# A theoretical study of dehydrogenation of cyclopentene on Pt(111)

Graciela Brizuela [a,c,*], Norberto Castellani [b,c]

[a] *Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301, USA*
[b] *Plapiqui (UNS-CONICET), Km 7 Camino de la Carrindanga, 8000 Bahía Blanca, Argentina*
[c] *Departamento de Física, Univesidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina*

## Abstract

The dehydrogenation of cyclopentene ($c$-$C_5H_8$) to cyclopentadienyl ($c$-$C_5H_5$) on Pt(111) is studied using a semiempirical molecular orbital method. Two possible mechanisms of reaction are considered. Results show that a sequential mechanism is favored over a simultaneous one. We also find a strong parallelism with previous theoretical results for $c$-$C_6H_{12}$ dehydrogenation to benzene. A bonding mechanism dominated by electron donation from $\pi$ orbitals of $c$-$C_5H_5$ into metal orbitals is found. Similar results have been reported for benzene adsorbed on Pt(111). © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Platinum; Cyclopentene; Dehydrogenation; ASED-MO

## 1. Introduction

Hydrocarbon conversion chemistry over metal surfaces represents an area of significant scientific and technological interest because of its importance in catalytic reforming. Platinum catalysts possess high activity for the conversion of aliphatic hydrocarbons to produce aromatic and branched species [1].

At the present it is widely accepted that long chain ($> C_5$) skeletal isomerization and dehydrocyclization reactions both have the same intermediate of $C_5$ cyclic nature [2,3]. A number of studies have been undertaken to elucidate the structure and chemistry of such molecules on Pt [4–10] and other transition metal surfaces [10–13]. The adsorption and dehydrogenation of cyclopentene ($c$-$C_5H_8$) on Pt(111) has been considered for the first time by Avery [4] using thermal desorption spectroscopy (TDS), work function changes (WFC) and electron energy loss spectroscopy (EELS). This molecule is easily dehydrogenated as the temperature of the substrate increases. To explain the different EELS spectra obtained during this heating process Avery [4] suggests that $c$-$C_5H_8$ tilts out of the surface, and that a cyclopentadienyl ($c$-$C_5H_5$) species is produced at nearly 250 K.

* Corresponding author. Fax: +54-1-607-253-5524; E-mail: gb40@cornell.edu

This species is stable to temperatures near that required for isomerization ($T \cong 500$ K) [4].

Later studies of Campbell et al. [8,10] based on bismuth postdosing TDS, X-ray photoelectron spectroscopic (XPS) and Auger electron spectroscopy (AES) support Avery's proposals. Moreover c-$C_5H_5$ has been identified as a stable intermediate on Cu(100) and Rh(111) arising from the dehydrogenation of either c-$C_5H_8$ or cyclopentadiene (c-$C_5H_6$) [11,13].

Most of the studies of dehydrogenation of cyclic hydrocarbons on transition metals are devoted to $C_6$ ring compounds, using a variety of surface analysis techniques [14–20]. In particular the dehydrogenation of cyclohexene (c-$C_6H_{10}$) to benzene on Pt(111) has been the subject of many studies as a model catalytic system [21–27]. This molecule, adsorbed to the surface with a di-σ-bonded geometry, begins to dehydrogenate at 180–200 K [24]. In the case of cyclohexane (c-$C_6H_{12}$), much of the interest has stemmed from the observation of a low C–H stretching frequency, associated with a molecule–surface interaction [14]. Originally it was supposed that dehydrogenation occurred in a simple step at 200 K. Even though there is now a growing body of evidence that a stable intermediate is produced, the underlying mechanism remains a subject of intense debate [17,24,25].

Kang and Anderson [28], using the atom superposition and electron delocalization molecular orbital (ASED-MO) method, studied the dehydrogenation of c-$C_6H_{12}$ to benzene on Pt(111). They suggest that the bonding to the surface is caused by C–H σ donation to the metal, which also serves to weaken the C–H bonds.

To the best of our knowledge no theoretical studies have been performed on the dehydrogenation of $C_5$ cycles. The objective of the present work is to study the dehydrogenation of c-$C_5H_8$ to c-$C_5H_5$ on Pt(111) at low coverage limit. For that purpose the ASED-MO formalism is used. Theory and model are considered in Section 2.

## 2. Theoretical method and adsorption model

Our calculations were performed using the ASED-MO method. In this quantum chemical technique an Extended Hückel (EH)—like Hamiltonian is used for the calculation of valence electron eigen-energies. The main modification is the substitution of the Wolfsberg–Helmholtz constant for off-diagonal elements by a distance dependent expression [29]. In addition, a pairwise repulsive term is included to take into account the repulsive interaction between screened cores, allowing the determination of equilibrium geometries for the adsorbed species. This formulation, which can be rationalized applying the Hellmann–Feynman theorem [29], has been successfully employed for the adsorption of CO and hydrocarbons on a series of pure transition metals and intermetallics [30–32].

Regarding the atomic basic sets, a full valence s + p + d for Pt, s + p for C and s for H of the Slater type was employed. The atomic parameters (ionization potentials IP and Slater's exponents of atomic orbitals) are listed in Table 1. The IP for the light elements (H, C) have been decreased by 1.0 eV and those of Pt increased by the same amount from tabulated values [33] in order to minimize exaggerated electron drifts.

The dehydrogenation of c-$C_5H_8$ to c-$C_5H_5$ on Pt(111) was studied within the cluster approach. The Pt(111) surface was represented by a 64 atoms cluster distributed in three layers of 27 (first layer), 19 (second layer) and 18 (third layer) atoms. This cluster has the same geomet-

Table 1
Atomic parameters

| Atom | Orbital | $H_{ij}$ (eV) | $\zeta_1$ | $\zeta_2$ | $c_1$ | $c_2$ |
|------|---------|---------------|-----------|-----------|-------|-------|
| C    | 2s      | −19.00        | 1.66      |           |       |       |
|      | 2p      | −10.26        | 1.62      |           |       |       |
| H    | 1s      | −12.60        | 1.20      |           |       |       |
| Pt   | 6s      | −11.00        | 2.55      |           |       |       |
|      | 6p      | −7.96         | 2.25      |           |       |       |
|      | 5d      | −11.60        | 6.01      | 2.40      | 0.6567 | 0.5715 |

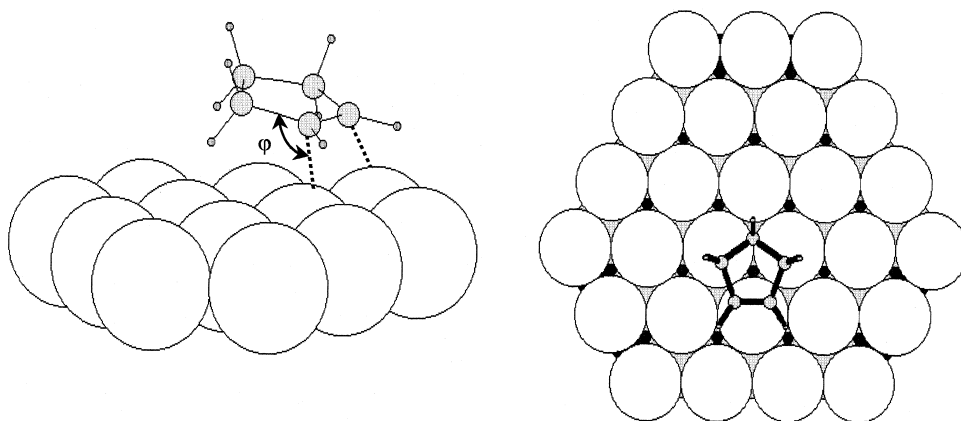Fig. 1. Adsorption geometry for c-$C_5H_8$/Pt(111).

ric periodicity of bulk Pt and no reconstruction was included for the first layer.

Energy ($E$) values reported in Section 3 were calculated making the following total energy difference:

$$E = E_T(\text{c-}C_5H_n/Pt_{64}) - E_T(\text{c-}C_5H_n)$$
$$- E_T(Pt_{64}) \tag{1}$$

where $C_5H_n/Pt_{64}$, c-$C_5H_n$ and $Pt_{64}$ refer to adsorbate-on-cluster system, the free c-$C_5H_n$ specie and the bare Pt cluster, respectively. The ASED-MO calculations are not accurate enough to predict reliable adsorption or dissociation energies, but provide reasonable adsorption geometries. The method gives correct orders for the site adsorption preference and for reaction trends. More details of this method are given in the literature [28–33].

A geometrical optimization of a cluster model for c-$C_5H_8$ and c-$C_5H_5$ on Pt(111) had been carried out previously using the ASED-MO method [34]. For each species the ring-surface distance ($d_{C5-Pt}$) was optimized to get the minimum total energy ($E_{ads}$) and hence to establish the site preference. This optimization was performed maintaining the other geometrical parameters fixed at the free molecule values [35,36]. For the most favored site a full optimization of interatomic distances and bond angles was done. The c-$C_5H_8$ molecule adsorbed in the most favored site and the angle of inclina-

tion of the $C_5$ ring can be seen in Fig. 1. The c-$C_5H_5$ species was considered to have a geometric orientation which is nearly parallel to the Pt surface, as proposed by Avery [4] (see Fig. 2). In both cases the molecule was placed near the center of the cluster to avoid undesirable border effects. Nevertheless, calculations performed with a smaller cluster of 25 atoms (distributed in three layers of 12, 7 and 6 atoms) gave almost the same trends as those obtained with the bigger cluster.

In the present study we have considered two possible mechanisms of dehydrogenation. In the first one, three hydrogen atoms were abstracted sequentially. In the second one they were abstracted simultaneously. In both mechanisms, the hydrogen atoms were transferred to hollow surface sites following linear trajectories. For the sequential mechanism the chosen steps are
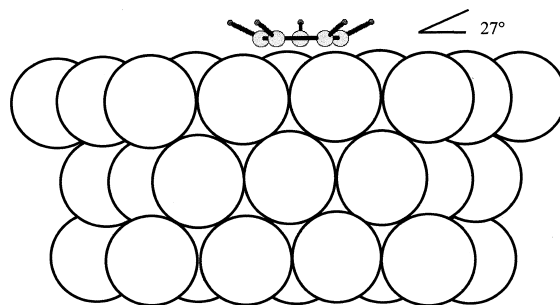


Fig. 2. Adsorption geometry for c-$C_5H_5$/Pt(111).
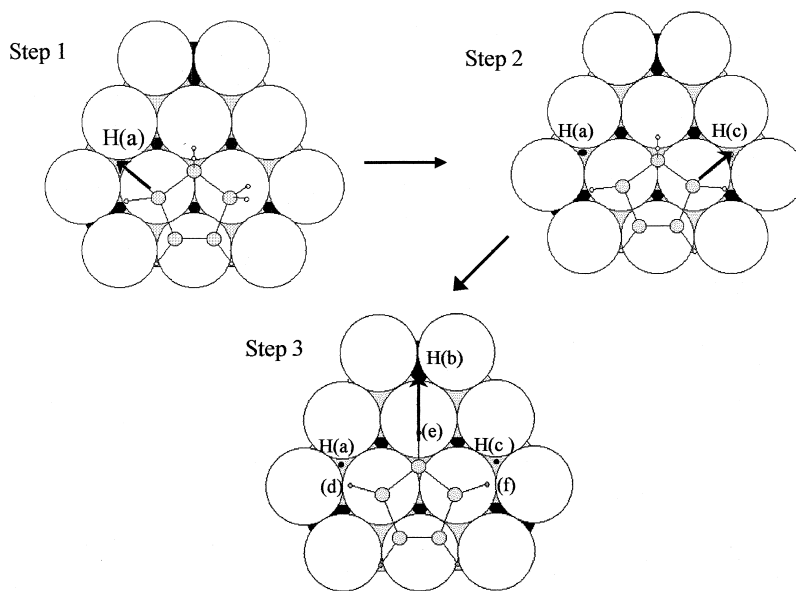
Fig. 3. Sequential mechanism of dehydrogenation of c-$C_5H_8$/Pt(111).

shown in Fig. 3. In the first step of this mechanism we stretched the C–H(a) bond of the c-$C_5H_8$ molecule, adsorbed in the most favored site. At the same time and linearly with this step we diminished the ring-C–H(d) angle, until this bond was coplanar with the $C_5$ ring (see Fig. 4). In the second step we carried out the same procedure with C–H(c) and C–H(f) bonds. The ring-surface distance ($d_{C5-Pt}$) was continuously optimized during the two mentioned hydrogen

abstractions. During the third hydrogen abstraction the C–H(b) bond was stretched, while the ring-C–H(e) angle ($\alpha$) was linearly diminished. In this step the angle of inclination of the $C_5$ ring ($\beta$) and the ring-surface distance ($d_{C5-Pt}$) were also optimized, as is shown in Fig. 5.

In the simultaneous mechanism of reaction hydrogen atoms were transferred concurrently to the hollow sites, according to a procedure which involved at the same time: C–H(a,b,c) bonds stretching, ring-C–H(d,e,f) angles de-
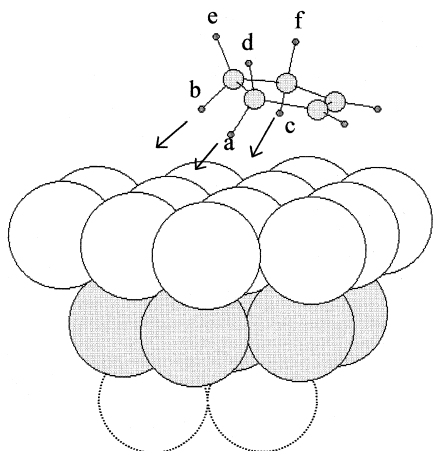


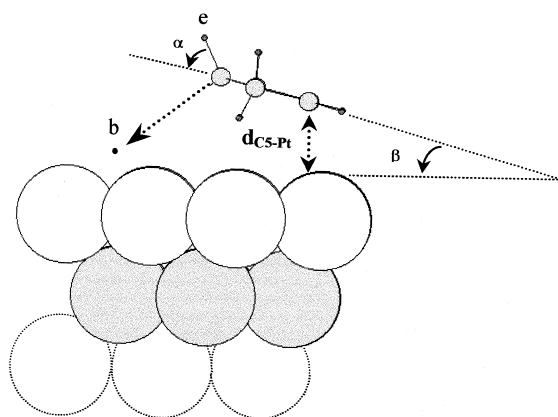Fig. 4. Lateral view of the mechanism of dehydrogenation of c-$C_5H_8$ /Pt(111).



Fig. 5. Geometrical rearrangement for the last hydrogen abstraction.

creasing, angle of inclination of the $C_5$ ring ($\beta$) and ring-surface distance ($d_{C5-Pt}$) optimizations.

In Section 3 the adsorption of the reactant (c-$C_5H_8$) and the product (c-$C_5H_5$) are discussed and afterwards, the analysis of our dehydrogenation models are considered.

# 3. Results and discussion

## 3.1. Reactant and product adsorption

The results corresponding to the geometrical optimization of c-$C_5H_8$ and c-$C_5H_5$ on Pt(111) are given in Table 2. We can observe that the adsorption energy ($E_{ads}$) for c-$C_5H_8$ is relatively small ($= -0.120$ eV), indicative of an interaction of physical nature between molecule and surface. We are in the presence of a weakly adsorbed molecule, which further dehydrogenates. Experimental results from Henn et al. [9] show that at low exposures ($< 0.23$ l) the amount of c-$C_5H_8$ undergoing dehydrogenation is at least 12 times greater than that which desorbs. Kang and Anderson [28] in a theoretical study, report $E_{ads}$ for c-$C_6H_{12}$ of about $-0.42$ eV, which is also a weakly adsorbed molecule on Pt(111). Furthermore experimental results also found that the reactant (c-$C_6H_{12}$) is weakly bonded to the Pt(111) surface, when comparing with the adsorption of the dehydrogenation product (benzene) [21–25].

The high coordination side, designed as 3CO (three-fold octahedral), is only slightly more favored than the other ones considered for c-$C_5H_8$ [34]. Notice that for this geometry the double C=C bond is placed just above a Pt atom (see Fig. 1). The $d_{C5-Pt}$ distance is relatively large ($= 3.5$ Å) in comparison with those corresponding to other unsaturated hydrocarbons (such as ethylene), in good correlation with a weaker ring-surface bonding. When the C–H, C=C and =C–H distances for the c-$C_5H_8$ free molecule are compared with those for the adsorbed molecule, no significant differences are observed, while the C–C distance undergoes a small relaxation of about 0.05 Å. These results are also an indication of a weak adsorbate–substrate interaction. An observation to be underlined is the fact that the molecule has an inclination angle $\beta$ with respect to the Pt plane (see Fig. 5). Notice that the value obtained for this angle increases the $\angle$C–C–Pt angle ($\varphi$ in Fig. 1) from 90 (without inclination) to 104°, which is close to the value of 107.8° reported for the saturated c-$C_5H_{10}$ molecule [34]. Although there are no direct experimental evidences of an inclined geometry for the c-$C_5H_8$ molecule, the interpretation given by Avery [4] to its EELS spectra is coherent with the existence of two inclined species (inferred by geometrical modeling) at angles of 30 and 70° with respect to the surface. Another indirect evidence of this inclination is the fact that c-$C_5H_8$ attains a maximum surface coverage higher than c-$C_5H_{10}$ adsorbed on Pt(111), where a plane geometry was proposed [6]. The ensemble requirement for the adsorption on the Pt(111) surface can be obtained combining TDS data with XPS measurements, as well as using the bismuth postdosing technique, indicating in both cases that 4 Pt atoms are necessary to adsorb one c-$C_5H_8$ molecule, while near 4.5 Pt atoms are necessary for c-$C_5H_{10}$ [9,10].

Table 2
Equilibrium chemisorptive properties for c-$C_5H_8$ and c-$C_5H_5$/Pt(111)

| Species | Site | $d_{C5-Pt}$ (Å) | $\alpha^{a}$ (°) | $\beta^{b}$ (°) | $d_{C-C}$ (Å) | $d_{C-H}$ (Å) | $d_{C=C}$ (Å) | $d_{=C-H}$ (Å) | $E_{ads}$ (eV) |
|---|---|---|---|---|---|---|---|---|---|
| c-$C_5H_8$ | 3CO | 3.5 | – | 15 | 1.67 | 1.20 | 1.44 | 1.18 | −0.121 |
| c-$C_5H_5$ | 3CT | 2.0 | 27 | 0 | 1.55 | 1.15 | – | – | −2.936 |

[a] Ring-C–H angle (see Fig. 2).
[b] Angle of inclination of the $C_5$ ring (see Fig. 5).

It should be mentioned that for the c-$C_5H_8$/Pt(111) system the XPS spectra of C1s level has a binding energy which is indicative of a preponderant sp$^3$ hybridization [9]. According to this, we note that both the monolayer and the multilayer of c-$C_5H_8$ present C1s-binding energy values which are very close to those corresponding to the monolayer and the multilayer of c-$C_6H_{12}$, respectively [9,37].

Table 2 also summarizes the results concerning the geometrical optimization of c-$C_5H_5$ on Pt(111). The $E_{ads}$ value is one order of magnitude greater than that corresponding to c-$C_5H_8$, pointing out that in this case an interaction of chemisorptive nature is present between molecule and surface. This observation is in agreement with the fact that c-$C_5H_5$ is a stable species up to 480 K. The adsorption site 3CT (three-fold tetrahedral) is the most favored one [34]. The $d_{C5-Pt}$ distance is notably shorter (= 2.0 Å) than that of c-$C_5H_8$, in concordance with our reasoning of a stronger adsorbate–metal interaction. Although at the present no experimental information relative to the geometrical equilibrium parameters for adsorbed c-$C_5H_5$ is available, a parallelism with the unsaturated six carbon rings could be made. Anderson et al. [33] studying the adsorption of benzene on Pt, Ni and Ag(111) find that the most favored site is that of highest coordination and that the adsorption energy is an increasing function of the coordination number. Equilibrium benzene-surface distances obtained for these geometries are very close (within ≅ 0.1 Å) to our result for c-$C_5H_5$ ($d_{C5-Pt}$). Moreover, theoretical studies of c-$C_6H_6$/Ni(111) allow to conclude a generalized preference for the tricoordinated sites [38–40]. Experimental studies of benzene on Pt, Ni and Ag(111) performed by Avouris and Demuth [41] and Lehwald et al. [42] show that benzene adsorbs on tricoordinated sites, disposing its molecular plane parallel to the metallic surface.

Jing and Whitten [40] in a theoretical ab initio study of the adsorption of benzene on Ni(111) report that the C–H bonds present an important bending-away angle of 8.5° with respect to the molecular plane. Experimental studies suggest the same behavior when benzene is adsorbed on Rh(111) [43]. An important bending-away angle ( = 20°) has also been reported by Anderson et al. [33] for benzene on Pt(111). These authors give an explanation of this molecular distortion which takes into account an optimization of the overlapping between the benzene $\pi(e_{1g})$ orbital and the d metallic orbitals. In our calculations for c-$C_5H_5$ the bending-away angle is even greater (with a value of 27°).

In order to reveal a possible rehybridization of c-$C_5H_8$ and c-$C_5H_5$ species the overlap population (o.p.) of C–C, C–H and C–Pt bonds and the net electronic charge are compared with those of the free species [34]. The results show that for the c-$C_5H_8$ molecule all these bonds undergo negligible modifications. Moreover the C–Pt bond is of no bonding character, in agreement with a negligible charge transfer between molecule and surface. On the other hand for c-$C_5H_5$ the C–C o.p. undergoes an important decrease ( ≅ 8.6%), a situation indicative of a significant weakening in C–C bonds. The C–H bond turns out more strengthened ( ≅ 3.2%). Both observations might be considered as a clear evidence of the hybridization of c-$C_5H_5$ valence molecular orbitals. Furthermore, this fact can be verified in the large o.p. value of bonding character between C and Pt atoms. A significant electron transfer ( ≅ 0.5 e$^-$) from the c-$C_5H_5$ molecule toward the surface has also been obtained [34].

The study of the electronic structure of c-$C_5H_8$ and c-$C_5H_5$ on Pt(111) using the electronic local density of states (LDOS) reveals that while c-$C_5H_8$ molecular orbitals hybridize very slightly, those of c-$C_5H_5$ undergo a much more important hybridization, as it can be appreciated in Fig. 6 [34]. These observations are in complete correlation with the o.p. analysis performed for C–Pt and C–C bonds.

Theoretical studies concerning benzene adsorbed on transition metal surfaces show that
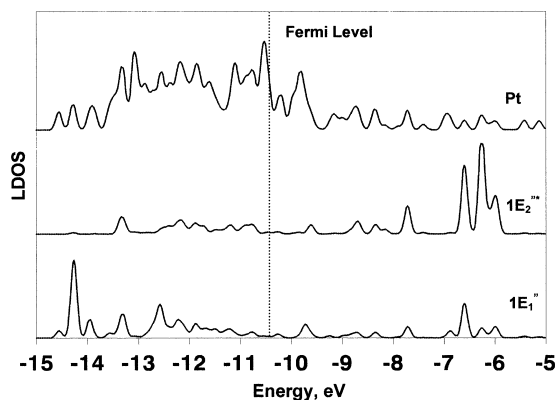
Fig. 6. Projected LDOS curves of $1E_1''$ and $1E_2''{}^{*}$ orbitals for c-$C_5H_5$ and LDOS of the Pt atom nearest to the ring.

benzene molecular orbitals also present an extended coupling with the d atomic orbitals of the metal [33,38–40]. In agreement with this observation, Campbell et al. [8] report that the binding energy value found for the C1s level of c-$C_5H_5$ on Pt(111) is very close to that obtained for benzene on the same metal.

### 3.2. Dehydrogenation reaction

For the sequential and simultaneous mechanisms of reaction considered in the present study the curves of energy vs. reaction coordinate are displayed in Figs. 7 and 8, respectively. From these curves we observe that in both cases the overall energetic balance is endothermic.

The activation energies ($E_{activ}$) calculated for our proposed mechanisms are shown in Table 3. It can be appreciated that the sequential mechanism ($\sum E_{activ} = 5.143$ eV) has lower combined activation barrier than the simultaneous one ($E_{activ} = 7.089$ eV). We can also observe that, when the second and third hydrogens are removed, the $E_{activ}$ becomes progressively lower. The $E_{activ}$ values for the first and second hydrogen abstractions are close because they have similar symmetry (see H(a) and H(c) in Fig. 3). However when the third hydrogen is removed the $E_{activ}$ diminishes even more. This lower value might be due to a $\sigma$ donation from the C–H bond to the metal through a three center
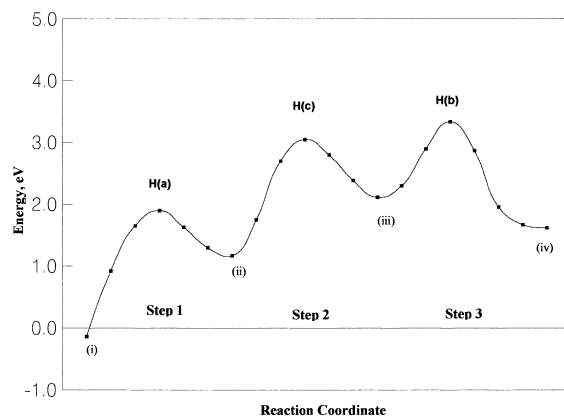


Fig. 7. Total energy vs. reaction coordinate for the sequential mechanism of reaction. From (i) to (ii): C–H(a) bond stretching, decreasing of the ring-C–H(d) angle and ($d_{C5-Pt}$) distance optimization. From (ii) to (iii): C–H(c) bond stretching, decreasing of the ring-C–H(f) angle and ($d_{C5-Pt}$) distance optimization. From (iii) to (iv): C–H(b) bond stretching, decreasing of the ring-C–H(e) angle, ($d_{C5-Pt}$) distance optimization and angle of inclination of the $C_5$ ring ($\beta$) optimization.

C–H–Pt bond, also proposed by Kang and Anderson for $C_6$ rings [28]. During the third C–H bond-breaking a direct interaction is possible with a Pt atom, located just below the hydrogen pathway towards a three-fold site (see Fig. 3). In addition, the ring has a lower $d_{C5-Pt}$ distance (= 2.2 Å). Consequently, this hydrogen atom is geometrically more favored than the others to generate a three center C–H–Pt bond, achieving a greater stabilization for the transition state. Another reason the lower $E_{activ}$ for the last
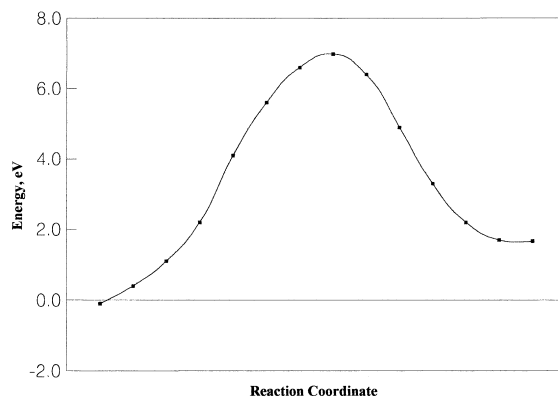


Fig. 8. Total energy vs. reaction coordinate for the simultaneous mechanism of reaction.

Table 3

Adsorption energies, ring-surface distances and activation energies for the sequential dehydrogenation of c-$C_5H_8$ and c-$C_6H_{12}^a$

| Adsorbate | c-$C_5H_8$ | c-$C_5H_7$ + H | c-$C_5H_6$ + 2H | c-$C_5H_5$ + 3H |
|---|---|---|---|---|
| $E$ (eV) | −0.121 | 1.168 | 2.115 | 1.670 |
| $d_{C5-Pt}$ (Å) | 3.5 | 3.5 | 2.2 | 2.2 |
| $E_{activ}^b$ (eV) | – | 2.014 | 1.880 | 1.249 |

| Adsorbate | c-$C_6H_{12}$ | c-$C_6H_{11}$ + H | c-$C_6H_{10}$ + 2H | c-$C_6H_9$ + 3H |
|---|---|---|---|---|
| $d_{C-Pt}$ (Å)$^c$ | 3.23 | 3.13 | 2.68 | 2.01 |
| $E_{activ}$ (eV) | – | 1.25 | 1.16 | 0.74 |

[a] c-$C_6H_{12}$ dehydrogenation results reported by Kang and Anderson [28].
[b] $E_{activ}$ = 7.089 eV for the simultaneous mechanism, $\sum E_{activ}$ = 5.143 eV for the sequential mechanism.
[c] Shortest C–Pt distance.

hydrogen transfer could be the stronger interaction between the surface and the product, c-$C_5H_5$. Indeed, as we mentioned above, this species undergoes an extended rehybridization of its $\pi$ orbitals.

Demuth et al. [14] in an EELS study observe a softening and broadening of the C–H bond stretching frequency upon adsorption of c-$C_6H_{12}$ on Pt(111) at 140 K. They suggest that this shift is associated with an attractive bonding interaction between hydrogen atoms and the surface. Other authors explain the softening in terms of the geometric match between C–H bonds of the adsorbate and high coordination sites of the substrate [44]. The exact fitting of C–H bonds on the hexagonal surface lattice gives the enhanced lower energy peak intensity, because the C–H to metal $\sigma$ donation is maximized when the C–H bonds are aimed directly at the surface metal atoms. They suggest that the C–H mode softening results from an interaction of lower axial C–H bonds with three-fold hollow sites [44].

The $E_{activ}$s corresponding to the sequential dehydrogenation of c-$C_6H_{12}$, reported by Kang and Anderson [28], are included in Table 3 in order to compare with our results. It can be see that these energies are lower than those corresponding to the dehydrogenation of c-$C_5H_8$. However $E_{activ}$s become lower with the progress of both reactions. Relative values, referred to the first hydrogen abstraction, are similar to

each other for $C_5$ and $C_6$ species ($\cong$ 7 and 43% for second and third hydrogen abstractions, respectively).

On the basis of their results Kang and Anderson [28] propose a mechanism for dehydrogenation where not all the six C–H bonds are simultaneously broken. The initial removal of a hydrogen atom from adsorbed c-$C_6H_{12}$ is the slowest step in the dehydrogenation process, followed by the formation of a partially dehydrogenated intermediate, c-$C_6H_9$, which loses three more hydrogen atoms in a relatively easy way. Once the loss of the first three hydrogen atoms has been completed the c-$C_6H_9$ molecule approaches very close to the surface to form three C–metal bonds. At this point the chair-shaped $C_6$ ring will begin to flatten in shape, and the last three hydrogen atoms will come off with low barriers, leading to a planar benzene. These authors consider that barriers are low because of C–H $\sigma$ donation to the surface through C–H–Pt bonds, previously mentioned.

Experimental studies find that c-$C_6H_{10}$ is formed as a surface intermediate in the dehydrogenation of c-$C_6H_{12}$ on Pt(111) [45]. The short lifetime of this intermediate is consistent with the idea that the initial dehydrogenation of c-$C_6H_{12}$ is the slowest step. Rodriguez and Campbell [24] report that the dehydrogenation of c-$C_6H_{10}$ on Pt(111) follows a mechanism in which four C–H bonds are broken before 350 K. It is not obvious whether this mechanism

involves a simultaneous breaking of four C–H bonds in a concerted step or a sequential dehydrogenation process, passing through species of stoichiometry between c-$C_6H_9$ and c-$C_6H_7$, which further decomposes. However, on the basis of the extremely low pre-exponential factor, the concerted mechanism can be considered unlikely. On the other hand for large exposures of c-$C_6H_{10}$ a new intermediate, with stoichiometry between c-$C_6H_9$ and c-$C_6H_8$, is formed and stabilized at 350 K. Indeed, several experimental studies of c-$C_6H_{12}$ and c-$C_6H_{10}$ dehydrogenation on Pt(111) propose a sequential mechanism, and the formation of an intermediate of c-$C_6H_9$ composition [17,18,20,25].

Henn et al. [9] determine the $E_{activ}$ for the dehydrogenation of c-$C_5H_8$ to c-$C_5H_5$ on Pt(111) (13.3 kcal/mol). This value is very similar to that determined for the conversion of c-$C_6H_{12}$ to benzene on the same metal (13.4 kcal/mol). This similarity is consistent with the fact that the C–H bonds being broken in each case belong to $sp^3$-hybridized carbons and in contrast with the higher $E_{activ}$ ($\cong 28$–$33$ kcal/mol), required for C–H breaking in $sp^2$-hybridized systems, such as adsorbed benzene or c-$C_5H_5$. Our theoretical results of the $E_{activ}$ for the dehydrogenation of c-$C_5H_8$ (40 kcal/mol) are higher than the experimental value. The limitations of the ASED-MO method to predict absolute values for energies were mentioned in Section 2. However we think that our results reproduce well the catalytic behavior of the studied system and contribute to understand the dehydrogenation reaction mechanism.

## 4. Conclusions

In the present paper we studied the dehydrogenation of c-$C_5H_8$ to c-$C_5H_5$ adsorbed on Pt (111) at low coverage limits. The calculations show that in our model of reaction a sequential mechanism is favored over a simultaneous one. We also find a strong parallelism with previous theoretical results for c-$C_6H_{12}$ dehydrogenation

to benzene. Moreover, there are considerable experimental analogies between the dehydrogenation of $C_5$ and $C_6$ cyclic hydrocarbons. A sequential mechanism is supported for c-$C_6H_{12}$ and c-$C_6H_{10}$ dehydrogenations, while no conclusive experimental evidences have been reported for $C_5$ cyclic molecules. Calculations for benzene and c-$C_5H_5$ adsorbed on Pt(111) suggest a bonding dominated by electron donation from $\pi$ orbitals of the dehydrogenated species into metal orbitals of the surface.

The mechanisms discussed in this paper require a large ensemble of free Pt atoms. We cannot rule out alternate mechanisms but comparing the two studied mechanisms, which involve similar molecular rearrangements, the sequential one results are preferred.

## Acknowledgements

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