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Catalytic Activity of Bulk Tungsten Carbides for Alkane Reforming

III. Reaction Mechanisms and the Kinetic Model

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This paper describes in close molecular detail the complex reactions which occur when a variety of hydrocarbons are adsorbed on fresh or oxygen-modified bulk tungsten carbide catalysts. On fresh tungsten carbide without oxygen, cracking reactions are the only reaction processes occurring; the results have been interpreted with a kinetic treatment which assumes successive carbon–carbon bond ruptures. The conditions under which the bulk tungsten carbide powders are treated with oxygen have a determinantal influence on their catalytic properties. If air is introduced at moderate temperature (350°C), an acidic character of the catalyst is observed which leads to a bifunctional mechanism. Cracking reactions are the most important processes, and corresponding mechanisms have been interpreted using the presence of OH surface groups leading to alkoxy species as intermediates. If air is introduced in flowing hydrogen at high temperature (700°C), the metallic character of the material is observed, leading to cracking and isomerization reactions explained via classical metallacyclobutane and σ-alkyl species, respectively.

1. INTRODUCTION

The catalytic properties of bulk tungsten carbides for alkane conversion have been widely studied. The work of Ribeiro *et al.* (1, 2) and Iglesia *et al.* (3) suggested the presence of a bifunctional mechanism when the surface is treated under oxygen; such a surface catalyses dehydrogenation and carbenium ion reactions typical of those occurring on reforming catalysts. As a result of our studies presented in Parts I and II of this series (4, 5), it has been pointed out that the catalytic activity for cracking and isomerization reactions can be strongly modified depending on the temperature at which the oxygen treatment is carried out. Moreover, the selectivity is also modified; it was observed that samples treated with air at 350°C for a few minutes (fm) or for 3 h [$WC_{(O\text{-}350)fm}$, $WC_{(O\text{-}350)3h}$] show a more acidic behaviour than a sample treated at a higher temperature (700°C), denoted $WC_{(O\text{-}700)4h}$, which exhibits a more metallic behaviour (5). To explain these results we propose in this paper various mechanisms capable of interpreting the catalytic results, and we include a discussion concerning the interaction of the active intermediates with the active surfaces or dual sites (6).

As the mechanism of paraffin cracking on tungsten carbide surfaces remains an important matter, we will first develop a kinetic scheme which explains the results obtained on bulk tungsten carbides without oxygen. This model makes clear the reason for the maxima observed in the curves relating to the cracking pattern. Then in Section 3 we will analyze the effect of treatments with air on the reaction pathways occurring on tungsten carbides. The extensive degradation of the starting reactant no longer occurs on these samples, and isomerization is favoured. This point will be discussed.

2. KINETIC MODEL FOR CRACKING REACTIONS ON BULK TUNGSTEN CARBIDES WC WITHOUT OXYGEN

In Part I of this series (4), the results obtained for the reformation of *n*-hexane, 2-methylpentane, and methylcyclopentane on WC without oxygen have been presented. The percentage yields of all the cracking products except methane exhibit a maximum when the reaction temperature is increased. A kinetic model assuming successive carbon–carbon bond cleavages can account for these results. First, the starting molecule must be adsorbed on the surface and then it can undergo a carbon–carbon bond breaking. After this first step, the resulting molecules can either desorb into the gas phase or undergo another carbon–carbon bond cleavage in the adsorbed state. At this stage, two reaction schemes are possible: either the successive carbon–carbon bond cleavage takes place in the adsorbed phase without desorption and readsorption of the molecule and once the molecule is desorbed into the gas phase it

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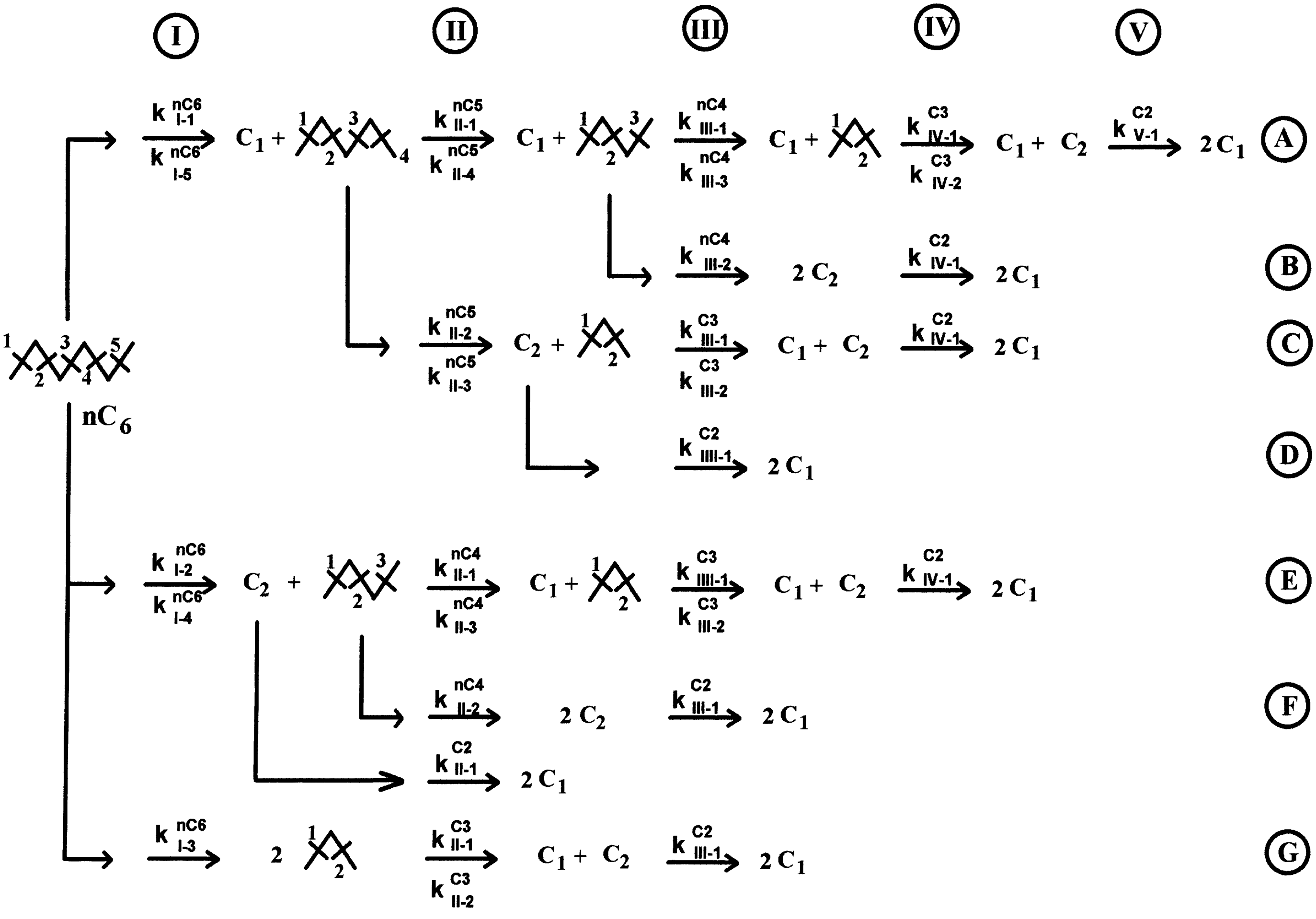


SCHEME 1

has no chance to be readsorbed, or between each carbon–carbon bond rupture a desorption–readsorption process of the corresponding molecule happens. As our results do not allow a choice between these two possibilities, the first assumption (cracking reactions happening in the adsorbed phase) has been chosen. Moreover, this model is simpler. The reaction process for the full decomposition of *n*-hexane by successive carbon–carbon bond cleavages is given in Scheme 1. For each carbon–carbon bond rupture a kinetic coefficient *k* with an exponent and an index is given. For instance, the coefficient $k_{\mathrm{I}-1}^{n\mathrm{C}_6}$ is the kinetic coefficient for the first carbon–carbon bond cracking involving the carbon–carbon bond labelled 1 in the *n*-hexane molecule. The exponent gives the molecule concerned by the reaction process, the roman numeral of the index giving the number of the carbon–carbon bond rupture, as indicated at the top of Scheme 1 by the roman numeral in the circle, and the arabic numeral being the number of the carbon–carbon bond in the molecule.

In a first simple approach, if all the kinetic coefficients, $k_{\mathrm{I}-i}^{n\mathrm{C}_6}$, whatever the number of the carbon–carbon bond concerned, are assumed to be equal, this means that all of the carbon–carbon bonds have the same chance to be broken at each reaction step, I–V, of the cracking reaction. It is easily possible to identify and count the molecules produced at each step of the process. For instance, from the reaction process of the *n*-hexane given in Scheme 1, it is easily deduced that the first carbon–carbon bond rupture, I, leads to $2\,\mathrm{C}_1 + 2\,\mathrm{C}_2 + 2\,\mathrm{C}_3 + 2\ n\mathrm{C}_4 + 2\ n\mathrm{C}_5$, i.e., a total of 10 molecules, each of the molecules representing 20% of the total. For the second carbon–carbon bond rupture, II, these molecules except for methane are transformed, giving new products whose percentages can be calculated by the same method. The yield% of the species produced at each carbon–carbon bond rupture can be determined and the concentration of each of the cracked products as a function of the number of the carbon–carbon bond cleaved are given in Figs. 1–3 for *n*-hexane, 2-methylpentane, and 3-methylpentane, respectively. As observed in the curves, the yield% of each molecule produced goes through a maximum, except for methane, which is of course the only molecule present after five carbon–carbon bond ruptures.

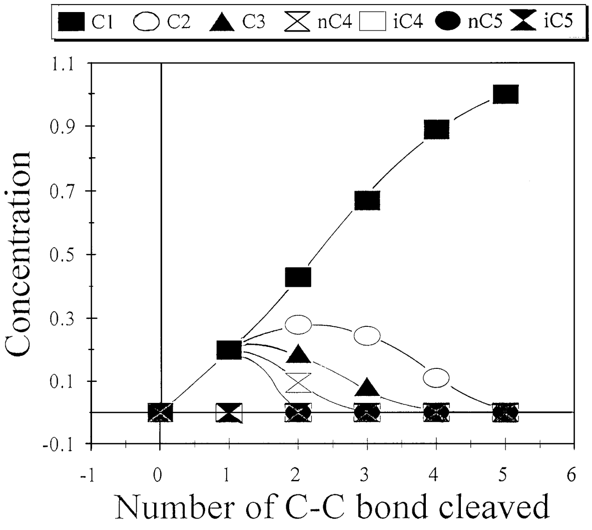


FIG. 1. *n*-Hexane cracking product concentration versus the number of carbon–carbon bond cleaved.

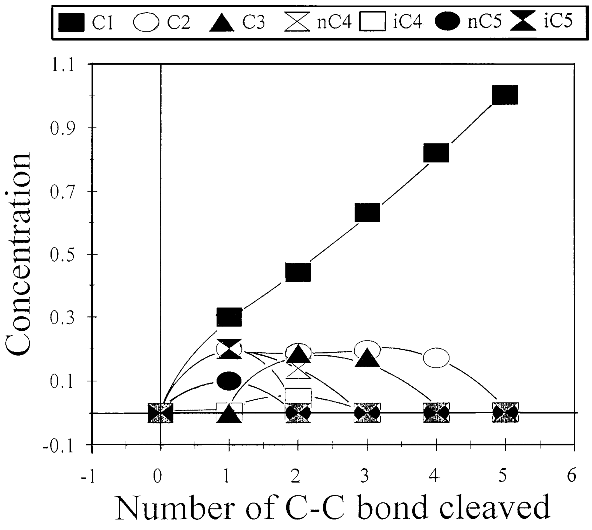


FIG. 3. 3-Methylpentane cracking product concentration versus the number of carbon–carbon bond cleaved.

As it is reasonable to assume that the number of the carbon–carbon bond cleaved increases as the reaction temperature increases; this scheme can account, at least qualitatively, for the experimental results presented previously (4).

If different values are now considered for the kinetic coefficient k (except for those which are actually equal, such as $k_{\mathrm{I}-1}^{n\mathrm{C}_6}$ and $k_{\mathrm{I}-5}^{n\mathrm{C}_6}$ due to the symmetry of the molecule), it is possible to establish relationships giving the production kinetics of each species concerned by the cracking process, as shown in Scheme 1 for the *n*-hexane molecule. However, several assumptions must be put forward.

First, the production rate of a molecule in the gas phase is given by the concentration of this molecule in the adsorbed phase, i.e., it is given by θ, multiplied by a desorption coefficient k_{des}.

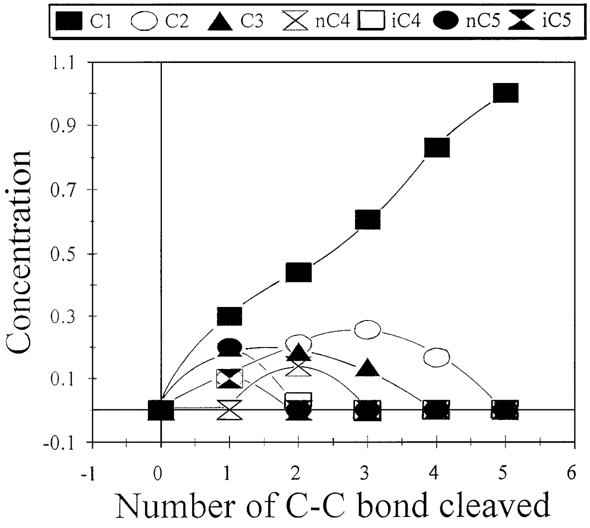


FIG. 2. 2-Methylpentane cracking product concentration versus the number of carbon–carbon bond cleaved.

Second, the concentration of one species in the adsorbed phase results from a stationary state between the formation process due to the cracking of a molecule of higher molecular mass and from the disappearance process due to the cracking and the desorption of this molecule into the gas phase. For instance, the concentration of *n*-pentane in the adsorbed phase produced by the cleavage of the carbon–carbon bond labelled 1 and 5 of the *n*-hexane molecule, as shown in Scheme 1, results from the equilibrium between the following rates:

$$\text{Formation rate}\qquad \frac{d\theta_{n\mathrm{C}_5}}{dt} = \theta_{n\mathrm{C}_6}\left[k_{\mathrm{I}-1}^{n\mathrm{C}_6} + k_{\mathrm{I}-5}^{n\mathrm{C}_6}\right] \qquad [1]$$

$$\text{Disappearance rate}\qquad \frac{d\theta_{n\mathrm{C}_5}}{dt} = \theta_{n\mathrm{C}_5}\left[\sum_{i=1}^{i=4} k_{\mathrm{II}-i}^{n\mathrm{C}_5} + k_{\mathrm{des.}}^{n\mathrm{C}_5}\right] \qquad [2]$$

At equilibrium the two rates are equal and

$$\theta_{n\mathrm{C}_5} = \frac{\theta_{n\mathrm{C}_6}\left[k_{\mathrm{I}-1}^{n\mathrm{C}_6} + k_{\mathrm{I}-5}^{n\mathrm{C}_6}\right]}{\sum_{i=1}^{i=4} k_{\mathrm{II}-i}^{n\mathrm{C}_5} + k_{\mathrm{des.}}^{n\mathrm{C}_5}}. \qquad [2']$$

The rate of $n\mathrm{C}_5$ production in the gas phase is given by:

$$r_{n\mathrm{C}_5} = \theta_{n\mathrm{C}_5} \times k_{\mathrm{des.}}^{n\mathrm{C}_5} = \frac{\theta_{n\mathrm{C}_6}\left[k_{\mathrm{I}-1}^{n\mathrm{C}_6} + k_{\mathrm{I}-5}^{n\mathrm{C}_6}\right]}{\sum_{i=1}^{i=4} k_{\mathrm{II}-i}^{n\mathrm{C}_5} + k_{\mathrm{des.}}^{n\mathrm{C}_5}} \times k_{\mathrm{des.}}^{n\mathrm{C}_5}. \qquad [3]$$

$\theta_{n\mathrm{C}_6}$ must be calculated assuming an equilibrium between a rate of formation and a rate of disappearance. The disappearance rate is simply given by:

$$\frac{d\theta_{nC_6}}{dt} = \theta_{nC_6}\left[\sum_{i=1}^{i=5} k_{\mathrm{I}-i}^{nC_6} + k_{\mathrm{des.}}^{nC_6}\right] \qquad [4]$$

The formation of the adsorbed *n*-hexane is the result of the adsorption of the *n*-hexane molecule on the free surface fraction $1-\theta_{\mathrm{H}}$–θ_{C}, where θ_{H} and θ_{C} are the surface fractions covered by hydrogen and by adsorbed hydrocarbons, respectively. As the $P_{\mathrm{H}_2}/P_{\mathrm{HC}}$ ratio is very high, it can be reasonably assumed that θ_{C} is negligible in comparison with θ_{H}, and the free surface fraction can be assumed to be equal to $1-\theta_{\mathrm{H}}$. The rate of formation of the fraction of the adsorbed *n*-hexane layer is given in Ref. (7):

$$\frac{d\theta_{nC_6}}{dt} = \frac{P_{\mathrm{HC}}}{\sqrt{2\pi m' kT}} \times [1-\theta_{\mathrm{H}}], \qquad [5]$$

where k is the Boltzmann constant and m' is the molecular mass of the hydrocarbon.

The hydrogen coverage can be determined by assuming an adsorption–desorption equilibrium (Langmuir isotherm) which leads to the following relationship:

$$\theta_{\mathrm{H}} = \frac{\left[\dfrac{P_{\mathrm{H}_2}}{\sqrt{2\pi mkT}} \times \dfrac{1}{\nu \exp-(E_{\mathrm{H}_2}/RT)}\right]^{1/2}}{1+\left[\dfrac{P_{\mathrm{H}_2}}{\sqrt{2\pi mkT}} \times \dfrac{1}{\nu \exp(-E_{\mathrm{H}_2}/RT)}\right]^{1/2}}, \qquad [6]$$

where m is the mass of the hydrogen atom. Assuming that hydrogen is dissociatively adsorbed on the surface, and that desorption happens by recombination of two adsorbed hydrogen atoms, P_{H_2} and E_{H_2} are respectively the stationary hydrogen pressure and the activation energy of the desorption process which is given by the following equation: $E_{\mathrm{H}_2} = 2\,E_{\mathrm{H}-M} - E_{\mathrm{H-H}}$, where $E_{\mathrm{H}-M}$ is the binding energy between the hydrogen atom and the catalyst, and $E_{\mathrm{H-H}}$ is the dissociation energy of the hydrogen molecule.

Due to the experimental conditions, $\theta_{\mathrm{H}} \approx 1$ and thus we may approximate

$$1-\theta_{\mathrm{H}} = \left[\frac{P_{\mathrm{H}_2}}{\sqrt{2\pi mkT}} \times \frac{1}{\nu \exp(-E_{\mathrm{H}_2}/RT)}\right]^{-1/2}. \qquad [7]$$

Combining [4], [5], and [7], it is easily found that

$$\theta_{nC_6} = \frac{P_{\mathrm{HC}}}{P_{\mathrm{H}_2}^{1/2}} \times \frac{[2\pi mkT]^{1/4}}{[2\pi m' kT]^{1/2}} \times [k_{\mathrm{H}_2}]^{1/2} \times \frac{1}{\sum_{i=1}^{i=5} k_{\mathrm{I}-i}^{nC_6} + k_{\mathrm{des.}}^{nC_6}}, \qquad [8]$$

with $k_{\mathrm{H}_2} = \nu \exp(-E_{\mathrm{H}_2}/RT)$.

Finally, combining [3] and [8], the production rate of the nC_5 molecule in the gas phase is given by

$$r_{nC_5} = \frac{P_{\mathrm{HC}}}{P_{\mathrm{H}_2}^{1/2}} \times \frac{[2\pi mkT]^{1/4}}{[2\pi m' kT]^{1/2}} \times [k_{\mathrm{H}_2}]^{1/2} \times \frac{2k_{\mathrm{I}-1-5}^{nC_6}}{\sum_{i=1}^{i=5} k_{\mathrm{I}-i}^{nC_6} + k_{\mathrm{des.}}^{nC_6}} \times \frac{k_{\mathrm{des.}}^{nC_5}}{\sum_{i=1}^{i=4} k_{\mathrm{II}-i}^{nC_5} + k_{\mathrm{des.}}^{nC_5}}, \qquad [9]$$

where, since $k_{\mathrm{I}-1}^{nC_6} = k_{\mathrm{I}-5}^{nC_6}$, we have written $k_{\mathrm{I}-1}^{nC_6} + k_{\mathrm{I}-5}^{nC_6} = 2k_{\mathrm{I}-1-5}^{nC_6}$.

The production rate for the other molecules nC_4, C_3, C_2, and C_1 can be calculated using the same method. However, it must be noted that several reactions can lead to these molecules and the resulting equations will be more complex. For nC_4 formation from *n*-hexane cracking, for instance, two processes must be taken into account as shown in Scheme 1: that in the first line after the second carbon–carbon bond rupture and that in the fifth line after the first carbon–carbon bond cleavage. Many more processes must be considered for C_3, C_2, and C_1 and their number increases as the number of carbon atoms decreases in the resulting molecule. For instance, 16 processes must be taken into account for the methane formation, as can be seen in Scheme 1. In one of these processes, the methane formation kinetics after the first carbon–carbon bond rupture in the first line of Scheme 1 is given by

$$r_{C_1} = \frac{P_{\mathrm{HC}}}{P_{\mathrm{H}_2}^{1/2}} \times \frac{[2\pi mkT]^{1/4}}{[2\pi m' kT]^{1/2}} \times [k_{\mathrm{H}_2}]^{1/2} \times \frac{2k_{\mathrm{I}-1-5}^{nC_6}}{\sum_{i=1}^{i=5} k_{\mathrm{I}-i}^{nC_6} + k_{\mathrm{des.}}^{nC_6}}, \qquad [10]$$

and the total methane formation kinetics is the sum of 16 expressions similar to the one written above. It is impossible to fit the expression given by this kind of model with the experimental curve due to the large number of adjustable parameters concerned. However, a general relationship can be drawn from the experimental results, where a maximum is observed as a function of the reaction temperature for the production rate for all the cracked products except methane.

The derivative of the logarithm of the production rate for methane with respect to temperature is given by

$$\frac{1}{dT} \times \frac{dr_{C_1}}{r_{C_1}} = \frac{1}{(RT)^2}\left[\frac{1}{2}E_{\mathrm{H}_2} + Ek_{\mathrm{I}-1-5}^{nC_6}\right] - \frac{1}{(RT)^2} \times \frac{\sum_{i=1}^{i=5} Ek_{\mathrm{I}-i}^{nC_6} \times k_{\mathrm{I}-i}^{nC_6} + Ek_{\mathrm{des.}}^{nC_6} \times k_{\mathrm{des.}}^{nC_6}}{\sum_{i=1}^{i=5} k_{\mathrm{I}-i}^{nC_6} + k_{\mathrm{des.}}^{nC_6}}, \qquad [11]$$

the second term of this expression being a mean value between all the $Ek_{\mathrm{I}-i}^{nC_6}$ and $Ek_{\mathrm{des.}}^{nC_6}$. All the values $Ek_{\mathrm{I}-i}^{nC_6}$, which are the activation energies of the carbon–carbon bond cleavages of the *n*-hexane, must not be very different, and if $Ek^{nC_6}_{\mathrm{des.}}$ is of the same order of magnitude or lower then $(1/dT)\times(dr_{C_1}/r_{C_1})$ is always positive and the methane production kinetics, by this process, is always increasing with the reaction temperature. The same result can be obtained for all of the other production processes of methane, and the whole rate of methane production does not exhibit a maximum if the activation energy for the desorption of a molecule is of the same order of magnitude or lower than the decomposition process of the corresponding molecule.

Returning to the production kinetics of nC_5, the derivative of the logarithm is given by

$$\frac{1}{dT}\times\frac{dr_{nC_5}}{r_{nC_5}} = \frac{1}{(RT)^2}\times\frac{E_{H_2}}{2} + \frac{1}{(RT)^2}\left[Ek^{nC_6}_{\mathrm{I}-1-5} - \frac{\sum_{i=1}^{i=5} Ek^{nC_6}_{\mathrm{I}-i}\times k^{nC_6}_{\mathrm{I}-i} + Ek^{nC_6}_{\mathrm{des.}}\times k^{nC_6}_{\mathrm{des.}}}{\sum_{i=1}^{i=5} k^{nC_6}_{\mathrm{I}-i} + k^{nC_6}_{\mathrm{des.}}}\right] + \frac{1}{(RT)^2}\left[Ek^{nC_5}_{\mathrm{des.}} - \frac{\sum_{i=1}^{i=4} Ek^{nC_5}_{\mathrm{I}-i}\times k^{nC_5}_{\mathrm{I}-i} + Ek^{nC_5}_{\mathrm{des.}}\times k^{nC_5}_{\mathrm{des.}}}{\sum_{i=1}^{i=4} k^{nC_5}_{\mathrm{I}-i} + k^{nC_5}_{\mathrm{des.}}}\right]. \quad [12]$$

The first and the second terms of this expression are positive for the first one, and low or zero for the second one. The third term can be negative if $Ek^{nC_5}_{\mathrm{des.}}$ is lower than all the $Ek^{nC_5}_{\mathrm{I}-i}$ activation energies for the pentane carbon–carbon bond ruptures. This is the condition given by the model to obtain a maximum in the kinetic production curves for the cracked molecules. The general conclusion is that the activation energy for the desorption of the corresponding molecule would be lower than the activation energy for the decomposition of this molecule, a result which is very reasonable.

3. REACTION MECHANISMS OF HYDROCARBON REFORMING IN THE PRESENCE OF OXYGEN

In Part II (Ref. (5)), we described the influence of oxygen on the activity and selectivity as a function of three different surface states resulting from oxygen introduction by a controlled air leak of ≈1–2% O_2 in H_2 at different temperatures and for different times:

—by an air leak at 350°C for a few minutes; this sample is denoted $WC_{(O\text{-}350)fm}$

—by an air leak at 350°C for 3 h, the catalyst will be denoted $WC_{(O\text{-}350)3h}$

—by an air leak at 700°C for 4 h; this will be denoted as $WC_{(O\text{-}700)4h}$.

These catalysts were designated the series of B samples.

(a) Whatever the starting acyclic molecule (hexanes or heptanes), no dehydrocyclisation is observed. The cyclic five-membered reactants (methylcyclopentane or ethylcyclopentane) are transformed less easily than the acyclic ones. The heptanes are more reactive than the hexanes, which are more reactive than the pentanes, which means that the greater the carbon atom number, or the greater the surface coverage, the larger the amount of hydrocarbon which is transformed (7–9). We already observed that on bulk tungsten carbides modified by oxygen the isomerization does not involve a cyclic mechanism via a methylcyclopentane intermediate (5), as is the case on Pt/Al_2O_3 (8).

(b) The temperature modification by oxygen is of high importance; we have observed (5) that fresh bulk tungsten carbides treated by chemisorbed oxygen at low temperature (−65°C), and on which catalytic experiments have been performed at 350°C, present behaviour similar to carbides treated by air at 350°C for a few minutes ($WC_{(O\text{-}350)fm}$). In contrast, the sample treated by air at 700°C, $WC_{(O\text{-}700)4h}$, behaves differently concerning the distribution of products. The $WC_{(O\text{-}350)3h}$ sample (5), treated for a longer time (3 h) with air at 350°C, shows intermediate properties, as confirmed by the minimum of conversion obtained for all the alkanes, except for 2,2-dimethylbutane.

(c) Concerning the extensive cracking, its contribution is more important when the carbon atom number of the starting molecule is high, such a molecule being more strongly adsorbed on the surface. Indeed, it has been shown that

(i) for pentanes there is no extensive cracking,

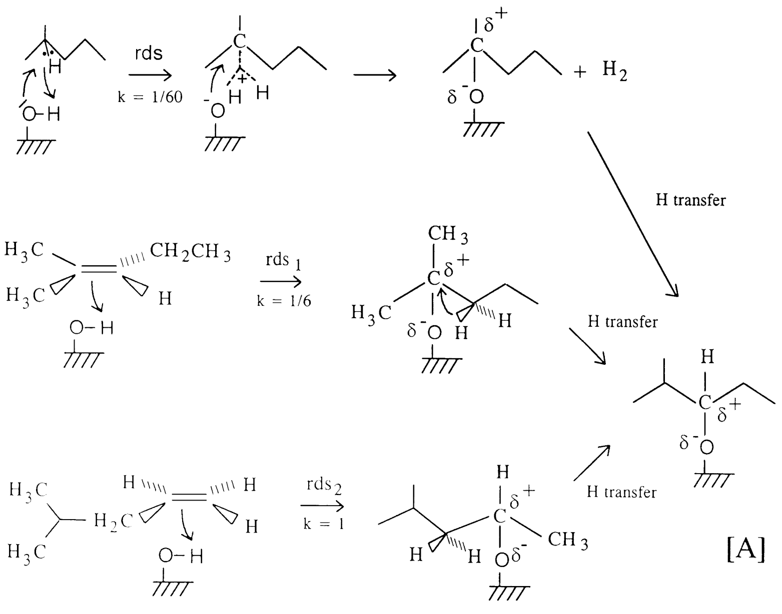
(ii) for hexanes there is only some repetitive cracking on the most modified sample, $WC_{(O\text{-}700)4h}$ (except for 2,2-dimethylbutane, which leads to extensive cracking on the three samples studied),

(iii) for heptanes this process occurs in most cases on the three samples.

3.1. Reaction Mechanisms on ($WC_{(O\text{-}350)fm}$), Modified by Chemisorbed Oxygen at Moderate Temperature (350°C)

On metallic catalysts with large metallic particles, such as alumina-supported platinum, by using carbon-13 labelled hydrocarbons we were able to determine that the rate determining step is the carbon–carbon bond breaking (10–11). It was possible to conclude that this process was the slowest one because no "abnormal labelled hydrocarbons" were found. Moreover, on this catalyst we checked that olefins and alkanes with the same carbon atom number react at the same rates, and that the methylcyclopentane reacts 10 times faster than the hexanes (8).

On all the WC oxygen-modified samples we observed that substituted cyclopentanes react more slowly than the alkanes in the same series. To investigate the reactivity on such samples, we tested olefins in order to determine if the C−H bond rupture could be the slowest step of the process. The total activity of the alkenes will be compared with those obtained from alkanes.



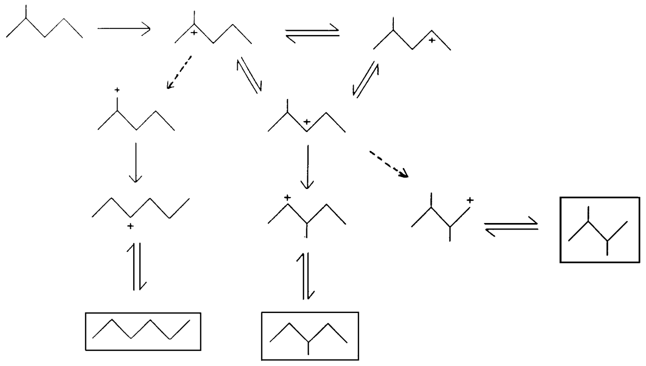
SCHEME 2

3.1.1. Reactions of olefins. The comparison of reactivity between 2-methylpentane, 2-methyl-2-pentene, and 4-methyl-1-pentene in the reforming reactions has shown that the WC$_{(O\text{-}350)fm}$ sample, treated at moderate temperature, presents some acidic properties (5). The 4-methyl-1-pentene, leading to the most reactive secondary carbenium ion, reacts 6 times faster than the 2-methyl-2-pentene, leading to the most stable tertiary and the least reactive ion, and 60 times faster than the corresponding alkane, the 2-methylpentane. These results show that the slow step on these samples (WC$_{(O\text{-}350)fm}$ and WC$_{(O\text{-}350)3h}$) is the carbon–hydrogen bond rupture from the alkane. Starting from the alkenes, the stability of the adsorbed olefin and of the carbenium ion plays a role in the reactivity of the olefin, as shown in Scheme 2.

In Scheme 2 the possible pathways leading to the intermediate species, [A], responsible for isomerization and/or cracking, starting from 2-methylpentane or 2-methyl-2-pentene or 4-methyl-1-pentene, have been compared. We propose that Brønsted acid sites arising due to the presence of OH groups on the surface are involved; carbenium ions are formed from olefins and a carbonium ion is formed from the alkane. In all cases the strength of the Brønsted acid and that of the neighbouring basic oxygen are important (12) and lead to surface alkoxy species, as already proposed by Cheng *et al.* (13).

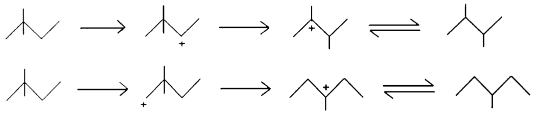
3.1.2. Reactivity of alkanes. On WC$_{(O\text{-}350)fm}$, which is the most acidic sample, the k_{tot} for *n*-heptane is about 4 times higher than for *n*-pentane (Table 9 in Ref. 5). On this sample, the deviations in reactivity between pentanes, hexanes, and heptanes are still more marked for the branched hydrocarbons than for the linear ones. Furthermore, for the same category of alkanes, the branched ones react more easily than the linear ones. This result on the sample modified at moderate temperature (WC$_{(O\text{-}350)fm}$) could easily be explained by an acidic mechanism. Indeed, under acidic conditions, among the alkanes having the same carbon atom number, the heat of formation for a tert-alkyl cation is lower than the heat of formation of a sec-alkyl cation, which is less important than for a primary cation (14). But this thermodynamic approach cannot by itself explain the reaction rates. We have to invoke the σ basicity concept first proposed by Olah (15). The tertiary C–H bond is more basic, so it will react faster than a secondary C–H bond, and in this case it may explain why 3-methylhexane, 3-methylpentane, and isopentane are more reactive than *n*-heptane, *n*-hexane, and *n*-pentane, respectively. It shows that the reactions are kinetically controlled.

Other results confirm our assumptions concerning the acidic properties of the WC$_{(O\text{-}350)fm}$ sample and the kinetic control of the reaction. Starting from 2-methylpentane (5), the 3-methylpentane is the main isomer, the *n*-hexane being unfavoured and 2,3-dimethylbutane not being detected on this sample. This could be explained by the following reactions (simplified Scheme 3) in which the height of the energy barrier controls the reaction selectivity. The most favoured isomer is the 3-methylpentane, because its formation involves no primary carbenium ions, whereas the formation of *n*-hexane requires a primary carbenium ion after hydride transfer and 2,3-dimethylbutane requires a primary carbenium ion after a methyl migration which is more improbable.



SCHEME 3

Starting from 2,2-dimethylbutane, on $WC_{(O\text{-}350)fm}$, only 2,3-dimethylbutane is formed among the isomers (5). That could be explained with carbenium ions as intermediates, as shown in the simplified Scheme 4.

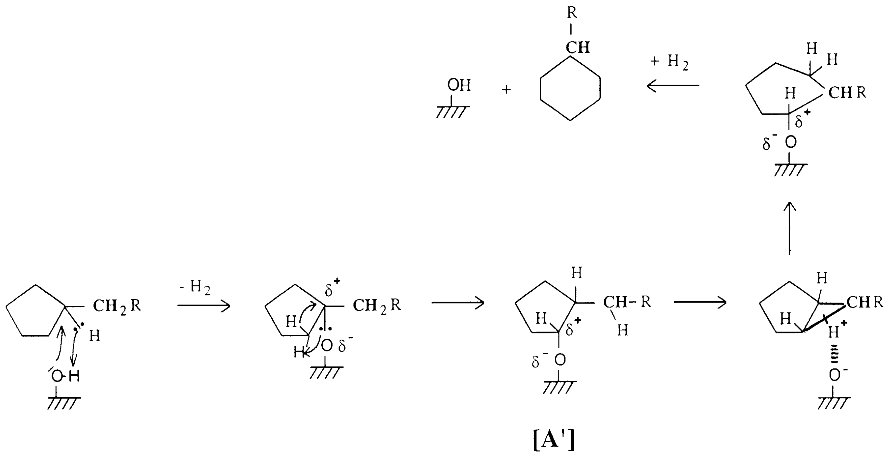


SCHEME 4

The 3-methylpentane production requires the generation of a primary carbenium ion, and the 2,3-dimethylbutane formation goes through an initial secondary carbenium ion. So, in the first case a favourable change of a secondary to a tertiary carbenium ion takes place, explaining why the 2,3-dimethylbutane formation is so easy. However, our speculations on an acidic behaviour, supposing carbenium or carbonium ions as reaction intermediates, are not supported by the data on their mode of formation: either protonation of the alkanes by Brønsted acidic sites (16) or hydride abstraction by a Lewis acis site (17). Moreover, does the skeletal carbon–carbon rearrangement imply a protonated cyclopropane, and what is the mode of interaction of the active intermediates with the surface? Some arguments are deduced from the results obtained with alkyl-cyclopentanes as test molecules.

3.1.3. Reactivity in ring enlargement of cyclo-alkanes. The results presented in Part II (5) have shown that methylcyclopentane and ethylcyclopentane led to the formation of cyclohexane and methylcyclohexane, respectively. To interpret the ring enlargement reaction we propose the mechanisms represented in Scheme 5. The carbenium ions formed in the first step are bound to the surface. The formation of several possible polarized surface (alkoxy) intermediates is shown in Scheme 5, in which we propose that chemisorbed oxygen is the active site and a concerted mechanism is involved between the "H" and "O" transfers. Then we obtain a surface alkoxy species [A′] as an intermediate species which is similar to [A] as given in Scheme 2.

On these catalysts ($WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$), ethylcyclopentane undergoes ring enlargement to methylcyclohexane with great ease because two secondary cations could be involved either on the endo- or exocyclic carbon of the [A′] species. On the other hand, for the methylcyclopentane ring enlargement one tertiary leading to only one secondary cation formation is possible; therefore this process is less easy than that for ethylcyclopentane ring enlargement.



R = H for methylcyclopentane
R = CH_3 for ethylcyclopentane

SCHEME 5

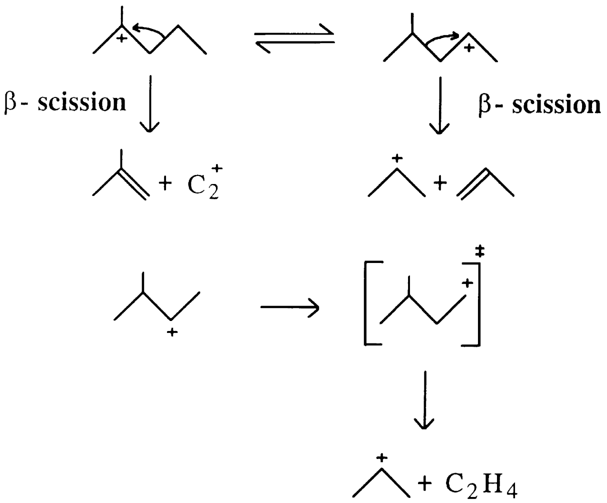
It has been observed, on the $WC_{(O\text{-}350)fm}$ sample, that the ring enlargement from ethylcyclopentane is about 7.5 times faster than that from methylcyclopentane.

Our proposal supposes that isomerization and ring enlargement take place by the rearrangement of alkoxy intermediates as already mentioned by McVicker *et al.* (18) and for which energy diagrams were determined by Kazansky (19), who pointed out that the most stable structure is a covalent ethoxy group.

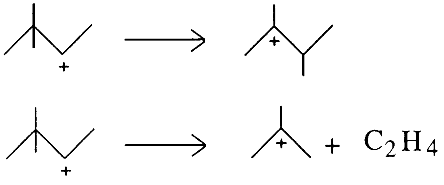
On acidic catalysts, the cyclohexane and the methylcyclohexane are obtained via pseudo cyclopropane stabilised by the inductive donor effect of the substituent group, and with the chemisorbed oxygen, the former effect being more important for ethyl than for methyl substituents. Thus, starting either from cyclohexane or from methylcyclohexane, we should in the same conditions preferentially isomerize the methylcyclohexane into ethylcyclopentane rather than isomerize the cyclohexane into methylcyclopentane, as was the case (see Tables 5 and 6 of Ref. 5).

3.1.4. Cracking of alkanes. Regarding the cracking reactions of alkanes, it is well known that, on acidic catalysts, β-scissions leading to the more stable secondary or tertiary alkyl cations are preferentially produced. Therefore, demethylation, which requires the formation of the least stable primary cations, will not occur.

If we examine how the alkanes are cracked on the acidic sample $WC_{(O\text{-}350)fm}$, we can observe that this process takes place mainly by carbenium ions. From 2-methylpentane, 3-methylpentane, and isopentane, the internal cleavages are favoured, giving mainly propane, *n*-butane, and propane, respectively. Moreover, starting from 2-methylpentane, the most stable ion and thus the least reactive carbenium ion, the tertiary one, leads to isobutane, and the less stable but more reactive ion, the secondary one, gives propane (simplified Scheme 6), and the latter case is favoured, as observed in our experimental results (see Table 2b of Ref. 5) on the $WC_{(O\text{-}350)fm}$ sample; the cracking of 2-methylpentane leads mainly to propane, but we have also some isobutane. For the isopentane cracking, a primary cation must be taken into account, as shown in the simplified Scheme 6.



SCHEME 6



SCHEME 7

We already mentioned that, among the hexanes, 2,2-dimethylbutane reacts the easiest, especially on the $WC_{(O\text{-}350)fm}$ catalyst, for both isomerization and cracking, although the cracking is more important. On an acidic catalyst, however, the formation of the secondary cation of 2,2-dimethylbutane is less favoured than the generation of a tertiary cation, for other hexanes, like 2-methylpentane or 3-methylpentane, its transformation into a tertiary carbenium ion (very stable) is very easy, as shown in the simplified Scheme 7.

In the same manner, the cracking of the 2,2-dimethylbutane would be easier on the acidic sample, $WC_{(O\text{-}350)fm}$, than on the other catalyst because in the former case the leaving group contains a tertiary cation, whereas starting from 2-methylpentane or 3-methylpentane, tertiary–secondary equilibrium may occur, which decreases the cracking rate. This also could explain why, in this sample, no neopentane is formed, involving in this case the formation of a primary cation, very unfavoured in acidic conditions.

The reason for the lower reactivity of cyclic hydrocarbons having five-membered rings (methylcyclopentane or ethylcyclopentane) in comparison to acyclic alkanes could be explained by the formation of cyclopentadienyl hydrocarbons leading to coke, their influence being the most important in acidic conditions (14).

In conclusion, for the samples treated by oxygen at moderate temperature, ($WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$), the different results obtained have pointed out the acidic behavior of this catalyst, and according to Kazansky (12), the close connection between Brønsted acid sites and the neighbouring basic oxygen clearly shows the dual nature of the active sites and that a concerted mechanism takes place.

3.2. Reaction Mechanisms on the Catalyst Sample ($WC_{(O\text{-}700)4h}$) Modified by Oxygen at High Temperature (700°C)

On the $WC_{(O\text{-}700)4h}$ catalyst the following points have been observed, as described in Part II (5).

—Starting from 2-methylpentane, *n*-hexane is present in a larger amount than 3-methylpentane in the isomers

(5) in comparison with the amount obtained for the $WC_{(O\text{-}350)3h}$ sample. Furthermore, 2,3-dimethylbutane and 2,2-dimethylbutane are detected; these observations suppose that, on the $WC_{(O\text{-}700)4h}$ sample, the isomerization proceeds via intermediates other than purely carbenium ions.

—On the $WC_{(O\text{-}350)fm}$ acidic sample, the ring enlargement from ethylcyclopentane is about 7.5 times faster than from methylcyclopentane, whereas, on the $WC_{(O\text{-}700)4h}$ sample, it is only about 1.4 times higher (see Fig. 8b of Ref. (5)).

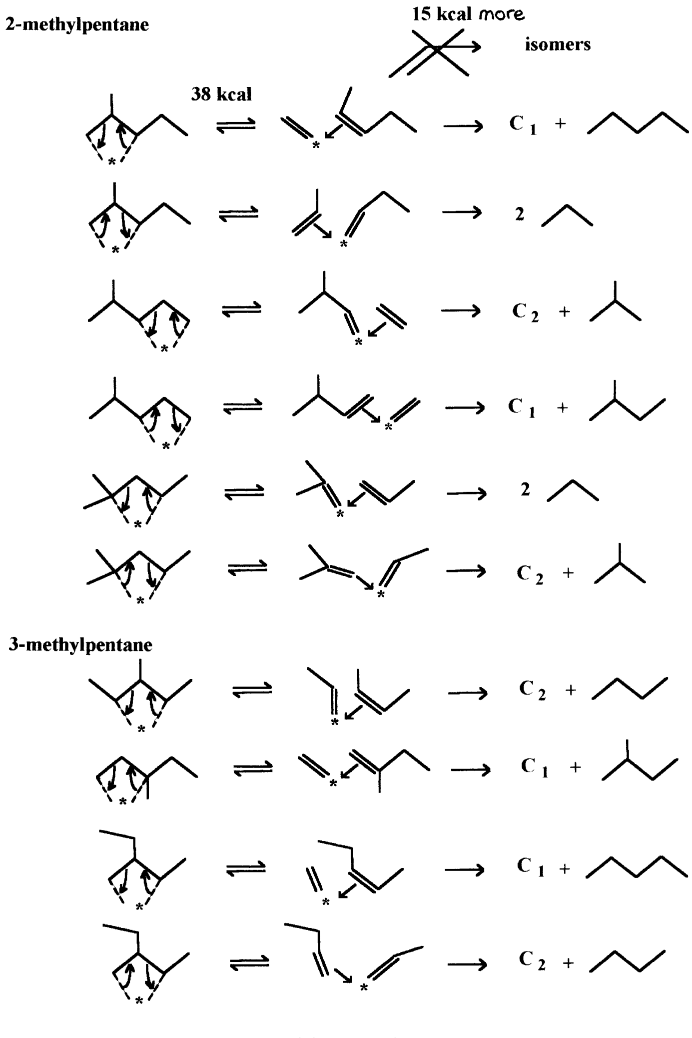
—It is known that methylcyclohexane dehydrogenates into toluene on metallic catalysts, but isomerizes into ethylcyclopentane on acidic metal oxides (14). On the $WC_{(O\text{-}700)4h}$ sample, the methylcyclohexane preferentially leads to toluene (64.4% of the total conversion).

—Furthermore, from the comparison of the total isomerization rates between the 2-methylpentane, the 4-methyl-1-pentene, and the 2-methyl-2-pentene, 2-methyl-2-pentene and 4-methyl-1-pentene isomerization proceeds respectively 1.25 and 3 times faster than for 2-methylpentane (see Table 9 of Ref. 5). We deduced that, on the $WC_{(O\text{-}700)4h}$ sample, the mechanism does not involve carbenium ion intermediates.

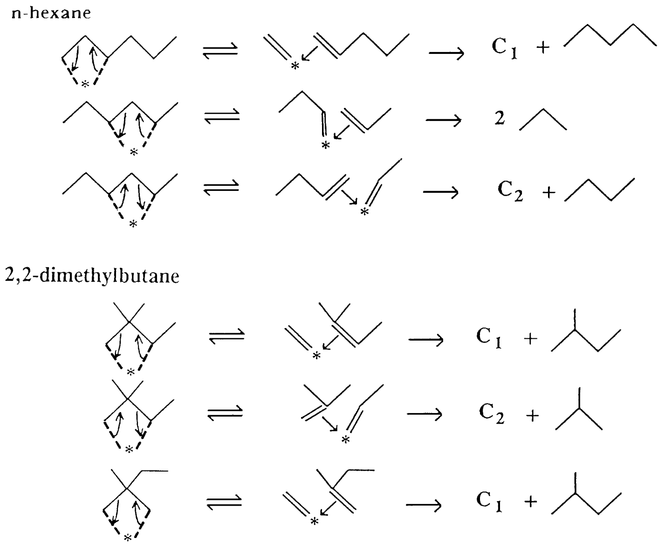
From these different results we may propose that the catalytic behaviour of the carbide treated at high temperature seems more metallic than acidic.

On the other hand, whereas for the previous catalyst, $WC_{(O\text{-}350)fm}$, we only examined the various selectivities in the carbon–carbon bond breaking and the differences in the reaction rates between alkenes and *n*-alkanes and isoalkanes to determine the skeletal mechanisms for the rearrangement of the paraffins, for the sample modified by oxygen at high temperature, $WC_{(O\text{-}700)4h}$, the apparent activation energies for cracking and for isomerization have been determined. The respective E_a values for the 2-methylpentane reaction are 38 and 17 kcal/mol on the $WC_{(O\text{-}700)4h}$ catalyst. From the results already published concerning the mechanisms of hydrogenolysis and of isomerization of hydrocarbons on metals (10), we were able to associate two different intermediate species when the values of the apparent activation energies were different by, at least, 10 kcal/mol. For these reactions on the $WC_{(O\text{-}700)4h}$ sample, we also can assume that two different kinds of intermediates are involved, one responsible for the cracking reaction with the higher E_a value, and the other for the isomerization reaction with the lower E_a value. Keeping this analogy between the results obtained on metals and those obtained on $WC_{(O\text{-}700)4h}$, it can then be supposed, according to the product distributions obtained from the various hydrocarbons studied previously (4, 5), that the isomerization could proceed via σ-alkyl intermediates, already proposed by McKervey *et al.* (20), and that the cracking implies more dehydrogenated species such as metallacyclobutane (8, 10, 21).

3.2.1. Cracking of alkanes. Concerning the cracking reactions, where the apparent activation energy is about 38 kcal/mol, metallacyclobutane intermediates explain very well the different cracking products observed. These adsorbed species, already investigated on platinum (10) and on tungsten (22), exhibit activation energies around 40 kcal/mol. The different cracking products from 2-methylpentane, 3-methylpentane, *n*-hexane, and 2,2-dimethylbutane, formed via adsorbed metallacyclobutane intermediates, are summarized in Scheme 8. The adsorbed metallacyclobutane species give a metallacarbene and an adsorbed olefin. It is well known (23, 24) that substituted metallacarbenes are rapidly isomerized via 1–2 hydrogen shift to adsorbed olefins. Reformation of the adsorbed metallacyclobutane is then much less probable than the hydrogenolysis of carbon–carbon bonds. Thus, it could be reasonable to think, as 38 kcal/mol has been found for the cracking activation energy, that in our case the adsorbed metallacyclobutane intermediates are only responsible for the cracking processes but not for the isomerization



SCHEME 8



SCHEME 8—*Continued*

reactions. Furthermore, the reformation of the metallacarbene and of the adsorbed olefin requires that the rotation barrier of the olefin is overcome before recombination of the carbon–carbon bond, leading to an isomer. The value of this rotation barrier is about 15 kcal/mol on platinum (8) and around 20 kcal/mol on tungsten (22) and increases with the branching. In our case, the apparent activation energy for the isomerization on the WC$_{(O\text{-}700)4h}$ sample is 17 kcal/mol. This model (Scheme 8) cannot account for the isomerization process for, if this model were justified, the total activation energy for isomerization would be $38 + 17$ kcal/mol $= 55$ kcal/mol. The metallacyclobutane intermediates leading to the cracking could explain why on this sample treated with oxygen at high temperature, 2,2-dimethylbutane (see Scheme 8) mainly gives cracking products, preferentially isopentane and isobutane, in contrast to all the other hydrocarbon previously studied. For the other hexanes, pentanes, and heptanes, the more severe the oxygen treatment, the more important the isomerization. In the case of 2,2-dimethylbutane, the larger amount of cracking products on this sample could be explained by the formation of metallacyclobutane on each side of a quaternary center. These adsorbed metallacyclobutane species do not lead to the formation of neopentane, coming from the C$_{I}$–C$_{IV}$ bond cleavage, because the quaternary carbon can no longer lose a hydrogen to generate a metallacyclobutane intermediate, so this mechanism explains very well the absence of neopentane in the cracking process of 2,2-dimethylbutane.

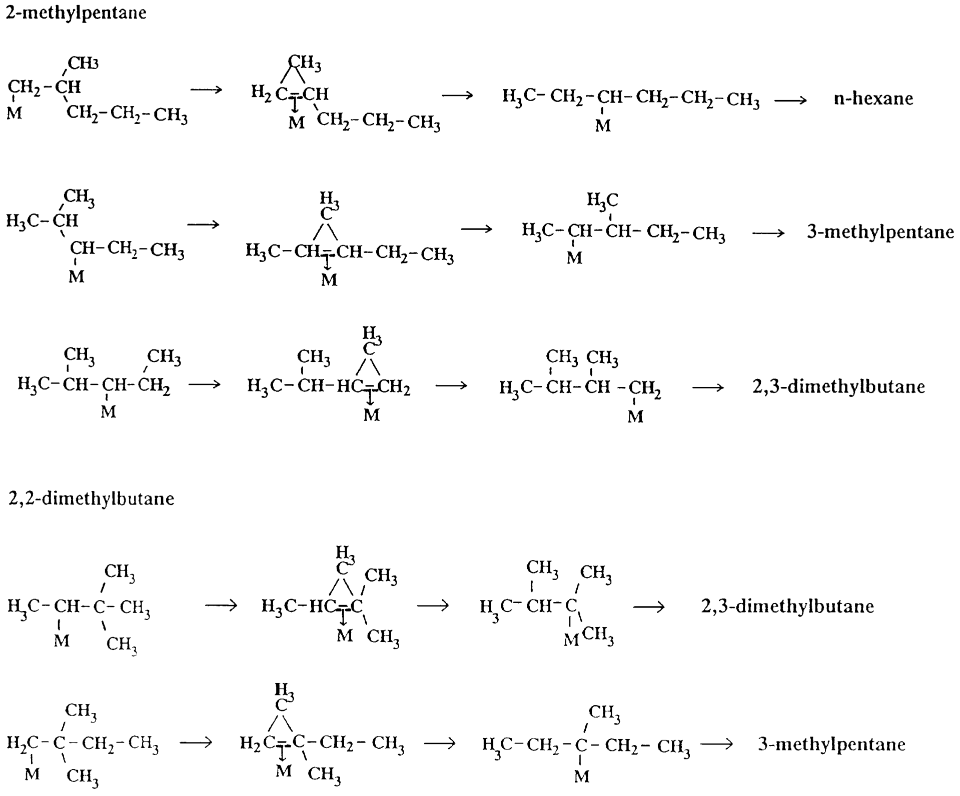
3.2.2. Isomerization of alkanes. Concerning the isomerization, whose activation energy is around 17 kcal/mol and where by ^{13}C tracer studies it was shown that the methyl transposition is predominant over the other alkyl bond shifts (25), it can be assumed that the isomerization proceeds via σ-alkyl intermediates (19). This metallic type of isomerization pathway, proposed by Rooney *et al.* (20, 26), does not lead to cracking but rather exclusively to isomerization (Scheme 9) and explains only the isomer formation by 1,2-bond shift, observed with the ^{13}C tracer studies.

In this mechanism the transient species implies the formation of three-center orbitals (19) as in the nonclassical carbonium ions, with simultaneous π-bonding to the metal; the formation energy of these transient species decreases with the leaving group size and is therefore favoured for a methyl shift. Looking at Scheme 9, this mechanism explains the formation of 3-methylpentane and 2,3-dimethylbutane on the WC$_{(O\text{-}700)4h}$ sample starting from 2,2-dimethylbutane, whereas on the acidic sample, WC$_{(O\text{-}350)fm}$, only 2,3-dimethylbutane was favoured in acidic conditions, as shown in Scheme 4. In the same manner, starting from 2-methylpentane or 3-methylpentane, *n*-hexane and 2,3-dimethylbutane could be obtained by σ-alkyl species, the *n*-hexane being unfavoured on the acidic sample modified by chemisorbed oxygen (5). We also observe the presence of 2,3-dimethylbutane which was not detected on the acidic catalyst because its formation requires the generation of a primary carbocation which is very unfavoured in acidic conditions.

3.2.3. Ring enlargement. Concerning the ring enlargement from methyl- or ethylcyclopentane, the same metallacyclobutane intermediates already invoked to account for the cracking reaction allow us to explain our observations on the catalyst WC$_{(O\text{-}700)4h}$ treated by air at 700°C. These reactions are summarized in Scheme 10. This mechanism includes ring opening by a metallacyclobutane mechanism, followed by carbene–olefin addition, and does not invoke a rotation barrier of the adsorbed olefin.

Let us recall that on the WC$_{(O\text{-}700)4h}$ sample the rate constant for ring enlargement was only 1.4 times higher for the ethylcyclopentane than for the methylcyclopentane, though on the acidic sample, WC$_{(O\text{-}350)fm}$, it was around 8 times higher. Via a carbenium ion mechanism (Scheme 5), the ethylcyclopentane ring enlargement proceeds more easily than from the methylcyclopentane. Via a metallacyclobutane mechanism, as shown in Scheme 10, there is no reason for such an important difference in reactivity. It has already been mentioned that on platinum films (8) methyl- and ethylcyclopentane produce approximately the same amount of ring enlargement products by metallacyclobutane intermediates.

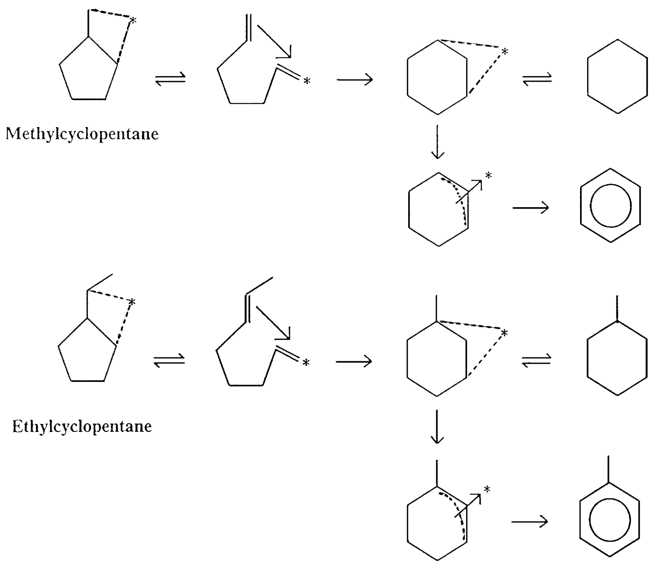
Starting from 2-methylpentane, isopentane, or *n*-pentane, the formation of homologation products has been observed on the WC$_{(O\text{-}700)4h}$ sample. It is well known that metallacyclobutane dismutation into a metallacarbene and an adsorbed olefin is involved in the olefin metathesis reaction (27). Thus, the metallacyclobutane species could also be invoked to explain the formation of homologation products.



SCHEME 9

4. CONCLUSIONS

The conditions under which bulk tungsten carbide powders are treated with oxygen have a determining influence on their catalytic properties for alkane reforming. If air is introduced at moderate temperature ($WC_{(O\text{-}350)fm}$ sample), an acidic character of the catalyst is observed, leading to a bifunctional mechanism. Cracking reactions are the most important and the corresponding mechanisms have been explained by the presence of OH surface groups leading to alkoxy species as intermediates. If air is introduced in flowing hydrogen at 700°C, the metallic character of the material is observed and the reaction takes place through the classical metallacyclobutane and σ-alkyl species leading to cracking and isomerization, respectively. This leads us to conclude that the different oxygen treatments generate different oxygen species responsible for the various mechanisms proposed, acidic or metallic, in agreement also with some very recent results (28).



SCHEME 10

On bulk tungsten carbide without oxygen, cracking reactions are the main reaction processes observed and the surface is much more reactive than in the presence of oxygen. Thus, at 350°C, methane is the only product detected. The maxima observed in the curves relative to cracking pattern as a function of reaction temperature have been explained by a kinetic scheme invoking successive carbon–carbon bond ruptures. If oxygen is added to the surface at moderate temperature (350°C), the same kinetic result is obtained, the only difference being a regular decrease of the surface area for the carbon–carbon rupture as the amount of oxygen adsorbed on the surface is increased.

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