization selectivity which increases when the surface of either Pt or Ir is covered by carbonaceous deposits. Thus, *this* selectivity change has to be ascribed primarily to the carbon(aceous) layer. The shift from hydrogenolytic (and with Pt also from isomerization) products to methylcyclopentane production, when achieved, is essentially the same with large as well as with small particles of both Ir and Pt.

DISCUSSION

First we make a short remark with regard to the selectivity of catalysts. We do not intend to overemphasize the implications of the fact that self-poisoning of the Ir surface leads to a higher activation energy and, simultaneously, to a higher selectivity for

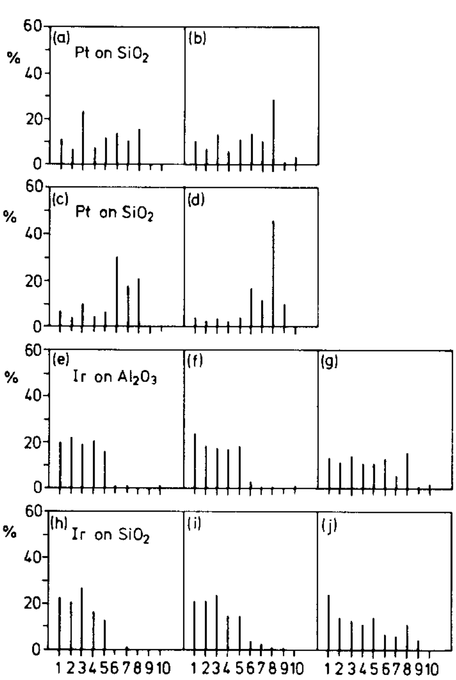


FIG. 4. Hexane skeletal rearrangements. A comparison of earlier results obtained with Pt (Ref. (*4*)) with those obtained with Ir. 1–5 are C_1–C_5; 6 = 2MP, 7 = 3MP; 8 = MCP; 9 = Be; 10 = cyclohexane. (a) 506 K, 10 ml/min flow, Pt/SiO$_2$ (4% wt, particle size ~2.4 nm) virgin surface; (b) 551 K, 10 ml/min flow, catalyst as in (a) after poisoning; (c) 539 K, 10 ml/min flow, Pt/SiO$_2$ (4% wt, particle size ~8 nm) virgin surface; (d) 627 K, 10 ml/min flow, catalyst as in (c) after poisoning; (e) 463 K, 9 ml/min flow, Ir/Al$_2$O$_3$ (10% wt, particle size ~18 nm) virgin surface; (f) 505 K, 9 ml/min flow, catalyst as in (e) after poisoning; (g) 581 K, 9 ml/min flow, catalyst as in (f) after poisoning; (h) 454 K, 9 ml/min flow, Ir/SiO$_2$ (1% wt, particle size ~1.5 nm) virgin surface; (i) 525 K, 9 ml/min flow, catalyst as in (h) after poisoning; (j) 611 K, 9 ml/min flow, catalyst as in (i) after poisoning.

hexane, but it is tempting to speculate that the processes on poisoned surfaces, which necessarily make use of smaller ensembles, reveal indeed a higher activation energy than the multisite processes on the virgin surfaces. A similar effect has already been observed with some other reactions (*22–24*) as well. Another explanation could be that on the virgin surfaces some reversible poisoning occurs, increasing in its extent with increasing temperature, while on the intentionally poisoned surface no such additional reversible self-poisoning can occur. This would lead to an observable difference in the apparent activation energies observed.

A second point to be discussed is the problem of isomerization selectivity. As one can see in Figs. 2 and 4, it is indeed possible to isomerize hexane with Ir. We know already that also with neohexane some isomerization is observed (*15*). However, in order to observe any isomerization one has to follow the skeletal reactions of hydrocarbons at sufficiently high temperatures and under conditions that Ir is partially covered by carbon(aceous) deposits (*5*). These conditions were most likely not fulfilled in experiments by those authors who reported a complete absence of isomerization with Ir catalysts.

The selectivity in the selective/non-selective (that is "without" or "with" hexane among the products) ring opening of methylcyclopentane similarly to the isomerization reactions, is controlled by a carbon(aceous) layer. A shift in selectivity of the ring opening caused by the deposition of a carbonaceous layer has been observed with both Pt and Ir (for Ir see Ref. (*26*) and this paper). The same shift from a selective to a nonselective mechanism can be caused with Pt (not with Ir) by diminishing the particle size.

Before we start to discuss the possible intermediates and likely explanations in more detail, some general remarks should be made. There are two reasons to conclude that 5C-intermediates are indeed present on the metal surfaces and in particular on Ir. These are (a) dehydrocyclization/5-ring opening reactions can hardly proceed without 5C-intermediates (there is no alternative) and (b) the isotopic labeling (*7, 8*) shows that isomerization on Ir is running via 5C complexes. While the number of C-atoms is known, all other features of these complexes are virtually unknown: we do not know to which extent the complexes are dehydrogenated, whether they are standing perpendicularly (more or less perpendicularly) to the metal surface or laying horizontally on it, whether the "perpendicular" complexes are bound by single or multiple bonds to the surface and, last but not least, how many atoms of the metal surface are involved in the formation or holding of the complex (*22*). We shall simplify below and discuss two types of complexes, namely single-site complexes and double-site complexes, the latter standing for all complexes with more than one metal atom involved. With regard to the other question, namely, how many bonds are formed between the complex and the metal surface, the following can be stated. There seems to be now no particular reason to speculate that carbyne-like structures Ir≡C— are the *sine qua non* intermediates of isomerization, since (i) there is some isomerization observed also with neohexane; and (ii) there is an appreciable isomerization observed with hexane, a molecule which cannot form simultaneously a double carbyne in 1,5 positions. However, with regard to other details of the possible complexes, the best choice is probably to leave the question open.

Possible complexes can be subdivided into two classes (*22*): (I) complexes standing (more or less) perpendicularly to the metal surface (*26*), and (II) complexes laying horizontally (*27*) on the surface and being most probably dehydrogenated to such an extent that their double bonds are conjugated. Complexes of the first class (I) have to be considered in their single and multiple (double) site forms, whereas complexes of the second class can be easily accommodated on single sites. Complexes of class I are schematically shown in Fig. 5.

A carbonaceous layer is a rather inert blocking material and therefore it is acceptable to discuss its effects in *geometrical* terms. If we do that, we shall find it very difficult to suggest an explanation of the effects of carbon(aceous) deposits on ring opening if the only type of complexes operating were the one-site complexes. Therefore, we have to assume that next to the single-site mechanism(s), also one or other multisite mechanism must operate.

Experience with other metal and alloy systems (for a review, see Ref. (*22*)) suggests that on surfaces where a sufficient number of contiguous sites is available the multisite complexes (complexes 5–8 of Fig. 5) are formed more easily than the single-site complexes (complexes of class II and the complexes 1–4 of Fig. 5). It may be expected that a carbon(aceous) deposit on the surface, poisoning by sulfur or alloying, may all cause then a shift from the first-mentioned to the latter-mentioned complexes. Let us analyze now whether there could be a reason why such a shift should lead to the appearance of hexane among the products of the MCP ring opening. We suggest that the following factors play a role in establishing the observed selectivity.

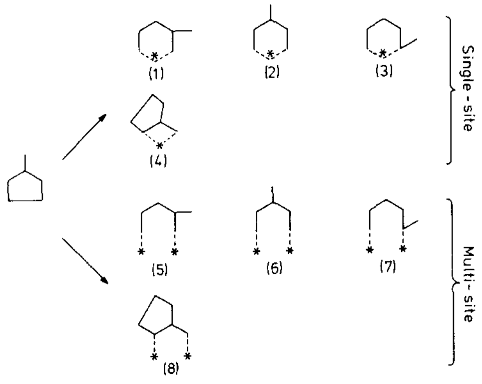
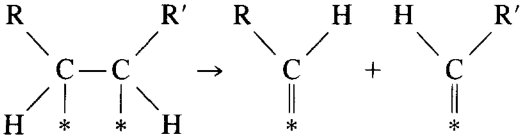


FIG. 5. Possible single (1–4) and multisite (5–8) intermediates of the ring closure/ring opening and of the 5C-("cyclic") isomerization. Only intermediates of class I are shown; the intermediates of class II should most probably be visualized as lying horizontally (π-complexed?) unsaturated species (for more details, see the text).

(i) Intermediates like (5) or (6) (Fig. 5) would be formed by a reaction reminiscent of hydrogenolysis of $\alpha\beta$-bonded species. It can be expected that carbons of the broken bonds are bound to the surface by multiple bonds, as, e.g.:



Then it is not unlikely that the asterisk site represents a hollow position in the valley, among two or more surface atoms. It is more difficult to force a branched carbon into this position and this factor, in our opinion, makes the intermediate (7) less probable than the intermediates (5) and (6). According to the experience (*5*) with hydrogenolysis of neohexane, neopentane, etc., the $\alpha\beta$-bound intermediates (5) and (6) should be formed on "clean" Ir easier than the $\alpha\gamma$-type intermediate (8).

(ii) One can also expect a difference in the behavior of metal atoms in the flat surfaces and on edges, corners, etc. When other conditions are equal, flat surfaces which are not covered by carbon(aceous) layers to a too high extent give rise to a fast formation of intermediates (5) and (6), since larger numbers of contiguous sites are available there. This is demonstrated by the production of mainly 2MP and 3MP on "clean" metal catalysts (Pt, Ir) and the absence of *n*-hexane among the products.

(iii) The observed fact that a carbon(aceous) layer forces the reaction to become less "selective" (i.e., more of *n*-hexane is formed) can thus be rationalized by two effects operating simultaneously: (a) the presence of carbon on the surface eliminates the large ensembles of contiguous sites, causing a shift from the multisite to the single-site intermediates of class I and class II; and (b) carbon atoms, most probably sitting in the hollow positions and on the planes (*2*, *3*) suppress the formation of (1–3)-intermediates and by that they increase the chance that the intermediate (4), which is otherwise more difficult to be formed, is formed. Also, the $\alpha\gamma$-intermediate (4) can be formed more easily on atoms positioned at the corners and the edges which are relatively free from carbon(aceous) deposits [carbon(aceous) deposits eliminate the flat surfaces more efficiently *2, 3*]

Effect (b) under (iii) is a particularly attractive explanation in view of the fact that diminution of the size of the Pt particles (which raises the relative amount of corner and edge atoms) leads to a promotion of the non-selective ring opening, i.e., promotion of hexane formation. However, diminution of particles alone is not sufficient to promote hexane formation from MCP in all cases, as the example of Ir shows. With Ir the valley positions evidently have to be blocked in any case. On the other hand, blocking alone would not be a sufficient explanation either, since the smallest particles of Pt are less poisoned than the large ones and they produce more hexane upon ring opening of MCP. Thus both effects have to be considered.

A definitive detailed explanation and a decision between the various possibilities is not yet possible, but it seems that the results presented above and analyzed in this discussion have already localized the problem to a rather narrow range of residual possibilities of explanation.

Finally, we should make two remarks on the particle size effect with regard to Ir: (1) this effect is not very pronounced with neohexane and it also depends on the structure of the carbonaceous layer (5); and (2) this effect is even smaller in MCP ring opening, a fact which has been already recognized (*10*).

In these respects Ir and Pt behave in a very different way. We tend to relate these facts to the observation that it is more difficult to self-poison Ir by carbon than Pt. This leads us to see the particle size effect as (mainly) an effect on the side reaction, the main factor influencing the selectivity being the extent, structure, and reactivity of the carbon(aceous) layer.

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