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Reactivity of 3-Methyl-Crotonaldehyde on Pt(111)

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The reactivities of an α,β-unsaturated aldehyde, 3-methylcrotonaldehyde, and of its two monohydrogenated products, 3-methyl-crotyl alcohol and 3-methyl-butyraldehyde, have been investigated on a well-defined Pt(111) surface by low-pressure adsorption, thermal desorption, and high-pressure gas-phase hydrogenation experiments. Two kinetic regimes have been found when varying the 3-methyl-crotonaldehyde partial pressure and, in both cases, a rate-determining step has been proposed. At the origin of the reaction the high selectivity for 3-methyl-crotyl alcohol can be accounted for by the nature of the most abundant C_5H_9O isomer adsorbed species, the latter being determined by geometric effects. The influence of the 3-methyl-crotonaldehyde partial pressure on selectivities can be easily explained by a competitive hydrogenation between this molecule and the 3-methyl-crotyl alcohol. A similar previous study on Pt(100) has shown a quite different behaviour, and this work underlines the importance of the crystalline orientation of the platinum surface on the observed selectivities.

1. INTRODUCTION

The selective hydrogenation of α,β-unsaturated aldehydes into unsaturated alcohols has become an important topic in heterogeneous catalysis because of its importance in the fine chemicals industry. Production of α,β-unsaturated alcohols is a key step in the preparation of molecules used in the field of perfumes, flavourings, and pharmaceuticals (Vitamin A) (1, 2). This selective hydrogenation of the carbonyl group is not an easy reaction and many studies have been devoted to it (3–12). Most of the working catalysts are based on dispersed Group VIII metals. It appears that, according to the system under study (influence of the support (5–7), of the additives (8, 9), of the organic compound (10–12)), the selectivity of the reaction is governed both by electronic and steric contributions. Nevertheless, clear-cut conclusions are often difficult to draw due to the complexity of the catalyst studied, and much remains to be known about this type of reaction.

Our group is currently studying the gas phase hydrogenation of an α,β-unsaturated aldehyde, namely 3-methylcrotonaldehyde, on several well-defined single crystal platinum surfaces used as model catalysts. The reactions are carried out at pressures near to atmospheric and the platinum surfaces are characterized under conditions relevant to surface science techniques. This approach has already led to interesting results concerning the hydrogenation of diolefines (13) and has proved to be very fruitful for a better understanding of the mechanisms of selective hydrogenations.

The present paper reports a study of the reactivity of 3-methyl-crotonaldehyde on Pt(111). The threefold symmetry of this face is expected to induce specific adsorption modes of the molecule, which may determine the selectivity. First, low-pressure adsorption and thermal desorption of 3-methyl-crotonaldehyde (3-MeCal), 3-methyl-crotyl alcohol (3-MeCol), and 3-methyl-butyraldehyde (3-MeBal) have been carried out to characterize the interactions of these organic compounds with Pt(111). Then, the hydrogenation of 3-MeCal has been extensively investigated and we report a kinetic study of this reaction. Finally, the hydrogenations of 3-MeCol and 3-MeBal, which result from the mono-hydrogenation of 3-MeCal, were also investigated for a better understanding of the parallel/consecutive reaction network (Scheme 1).

2. EXPERIMENTAL

2.1 Preparation of the Sample

The Pt(111) sample was a 2-mm thick, 1.5-cm^2 disk of 5 *N* platinum (Sogemet). The crystal was oriented to within 1° off the (111) face by X-ray back-reflection diffraction and was cut by the spark erosion technique. The sample was then mechanically polished up to 0.5 μm and annealed under ultra-pure hydrogen at T = 1380 K for 24 h. In order to avoid any catalytic activity from the edge of the crystal, the latter was covered with a SiO_2–Al_2O_3 coating. The sample was resistively heated by tungsten wires. Temperatures were measured by a chromel–alumel thermocouple touching the edge of the sample. The cleaning of the surface was achieved by repeated cycles of argon ion bombardment ($P_{Ar} = 3 \times 10^{-4}$ Torr, T = 300 K), low-pressure oxygen treatment ($P_{O_2} = 5 \times 10^{-7}$ Torr, T = 300 K), and annealing at about 1200 K (1 Torr = 133.3 Pa). The state of the surface was controlled by

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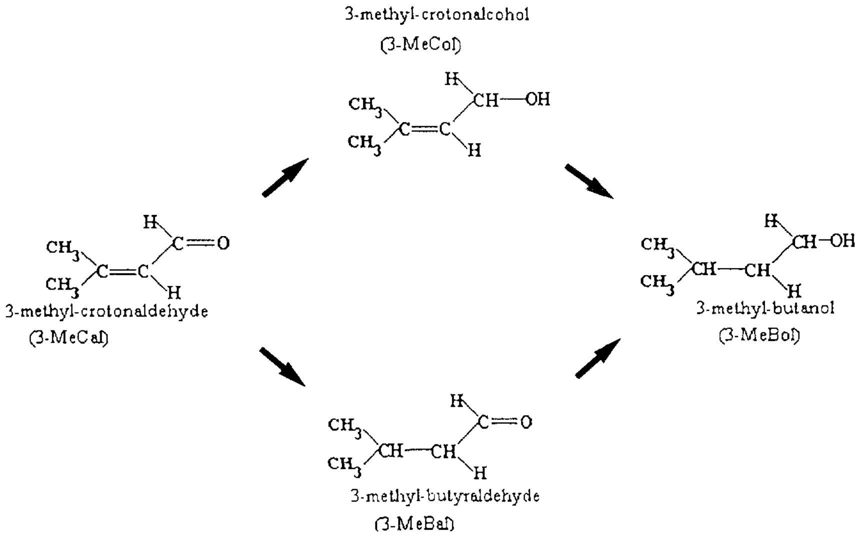


SCHEME 1. Reaction network for the hydrogenation of 3-methyl-crotonaldehyde.

Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) before and after every catalytic test.

2.2 *Low-Pressure Adsorption and Thermal Desorption Experiments*

For each of the organic molecules, low-pressure adsorptions were performed at $T = 353$ K and 10^{-8} Torr pressure. The adsorption kinetics on Pt(111) were followed by monitoring $I_{C(272eV)}/I_{Pt(237eV)}$ in the differential mode by AES using cylindrical mirror analyzer (Riber O.P.C. 105) with a primary beam energy of 2.0 keV and a modulation voltage of 4 V peak-to-peak. Temperature-programmed desorption experiments were performed using a linear heating rate of 20 K s^{-1} and were monitored by a quadrupole mass spectrometer (Leybold IQ 200).

2.3 *Catalytic Reactions*

For each catalytic reaction, the sample was transferred by a rod from the analysis-preparation chamber onto an identical sample carrier located in a stainless steel ultrahigh vacuum reaction chamber. The catalyst temperature was stabilized at $T = 353$ K, and then the reaction chamber was isolated from the analysis chamber and connected to a glass-made reactor. The reactions were carried out in the presence of a homogeneous mixture containing a large excess of hydrogen ($P_{H_2}/P_{3\text{-MeCal}} = 10^4$), and in order to avoid any transport limitation phenomenon the circulation of the gases was ensured by a pump whose flow rate was equal to 2 liter/min. The catalytic reaction was monitored by an on-line gas-phase chromatograph (Intersmat). At the end of the reaction the gases were evacuated by a turbomolecular pump and the sample was transferred back into the analysis chamber.

3. RESULTS

3.1. *Low-Pressure Adsorption and Thermal Desorption Experiments*

For the three organic compounds the adsorption has been conducted at 353 K and under a partial pressure of 10^{-8} Torr. In order to limit the cracking of the adsorbed molecules, the incident electron beam of the Auger gun was focused onto the surface only during the recording time. Figure 1 represents the carbon peak-to-peak Auger intensity ratio $I_{C(272\text{ eV})}/I_{Pt(237\text{ eV})}$ versus time for the three organic compounds. The initial sticking coefficients have been estimated using the calibration of graphite on Pt(111) established by Biberian and Somorjai (14) and are reported in Table 1. These sticking coefficients show that 3-MeCal and 3-MeCol have similar affinities on Pt(111), and that 3-MeBal is less reactive on this surface. Moreover, when the rate of adsorption tends to zero (existence of a plateau), the corresponding coverage can be calculated,

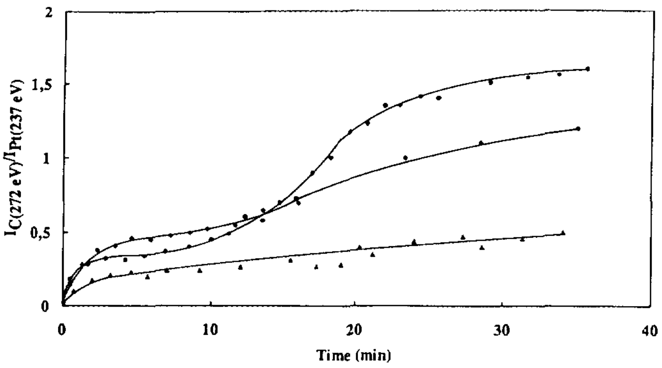


FIG. 1. Kinetics of adsorption on Pt(111) at 353 K and 10^{-8} Torr pressure. (●) 3-MeCal; (▲) 3-MeBal; (◆) 3-MeCol.

TABLE 1

Initial Sticking Coefficients, Final Coverages (Expressed by the Number of Surface Platinum Atoms for One Molecule) and Adsorption Energies for the Different Organic Compounds Adsorbed on Pt(111)

Organic compounds	Initial sticking coefficient	$I_{C(272\ eV)}/I_{Pt(237\ eV)}$	Final coverage (molecule/n Pt)	Temperature of desorption (°K)	Adsorption energy (kJ/mol)
3-methyl-crotonaldehyde	0.6	0.4	n = 10	433	51
		1.6	n = 3		
3-methyl-crotylalcohol	0.5	—	—	440	49
3-methyl-butyraldehyde	0.3	0.4	n = 10	403	36

with an estimated error of 10 to 20% considering five carbons per molecule. The absence of a plateau for the adsorption of 3-MeCol probably comes from a partial dehydrogenation or cracking of this molecule on the surface. For $I_{C(272\ eV)}/I_{Pt(237\ eV)} = 0.4$, the adsorption curves of 3-MeCal and 3-MeBal have a "plateau," which corresponds to a coverage of one molecule for ten platinum atoms and which may be accounted for by a flat adsorption of these molecules with repulsive interactions on Pt(111). The further increase in the rate of adsorption of 3-MeCal, and the existence of a second plateau near $I_{C(272\ eV)}/I_{Pt(237\ eV)} = 1.6$ may come either from a partial cracking on the surface or from the existence of a second adsorption mode of this molecule, which would correspond to one molecule for three platinum atoms and which would be favoured at high coverages.

Temperature-programmed desorptions have been carried out immediately after various exposures for the three molecules. For each of these molecules one desorption curve has been plotted in Fig. 2. As long as these curves are dissymmetric and the desorption temperatures do not vary with coverage, one can perform a comparative estimation of the adsorption energies using the model established by Chan *et al.* for a nondissociative first order process (15). The model of Chan *et al.* assumes weak interactions between the molecules, which is reasonable at low coverage, simple analytical expressions give the activation energy of desorption, sticking coefficient, and adsorption energy using the spectral peak width and the temperature at which the maximum rate of desorption occurs (see Table 1).

These results show a lower adsorption strength for 3-MeBal and support the fact that 3-MeCal and 3-MeCol have similar reactivities on Pt(111), which suggests a possible competitive hydrogenation process between these two molecules.

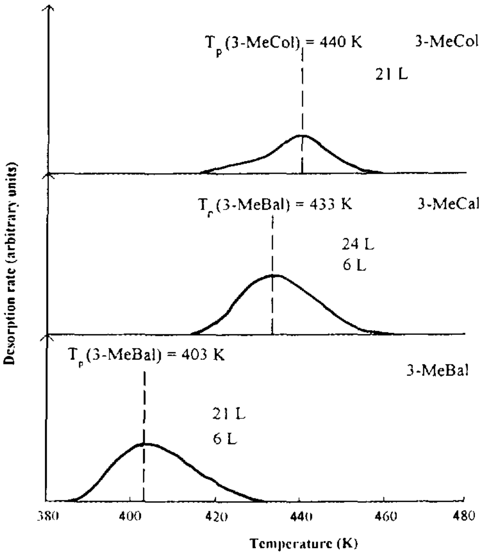


FIG. 2. Thermal desorption profiles of 3-MeCal, 3-MeBal, and 3-MeCol adsorbed on Pt(111) at 353 K after different exposures (expressed in Langmuir units, 1 L = 10^{-6} Torr s). Heating rate $\beta = 20\ K\ s^{-1}$. Desorption rates are plotted in arbitrary units. T_p is the peak maximum temperature.

3.2. *"High"-Pressure Hydrogenation of 3-Methyl-Crotonaldehyde*

The reaction has been carried out under the following "standard" experimental conditions:

$$P_{H_2} = 400\ \text{Torr},\ P_{3\text{-MeCal}} = 20 \times 10^{-3}\ \text{Torr, and}\ T = 353\ \text{K}.$$

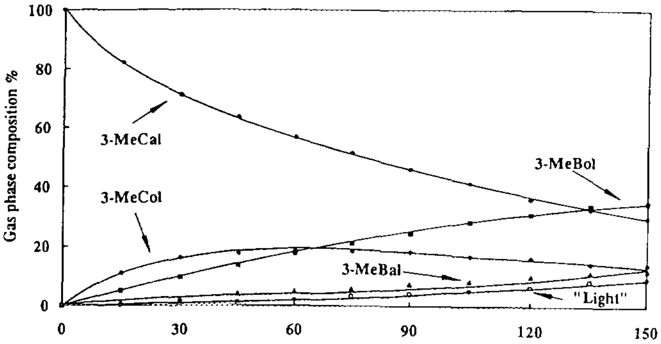


FIG. 3. Hydrogenation of 3-MeCal on Pt(111) with $P_{(H_2)} = 400$ Torr, $P_{(3\text{-MeCal})} = 2 \times 10^{-2}$ Torr, and $T = 353$ K.

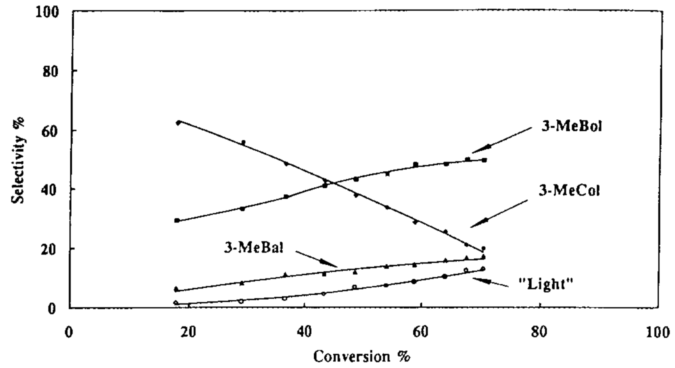


FIG. 4. Selectivity versus conversion for the hydrogenation of 3-MeCal on Pt(111) with $P_{(H_2)}$ = 400 Torr, $P_{(3\text{-MeCal})} = 2 \times 10^{-2}$ Torr, and T = 353 K.

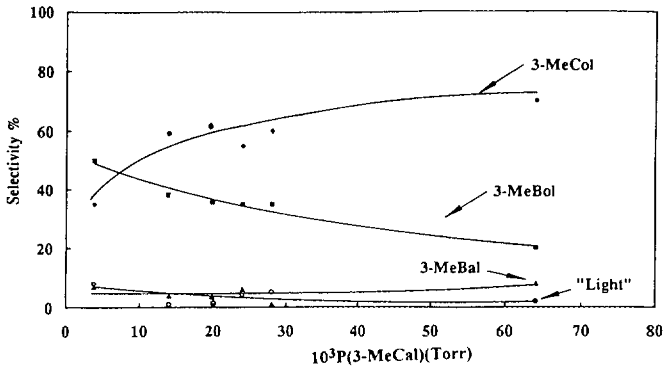


FIG. 6. Influence of the 3-MeCal partial pressure on the selectivity at 10% conversion. T = 353 K, $P_{(H_2)}$ = 400 Torr, and 4×10^{-3} Torr < $P_{(3\text{-MeCal})} < 6.4 \times 10^{-2}$ Torr.

Figure 3 shows the time course of the reaction. It indicates the following:

(i) For the whole reaction, the fractions of 3-MeBal and "light" C_4 and C_5 products (mainly isobutene, but also some fractions of isobutane, methyl-butene and methyl-butane) remain small (<10%);

(ii) at the beginning of the reaction, 3-MeCol is the most abundant product, but there is also a significant fraction of saturated alcohol (3-methyl-butanol). Nevertheless, with increasing conversion the saturated alcohol becomes the main product because of the rehydrogenation of 3-MeCol.

Complementary changes in the saturated alcohol and 3-MeCol are obvious in Fig. 4, in which the selectivity for each product is plotted versus conversion.

The activity has been characterized by the turn-over number (TON), i.e., the number of molecules of 3-MeCal converted per second and per surface atom at the start of the reaction, assuming a surface atomic density of 1.5×10^{15}at/cm^2 for Pt(111):

$$\text{TON} = 20 \times 10^{-2} \text{mol at}^{-1}\,\text{s}^{-1}.$$

The consumption rate decreases with increasing conversion. Nevertheless, the reaction does not seem to be drastically poisoned, since at 60% conversion, the TON is still equal to 4.5×10^{-2} mol at^{-1} s^{-1}.

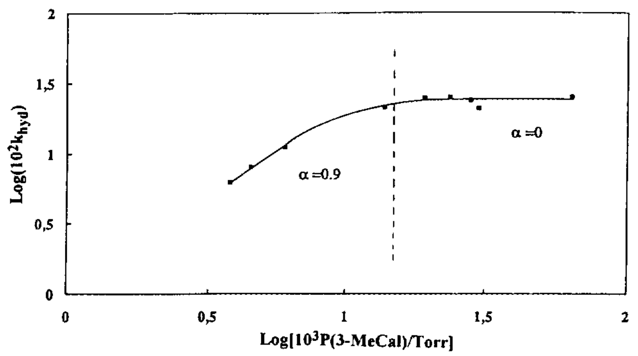


FIG. 5. Rate variation with 3-MeCal partial pressure for the overall hydrogenation; T = 353 K, $P_{(H_2)}$ = 400 Torr, and 3×10^{-3} Torr, < $P_{(3\text{-MeCal})} < 6.4 \times 10^{-2}$ Torr.

Influence of 3-methyl-crotonaldehyde partial pressure. The influence of 3-MeCal pressure on the activity has been investigated between 3×10^{-3} and 64×10^{-3} Torr, for P_{H_2} = 400 Torr and T = 353 K. The kinetic partial order α has been determined at the start of the reaction. Results are plotted in Fig. 5 and are summarized below:

$$3 \times 10^{-3}\,\text{Torr} < P_{3\text{-MeCal}} < 15 \times 10^{-3}\,\text{Torr} \qquad \alpha: 0.9 \rightarrow 0$$

$$15 \times 10^{-3}\text{Torr} < P_{3\text{-MeCal}} < 64 \times 10^{-3}\,\text{Torr} \qquad \alpha = 0.$$

It appears in Fig. 6 that, depending on the 3-MeCal partial pressure, the two main products are 3-MeCol and saturated alcohol, and that the fractions of "light" products and 3-MeBal remain always low. Moreover, when increasing the 3-MeCal partial pressure, the selectivity for 3-MeCol increases. Consequently, with increasing conversion of 3-MeCal, the selectivity for saturated alcohol increases to the detriment of 3-MeCol (see Fig. 4).

Influence of hydrogen partial pressure. As for 3-MeCal, the influence of hydrogen has been investigated at T = 353 K. However, because of the change of kinetic regime with varying 3-MeCal partial pressure, the partial order towards hydrogen (β) has been determined for two different values of the 3-MeCal partial pressure, 7×10^{-3} and 16×10^{-3} Torr. The results are:

$$P_{3\text{-MeCal}} = 7 \times 10^{-3}\,\text{Torr},\ 100\,\text{Torr} < P_{H_2} < 400\,\text{Torr}$$

$$\beta = 0 \text{ or slightly positive}$$

$$P_{3\text{-MeCal}} = 16 \times 10^{-3}\,\text{Torr},\ 100\,\text{Torr} < P_{H_2} < 400\,\text{Torr}$$

$$\beta = 0.5.$$

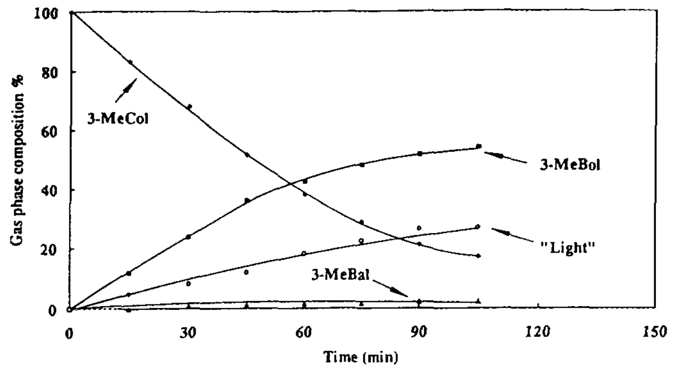


FIG. 7. Hydrogenation of 3-MeCol on Pt(111); $T = 353$ K, $P_{(H_2)} = 400$ Torr, and $P_{(3\text{-MeCol})} = 1.8 \times 10^{-2}$ Torr.

In addition, whatever the 3-MeCal partial pressure, our results have shown that the selectivity is not affected by the hydrogen partial pressure.

3.3. *Hydrogenation of 3-Methyl-crotylalcohol and of 3-Methyl-butyraldehyde*

Hydrogenations of 3-MeCol and of 3-MeBal have been carried out at $T = 353$ K and $P_{H_2} = 400$ Torr. The partial pressures were 18×10^{-3} and 36×10^{-3} Torr respectively for the former and the latter organic compounds. The time courses of these two hydrogenation reactions are plotted in Figs. 7 and 8.

The rate of consumption of 3-MeCol is constant until 50% conversion. This means a zero order with respect to this molecule, which saturates the available surface of the catalyst. The TON at 0% conversion is equal to 15×10^{-2} mol at^{-1} s^{-1}, and thus 3-MeCol and 3-MeCal have similar reactivities on Pt(111). Moreover, besides the formation of saturated alcohol, C_4 and C_5 hydrocarbons appear in the gas phase. The selectivity for hydrocarbons is equal to 25% throughout the reaction. Finally, a very small amount of 3-MeBal is produced through a mesomerism equilibrium; this process, favoured at high temperature, has already been noticed by several authors (16).

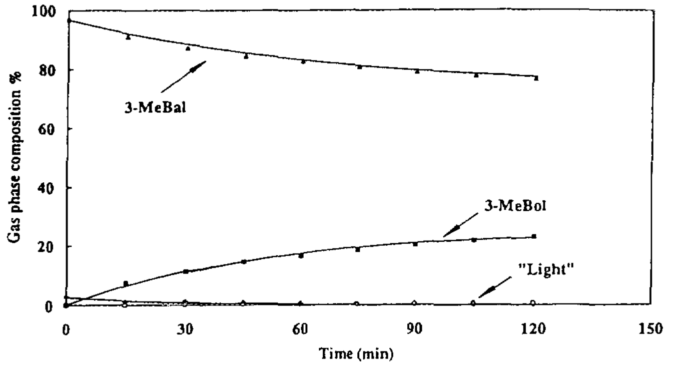


FIG. 8. Hydrogenation of 3-MeBal on Pt(111); $T = 353$ K, $P_{(H_2)} = 400$ Torr, and $P_{(3\text{-MeBal})} = 3.6 \times 10^{-2}$ Torr.

The hydrogenation of 3-MeBal appears to be a slow reaction. Indeed, the TON decreases rapidly to 3×10^{-2} mol at^{-1} s^{-1}. This hydrogenation leads to saturated alcohol, without any hydrogenolysis reaction.

4. DISCUSSION

4.1. *Activity*

The kinetic partial orders obtained from our experiments show that the hydrogenation of 3-MeCal (C_5H_8O) on Pt(111) proceeds with a change in kinetic regime when varying the partial pressure of the organic molecule. In the "high-pressure" kinetic regime ($P_{C_5H_8O} > 15 \times 10^{-3}$ Torr), the zero order with respect to the unsaturated aldehyde indicates that the surface is saturated with 3-MeCal. We propose the existence of C_5H_9O adsorbed species to explain the half unity order with respect to hydrogen according to the same reaction as the one proposed by Gonzo and Boudart for the hydrogenation of cyclohexene on supported palladium (17),

$$H_2 \overset{K_1}{\rightleftharpoons} 2H* \qquad [1]$$

$$C_5H_8O \overset{K_2}{\rightleftharpoons} C_5H_8O* \qquad [2]$$

$$C_5H_8O* + H* \overset{K_3}{\rightleftharpoons} C_5H_9O* \qquad [3]$$

$$C_5H_9O* + H* \xrightarrow{k_4} C_5H_{10}O*, \qquad [4]$$

where the asterisks (*) indicate adsorbed species.

We assume that at 353 K hydrogen chemisorption on Pt(111), step 1, is in equilibrium and is a dissociative process. Under a large excess of hydrogen, the dissociative adsorption of C_5H_8O must be a very slow process and an equilibrated nondissociative adsorption of C_5H_8O is a reasonable hypothesis (step 2). The addition of a first hydrogen is reversible (step 3), the addition of a second hydrogen is the rate-determining step with rate constant k_4 through a Langmuir–Hinshelwood process. This implies that the most abundant species is the half-hydrogenated state C_5H_9O*. Under the preceding assumptions, we have

$$[C_5H_9O*] \gg [*] \gg [H*] \Rightarrow [L] \approx [C_5H_9O*],$$

where $[L]$ is the number of active sites per unit area of metal, $[*]$, $[C_5H_9O*]$, and $[H*]$ are respectively the concentrations of free sites, half-hydrogenated species, and atomic hydrogen. The rate of the overall reaction is then given by

$$V_{\mathrm{hyd.}} = V_4 = k_4[C_5H_9O*]\cdot[H*] = k_4\cdot[L]\cdot K_I^{1/2}\cdot P_{H_2}^{1/2}.$$

In the "low-pressure" regime ($P_{C_5H_8O} < 15 \times 10^{-1}$ Torr), the kinetic partial order towards 3-MeCal goes from 0.9 to 0 when the partial pressure is increased, whereas the hydrogen partial pressure has no influence on the rate of the overall hydrogenation reaction ($\beta = 0$). In the low-coverage region, the initial part of the curve of Fig. 5, we propose that the kinetics are limited by the adsorption of C_5H_8O on the platinum surface. If we assume a Langmuir isotherm, the coverage of the Pt(111) surface with C_5H_8O* species obeys the following law: $\theta_{C_5H_8O} = b \cdot p^n_{C_5H_8O}$, where b is a constant and n varies continuously between 1 at low pressure and 0 at higher pressure. This low coverage of C_5H_8O* may seem surprising at a partial pressure of 10^{-3} Torr; this is due to a preferential adsorption of hydrogen which displaces the isotherm of adsorption of 3-MeCal towards higher pressures. The Langmuir approximation, in particular the absence of interactions, is likely to be valid for values of the coverage below 0.5; for higher values, the reaction is still limited by the adsorption state but the exact meaning of the kinetic order is not known.

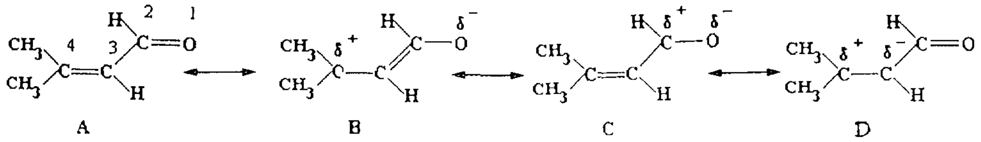
4.2. Selectivity

On the basis of the kinetic results, we arrive at the conclusion that, in the "high-pressure" regime, the most abundant adsorbed species is C_5H_9O*. In these conditions, our results concerning the selectivity indicate that at the start of the reaction, 3-MeCol, which results from the hydrogenation of the C=O bond, is the most abundant product. We can tentatively relate the observed selectivity to the conformation of the C_5H_9O* adsorbed species, which depends on the first addition of hydrogen. The partial positive charges on C_2 and C_4 suggested by the most favoured resonance structure in Scheme 2 make possible a nucleophilic attack by $H^{\delta-}$ species. The presence of these $H^{\delta-}$ adsorbed species has already been tentatively proposed by Noller and Lin to explain the mechanism of hydrogenation of 3-MeCal on Ni–Cu/Al_2O_3 catalysts (18). The almost-filled d orbitals of platinum act as electron pair donors and induce the presence of $H^{\delta-}$ on the surface, through a metal-to-hydrogen electron transfer.

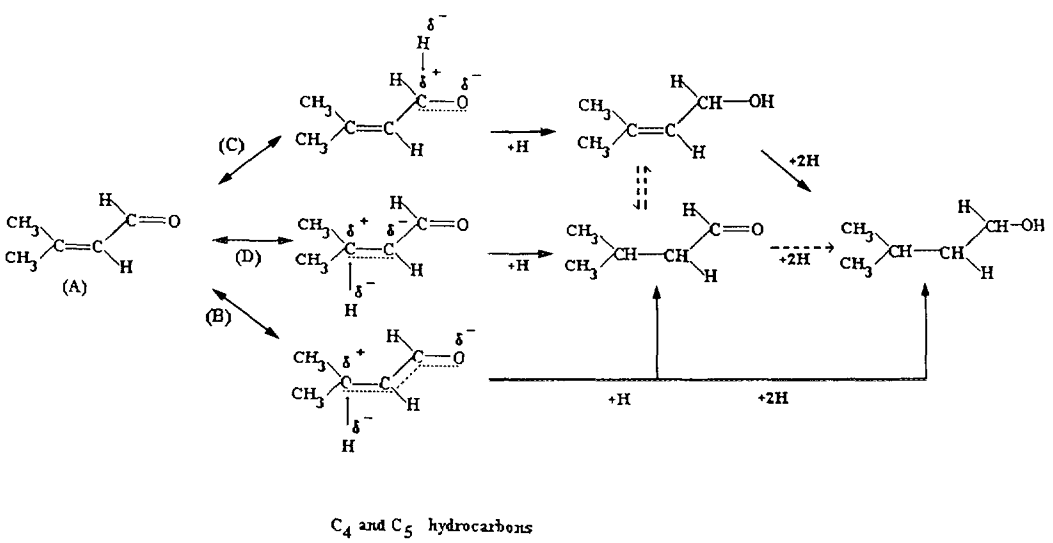
Several reasons may explain why the C=O activation (resonance structure C) is more favoured on Pt(111) than the C=C activation (resonance structure D). First, it is well known in organic chemistry that among the structures shown in Scheme 2 structure C is one of the most abundant. If we suppose that this trend is not affected by the adsorption of the molecule on platinum, we can understand why nucleophilic attacks are more likely to occur on C_2. Second, it is well known that the lower the electronic density on platinum atoms, the more the C=C bond is activated (10). Such atoms with low electronic density, which can exist on surfaces of high rugosity, are absent on Pt(111) and thus the activation of the C=C bond is more difficult on this flat surface. Third, the activation of the C=C bond is difficult because the accommodation of the two methyl groups is hindered by the threefold symmetry of the flat Pt(111) face. Such a steric effect has already been put forward by Beccat *et al.* (19). In the hydrogenations of 3-MeCal and of crotonaldehyde on Pt(111), these authors showed that the selectivity for unsaturated alcohol was higher in the former case because of the additional methyl group. The above interpretation can account for the high selectivity for 3-MeCol, and the low selectivity for 3-MeBal at the beginning of the reaction (Fig. 4).

The selectivity (extrapolated to 0% conversion) for saturated alcohol is equal to 20%. This implies that part of the produced saturated alcohol comes from a double hydrogenation of 3-MeCal without desorption of the intermediary product. This is likely to occur through the resonance structure B in Scheme 2, where the whole conjugated system is activated. This activation mode is stabilized by mesomerism, but requires the accommodation of the C=C bond, which is less favoured than the single activation of the C=O bond. This activation mode has already been proposed in one of our recent papers for the hydrogenation of 3-MeCal on Pt(100) to explain the formation of hydrocarbons (20). Besides the formation of saturated alcohol, this activation mode can account for the formation of the small amount of saturated aldehyde and of C_4 and C_5 hydrocarbons by hydrogenolysis reactions.

In the following part of the discussion, we focus on the



SCHEME 2. Mesomeric equilibria involving the most likely structures of 3-MeCal.



SCHEME 3. Reaction scheme for the hydrogenation of 3-MeCal on Pt(111). Slow unfavoured reactions are denoted by dashed arrows.

influence of the reactant pressures on the variations of the selectivities. Figure 6 indicates that an increase in the 3-MeCal partial pressure increases the selectivity for 3-MeCol and complementarily decreases the selectivity for saturated alcohol. The reverse trend is observed for the variation of selectivity with conversion (Fig. 4) and may be explained by a change in the gas-phase compositions throughout the reaction. The time course of the reaction in Fig. 3 indicates that 3-MeCol is rehydrogenated on Pt(111) before the complete disappearance of 3-MeCal, which means that the hydrogenations of these two molecules are competitive. At high 3-MeCal partial pressure, the surface is saturated with this molecule and the readsorption of 3-MeCol is difficult. At lower partial pressure the rehydrogenation of 3-MeCol becomes easier to the benefit of saturated alcohol. Support for this competitive process is given both by the hydrogenation of 3-MeCol and 3-MeBal and by low-pressure adsorption and thermal desorption experiments. Figures 1 and 2 show that, on the one hand, 3-MeCal and 3-MeCol have comparable sticking coefficients and adsorption energies, and they also display similar reactivities (Fig. 7). On the other hand, 3-MeBal has a lower sticking coefficient and also a lower adsorption energy which can account for its lower reactivity on Pt(111) (Fig. 8). Under the "standard" experimental conditions, the concentration of this saturated aldehyde remains low and its rehydrogenation is not possible. It has already been noted that the hydrogenation of the saturated aldehyde is more difficult than the hydrogenation of unsaturated alcohol (21). This may be due to energetic reasons because of the higher C=O energy bond (715 kJ/mol) compared to the C=C energy bond (615 kJ/mol).

The above discussion suggests the following sequence of hydrogenation probabilities:

$$\begin{aligned}&\alpha,\beta\text{-unsaturated C=O bond}\\&\quad > \text{concerted C=C/C=O bonds}\\&\quad > \text{alcohol C=C bond} > \text{saturated C=O bond.}\end{aligned}$$

A reaction scheme for the hydrogenation of 3-MeCal on Pt(111) is given in Scheme 3. A double hydrogen addition to the B surface intermediate has been considered in order to account for the initial selectivity towards the saturated alcohol close to 18%.

This reaction scheme is quite different from what has been found in the same experimental conditions for the hydrogenation of this molecule on Pt(100) (20). Because of the fourfold symmetry of the Pt(100) the accommodation of the two methyl groups is easier. The activation of the whole conjugated system via resonance structure B is then more favoured and thus C_4 and C_5 hydrocarbons producd by hydrogenolysis reactions are the main products. The comparison between these two faces proves the importance of the structure of the single crystal platinum surface. It determines the most favoured activation mode and thus the observed selectivities.

5. CONCLUSIONS

For the hydrogenation of 3-MeCal on Pt(111) our results show that there are two kinetic regimes. In the "low-pressure" regime ($P_{3\text{-MeCal}} < 15 \times 10^{-3}$ Torr), the great excess of hydrogen displaces the adsorption isotherm of the organic compound and the reaction is limited by the available quantity of adsorbed 3-MeCal. In the "high-pressure" regime ($P_{3\text{-MeCal}} > 15 \times 10^{-3}$ Torr), the C_5H_9O* adsorbed species is proposed to be the most abundant intermediate on the surface and the addition of a second hydrogen to this adsorbed species is the rate-determining step.

At low conversion, the selectivity for 3-MeCol is high. It has been accounted for by the nature of the most abundant C_5H_9O* isomer. The latter is proposed to be formed by nucleophilic attacks, mainly governed by steric effects. The influence of the 3-MeCal partial pressure on selectivity can be simply explained in terms of competitive hydrogenations of 3-MeCal and 3-MeCol.

This study shows that the hydrogenation of an α,β-unsaturated aldehyde such as 3-MeCal on platinum is structure sensitive. Similar hydrogenation experiments of this molecule on other single crystal platinum surfaces are currently under study in order to investigate further the influence of the geometry of the surface on the selectivity.

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