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Competitive C=C and C=O Adsorption of α–β Unsaturated Aldehydes on Pt and Pd Surfaces in Relation with the Selectivity of Hydrogenation Reactions: A Theoretical Approach

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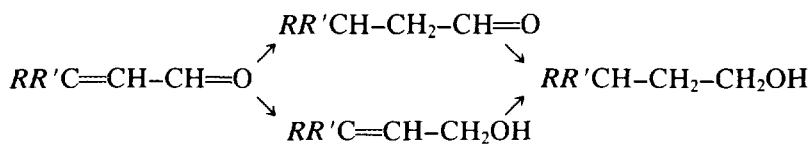
The adsorption geometries of acrolein, crotonaldehyde, methylcrotonaldehyde (prenal), and cinnamaldehyde on Pt and Pd surfaces have been studied by means of semiempirical extended Hückel calculations: Pt(111), Pt(100), Pt(110), and Pd(111) surfaces, and steps on Pt(111) have been compared. Depending on the face and the substituents of the organic molecule, the adsorption geometries are totally different: a di-σ form is preferred on Pt(111), a planar η_4 one on Pd(111) and Pt(100), and a π_{CC} one on Pt(110) and on the step. These preferred adsorption modes allow one to explain the selectivity observed during the hydrogenation of prenal on these well-defined surfaces. The results obtained in this work also allow one to understand the behavior of different metal catalysts towards the hydrogenation of the α–β unsaturated aldehydes. © 1995 Academic Press, Inc.

I. INTRODUCTION

The selective hydrogenation of the α–β unsaturated aldehydes is a well-documented reaction with important applications in the industrial field. It gives three types of products following Eq. [1]: the C=C double bond is hydrogenated giving a saturated aldehyde or the C=O double bond is involved yielding an unsaturated alcohol; finally, a total hydrogenation can occur and a saturated alcohol is obtained. The most important product, from an industrial viewpoint is the unsaturated alcohol. This compound is also the most difficult to obtain (1) since it is known that, generally, a C=C double bond hydrogenates more easily than a C=O double bond (2). Therefore many studies have been devoted to improving the selectivity towards the unsaturated alcohol, especially by choosing efficient supports (3–5), by adding promoters to metals of Group VIII (6–8) or by using a metal alloy (9–12). It is thus important to identify which parameters orientate the hydrogenation towards one or the other double bond of the molecule. In the case of catalytic hydrogenation, it is generally assumed that the reactive bond is the one involved in chemisorption on the surface. Therefore the problem of selective hydrogenation can be reduced in a first rough approximation to determine the electronic factors which control the adsorption mode of α–β unsaturated aldehydes on the surface. In previous work, we have studied in detail from a theoretical viewpoint the adsorption of both isolated double bonds (C=C(4); C=O(5)) on the well-defined (111) and (110) surfaces of platinum and palladium and on steps on Pt(111). These results can be used as a basic starting point to study the competitive adsorption of these two double bonds in α–β unsaturated aldehydes.

Our calculations are related to reactions at the solid-gas interface. Most of the experimental studies, however, are made in solution and with dispersed catalysts. Nevertheless, a few reactions have been realized in the gas phase and with well-defined metallic surfaces (10, 15). The hydrogenation of crotonaldehyde and methylcrotonaldehyde (prenal) has been studied over Pt(111) and $Pt_{80}Fe_{20}$(111) single crystals (10). The selectivity in unsaturated alcohol increases when the C=C bond is substituted by a second methyl group and when changing the catalyst from Pt(111) to $Pt_{80}Fe_{20}$(111). Therefore crotonaldehyde on Pt(111) selectively yields the saturated aldehyde and prenal preferentially yields the unsaturated alcohol, although the selectivity is moderate. The other papers (15) deal with the hydrogenation of prenal on



[1]

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Pt(100) (15a), Pt(111) (15b), Pt(110) (15c), and steps on Pt(111) (15c). On Pt(111), the same result is obtained as in Ref. (10): the unsaturated alcohol is the major product. At high conversion, saturated alcohol coming from total hydrogenation is also produced. Light compounds arising from cracking of the molecule are present in a very small amount. For prenal on Pt(100), the main difference with Pt(111) is the large amount of light products even at low conversion. The three possible hydrogenated products are obtained, i.e., the saturated aldehyde, the unsaturated, and the saturated alcohols, but in low yields. The selectivity in unsaturated alcohol increases with the partial pressure of prenal. On Pt(110), hydrogenation of prenal gives the saturated aldehyde with high selectivity and a small fraction of saturated alcohol. At high conversion, this aldehyde is further hydrogenated to saturated alcohol. The amount of light products is low. On a step of Pt(111), the unsaturated alcohol is the major product. However, the saturated alcohol and the saturated aldehyde are also obtained. At high conversion, the unsaturated alcohol is totally hydrogenated and the saturated alcohol becomes the major product together with the saturated aldehyde. Light products are present in small amount. At high partial pressure of prenal, the unsaturated alcohol is the major product. These experimental results show, therefore, that the selectivity of the hydrogenation of α–β unsaturated aldehydes is strongly dependent on the nature of the crystal face.

Experimental papers dealing with the adsorption modes of α–β unsaturated aldehydes are rare. Two recent works are concerned with the adsorption of acrolein on Rh(111) and Pd(111) (16). In both, acrolein is found to be initially bound in an η_2(CO) configuration which upon heating yields an η_4 (C, C, C, O) mode.

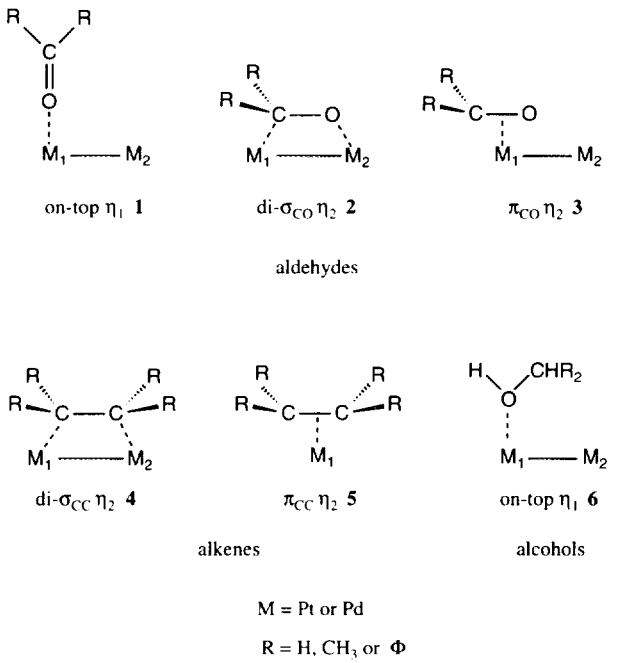
The purpose of the present work is to analyze the factors which govern the adsorption of α–β unsaturated aldehydes towards the C=O or the C=C bond, by using the results previously obtained for the simple ethylenic compounds or aldehydes considered as synthons (13, 14). We will first recall these results and add some new molecules which have not been studied before. Effectively, the formation of the dihydrogenated product can depend on the relative adsorption strength of the monohydrogenated products compared with the reactant (unsaturated aldehyde). We will therefore study the adsorption of simple compounds arising from the hydrogenation of α–β ethylenic aldehydes, that is, for example, saturated and unsaturated alcohols.

Acrolein will be studied in detail as a model for α–β unsaturated aldehydes. Its adsorption modes on Pt(111), Pt(100), Pt(110), and Pd(111), and steps will be considered and compared. Substituents will then be added on the ethylenic double bond: one CH_3 (crotonaldehyde or butenal), two CH_3 (prenal or 3-methylbutenal), or a phenyl group (cinnamaldehyde) giving the most experimentally studied unsaturated aldehydes. These adsorption properties of α–β unsaturated aldehydes on different faces will finally be analyzed in terms of qualitative trends for selective hydrogenation on real catalysts.

II. THEORETICAL MODEL

The calculation procedure has already been described elsewhere (13, 14). The extended surface of the metals is modelled by finite clusters. On these clusters, a correction of the edge effects has been performed, dividing them into a core part containing all atoms with their complete first neighbor environment, and an outer shell including all atoms whose coordination is affected by the cluster formation. The molecular orbitals of the entire cluster are calculated and projected on the core part. The electronic filling of these orbitals is done until the core part receives the correct electron count. This contrasts with the usual calculation where the electron filling is stopped when the entire cluster has the correct electron count and ensures a better description of the "true" surface, where the adsorption takes place. A cluster of 49 atoms (core of 15 atoms) is used for a (111) face, 44 atoms (core of 12 atoms) for a (110) face and 52 atoms (core of 16 atoms) for a (100) face; these clusters are called Pt_{49} (or Pd_{49}), Pt_{44}, and Pt_{52}, respectively. The calculations are of the extended Hückel type. The electronic parameters for carbon, oxygen, hydrogen, platinum, and palladium have been carefully chosen in order to obtain a coherent description of the electronic structure. The determination of these parameters and their values are given in Refs. (13) and (14). Because of the large number of orbitals, a Gaussian broadening of the discrete spectrum has been used in order to represent the results in terms of density of states (DOS) and crystal orbital overlap population (COOP) curves, usual for studying periodic infinite solids.

Among all possible adsorption modes of the unsaturated functions only the best geometries are considered. These basic coordinations are shown in Scheme 1: for aldehydes, the η_1 on-top adsorption **1** by the oxygen atom and the η_2 lateral interactions **2** and **3** through the double bond, for alkenes, two η_2 lateral adsorption modes **4** and **5** through the double bond and for alcohols the η_1 on-top adsorption **6** by the oxygen lone pair. The adsorption of the multifunctional molecules considered in this paper will be built from a combination of these simple coordination modes. The metal atoms are in their bulk geometry (Pt–Pt = 2.77 Å; Pd–Pd = 2.75 Å) and the bonding distances are kept fixed in all models: *M*–O, 2 Å; *M*–C, 2.1 Å; C–C(CH_3), 1.52 Å; C–C (Φ), 1.50 Å; C–C in Φ, 1.40 Å. For the η_1 interaction, the gas phase geometry of the molecule is used (C=C, 1.34 Å; C=O, 1.22 Å).



SCHEME 1

For the η_2 adsorption, the molecule is pyramidalized in the following way: bond lengths, bond angles and torsional angles are varied linearly and optimized with respect to a parameter "h" which represents the hybridization between the sp^2 geometry ($h = 0$) and the sp^3 geometry ($h = 1$). For each adsorption type, either planar η_1 or pyramidalized η_2, the best conformation of the substituents has been searched.

Even if we consider a fixed M–C or M–O bond length, an adsorption minimum does exist for these molecules in the calculations: the "optimized" bond length is 0.1–0.2 Å shorter than the standard one used here. This is due to the absence of nuclei-nuclei interactions (repulsive) in the EH framework (32). The same M–C or M–O distance is therefore used for all adsorption modes. However, these distances are known from model organometallic systems and from LEED crystallography to be rather constant (sum of covalent radii). A variation of 0.1 Å in these bond lengths (typical upper bound for such a M–C or M–O variation) results in a change of the adsorption energy of 2–3 kcal/mol.

As introduced in previous papers (13, 14), an important step for the analysis of the binding of molecules on metal surfaces is the distinction between two-electron stabilizing interactions and four-electron destabilizing ones. The former are quantified by the sum ET of the absolute values of the electron transfers between the organic molecule and the cluster, either electron donation or back bonding and involve the classical frontier orbital interactions. The latter involve the interactions between occupied orbitals on the molecule and full states on the surface. From perturbation theory, the interaction between two occupied orbitals can be qualitatively described by the square of their overlap. For a given occupied molecular orbital of the organic molecule, these squared overlaps are summed over all occupied states of the cluster, in order to yield its total individual contribution to the electronic repulsion. These contributions per adsorbate occupied molecular orbital can finally be added to give the total square overlap value S^2 between the adsorbate and the surface filled states. The binding energy BE (taken as the difference between the energy of the system cluster + adsorbate and the energies of the naked cluster and the free molecule in its gas phase geometry) reflects the balance between the two types of interactions. A negative value means a bonding adsorption.

This extended Hückel approach enables us to perform a series of calculations on several adsorption modes of organic molecules on surfaces modelled by large clusters but has well-known limitations. Such a method is most powerful in the qualitative comparison between related systems and in the molecular orbital analysis of their differences. Our purpose is to present here such a comparative study for the possible adsorption modes of α–β unsaturated aldehydes on a Pt or Pd surface in order to determine the qualitative trends when changing substituents on the molecule or the type of metal surface, in relation with the selective hydrogenation of these adsorbates.

III. ADSORPTION OF BASIC FRAGMENTS: SUBSTITUENT EFFECTS

III.1. Adsorption on Pt(111)

The results obtained for formaldehyde, acetaldehyde and acetone have been commented on extensively in Ref. 14 and will be recalled here briefly (Table 1). The preferred adsorption mode is η_2 di-σ for the aldehydes but is η_1 on-top for acetone. We have explained in detail previously that this result is essentially due to a steric interaction of the methyl substituents with the surface in the di-σ geometry as indicated by the increase of the repulsive interaction (S^2 value) from H_2CO to $(CH_3)_2$ CO, together with a small decrease of the electron transfers.

Compared to the η_1 on-top form of formaldehyde, the η_1 on-top form of methanol is less stable. However, the total electron transfer is better (0.32 versus 0.29). This is due to the mixing of the oxygen lone pair with a π_{CH_3} orbital that reinforces its donor character. Once again, the repulsive four-electron interactions are determinant. The presence of a methyl on the oxygen introduces a destabilization compared to formaldehyde (S^2 = 3.48 compared to 2.74). The interaction between the methyl

TABLE 1

Binding Energies (in kcal/mol) for the Adsorption Modes of Simple Unsaturated Molecules

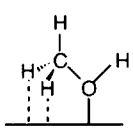
	Pt(111)	Pd(111)	Pt(110)
H_2CO			
On-top	−11.0	−10.4	−13.4
Di-σ	−22.9	−31.8	−27.0
π	−5.7	−19.0	−13.0 (−11.7)[a]
CH_3CHO			
On-top	−11.0	−10.4	
Di-σ	−14.7	−25.5	
π	+2.2	−13.3	
$(CH_3)_2CO$			
On-top	−11.0	−10.3	−13.3
Di-σ	−6.1	−19.1	−15.2
π	+10.3	−7.8	−4.1 (−1.7)[a]
CH_3OH			
On-top	−7.5	−8.3	
C_2H_4			
Di-σ	−15.3	−18.2	−19.5
π	−7.8	−15.9	−19.3 (−15.0)[a]
$CH_3CH{=}CH_2$			
Di-σ	−10.8	−15.8	−17.6
π	+0.6	−13.5	−17.0
$(CH_3)_2C{=}CHCH_3$			
Di-σ	−0.7	−13.2	
π	[b]	−5.1	
$\Phi CH{=}CH_2$			
Di-σ	−8.6	−22.2	
π	−4.8	−26.8	

Note. A negative value means a bonding state.

[a] The value in parentheses concerns the $\pi(\parallel)$ adsorption (see text) and the other value the $\pi(\perp)$ adsorption.

[b] Not calculated because too unstable.

and the surface has been experimentally detected by the presence of a ν(CH) vibration mode at 2930 cm^{-1} in the electron energy loss (EEL) spectrum of CH_3OH adsorbed on Pt(111) (17). Our calculation shows also the existence of a small positive overlap population between the hydrogens of the methyl group and the surface (**7**),



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together with a small negative overlap population between the carbon and the surface.

The effect of substituents on an ethylenic C=C double bond has been studied following the same way. The adsorption modes of propene, 2-butenes, 2-methyl 2-butene, and styrene have been compared and explained in Ref. (13b). Af for the η_2 form of aldehydes, the substitution by methyls or a phenyl results in a decrease of the binding energies, both for the di-σ_{CC} and the π_{CC} modes. This is also due to an increase of the repulsive interactions of the substituents with the surface which cannot be compensated by the concomitant increase of the electron transfer, due to a better donor character.

In conclusion, alkyl and aryl subtituents destabilize the η_2 adsorption modes of both carbonyl and ethylenic compounds on a Pt(111) surface because of steric-like repulsions between the substituents and the surface.

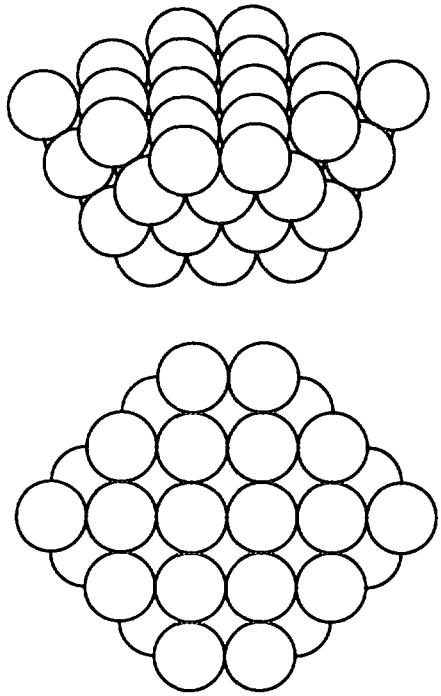
III.2. Adsorption on Pd(111)

The important points for comparing Pd and Pt is that the Pd bulk has a slightly higher Fermi level than Pt and, more important, a *d*-band width significantly reduced compared to that of Pt, which means that the radial expansion of the Pd *d* orbitals is smaller than that of the Pt *d* orbitals. As a consequence, the overlaps of these orbitals with the orbitals of the adsorbate molecule are reduced on Pd and the result is a weakening of the interactions between the molecule and the surface, especially the four-electron interactions whose preponderant role has already been underlined. Therefore, the more important the four-electron interactions, the more stabilized are the corresponding adsorption geometries when Pd replaces Pt. This is the reason why the η_2 modes are more strongly bound on Pd(111) than on Pt(111), particularly the π geometries (13, 14) (see Table 1). For example, the best adsorption form for acetone on Pd(111) is the di-σ one while it was on-top on Pt(111). Due to the decrease of the repulsive interactions on Pd, the effect of the substitution on the binding energy is much reduced and even 2-methyl 2-butene is bound to the surface.

Styrene represents a special case since its adsorption energy is larger than that of ethylene, especially the π_{CC} geometry. In fact, we have shown that the phenyl ring takes part in the bonding in a kind of trihapto structure (13b).

III.3. Adsorption on Pt(110)

The results for adsorption of formaldehyde, acetone and ethylene are given in Table 1. The (110) face is more open than the (111) face since each surface atom has seven neighbors instead of nine. As explained in previous papers (13, 14) this results in smaller four-electron repulsive interactions on Pt(110) than on Pt(111). Therefore, all adsorption geometries have a better binding energy on Pt(110) especially the η_2 ones, for which the repulsive interactions are important on Pt(111) and significantly released on Pt(110). We have also seen that the π geometries are more sensitive than the di-σ ones to these repulsive interactions. As a consequence the π geometries are



SCHEME 2

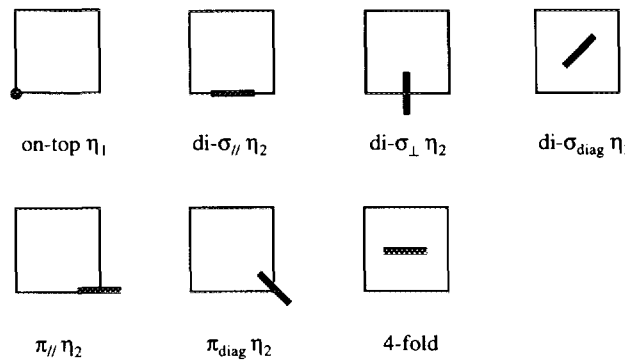
more stabilized on Pt(110). Because of the anisotropy of the (110) surface, there are two kinds of π geometries, one parallel and the other perpendicular to the atomic row. In the $\pi(\perp)$ geometry, the repulsive interactions are even more reduced owing to the suppression of the interactions with the neighboring atoms in the same row.

The systematic study of the substituent effects has only been undertaken on Pt(110) for the C=O function (14b). The substituted molecules being more sensitive to repulsions, the η_2 forms are more stabilized on Pt(110) in comparison with Pt(111). This is illustrated by the results obtained for acetone which prefers the η_2 di-σ geometry on Pt(110), contrary to Pt(111), and can be extended to the substituted ethylenic compounds.

III.4. Adsorption on Pt(100)

The (100) face of platinum has not been considered in our previous papers and therefore will be presented here in more detail for formaldehyde and ethylene. The (100) surface is represented by a cluster of 52 atoms shown in Scheme 2, of comparable size with clusters used before for Pt(111) and Pt(110). The surface layer is a square lattice. Beside the usual on-top, di-σ (called here di-$\sigma(\|)$) and π (called here $\pi(\|)$ adsorption geometries, one can find new adsorption modes as depicted in Scheme 3.

Two forms can be discarded, the di-$\sigma(\perp)$ and the 4-fold ones. Their binding energies in the case of formaldehyde are +22.5 and −3.2 kcal/mol respectively. For these two



SCHEME 3

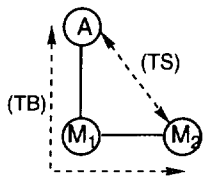
forms, both C and O interact with two Pt atoms. We have already explained (14) that on platinum, which has a broad and almost filled *d*-band, adsorption forms involving many metal atoms show large two-electron interactions but also very strong repulsive four-electron interactions, which results in poorly stable situations.

The binding energies for the other adsorption geometries shown in Scheme 3 are given in Table 2. For both formaldehyde and ethylene, the best form is the di-$\sigma(\|)$ one, as was the case on the other studied surfaces (111) and (110) (13, 14). The hybridization has been optimized for C_2H_4 and the same parameter as on Pt(111) has been found (h = 0.8). As in the case of the adsorption on Pt(110), the energy difference between the di-$\sigma(\|)$ and the $\pi(\|)$ forms is smaller for the adsorption on Pt(100) than it is on Pt(111). By comparison with previous results (13, 14) we find that the repulsions on Pt(100) are intermediate between those on Pt(111) and on Pt(110). The total electron transfer does not vary greatly between the three faces but is nevertheless smaller on Pt(100). These results can be explained by comparing the metal atom environment on the three surfaces. On a (100) surface, each atom

TABLE 2

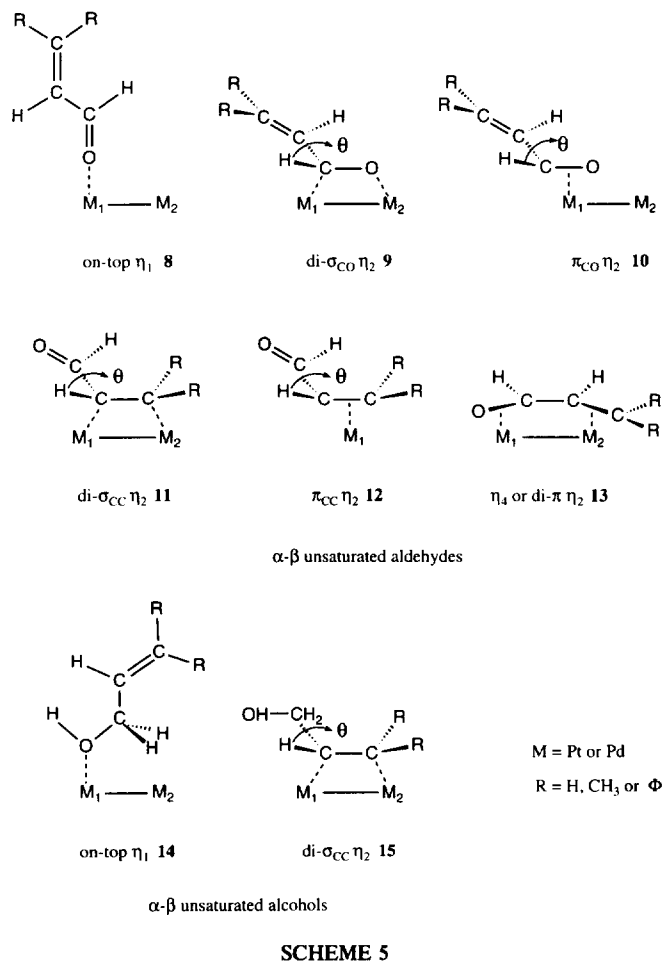
Binding Energies (BE in kcal/mol), Total Electron Transfers (ET), and $S^2 \times 10^2$ for Adsorption of Formaldehyde and Ethylene on $Pt_{52}(100)$

	On-top η_1	Di-$\sigma(\|)$ η_2	Di-σ(diag) η_2	$\pi(\|)$ η_2	π(diag) η_2
H_2CO					
BE	−8.7	−22.6	−10.8	−8.4	−6.1
ET	0.29	1.22	1.27	1.02	1.02
S^2	2.65	4.49	6.22	4.33	4.56
C_2H_4					
BE	—	−15.9	+0.28	−11.6	−9.7
ET	—	1.36	1.41	0.96	0.96
S^2	—	8.22	10.64	7.93	8.32



SCHEME 4

has eight neighbors, four in the first layer and four in the second one. Therefore its coordination is intermediate between that on a (111) face (9) and that on a (110) face (7). This environment of the surface atom has only a small effect on the attractive interactions with an adsorbate since the orbitals involved in the adsorption are mainly d_{z^2} and d_{xz}, which are perpendicular to the surface and therefore little affected by a change in coordination. On the contrary, repulsive interactions are very sensitive to the surface site coordination. Two types of metal atoms can be distinguished on the surface: those directly bonded to the adsorbate (M_1) and those which have only secondary overlaps with the molecule (M_2) (see Scheme 4). The repulsive interactions between the adsorbate and metal atoms M_2 can happen either by a direct through-space overlap (TS) or by an indirect through-bond overlap (TB) via the orbitals of atoms M_1 (14). The former type is predominant. These four-electron repulsions coming from surface atoms coordinated to the site but not directly bonded to the molecule represent a large part of the total repulsion and, as a consequence, the less coordinated the metal atoms on the surface, the smaller are the repulsive interactions with the adsorbate. This explains why the repulsions decrease in the order Pt(111), Pt(100), Pt(110).



SCHEME 5

The result of the balance between attractive and repulsive interactions is that both formaldehyde and ethylene have a similar behavior on Pt(100) and Pt(111): they have the same preferred adsorption mode (di-σ) with the same binding energy and the same hybridization. This latter point is in agreement with experimental data (18). It is shown indeed that ethylene has the same EEL spectrum on Pt(111) and on Pt(100). This means that the geometry is identical on both surfaces.

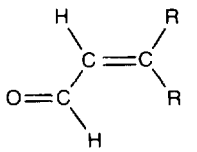
In conclusion to this section, the adsorption modes of a C=C or a C=O double bond and of an alcohol function have been considered on various surfaces. The preferred forms have been explained by means of electronic and steric arguments. These basis functions will now be considered to form complex molecules and their competitive adsorption will be studied in the light of the previous results.

IV. ADSORPTION OF COMPLEX MOLECULES: α–β UNSATURATED ALDEHYDES AND ALCOHOLS

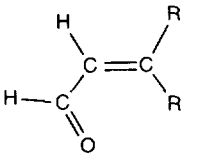
In this section, we will treat in detail the adsorption modes of acrolein on Pt(111), Pd(111), Pt(110), and Pt(100) surfaces. The case of a step on Pt(111) will also be addressed. Then the influence of substituent groups on the preferred adsorption modes will be underlined. The following molecules will be considered: *trans*-2-butenal or crotonaldehyde, methyl-3-butenal or prenal, phenylpropanal or cinnamaldehyde. Finally, the adsorption of propenol and 3-methyl-2-butenol, resulting from the hydrogenation of acrolein and prenal, will also be studied, since their adsorption can be competitive with that of the reactants. For these polyfunctional molecules, several possible structures can be compared. For adsorption through the C=C double bond, these aldehydes are just alkenes substituted by a CHO group and the considered geometries are then di-σ_{CC} and π_{CC} (see Scheme 5). For adsorption through the C=O double bond, they are aldehydes substituted by a vinyl group and the considered geometries are on-top, di-σ_{CO} and π_{CO}. However, a new structure can be envisaged where the adsorption involves both the C=C and the C=O double bonds, in a quasi

planar geometry. This form **13** is called η_4 in Scheme 5. Unsaturated alcohols can be considered as substituted alcohols or alkenes and hence two possible adsorption geometries can exist, namely on-top and di-σ_{CC}.

For gas phase α–β unsaturated aldehydes, the best conformation is trans (**16a**). However, on surfaces, owing to some supplementary interactions, the *cis* (**16b**) can become more stable, as will be shown in the following.



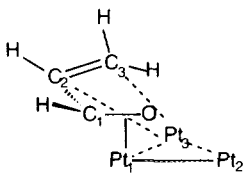
16a



16b

IV.1. Adsorption on Pt(111)

IV.1.a. Acrolein CH_2=CH–CHO. For each η_2 adsorption mode (CC or CO), the best conformation of the substituent (either CH_2=CH or CHO) has been searched by varying the dihedral angle CCCO called θ (see Scheme 5). The adsorption through the C=O bond is presented first. For the di-σ_{CO} geometry, where the pyramidalization is total (h = 1), the best conformation is the trans one with $\theta = -160°$. This rotation allows the π_{CC} orbital to become parallel to the hybridized π_{CO} orbital and therefore restores the conjugation. The cis configuration is preferred for the π_{CO} geometry (θ = 20°). A small stabilizing interaction occurs between Pt_3 and the vinyl group (see **17**) so that this group prefers to come nearer the surface, which tends to reduce the hybridization. The overlap populations are 0.14 and 0.09 between Pt_3 and C_3 and C_2 respectively.



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The binding energies (BE) are given in Table 3. Despite this secondary interaction, the π_{CO} form remains far less stable than the di-σ_{CO} one, as was the case for simple aldehydes. Let us compare the results with those obtained for acetaldehyde CH_3CHO (Table 1). For the on-top geometry, there is no difference; the methyl and the vinyl substituents behave similarly. This comes from the fact that the molecular orbitals involved in the on-top adsorption are the oxygen lone pairs which are localized on oxygen and only slightly influenced by substituents on the carbon. For the di-σ_{CO} geometry, the BE is slightly higher for acrolein, with a better electron transfer and a larger S^2. The better electron transfer is easily explained: by conjugation with the vinyl group, the π^*_{CO} orbital goes down in energy and becomes lower than in formaldehyde, yielding a better transfer. In CH_3CHO, the methyl group, a σ-donor, induces an opposite situation.

Let us consider now the adsorption of acrolein through the C=C bond. For the di-σ_{CC} geometry, where the hybridization parameter is 0.8, the rotation angle θ has been varied and the binding energy has been plotted versus θ in Fig. 1 (θ = 0° and θ = 180° correspond to *cis* and *trans* configurations, respectively). Three minima appear, for θ = 30°, 120°, and 210° (−150°), with binding energies of −13.8, −15.6, and −14.6 kcal/mol respectively. The first and the third ones correspond to the *cis* and the *trans* conformations with a rotation of 30° allowing the conju-

TABLE 3

Binding Energies (BE in kcal/mol), Total Electron Transfers (ET), and $S^2 \times 10^2$ for Adsorption of Acrolein on Pt_{49}(111), Pd_{49}(111) and Pt_{52}(100)

	On-top	Di-σ_{CO}	Di-σ_{CC}	π_{CO}	π_{CC}	η_4
Pt(111)						
BE	−11.0	−15.7	−17.8	−3.6	−11.2	−8.3
ET	0.26	1.27	1.66	1.26	1.28	1.63
S^2	2.67	6.19	11.85	8.77	11.85	13.08
Pd(111)						
BE	−10.5	−26.2	−26.7	−18.3	−25.5	−31.9
ET	0.20	1.24	1.24	1.02	1.03	1.38
S^2	1.54	3.37	7.35	4.83	7.07	7.97
Pt(100)						
BE	−8.8	−16.3	−16.6	−2.9(*trans*)	−16.5	−27.9
ET	0.29	1.24	1.72	1.02	1.25	1.91
S^2	2.58	5.59	11.68	5.19	10.55	13.65

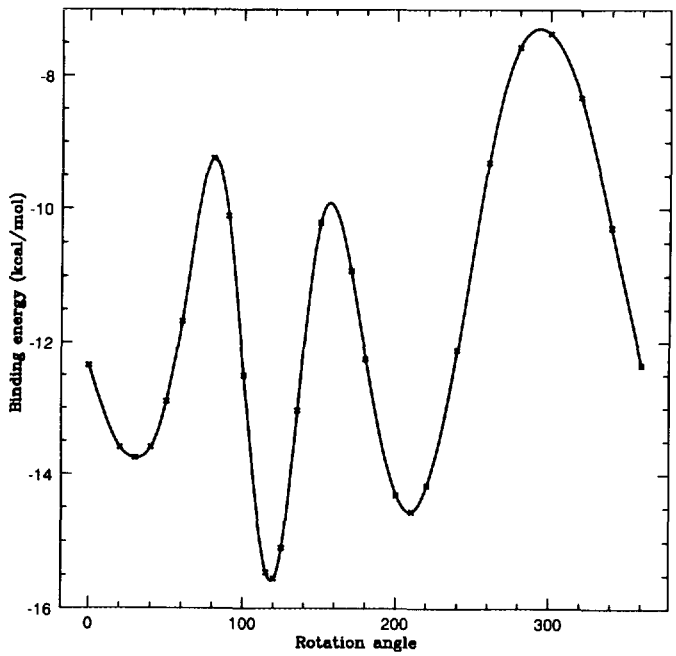


FIG. 1. Di-σ_{CC} geometry for acrolein on $Pt_{49}(111)$. Variation of the binding energy versus the rotation angle θ shown in Scheme 5.

gation between the π_{CO} and the hybridized π_{CC} orbitals to be restored, as explained before. The binding energy is better than that of propene (Table 1). Effectively, the electron transfer (1.46 e^-) is better and, above all, the repulsive interactions are far smaller ($S^2 = 8.69 \times 10^{-2}$ versus 10.17×10^{-2}). The CHO electron-acceptor and the CH_3 electron-donor groups have opposite effects on the π^*_{CC} orbital and therefore the back-bonding electron transfer into this orbital is better for acrolein than for propene. Both groups induce a shift up of the π_{CC} orbital so that the donation transfer from it is roughly the same. Nevertheless, the main difference between the CHO and the CH_3 groups is the lower steric hindrance of the former.

The second minimum is the most interesting. It corresponds to a conformation where the two double bonds (or former double bonds) are perpendicular, completely breaking their conjugation but allowing the oxygen atom to approach the surface and, especially, to become close to atom Pt_5 (see **18**). The Pt_5O distance is 2.07 Å.

A real bond is formed between Pt_5 and O, reflected by an overlap population of 0.279, which has to be compared with the overlap population between Pt_1 and O in the on-top geometry (0.335). The orbitals of Pt_5 involved in the interaction are mainly d_{z^2}, which loses 0.52 e^- and to a less extent d_{xz} (−0.11 e^-), p_z (+0.1 e^-) and s(−0.07 e^-). Therefore, the interaction of the oxygen atom with Pt_5 looks like the interaction observed in the on-top geometry of aldehydes which has been described in Ref. (14). It can be illustrated, for example, by the DOS and COOP curves given in Fig. 2. The DOS curve projected on d_{z^2}

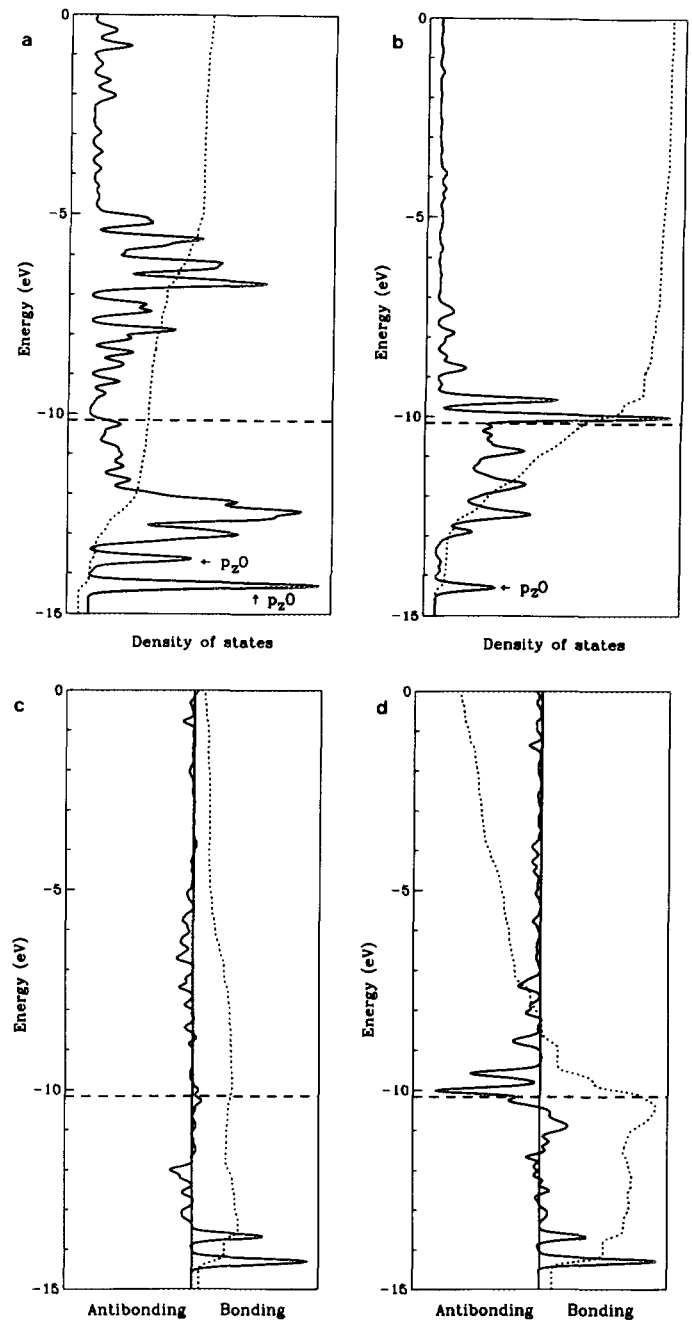
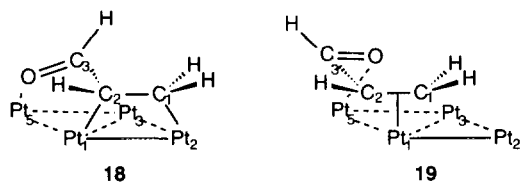


FIG. 2. Acrolein on $Pt_{49}(111)$: DOS curve projected (a) on s Pt_5; (b) on d_{z^2} Pt_5 – COOP curves; (c) between s Pt_5 and p_zO; (d) between d_{z^2} Pt_5 and p_z O.



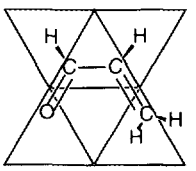
Pt_5 shows that this orbital has been partly pushed above the Fermi level by interaction with p_zO. In the DOS projected on s Pt_5, peaks also appear corresponding to p_zO. The COOP curves show the bonding and antibonding parts of these interactions.

In conclusion, the best conformation for the di-σ_{CC} adsorption mode is a trihapto geometry where the interaction occurs both through the π_{CC} system and through the oxygen atom lone pairs. If the overlaps between orbitals of oxygen and orbitals of the Pt atoms other than 1 and 2 are suppressed, the quantitative effect of the interaction through oxygen is measured. By doing that, the binding energy is decreased by 2.7 kcal/mol. To improve the interaction of the oxygen atom with the surface, the CHO group can be put nearer the surface by diminishing the hybridization on its side in order to have a distance of 2 Å between Pt_5 and O. The binding energy becomes −17.8 kcal/mol, as given in Table 3 and the overlap population 0.319.

For the π_{CC} geometry also (where $h = 0.5$), the rotation of angle θ shows several values for which O comes close to Pt surface atoms. For $\theta = 130°$, O is close to both Pt_1 and Pt_5, giving a bridge-like interaction. We have seen previously (14) that such an interaction is less favorable than the on-top one. Then this geometry must be excluded. The best conformation corresponds to a *cis* geometry with $\theta = 39°5$ (**19**). The Pt_5O distance is 2.0 Å and the overlap population 0.241. The same type of interaction as before occurs between the oxygen lone pairs and the surface. This explains why the π_{CC} geometry is far more stable for acrolein than is expected if one refers to the values obtained for propene (Table 1).

Let us now study the tetrahapto form **13** called η_4 in Scheme 5. It is in fact a di-π adsorption mode, which interacts with the surface through both the C–C and the C–O double bonds in a π geometry as shown in **20**. In this form, the three carbon atoms and the oxygen are in a plane parallel to the surface. The hydrogens must be tilted away from the surface in order to obtain the necessary hybridization. Effectively, the binding energy for the totally planar molecule with only C_1 pyramidalyzed is small (−2.6 kcal/mol). However, the degree of pyramidalization must not be too high, in order to maintain partial conjugation between the two double bonds. The best geometry found corresponds to $h = 0.5$ for both double bonds. By distorting slightly the molecule, one obtains correct distances: $Pt_2C_1 = Pt_2C_2 = Pt_1C_3 = 2.1$ Å, $Pt_1O = 2$ Å. The binding energy (−8.3 kcal/mol) is small despite the high electron transfer. The repulsive four-electron interactions are very important since a great number of atoms are involved in the adsorption. The small BE was expected: the π_{CC} and even more the π_{CO} modes are not very stable and their combination cannot give a binding energy better than the sum of the separated CC and CO π adsorptions (−1.0 −9.8 = −10.8 kcal/mol), because of the smaller hybridization parameter and the rotation with respect to Pt_1Pt_2.

A di-σ form (metallacycle) in which the molecule is bound by its extremities and perpendicular to the surface has also been tested (**21**). In this geometry, the molecule is planar and the double bond has migrated. The binding energy is −8.0 kcal/mol, similar to that of the η_4 form.



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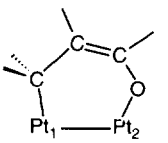

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In conclusion, acrolein adsorbs on Pt (111) in a di-σ_{CC} geometry. The stability of this form is increased by a secondary interaction of the oxygen atom with the surface, giving in fact a trihapto geometry (di-σ_{CC} + η_1O).

IV.1.b. Substituent effects: crotonaldehyde, prenal, and cinnamaldehyde. The results obtained when one or two methyls are fixed on the C=C double bond are given in Table 4. Only the three best geometries are considered: on-top, di-σ_{CO} and di-σ_{CC}. As we have already observed (Table 1), the on-top geometry is not affected by the substitution. The adsorption energy of the di-σ_{CO} form decreases only slightly when methyls are present. Effectively, the substituents are not directly linked to the C=O bond and do not introduce a supplementary repulsive interaction. Nevertheless, the donor effects of the methyls are transmitted through the C=C bond and π^*_{CO} goes up in energy, yielding a smaller electron transfer. Obviously, the substitution has a great influence on the di-σ_{CC} adsorption mode. The same decrease in the binding energy is observed as for alkenes (Table 1). The main influence of the methyl substituents is to strongly increase the four-electron repulsion component of the interaction and hence to make the adsorption through the C=C bond more difficult. Direct steric-like methyl-surface interactions are mostly responsible for this effect. The consequence is that the di-σ_{CC} form, which was the most stable for acrolein, becomes less stable for crotonaldehyde and prenal: substitution induces a change in the adsorption mode. This result is illustrated by the curves of Fig. 3 where the BE's of the three modes are plotted versus the number of methyls. The fact that the BE of the di-σ_{CC} mode decreases upon substitution is independent of the precise extended Hückel parametrization. However, the crossing point between BE(di-σ_{CC}) and BE(di-σ_{CO}) depends on the chosen H_{ii} parameters for C, H, and O. If their H_{ii}'s are decreased by 0.2 eV, the crossing occurs between crotonaldehyde and prenal, i.e.

TABLE 4

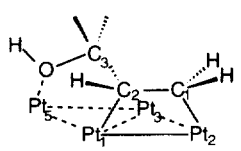
Binding Energies (BE in kcal/mol) of Acrolein, Crotonaldehyde, Prenal, Cinnamaldehyde, Propenol, and 3-Methyl-propenol on $Pt_{49}(111)$

	On-top	Di-σ_{CO}	Di-σ_{CC}
CH_2=CH-CHO	−11.0	−15.7	−17.8
CH_3CH=CH-CHO	−11.0	−14.2	−11.9
$(CH_3)_2C$=CH-CHO	−11.0	−13.5	−6.6
ΦCH=CH-CHO	−11.0	−14.1	−8.9
CH_2=CH-CH_2OH	−8.3	—	−15.6
$(CH_3)_2C$=CH-CH_2OH	−8.4	—	−3.6

for crotonaldehyde the di-σ_{CC} mode is still favored over the di-σ_{CO} mode. As a consequence, it is not possible, with this method of calculation, to determine where this crossing occurs but only to decide on the BE trend. Compared to experimental data, the parameter set chosen for the calculations seems to slightly favor the C=O adsorption against the C=C one. This effect, however, is rather small and does not affect the qualitative comparisons.

For cinnamaldehyde, the same result is obtained. The di-σ_{CO} adsorption geometry is the most stable, due to the large size of the phenyl ring. The difference with the di-σ_{CC} form is larger than for crotonaldehyde.

IV.1.c. Unsaturated alcohols CR_2=CH–CH_2OH (R = H or CH_3). Two adsorption modes are compared: the on-top and the di-σ_{CC} (see Scheme 5). The former is only slightly more stable than that of methanol. For the di-σ mode, many configurations have been tested. Two of them are interesting. In the first one, the oxygen atom is far from the surface and has no interaction with it. The binding energy is −10.0 kcal/mol, identical to that found for propene (Table 1). In the second one, the oxygen atom is at 2 Å distance from Pt_5 as shown in **22**.



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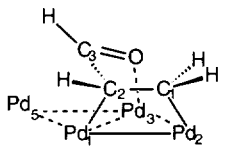

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There is a strong interaction between them, reflected by a large overlap population of 0.312. The binding energy is now −15.6 kcal/mol, much greater than that of the on-top geometry. Therefore propenol like acrolein adsorbs on Pt(111) in a trihapto geometry associating a di-σ_{CC} interaction and an on-top one through oxygen.

As expected, the presence of methyls on the C=C bond strongly decreases the binding energy of the di-σ_{CC} form, which becomes only slightly bonding. Therefore, 3-methyl-2-butenol adsorbs in the on-top form on Pt(111) (Table 4).

In conclusion, the adsorption of the α–β unsaturated aldehydes depends on the substitution of the C=C double bond. The more substituted this bond, the more favored is the adsorption through the C=O bond. In all these unsaturated aldehydes and alcohols, the adsorption through C=C is stabilized by a supplementary interaction between the oxygen atom and the surface.

IV.2. Adsorption on Pd(111)

The same adsorption geometries as on Pt(111) have been considered on Pd(111) and the results are given in

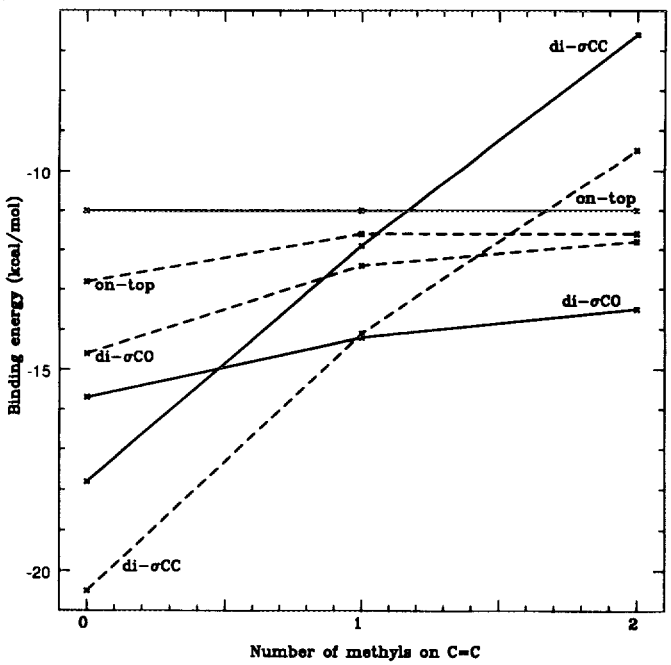


FIG. 3. Acrolein on $Pt_{49}(111)$. Variation of the binding energies for the on-top, di-σ_{CC}, and di-σ_{CO} geometries as a function of the substitution of the C=C bond. Solid lines: normal H_{ii}'s for C, H, and O; dashed lines: H_{ii}'s 0.2 eV lower (see Section IV.1.b).

TABLE 5

Binding Energies (BE in kcal/mol) of Acrolein, Crotonaldehyde, Prenal, Cinnamaldehyde, and Propenol on Pd_{49}(111)

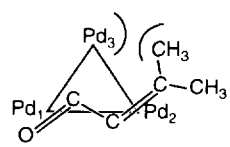
	On-top	Di-σ_{CO}	Di-σ_{CC}	π_{CO}	π_{CC}	$\eta_{4(di-\pi)}$
CH_2=CH-CHO	−10.5	−26.2	−26.7	−18.3	−25.5	−31.9
CH_3CH=CH-CHO	−10.4	−24.0	−22.9	−16.3	−21.6	−29.3
$(CH_3)_2C$=CH-CHO	—	−25.3	−18.8	−9.6	−13.0	−18.3
ΦCH=CH-CHO	−10.4	−24.4	−27.1	−19.9	−34.5	−37.6
CH_2=CH-CH_2OH	−9.0	—	−23.7	—	−14.6	—

Tables 3 and 5. The effect of changing the metal from Pt to Pd on the adsorption modes of aldehydes and alkenes has been described at the beginning of this paper. The same trends are observed for α–β unsaturated compounds (compare Tables 4 and 5). Both adsorptions through C=O and C=C bonds are favored compared to Pt(111), the former more than the latter. As before, a rotation of θ (Scheme 5) has been performed for the di-σ_{CC} and π_{CC} adsorption geometries of acrolein on Pd(111). The hybridization is smaller on Pd than on Pt (h = 0.6 for di-σ_{CC} and h = 0.3 for π_{CC}) so that the minima of the curve (BE versus θ) do not occur for the same values of θ. For the di-σ_{CC} geometry, three minima also exist for θ = 40°, 144°, and 200° (−160°) with BE = −23.0, −22.4, and −22.1 kcal/mol, respectively. The first minimum can be improved by optimizing the hybridization on the CHO side so that the oxygen atom is at 2 Å distance from Pd_3. BE becomes −26.7 kcal/mol with a Pd_3O overlap population of 0.21. Therefore, the best conformation for the di-σ_{CC} geometry of acrolein on Pd(111) corresponds to a cis conformation (**23**) while it is trans on Pt(111).

For the π_{CC} geometry, two minima are found for θ = 24° and 190° (−170°) with BE = −25.5 and −21.5 kcal/mol, respectively. The former corresponds to a *cis* conformation with Pd_3–O = 2 Å and a Pd_3O overlap population of 0.14. An important feature is that, on Pd(111), the π_{CO} and π_{CC} adsorption geometries become competitive with the di-σ ones, as was the case for the isolated CC and CO functions.

Let us comment now on the η_4 mode which, as we said before, is a di-π geometry. We have seen that the pyramidalization is smaller on Pd(111) than on Pt(111): the molecule can hence remain more planar. We have also seen that, the more numerous the atoms involved in the interaction, the more important are the four-electron interactions and therefore the larger is the decrease of these interactions when Pd replaces Pt. Effectively, the S^2 value of the η_4 mode which was the largest for acrolein on Pt(111), is of the same order of magnitude as that of di-σ_{CC} or π_{CC} on Pd(111). (See Table 3). Since the electron transfer is also the largest for that geometry, the η_4 mode is the best one for acrolein on Pd(111). This result is in good agreement with the experimental data (16) (see Introduction).

For the effect of methyl substituents, the same trends are observed as on Pt(111). However, since the repulsive interactions are less important on Pd, the substituents will have a significantly smaller effect on the adsorption through the C=C bond. Effectively the binding energy of the di-σ_{CC} mode does not decrease much when one and two methyls are added. The same observation has been made for the ethylenic compounds (Table 1). As a consequence, the η_4 geometry is still the best one for crotonaldehyde. However, this is not the case for prenal, for which the di-σ_{CO} form is preferred. For prenal, the trans conformation is more stable than the *cis* by 5 kcal/mol and therefore the best η_4 form is also trans, as shown in **24**. However, a steric hindrance exists between Pd_3 and



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CH_3 which can be released by increasing the hybridization of the carbon bearing the two methyls and twisting the C=C bond. Nevertheless this induces a decrease in the two-electron interactions with the surface and therefore a less stable η_4 form.

The case of cinnamaldehyde is interesting. It has been pointed out in Section III.2 that the phenyl ring of styrene has a nonnegligible stabilizing interaction with the surface. The same phenomenon occurs for cinnamaldehyde, which explains that the adsorption geometries through the C=C bond are more stable than those through the C=O bond, especially the π_{CC} one. For the same reason, the η_4 mode is again the most stable of all the adsorption modes. These interactions between the phenyl ring and the surface are reflected by Pd–C overlap populations in the range of 0.07.

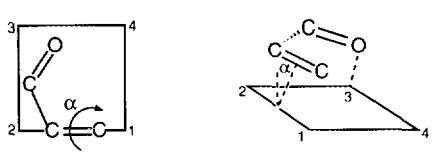
Finally propenol adsorbs on Pd(111) as on Pt(111) in a trihapto geometry (see **22**), involving both the C=C bond (di-σ) and an oxygen lone pair. The Pd_5O overlap population is 0.241. The participation of the oxygen in the adsorption of propenol on Pd is confirmed by experimental results (16): the HREEL spectrum of allylic alcohol (propenol) shows evidence that "both the oxygen function and the hydrocarbon backbone of the molecule bind strongly to the surface metal atoms." In this work also the desorption temperatures of several molecules have been noted. For example, acrolein, allylic alcohol and propanal desorb at the same temperature (200 K) in their η_1 mode. Our results are in agreement with these experimental data (see Table 5 for acrolein and propenol and Table 1 for ethanal).

In conclusion, the most interesting feature is that adsorption of α–β unsaturated aldehydes on Pd(111) occurs through both double bonds in a tetrahapto di-π geometry when the C=C bond is unsubstituted or monosubstituted. When this bond is disubstituted, the di-σ_{CO} geometry is the most stable one.

IV.3. Adsorption on Pt(100)

On this surface, only the most stable adsorption geometries found for formaldehyde and ethylene (Table 2) have been considered, that is di-σ ($\parallel$) and π ($\parallel$). As on the other surfaces, a η_4 form has also been studied, where both the C=C and the C=O bonds are involved. Its geometry will be described further. Let us comment first on acrolein. The results are given in Table 3. As on the other surfaces, the angle θ around the single C=C bond has been varied. For the di-σ_{CO} and the π_{CO} geometries, the *trans* conformation is the most stable, with θ = 200° (−160°) and 210° (−150°) respectively. However, the *cis* conformation with θ = 10° is only 1 kcal/mol above it. As on Pt(111), the π_{CO} form is very unstable.

Concerning the di-σ_{CC} geometry, with a pyramidalization of h = 0.8, only two minima are found corresponding to the trans conformation (θ = 200° (−160°)) and the cis conformation (θ = 20°). The geometry of the (100) surface is not the same as that of the (111) surface and therefore the secondary interactions of the oxygen atom with the surface atoms occur for different angles. In the cis conformation (θ = 20°), both C and O are close to Pt_3 (**25**) and



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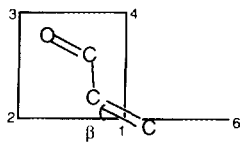
their overlap populations with it are positive. In order to improve these interactions, we have first decreased the pyramidalization on the side of CHO until h = 0.6. Then we have tilted the C=C bond around the Pt_1–Pt_2 axis by an angle α until the Pt_3–O distance is 2 Å (α = 11.6 Å). The overlap population Pt_3O is then 0.196 and the best binding energy is −16.6 kcal/mol. Therefore, there is a compromise between the binding of the C=C bond and that of the oxygen: the local arrangement of the C=C bond is slightly altered, which is compensated by an improvement of the O binding.

For the π_{CC} form for which the hybridization parameter is 0.5, three interesting geometries are found. The first one is the classical *trans* conformation with θ = 210° (−150°) (BE = −10.5 kcal/mol). The second is also trans but with θ = 130° and a rotation angle β of 18° (see **26**) so that the Pt_3–O distance is 2 Å (BE = −9.8 kcal/mol).



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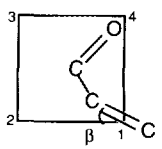

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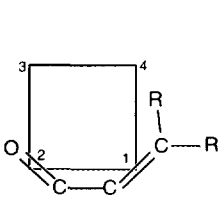
The third one corresponds to the *cis* conformation with θ = 50° and a rotation angle β of 8.3° (**27**). This is the best π_{CC} mode with a binding energy of −16.5 kcal/mol and a Pt_4O overlap population of 0.305. Therefore, the adsorption modes involving the C=C bond are further stabilized by a secondary interaction between the oxygen lone pair and the surface, as is the case for Pt(111).

For the η_4 form, several geometries have been tested. The first is the di-π (**28**) looking like that found on Pt(111) or Pd(111). For the same reason as on Pt(111) this form is not very stable (BE = −11.3 kcal/mol): this is due to the instability of the π_{CO} geometry (Table 3).



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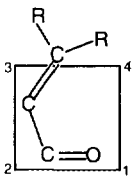

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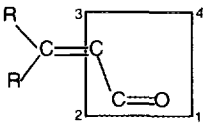

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However, the geometry of the (100) surface allows another structure to be investigated, contrary to the case of Pt(111). The results of Table 3 show that for acrolein on Pt_{52}(100) three geometries are roughly equivalent, di-σ_{CO}, di-σ_{CC} and π_{CC}. Hence, we can try to combine π_{CC} and di-σ_{CO} to obtain a η_4 form. Effectively, geometry **29** has been found to be the most stable of all with BE = −27.9 kcal/mol. In order to ensure good distances between Pt_3 and C=C, the C=O bond has been slightly shifted away from the plane perpendicular to Pt_1–Pt_2.

TABLE 6

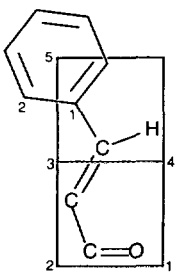
Binding Energies (in kcal/mol) of Acrolein, Crotonaldehyde, Prenal, and Cinnamaldehyde on Pt_{52}(100)

	Di-σ_{CO}(‖)	Di-σ_{CC}(‖)	π_{CC}(‖)	$\eta_{4(di-\sigma+\pi)}$
CH_2=CH-CHO	−16.3	−16.6	−16.5	−27.9
CH_3CH=CH-CHO	−14.5	−13.2	−10.6	−22.7
$(CH_3)_2C$=CH-CHO	−13.5	−3.9	−3.0	−18.0
ΦCH=CH-CHO	−15.1	−13.6	−10.4	−26.1

The substitution of the C=C bond by methyls has the same effect as before, that is the di-σ_{CC} and π_{CC} forms are destabilized compared to the di-σ_{CO} form (see Table 6). This destabilization is smaller than on Pt(111) because the repulsive interactions are decreased on Pt(100), except for prenal for which methyls cannot be easily accommodated on the surface in a trans structure like **26** (contact with Pt_6) or in the *cis* conformation **25** (contact with Pt_4).

For crotonaldehyde (one CH_3), the η_4 form **29** is again the most stable. For prenal, the η_4 form in this geometry is totally impossible because one methyl is too close to Pt_4. Nevertheless, a η_4 form can be found for prenal with the different geometry shown in **30**. In this geometry, the C=O bond still adsorbs di-σ and the C=C bond adsorbs π(‖) instead of π(diag) as in **29**. In such a geometry, the two methyls can more easily be kept at a sufficient distance away from the surface atoms. It results that, for prenal, the η_4 form is also the most stable.

Cinnamaldehyde behaves approximately like crotonaldehyde. However, owing to some small interactions between the phenyl ring and the surface, the η_4 form is far more stable: in geometry **31**, the phenyl ring has a good



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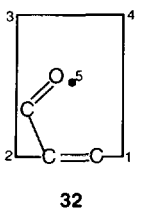
position to interact with Pt_5, which results in positive overlap populations of 0.046 and 0.067 for Pt_5C_1 and Pt_5C_2, respectively. Since on Pt(100) the repulsions are smaller than on Pt(111), the stabilizing two-electron interactions of the phenyl ring tend to overcome the destabilizing four-electron ones in that case and induce a global stabilization.

As a conclusion, a Pt(100) surface behaves differently from a Pt(111) surface for the adsorption of α–β unsaturated aldehydes. The preferred adsorption geometry is η_4 (di-σ_{CO} + π_{CC}) for all the studied molecules, whatever the substituents.

IV.4. Adsorption on Pt(110)

Four adsorption geometries have been considered, di-σ_{CC}, di-σ_{CO}, π_{CC}(⊥) and η_4. It is known from the calculations on olefins (13a) that the π_{CC}(‖) form is less stable than the π_{CC}(⊥) one. It is, therefore, discarded (see Table 1). Let us consider first acrolein (Table 7). As in the previous cases, the angle θ around the single C–C bond has been optimized. For the di-σ_{CO} geometry (hybridization h = 1), the *trans* conformation with θ = 200° (−160°) has been found to be the most stable, as on the other Pt surfaces. For the di-σ_{CC} geometry, two minima have been found for θ = 30° (*cis* form) and θ = 210° (−150°) (trans form) with a binding energy of −19.2 and −19.8 kcal/mol, respectively. Because of the distance between the atomic rows on the (110) face, the oxygen atom cannot approach sufficiently a surface atom to give a secondary interaction as on the other surfaces. On the contrary, by varying θ, this atom comes close to Pt_5, an atom of the second layer (**32**) with which the interaction is rather repulsive (small negative overlap populations). An additional stabilization by the oxygen atom of the di-σ_{CC} coordination is, therefore, not possible on Pt(110).



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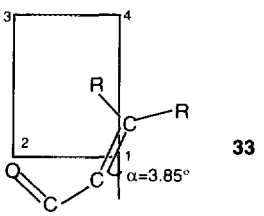

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For the π_{CC}(‖) geometry also, no stabilizing secondary interactions are found and this form remains less stable. On the contrary, the π_{CC}(⊥) geometry is greatly stabilized by an interaction between the oxygen and the neighboring Pt atom on the same row, as shown in **33** (R=H). For the π geometry on Pt(110), the hybridization is weak (h = 0.4) (13) and, therefore, the approach of the oxygen to the surface is made easier than on the other

TABLE 7

Binding Energies (in kcal/mol) of Acrolein, Crotonaldehyde, Prenal, and Cinnamaldehyde on $Pt_{44}(110)$

	Di-$\sigma_{CO}(\parallel)$	Di-$\sigma_{CC}(\parallel)$	$\pi_{CC}(\perp)$	$\eta_{4(di-\pi)}$
CH_2=CH-CHO	−21.3	−19.8	−28.2	−26.8
CH_3CH=CH-CHO	−20.2	−16.6	−25.5	−23.8
$(CH_3)_2C$=CH-CHO	−19.8	−11.5	−21.9	−14.3
ΦCH=CH-CHO	−20.1	−19.1	−24.7	−25.9

surfaces. With $\theta = 50°$ and a small angle $\alpha = 3.85°$, O becomes at a 2-Å distance from Pt_2 and a strong interaction occurs (overlap population 0.319) yielding a great stabilization of the $\pi_{CC}(\perp)$ geometry, which becomes in fact a trihapto form (BE = −28.2 kcal/mol compared to −18.9 kcal/mol for the *trans* form ($\theta = -160°$) where this interaction is suppressed).

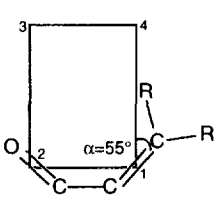
For the η_4 geometry, only the di-π conformation along the row (**34**) can exist, as on the (111) surface. It is slightly less stable than the $\pi_{CC}(\perp)$ one. This result is easily explained by comparing the binding energies of the on-top and the π_{CO} geometries of H_2CO (Table 1) which are almost identical. The conformation shown in **33** is in fact a $\pi_{CC}(\perp)$ + on-top(O) geometry and therefore its binding energy would be identical to that of η_4 (**34**) if the latter was not destabilized by rotation of both π bonds ($\alpha = 55°$). In conclusion, acrolein on Pt(110) prefers the trihapto $\pi_{CC}(\perp)$ + (O) adsorption mode; the η_4 one, however, is not far away in energy.

The substitution by methyls gives the results shown in Table 7. The effects are the same as those described for the other surfaces: the adsorption modes through C=O bond are only slightly affected. On the contrary, the adsorption modes through the C=C bond are more sensitive to the substitution. Nevertheless, the (110) face is more open than the (111) and the (100) faces and the repulsive interactions are less important. As a consequence, the binding energies for the adsorption through C=C decrease less than on the other faces when going from acrolein to prenal, especially that of the $\pi_{CC}(\perp)$ mode. Effectively, in such a geometry the two methyls are located over the trough of the (110) surface, and therefore are far from any surface atoms, yielding only small repulsive interactions (**33**, $R = CH_3$). The same trend has been observed for acetone compared to formaldehyde (Table 1). The consequence is that, on Pt(110), the $\pi_{CC}(\perp)$ geometry remains the most stable form even for prenal, because the electronic repulsion induced by the CH_3 groups is smaller on this low coordination site.

An exception is the large decrease in BE for the η_4 form of prenal. The trans conformation of prenal being more stable than the cis in the gas phase, the η_4 geometry **35** has been considered. One methyl is too close to Pt_6 and, finally, prenal prefers the cis η_4 geometry **34** ($R = CH_3$) where the methyls are further from the platinum atoms. Nevertheless, the repulsive interactions are still nonnegligible with Pt_4 and Pt_6 and the η_4 geometry of prenal is far less stable than the $\pi_{CC}(\perp)$ form, due to geometric constraints.

The behavior of cinnamaldehyde only differs from that of acrolein and crotonaldehyde in that the η_4(di-π) geometry is slightly preferred to the $\pi_{CC}(\perp)$ one. In these two geometries, as well as in the di-σ_{CC} one, the phenyl ring has small stabilizing interactions with the surface, which explains the large BE of the di-σ form.

In conclusion, the preferred adsorption geometry on Pt(110) is the trihapto $\pi_{CC}(\perp)$ + (O) one for acrolein, crotonaldehyde and prenal, but the η_4 one for cinnamaldehyde. Nevertheless, except for prenal, the energy difference between these two modes is small, and they can compete on the surface.



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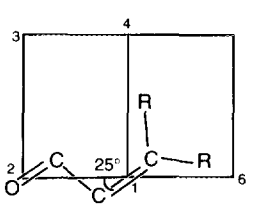

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IV.5. Adsorption on a Stepped Pt(111) Surface

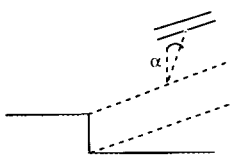
The adsorption modes of carbonyl compounds and of ethylene on a [n(111) × (100)] step of a Pt(111) surface have been previously studied (14b, 19). Such a step is constructed by removing half of the first layer of the cluster used to study the flat (111) surface. In order to have a good description of the atoms on the two generated terraces, the cluster must have a sufficient number of shells and, therefore, a cluster of 114 atoms is used to build the step. Depending on the side where the half layer is removed, a [n(111) × (100)] or a [n(111) × (111)] step can be generated. Only the first one is considered here. A cluster of 96 atoms (called Pt_{96}) with a core of 40 atoms, is then obtained.

TABLE 8

Binding Energies (in kcal/mol) of Acrolein, Prenal, and Cinnamaldehyde on a Stepped Pt(111) Surface

	Di-σ_{CO}	Di-σ_{CC}	$\pi_{CC}(\perp)$	$\eta_{4(di-\pi)}$
CH_2=CH-CHO	-21.4	-19.8	-25.7	-24.5
$(CH_3)_2$C=CH-CHO	-19.5	-11.3	-19.0	-11.1
ΦCH=CH-CHO	-20.0	-16.0	-23.0	-22.7

It has been shown previously that on a step, the adsorbed molecules are tilted with an angle α on the step edge (see **36**). The optimization of α gives 20° for aldehydes (adsorption of C=O) (14b) and 27° for olefins (adsorption of C=C) (19). This tilt allows a release of the repulsive interactions of the substituents with the terrace.



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The same tilt has been applied to α-β unsaturated aldehydes. In all cases, the tilted geometry is more stable than the orthogonal one, even for the di-σ_{CC} form **18** where the tilt suppresses the stabilizing interaction of the oxygen with the terrace.

The similarity in the behavior of a Pt(110) and a stepped Pt(111) surfaces has been pointed out (14b, 19). In particular the two best geometries are the same on both surfaces, that is $\pi_{CC}(\perp)$ and η_4 for acrolein and cinnamaldehyde and $\pi_{CC}(\perp)$ and di-σ_{CO} for prenal. On the step, the $\pi_{CC}(\perp)$ geometry is also a trihapto one, looking like **33** with $\alpha = 8°$. A PtO overlap population of 0.31 is obtained. As on Pt(110), prenal cannot adopt a η_4 geometry owing to the repulsive interaction of one methyl with the neighbouring atom on the step (like Pt_6 in **34** or **35**).

In conclusion, on a [n(111) × (100)] step of a Pt(111) surface, acrolein and cinnamaldehyde prefer the trihapto $\pi_{CC}(\perp)$ + (O) form over the η_4 one but the energy difference is very low and the two forms can again compete. For prenal, the competition is between the $\pi_{CC}(\perp)$ and the di-σ_{CO} forms, the η_4 form being far less stable (see Table 8).

IV.6. Summary and Conclusion of the Adsorption Study

The study of the adsorption of α-β ethylenic aldehydes on various metals (Pt and Pd) and various faces ((111), (100), (110)) and steps has shown that the preferred modes are strongly dependent on the nature of the metal and of the crystal face. Generally speaking, the substitution of the C=C bond decreases the binding energies of the η_2(CC) adsorption geometries, which can induce a modification of the preferred adsorption geometry for substituted and unsubstituted molecules.

The following trends can be pointed out:

—on Pt(111), acrolein prefers a trihapto di-σ_{CC} + (O) mode but crotonaldehyde, prenal, and cinnamaldehyde prefer the di-σ_{CO} one.

—on Pt(100), a η_4 geometry bound both by the C=C and the C=O bonds is strongly preferred whatever the substituents.

—on Pt(110), adsorption through the C=C bond is preferred in a $\pi(\perp)$ geometry (trihapto form), except for cinnamaldehyde for which the η_4(di-π) mode is slightly favored.

—on a [n(111) × (100)] stepped surface, the $\pi_{CC}(\perp)$ geometry is in competition with the η_4 one for acrolein and cinnamaldehyde and with the di-σ_{CO} one for prenal.

—on Pd(111) finally, the η_4 geometry is preferred except for prenal for which the di-σ_{CO} form is the most stable.

Therefore, the Pt(111) surface which yields a strong four-electron repulsion with the adsorbate, gives di-σ adsorptions, while a reduction of this repulsion, by changing the face to a more open one or by going to palladium, tends to favor η_4 or π coordinations.

In the next section, we will use these results to rationalize some experimental data concerning the selectivity of the hydrogenation of the unsaturated aldehydes.

V. DISCUSSION

Trends in Selective Hydrogenation

The previous results on the preferred adsorption modes of unsaturated aldehydes and of the possible monohydrogenated products can have important implications on the selective hydrogenation process even though they constitute only a very partial description of the reaction path. Our argumentation rests on the hypothesis that the double bond which is first hydrogenated is the one involved in the chemisorption on the surface. Two mech-

anisms have been proposed for the hydrogenation of the C=C bond in α–β unsaturated aldehydes: these are the classical Horiuti–Polanyi (20) mechanism which involves a 1–2 addition process on a di-σ adsorbed species and a mechanism involving a 1–4 addition process (21) which would be preferred on a η_4 geometry. The latter process leads to the formation of an enol that isomerizes to the same saturated aldehyde as the 1–2 process. Therefore, the two processes yield C=C bond hydrogenation. When the adsorptions through the two double bonds happen together (η_4 mode) the kinetic factor plays an important role: generally speaking a C=C bond hydrogenates more easily and quickly than a C=O one (10, 15b, 21). Moreover, metals do not all have the same efficiency in the hydrogenation of a C=C or C=O double bond. Carbonyl groups are usually hydrogenated over platinum while no hydrogenation has been reported over palladium for aliphatic aldehydes (21b, 22). On the contrary, palladium is more efficient than platinum in the hydrogenation of alkenes (21b, 22).

When the first hydrogenation is determined, the second step is to analyze the adsorption competition between the monohydrogenated products (saturated aldehydes or unsaturated alcohols) and the reactant itself. A stronger adsorption of the reactant would prevent, by competitive adsorption, the further reaction of the monohydrogenated products, yielding a selective partial hydrogenation until high reactant conversion is reached. In the following we consider successively the various surfaces we have studied.

Pt(111). On Pt(111), there is competition between the C=C and the C=O di-σ coordinations. The more substituted the C=C bond, the less stable is the adsorption through this bond and therefore the more likely it is for hydrogenation to occur at the C=O bond giving the unsaturated alcohol. This is the result described by Beccat *et al.* who obtain a better selectivity in unsaturated alcohol with prenal (56%) than with crotonaldehyde (10%) (10). This hydrogenation of prenal is very selective in partially hydrogenated products. Indeed, 3-methyl-butenol (the monohydrogenated product) adsorbs in the η_1 on-top geometry through the lone pair of oxygen (see Table 4), with an adsorption energy lower than that of the di-σ_{CO} mode of prenal. By competition of adsorption, the saturated alcohol 3-methyl-butanol can only be obtained when 3-methyl-butenol can adsorb and react, that is at high conversion or at low partial pressure of prenal. This is the result obtained by Birchem *et al.* (15b) who operate with conditions different from those of Beccat *et al.*

The case of crotonaldehyde is more difficult since its preferred adsorption geometry (di-σ_{CC} or di-σ_{CO}) is dependent on the choice of parameters in the calculation (see Fig. 3). It is suggested that these two modes have a similar adsorption energy which results, for kinetic reasons, in a poor selectivity in unsaturated alcohol.

Following the same trends, acrolein is adsorbed and hydrogenated on the C=C bond yielding propanal, which would be di-σ_{CO} coordinated like ethanol (BE = −14.5 kcal/mol) and could then be desorbed by competition with acrolein in the gas phase. Therefore propanal should be obtained with a rather good selectivity on Pt(111).

On the contrary, for cinnamaldehyde the di-σ_{CC} geometry is strongly destabilized, as for prenal. Therefore, the hydrogenation of cinnamaldehyde on Pt(111) would lead to the unsaturated alcohol with a better selectivity than in the case of crotonaldehyde.

Pt(100). On Pt(100), a tetrahapto η_4 form has been found to be the most stable, which means that both double bonds are involved in the adsorption and are therefore able to be hydrogenated, with a kinetic preference for the C=C bond. Moreover, this η_4 form being less hybridized than the di-σ ones, that is to say flatter on the surface, the methyl substituents are closer to the surface and can be easily dehydrogenated, which yields cracking products. It has been effectively shown, both experimentally (23) and theoretically (24) than olefinic compounds can decompose on Pt in H_2 and carbon fragments by abstraction of hydrogen by the platinum atoms. For this, it is necessary that a CH bond is close to the metal surface. In our calculations, we found, in agreement with the results of Anderson *et al.* (24), that for certain conformations of the methyls, a positive overlap population exists between hydrogens and platinum atoms, indicating an interaction between them and the possibility of forming a Pt–H bond.

This is experimentally verified (15a): the main products obtained during the hydrogenation of prenal on Pt(100) are "light" hydrocarbons arising from cracking. Besides them, the oxygenated products, obtained in low yield, consist of the three possible molecules, unsaturated aldehyde, unsaturated and saturated alcohols. The surface is rapidly saturated by carbon or oxygen fragments and the conversion is low (30%).

One interesting possibility in order to increase the selectivity in unsaturated alcohol is to increase the partial pressure of prenal. Indeed, the η_4 form, poorly selective, needs more atom sites on the surface (3) than the selective, but somewhat less stable, di-σ_{CO} mode (2) (see Table 6). Increasing the coverage in prenal can therefore favor the di-σ_{CO} coordination, which can yield a denser packing, and improve the selectivity in unsaturated alcohol. This is effectively the case experimentally (15a). For acrolein, crotonaldehyde, and cinnamaldehyde, for which the η_4 form is largely preferred, the selectivity in unsaturated alcohol would be lower with a large amount of light hydrocarbons.

Pt(110). On Pt(110) the situation is quite different. The best adsorption form found by our calculations is the π_{CC} one. Therefore, on this surface, the hydrogenation is supposed to yield mainly the saturated aldehyde by hydrogenation of the C=C bond. Hydrogenation of prenal has been performed experimentally on Pt(110) (15c) and effectively, the major product is 3-methyl-butanal at the beginning of the reaction, with small amounts of light products. The formation of these products can be explained by the weak hybridization of the $\pi_{CC}(\perp)$ geometry (see section IV.4), which allows the substituents to approach the surface, like in a η_4 form, and then induces cracking reactions. When the conversion increases, the saturated aldehyde which can strongly adsorb in the di-σ_{CO} mode (BE = ca. −19 kcal/mol) is itself hydrogenated and a large amount of saturated alcohol is obtained. A large partial pressure of prenal leads to a decrease in the selectivity in saturated aldehyde with the appearance of unsaturated alcohol. Effectively, the $\pi_{CC}(\perp)$ geometry is in fact a trihapto form involving three metal atoms. When the prenal pressure increases, the $\pi_{CC}(\perp)$ mode in this geometry, as well as the η_4 one, is no longer favored on the surface. (The binding energy of the $\pi_{CC}(\perp)$ geometry without the Pt–O interaction is only −13.4 kcal/mol). Therefore, the best adsorption mode at high coverage would be the di-σ_{CO} one (see Table 7), because it needs less surface atoms, which explains the formation of the unsaturated alcohol. For the other studied molecules, at low coverage on Pt(110), the preferred adsorption mode is also π_{CC} (or η_4 for cinnamaldehyde) which would yield a low selectivity in unsaturated alcohol. However, at high coverage, the di-σ_{CO} coordination should be again preferred, because it is only slightly less stable. In consequence, at high coverage, the selectivity in unsaturated alcohol would be better, as explained for prenal.

Step on Pt(111). At a step on Pt(111), there is a competitive adsorption between the $\pi_{CC}(\perp)$ and the η_4 forms for acrolein and cinnamaldehyde, as on Pt(110). For kinetic reasons (easier hydrogenation of the C=C bond), the major product would be the saturated aldehyde coming from $\pi_{CC}(\perp)$, accompanied by a smaller amount of saturated and unsaturated alcohols and light products. The situation is different for prenal for which the $\pi_{CC}(\perp)$ form is in competition with the di-σ_{CO} mode. Effectively the experimental results (15c) show that, at the beginning of the reaction, the major product is the unsaturated alcohol arising form the di-σ_{CO} form. Saturated alcohol and saturated aldehyde (from the π_{CC} form) are also obtained. The presence of this saturated aldehyde is the main difference between the flat Pt(111) face and a step. It is due to the possibility for prenal to adsorb through the C=C bond on the step (π_{CC}) because of smaller repulsions. The unsaturated alcohol has a binding energy similar to that of prenal: for the π_{CC} form of 3-methyl-butenol a binding energy of −18.1 kcal/mol has been calculated in this work. Therefore this molecule, when formed, competes with prenal and is also hydrogenated, which explains why great amounts of saturated alcohol are obtained when the conversion increases. The selectivity toward unsaturated alcohol can be improved when the partial pressure of prenal is increased. Effectively, as previously described, the $\pi_{CC}(\perp)$ geometry, that is also a trihapto one on the step, is no longer favored and prenal only adsorbs in the di-σ_{CO} form which yields preferentially the unsaturated alcohol.

Pd(111). On Pd(111), finally, the best adsorption form is the η_4 one, except for prenal which prefers the di-σ_{CO} geometry. Generally speaking, Pd(111) would behave like the Pt(100) surface, that is it should yield cracking products, perhaps in lower yield since this face is less open. Among the oxygenated products, the saturated aldehyde would be the major product since Pd is known to be a poor catalyst for the hydrogenation of the C=O bonds. To our knowledge, the only experimental data dealing with hydrogenation of α–β unsaturated aldehydes on Pd(111) are those obtained during TPD experiments used to study the interactions of acrolein with a Pd(111) surface (16). During these experiments, propanal is formed as the unique product arising from hydrogenation of some part of the adsorbed acrolein.

On the contrary, prenal, which is preferentially adsorbed on Pd(111) in the di-σ_{CO} form, would be unreactive with respect to hydrogenation since palladium does not hydrogenate aliphatic aldehydes. There is no experimental evidence of this prediction.

In conclusion, the determination by our calculations of the preferred adsorption modes of α–β unsaturated aldehydes gives good trends for explaining the selectivity of their hydrogenation reactions on well defined surfaces. Our results are in good agreement with the available experimental data. Nevertheless, real catalysts are seldom pure metallic surfaces but rather small particles of metal dispersed on a support, inert or not. Can we explain the selectivity obtained in those cases?

The hydrogenation of α–β unsaturated aldehydes on Pt dispersed on an inert support (C or SiO_2) gives a high selectivity in the saturated aldehyde. This is the case for acrolein (12d, 25) crotonaldehyde (3a–b, 6) and to a lesser extent for cinnamaldehyde, which also yields the unsaturated alcohol (4, 11b). Moreover, it has been shown for cinnamaldehyde and citral that the increase in the size of the metallic particles improves the selectivity in unsaturated alcohol (4, 26). There is less information for palladium. Nevertheless, cinnamaldehyde on Pd/C gives also the saturated aldehyde but with a large amount of the totally saturated alcohol (4, 27, 28). In the same

conditions, crotonaldehyde only gives the saturated aldehyde and no saturated alcohol (27). When a metallic salt such as $FeCl_2$ is added on platinum, the selectivity towards the unsaturated alcohol increases. On palladium, on the contrary, the addition of $FeCl_2$ suppresses the formation of the saturated alcohol and gives 100% saturated aldehyde (27).

Small metallic particles deposited on an inert support are usually represented by cubooctahedra presenting faces such as (111) and (100), and edges. For example, it has been shown by electron spectroscopy that small platinum particles supported on graphite present the (111) and (100) faces for catalytic reaction (29). Our calculations have shown that α–β unsaturated aldehydes are much more strongly bound on the (100) face and on a step than on the (111) face (compare Tables 4, 6, 7, and 8). Therefore, we can make the assumption that the adsorption and the hydrogenation would take place preferentially on the (100) face and on edges and not on the (111) face, in a first stage. On the (100) face of platinum, the adsorption for all aldehydes is η_4 (Table 6) following our calculations. The experimental study of the variation of the X-ray absorption coefficient of Pt when crotonaldehyde is adsorbed leads to the conclusion that adsorption occurs through both double bonds, in agreement with our results (30). The authors conclude that the hydrogenation of crotonaldehyde could yield selectively the saturated aldehyde because the hydrogenation of the C=O bond does not have an appreciable rate at low conversion.

Another explanation is possible: we have seen before that the hydrogenation of prenal on Pt(100) gives cracking products and a low conversion because of poisoning of the surface by these fragments. Therefore, one can imagine that the first hydrogenation on the (100) face is rapidly inhibited and that the only available faces become the (111) ones, leading also preferentially to the saturated aldehyde in the case of monosubstituted aldehydes.

No saturated alcohol is obtained with platinum because the saturated aldehyde formed is not sufficiently adsorbed on Pt to compete with the reactant and desorbs. Effectively, we have seen that saturated and unsaturated aldehydes have similar binding energies for the di-σ_{CO} form (compare CH_3CHO and acrolein or crotonaldehyde on Pt(111)). Therefore the saturated aldehyde on Pt(100) would have a BE in the range of -14 to -15 kcal/mol (Table 6), far smaller than that of the η_4 geometry.

To improve the selectivity in unsaturated alcohol, a first possibility, for prenal or cinnamaldehyde, is to favor the (111) face of platinum since this is the only face on which the di-σ_{CO} geometry can be preferred (if we except the step for prenal). This can be done by trying to expose preferentially this face either by making large particles or by using supports on which epitaxy can occur. Step and edge atoms should be avoided because they tend to favor C=C coordination. Another possibility is to improve the adsorption and the reactivity of the C=O bond compared to the C=C one. We have seen before that the main attractive effect in the adsorption of aldehydes on surfaces was the backdonation from the metal orbitals into π^*_{CO}. When this orbital is shifted down, the interaction is better and the adsorption stronger. This shift can be obtained when the C=O bond is complexed by Lewis acids which have been shown to increase the selectivity of platinum catalysts towards unsaturated alcohol. The same effect is obtained when the orbitals of Pt are shifted up. This is the case for Pt on graphite, which has been shown to increase the charge density of platinum by charge transfer (4, 11b), or for Pt–Fe and Pt–Sn alloys. The consequence is a better backbonding into π^*_{CO} and also a worse donation from the π_{CC} orbital which leads to a preferred C=O adsorption for Pt on graphite or for these alloys.

On Pd(111) the preferred adsorption mode is η_4 except for prenal. From the case of platinum, we can assume that on Pd(100) it would also be η_4. Consequently, the product of the hydrogenation on palladium would rather be the saturated aldehyde, since this metal is a good catalyst for hydrogenating the C=C bond but a very poor one for hydrogenating the aliphatic C=O bonds. This is effectively the case for crotonaldehyde. It is known, however, that palladium can hydrogenate the aromatic aldehydes. Therefore, it is assumed that it can hydrogenate the C=O bond of cinnamaldehyde which is vinylogue with benzaldehyde. Since cinnamaldehyde is η_4 on Pd, the C=O bond can be hydrogenated together with the C=C one, giving the saturated alcohol. This explains why on palladium the saturated alcohol is obtained with a high yield as primary product during the hydrogenation of cinnamaldehyde. When a metallic salt is added ($FeCl_2$) the adsorption of the C=O bond is favored, as explained before. However, both the di-σ_{CO} and the η_4 modes involve the C=O bond and hence both would be stabilized. Therefore the η_4 mode would be still preferred and the production of the unsaturated alcohol would not be improved, as is the case on platinum.

Our calculations also allow us to explain why osmium and iridium are selective in unsaturated alcohols without promoters or alloying. We have seen that adsorption of the C=C bond is very sensitive to the substitution because the role of the four-electron repulsive interactions is important. The larger the radial expansion of the *d* orbitals of the metal, hence the broader the *d*-band width, the stronger the repulsive interactions (see the comparison Pd/Pt in Section III-2), and therefore the more improbable the C=C adsorption. Now, osmium and iridium have a much larger *d*-band width than platinum (31),

which implies that the adsorption through C=O would be preferred leading selectively to unsaturated alcohols. In addition these metals have a less filled *d*-band, which results also in a diminution of the repulsive effects.

VI. CONCLUSION

The adsorption mode of an α–β ethylenic aldehyde on a metal surface is strongly dependent on the nature of the metal and the type of exposed crystal face. The knowledge of these adsorption modes is of great importance for understanding the selectivity of the hydrogenation of α–β unsaturated aldehydes. From the present calculations, we can conclude that there are two basic reasons not to obtain the hydrogenation of the C=O bond and hence the desired unsaturated alcohol.

The first one is simply that the C=O π system is not utilized in the molecular adsorption. This is the case when the C=C bond is only involved in the chemisorption (e.g. in a di-σ_{CC} coordination) eventually complemented by an interaction of the oxygen lone-pair with the surface. This is the typical situation for a platinum catalyst. The cure in that case can be to decrease the binding of the C=C part, which can be done by an increase of the repulsive four-electron interactions with the surface, either by larger substituents (CH_3 instead of H) or by using metals with more extended d orbitals like osmium or iridium. The dense (111) metal face is also not very favorable for the C=C coordination, and a greater participation of this face in the catalyst surface, with large faceted particles or by support epitaxy, can improve the selectivity. The second remedy is symmetrically to favor the interaction of the C=O π system with the surface. Lewis acid promoters would activate the carbonyl and lower the acceptor π^*_{CO} orbital, giving that result. Another possibility is to enrich the surface with electrons by interaction with an active support (graphite or TiO_2) which tends to favor the back-bonding interactions with π^*_{CO} to a larger extent than with π^*_{CC}, favoring C=O coordination. In any case, substituents on the C=O (ketones) should be strongly avoided.

The second basic reason for a poor C=O hydrogenation is an η_4 adsorption where both double bonds are involved in a quasi-planar situation. In that case, the hydrogenation of the C=C bond is generally favored for kinetic reasons. This situation is present when the four-electron repulsions between the surface and the molecule are small and this is the typical case for a palladium catalyst. Such a situation is difficult to improve. Lewis acids for example stabilize both the η_4 and the di-σ_{CO} mode in about equal amounts and are not efficient. Palladium is therefore intrinsically a poor catalyst for selective hydrogenation of the C=O bond of an α–β ethylenic aldehyde. It should be noted that this η_4 adsorption is also present for the open faces or steps of a platinum catalyst and those should be therefore minimized in the catalyst as explained just above.

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