A Quantum Chemical Approach to the Influence of Platinum Surface Structure on the Oxygen 
Electroreduction Reaction

C. F. Zinola and A. J. Arvia*

Instituto de Investigaciones Físicoquímicas Técnicas y Aplicadas (INIFTA), Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, (1900) La Plata, Argentina

G. L. Estiu and E. A. Castro

Programa de Química Inorgánica (QUINOR), Universidad Nacional de La Plata, Casilla de Correo 962, (1900) La Plata, Argentina

Received: January 21, 1994; In Final Form: May 2, 1994* 

The O2 electroreduction reaction (OERR) on Pt behaves as a structure sensitive reaction whose peroxy intermediates are formed in a greater extent on Pt(100) than on Pt(111) surfaces. A semiempirical quantum chemistry interpretation of this behavior is achieved on the basis of the study of [Pt]xO2OH systems, where N, the number of atoms in the Pt cluster, equals 18 and 25. Calculations indicate that dissociative O2 electroadsorption on Pt(111) and molecular O2 on Pt(100) are favored. As a result of the interactions of O2 and OH in adjacent positions, hydroperoxide intermediates are formed on Pt(100) leading to the possibility of having H2O2 as product from the OERR.

1. Introduction

The molecular oxygen electroreduction reaction (OERR) on Pt in acid solutions is one of the most relevant electrochemical reactions.1-3 It has been interpreted by a complex mechanism involving first the adsorption of molecular O2, followed by a charge transfer step and desorption of electroreduced adsorbates, finally leading to H2O as the main product, and to H2O2 as minor product.4-6

Recent OERR kinetic data have shown different current density vs electrode potential relationships, depending on the topography of the Pt electrode in both acid7,8 and alkaline solutions.9 To account for these results,5,10-12 a more adequate interpretation of the OERR kinetics can be given by considering that there is a competition between the four-electron electroreduction to H2O and the two-electron electroreduction to H2O2, which can further decompose to H2O. The relative contribution of each reaction depends on the Pt surface crystallography, the applied potential, and the nature and concentration of anions in the solution.13,14 The value of θs, the stationary Pt surface coverage by O-containing adsorbates in O2-saturated solution, changes almost linearly with the applied potential for all Pt surfaces.7 However, values of θs are greater for Pt(100) than for Pt(111) and polycrystalline (pc) Pt, implying for the former an additional contribution to θs from other oxygenated adsorbed species.

The formation of H2O2 in the course of the OERR in aqueous solutions was almost twice as much for Pt(100) than for Pt(111) and pc Pt electrodes.7 The difference indicates either a more strongly adsorbed peroxy species or a faster H2O2 decomposition on Pt(111) and pc Pt surfaces. Furthermore, the higher contribution of peroxy intermediates to the OERR on Pt(100) can explain the greater θs values found in O2-saturated acid solutions.7

The difference in the electronic characteristics of adsorption sites, resulting from the different crystallographic structures, leads to a topology dependence of the heterogeneous catalytic reaction kinetics. It has recently been found for the OERR on faceteds8 and single crystal9 Pt electrodes that there is a structure sensitivity in both acid and alkaline media, with a larger relative contribution of the two-electron reaction pathway on Pt(100) than on Pt(111) and pc Pt. There facts were assigned to different interactions between O2 and the reaction intermediates with Pt(100) and Pt(111) surface structures.

Both experimental gas-phase15-18 and theoretical19-24 studies have shown different characteristics of O2 adsorption on Me(100) and Me(111) surfaces (Me = transition metal). Thus, adsorbate configurations, resulting from molecular O2 adsorption on Pt(100) (5 × 20) surfaces, depend on the degree of reconstruction of the Pt surface, as it can be inferred from thermal desorption spectroscopy (TDS) and X-ray photoemission measurements.25 Activation energies of ca. 0.4 eV were found by molecular beam studies15 for the dissociative adsorption of O2 on Pt(100) with an enhancement of the sticking probability and no change on the threshold dissociation energy between 300 and 600 K.

Otherwise, on Pt(111), molecular O2 only predominates with respect to the O adatom, at temperatures below 120 K.26 Electron energy loss spectroscopy (EELS) data show a primary vibrational mode at 870 cm−1, which is characteristic of peroxy-type species.26,27 According to near edge X-ray adsorption fine structure studies (NEXAFS),28-31 molecular O2 lies with the intermolecular axis parallel to the metal surface, in agreement with EELS detection of peroxy species. Likewise, O adatoms predominant at temperatures higher than 170 K, since a single vibrational mode at 490 cm−1, attributed to the O P stretching frequency, is detected.26,32 Hence, the different behavior of the O2(gas)/Pt(111) and O2(gas)/Pt(100) systems provides a first indication of different surface structure O2-Pt interactions which, in principle, could be reflected to some extent in the OERR on different Pt substrates.

Theoretical calculations are mainly related to lower-atomic-number transition metals.19-21,23,24 To our knowledge, no previous theoretical study of the Pt3O2 system has involved either the optimization of the adsorbate structure or the influence of the applied potential.

In this paper, the interaction of an O2 molecule with Pt(100) and Pt(111) cluster surfaces is analyzed at a molecular orbital level, as a first step to understand the influence of the electrode topology on the OERR mechanism. In this way, the selective generation of peroxy species on Pt(100) can be justified on the basis of the involved molecular orbital interactions and the different nature of the adsorbent intermediates on both surfaces.

© 1994 American Chemical Society
2. Methodology

2.1. Calculation Procedure. For the treatment of large polyatomic systems, computational chemistry deals, nowadays, with a compromise between an overall description of the entire system and a more detailed treatment of a properly selected part of it. This situation particularly applies to transition metal structures, which have to be drastically minimized for an adequate ab initio, local density functional, or even semiempirical calculation at a good correlation level.33–36 In contrast to this simplification of the system, the improvement of simpler methods, which are capable of handling the system as a whole, have regained acceptability. This is the case of the extended Hückel molecular orbital (EHMO) method developed by Hoffman,35 which was initially used for a reasonable description of the structural and electronic properties of systems at a frozen geometry. Improvements of this method are mainly related to the addition of two-body electrostatic correction terms.38–42 Accordingly, $E_T$, the total energy of the system, is calculated from the contribution of two terms:

$$E_T = \Delta E_{EHMO} + E_{rep}$$

where $\Delta E_{EHMO}$ is the EHMO binding energy, calculated as the difference between $E_{EHMO}$, the noncorrected EHMO total energy and the summation of the monoelectronic terms; $b_\mu^0$ and $E_\mu^0$ are the occupation number and the valence state ionization potential (VSIP) of the $\mu$th atomic orbital. The correction implies the addition of $E_{rep}$, the repulsion energy,

$$E_{rep} = \sum_A \sum_{\lambda < \alpha} E_{AB}$$

where $E_{AB}$ is the electrostatic repulsion energy between atoms $A$ and $B$ separated by the distance $R_{AB}$. $E_{rep}$ is a pairwise additive term which can be either explicitly calculated for a given pair of atoms38,39,42 or determined from binding energy differences when inner orbitals are either considered or neglected.40,41

Calzaferri et al.42–46 have reformulated the EHMO method by including the following two main modifications.

i. A repulsion energy that explicitly considers both atoms of a given pair,

$$E_{AB} = \frac{Z_A Z_B}{R_{AB}^{1/2}} \left[ Z_A \int \frac{\rho_B(p)}{|r_A - r|} dr + Z_B \int \frac{\rho_A(p)}{|r_B - r|} dr \right]$$

where $Z_i$, $R_i$ and $\rho_i$ are the nuclear charge, position, and electron density of atom $i$, ($i = A, B$), where atom $B$ is more electronegative than atom $A$. The second right-hand side term in eq 4 is the arithmetic mean of $A-B$ and $B-A$ attractive interaction energies.

ii. A distance-dependent exponential factor that modifies the off-diagonal EHMO matrix elements according to

$$H_{\mu\nu}^{AB} = \frac{1}{2} K_{AB} (H_{\mu\nu} + H_{\nu\mu}) S_{\mu\nu}$$

where $K_{AB}$ and $\delta$ are adjustable parameters related by the expression

$$K_{AB} = 1 + \kappa \exp[-\delta (R_{AB} - d_0)]$$

$K_{AB}$ is the EHMO-$K$ parameter used in the off-diagonal Hamiltonian matrix elements, $H_{\mu\nu}^{ab}$, $\mu$ and $\nu$ being the $\mu$th and the $\nu$th orbitals of atoms $A$ and $B$, respectively. $d_0$ is the sum of the atomic radii of $A$ and $B$. $K_{AB}$ and $\delta$ are empirical parameters.

Such a formulation has been demonstrated to be a careful parametrization of the reformulated EHMO method allows us to optimize the geometry of either simple42–46 or organometallic complex molecules46 at a level that can be compared with high-quality calculations.

The preceding calculation procedure was employed to analyze the interaction of a single $O_2$ molecule with Pt(111) and Pt(100) cluster surfaces, including the influence of an applied electrical potential. Because of the complex nature of the electrochemical interface, which involves the solution constituents, adsorbates, and substrate, the interaction energy resulting from coadsorbed species was considered to find out whether $O_2$ dissociation is favored and to envisage the stability of adsorbates and final products, which can be related to the OER on different Pt electrode surfaces.

2.2. Calculation Details. Values of the VSIP in eq 5 are experimentally based, and valence orbitals are of the Slater form. The $O_2$ molecule-Pt site interactions are represented as an adsorbed ensemble, which is characterized by its specific VSIP. The VSIP value, which defines the equilibrium potential of the system, i.e., the zero applied potential condition, results when the charge transfer at the equilibrium distance of each intranuclear bond is close to that predicted for the adsorbed ensemble from the electronegativity difference, according to Pauling's ionicity relationship.53 VSIP values, adjusted in this way, are assembled in Table 1.

Following the previously described method,44 VSIP and Slater orbital exponents were taken from refs 46 and 54 for the substrate and the adsorbate, respectively. Values $\delta = 0.035$ nm$^{-1}$ and $K_{AB} = 1.75$ have been set in eq 6. Results from different $K_{AB}$ values ($1.5 \leq K_{AB} \leq 2.0$) have also been compared, and the $K_{AB}$ that best describes bond lengths and adsorption energies in Pt for testing clusters has been adopted. The VSIP adjustment to charge-transfer conditions was made for different $(K, \delta)$ pairs. The best set of $K$, $\delta$, VSIP, and Slater orbitals was finally chosen from the description of the adsorption interactions.

As a positive applied electric potential ($E$) shifts downward the metal energy Fermi level and vice versa, changes in the electrode potential were simulated by either decreasing or increasing the absolute value of the metal VSIP from the reference equilibrium value, for negative or positive charging, respectively.53–56 (Table 1). The $\Delta(\text{VSIP})/\Delta E$ value was set equal to 1, as there was no other clear experimental evidence which could justify a different choice.

High spin bulk superimposable bilayer Pt$_N$ clusters, with the number of atoms $N = 18$ and $N = 25$ for Pt(100), and $N = 18$ for Pt(111), (Figure 1), were used to model Pt surfaces. Clusters were geometrically built up, keeping the Pt-Pt bond length, $r_{Pt-Pt}$, constant at 0.277 nm. This figure, which has been used in previous calculations,55,56 agrees with the Pt-Pt interatomic distance in bulk Pt.57 The open shell configuration of the $O_2$ molecule ($\Sigma^+_g$) has been considered in the definition of the spin magnetic
moment of the PtN2O2 adsorbed ensemble which, according to the d-rule,48 involves at least one electron in each d-band molecular orbital.

Different types of adsorption sites can be defined on Pt single crystals, namely, on-top (1-fold), bridge (2-fold), and hollow (higher coordinated sites). Hollow sites are associated with a 5-fold coordination of an O atom on Pt(100) (four Pt atoms of the topmost layer and one Pt atom from the underlying layer). Otherwise, either three or four Pt atoms may define the hollow coordination in Pt(111), depending on whether the fcc or the hcp local symmetry, i.e., the (3-1) or the (3-3) hollow site, respectively, is involved. The interaction of an O2 molecule with these sites defines several adsorption configurations (see section 3.1).

The interaction of a single O2 molecule with a Pt surface was initially considered, but the OER in aqueous environments also involves H2O and other coadsorbed intermediates on the Pt surface. In the 0.60-1.00-V (vs reversible hydrogen electrode) potential range, where O2 adsorption takes place, there is an important contribution of adsorbed OH species. Therefore, the stability of the adsorbed ensemble, constituted by O2, OH, and Pt sites, was evaluated as a function of the applied potential. While the coordinates of the Pt atoms were kept frozen in the calculations, the Pt-O, O-O, and O-H distances and angles were fully optimized to minimum energy.

3. Results and Interpretation

3.1. Interaction of a Single O2 Molecule with Pt(111) and Pt(100) Cluster Surfaces: The Most Likely Stable Configuration of the Adsorbed PtN2O2 Ensemble. Because of the important role of O2 frontier orbitals (π, π*) in the interaction with the Pt surface, adsorption geometries with the O-O interatomic bond parallel to the Pt surface plane are likely to occur. However, the "parallel" (side-on) and the "perpendicular" (end-on) configurations were compared. Among possible configurations, the most important ones are those which involve either the coordination of one O atom to a single surface site (1-fold, bridge and hollow coordination) (Figure 2a-c) or the simultaneous coordination of both O atoms from O2 to a unique surface site (on-top side-on or bridge side-on configuration) (Figure 2d,e).

The geometry of each adsorbate configuration was fully optimized in bond distances and planar and dihedral angles, taking into account the orientation of the O-O bond relative to the Pt-Pt bond in the lattice.

The geometrical characteristics and relative stabilities of each adsorbate structure are compared in Table 2. Binding energies, BE, were calculated as

\[ BE = -(E_{T,PtO2} - E_{T,Pt} - E_{T,O2}) \]  

where \( E_{T,PtO2} \), \( E_{T,Pt} \), and \( E_{T,O2} \) are the total energy, of PtN2O2, PtN, and O2, respectively, resulting from eq 1. The \( E_{T,O2} \) value results from a full optimization of the \( 2\pi \) configuration, which is known to be the most stable one. From these calculations, \( r_{O-O} \), the equilibrium O-O bond length in an isolated O2 molecule, \( = 0.133 \) nm, a figure which is 6% greater than the experimental

\[ r_{O-O} \text{ value,}^{59,60} \text{ and a dissociation energy of } 2.02 \text{ eV was also calculated. The reproducibility of diatomic O2 experimental data was also considered for the parameter selection.} \]

The optimization of the adsorbed ensemble geometries implies the simultaneous modification of \( r_{O-O} \) and \( r_{Pt-O} \) O-O and Pt-O bond lengths, respectively, Pt-Pt-O and Pt-Pt-O planar angles, and Pt-Pt-O-O and Pt-Pt-Pt-O dihedral angles. To establish
TABLE 2: Molecular O₂ Binding Energies, BE, Repulsion Energies, RE, Optimized Pt-
O and O-O Distances (R_{Pt-O} and r_{O-O}), and Perpendicular Distance from the O Atom Closer to
the Plane of the Pt Surface (h), for Different [Pt(111)]₆O₂
and [Pt(100)]₆O₂ Configurations at Zero Potential

|                  | BE (eV) | RE (eV) | r_{O-Pt} (nm) | r_{O-O} (nm) | h (nm) |
|------------------|---------|---------|---------------|--------------|--------|
| Pt(111)          |         |         |               |              |        |
| on-top-end-on    | -1.9213 | 5.5997  | 0.189         | 0.120        | 0.189  |
| bridge-end-on    | -1.2655 | 5.5839  | 0.217         | 0.116        | 0.168  |
| bridge-side-on   | -2.5920 | 6.2410  | 0.185         | 0.138        | 0.171  |
| on-top-side-on   | -1.3225 | 7.9341  | 0.177         | 0.258        | 0.129  |
| hollow (3-1)     | 0.9211  | 12.4382 | 0.167*        | 0.220        | -0.006 |
| hollow (3-3)     | 2.2500  | 11.3150 | 0.167*        | 0.220        | -0.006 |
| Pt(100)          |         |         |               |              |        |
| on-top-end-on    | -2.3653 | 5.5459  | 0.185         | 0.120        | 0.185  |
| bridge-end-on    | -1.8283 | 4.8146  | 0.207         | 0.130        | 0.155  |
| bridge-side-on   | -4.0749 | 7.3146  | 0.180         | 0.119        | 0.161  |
| on-top-side-on   | -3.3177 | 8.5790  | 0.172         | 0.243        | 0.121  |
| hollow           | 1.5971  | 7.9083  | 0.196*        | 0.218        | -0.019 |

---

Figure 3. Potential energy hypersurface for the bridge side-on O₂
adsorption configuration on [Pt(100)]₆ at 0 eV.

whether molecular or dissociative O₂ adsorption takes place, it
is convenient to analyze the energy change with r_{O-Pt} and r_{O-O},
that is, through the potential energy hypersurface (Figure 3).
This diagram was constructed for each Pt₆O₂ adsorbate ensemble
configuration on Pt(111) and Pt(100) clusters, with the simulta-
nous variations of r_{O-O} and the Pt-Pt-O planar angle (in fact
r_{O-Pt}). The most likely reaction pathway for the O₂ dissociation
was followed through the minimum energy path in the potential
energy profile. For the bridge side-on configuration, the likely
pathway for the dissociation process involves first the opening of
the planar angle from 64° to 80°, i.e., r_{O-O} from 0.12 to 0.18 nm,
then a change in the Pt-O bond length from 0.18 to 0.165 nm,
and finally the perpendicular configuration of O atomic species
is accomplished. Most of the changes in the potential energy
values for the O₂ dissociation are due to the elongation of the
O-O bond distance; therefore it is reasonable to admit only r_{O-Pt}
for the definition of the reaction coordinate of the potential energy
diagram. For this purpose, 0.001 nm stepwise variations in r_{O-Pt}
were searched for minimum energy from the initial r_{O-Pt} = 0.080-
nm value up to those at which O₂ dissociation occurs. Then, for
a fixed r_{O-O} value, other coordinates were fully optimized (Table 2).
Optimized geometries correspond to local minima in the
energy vs r_{O-Pt} plot. These minima do not necessarily imply that
O₂ dissociation is excluded (Figure 5a,b). As a better description
of the potential energy curves for dissociation processes at distances
larger than that of equilibrium, the extended Hückel binding
energy, BE, can be corrected by means of either a self-consistent
charge iteration or the addition of an electrostatic interaction
term between the positive and negative species. The stability of the Pt₆O₂ ensemble can be determined from the energy barrier
that has to be surmounted to go from molecular O₂ to a single
O atom coordinated adsorbate ensemble. According to data
shown in Figure 5a,b, local minima in the energy vs r_{O-Pt} plot are
not clearly defined for some configurations, i.e., hollow adsorption
on Pt(100) and bridge side-on adsorption on Pt(111). Neverthe-
less, in these cases, an inflection point in the energy vs r_{O-Pt}
data (unobservable in the energy scale used in the plot) allowed us
to calculate the geometric properties of the adsorbates at that point
(Table 2).

For the different adsorbate configurations, σ and π O₂ orbitals
are involved, their relative weight depending on the specific
geometry of the adsorption site.

For the linear on-top-end-on coordination (Figure 2a,f) the
interaction of the π O₂ molecular orbital with the (dₘ⁢ₙ, dₓ) Pt
atomic orbital is more important than that of the σ O₂-dₓ Pt,
the z axis being perpendicular to the Pt surface (Figure 4a,f).
The contribution of the σ* O₂ molecular orbital to the stability of the
(σ) Pt atomic orbitals is negligible. The net interaction can be
described as a charge transfer to the Pt surface which, being
similar for both Pt(111) and Pt(100) (Table 3), reflects the local
character of the linear bond.

Otherwise, bridge end-on coordination (Figure 2b,g) implies a
greater stabilization of the σ O₂ molecular orbital, through a
bonding interaction with adjacent Pt atom dₓ₋ₙ orbitals, rather
than a π-type interaction (Figure 4c,g), which involves a
coordination of π orbitals from both Pt and O₂. However, the
more important π interaction on Pt(100) than on Pt(111) appears
to be responsible for the greater stability of the bridge end-on
coordination geometry in Pt(100), and π orbitals are not really
hybridized for a further contribution to Pt-Pt bonding. In spite

---

TABLE 3: Net Charges (q₀₁ and q₀₂) and σ and π Mulliken Populations in the O Atoms (MP₄(O₁₂) and MP₄(O₁₂)), for
Different [Pt(111)]₆O₂ and [Pt(100)]₆O₂ Configurations, as Described in Table 2

|                  | q₀₁ (e) | MP₄(O₁₂) | MP₄(O₁₂) |
|------------------|---------|----------|----------|
|                  |         |          |          |
| free O₂          | 0       | 3.4737   | 2.5263   |
| Pt(111)          |         |          |          |
| on-top-end-on    | 1.5323  | 2.5353   | 1.9322   |
| bridge-end-on    | 1.5741  | 2.4733   | 1.9525   |
| bridge-side-on   | 0.8598  | 2.7251   | 2.4150   |
| on-top-side-on   | 0.7686  | 2.8708   | 2.3604   |
| hollow (3-1)     | 1.6933  | 2.4457   | 1.8609   |
| hollow (3-3)     | 1.5551  | 2.4704   | 1.9743   |
| Pt(100)          |         |          |          |
| on-top-end-on    | 1.5204  | 2.5247   | 1.9548   |
| bridge-end-on    | 1.4390  | 2.5284   | 2.0324   |
| bridge-side-on   | 1.1868  | 2.6595   | 2.1137   |
| on-top-side-on   | 0.6294  | 2.8579   | 2.5110   |
| hollow           | 1.6569  | 2.5687   | 1.7741   |

---

The Journal of Physical Chemistry, Vol. 98, No. 31, 1994 7569
Figure 4
Figure 4 (Continued)
of the shorter Pt–O bond length on Pt(100), the lower repulsion energy value (Table 2) is due to the fact that the electron density is lower in the less densely packed Pt(100) structure than in that of Pt(111). The lower repulsion energy value also contributes to the stability of bridge end-on coordinated adsorbate. Both σ and π interactions imply a charge transfer to Pt, as can be inferred from the decrease in σ and π Mulliken populations in O atoms (Table 3). These populations were defined according to the x, y, and z axis contributions to the σ and π orbitals. Unfortunately, no direct comparison of the σ and π relative Mulliken population values of Pt(111) and Pt(100) can be made because the equilibrium geometries to which the data belong are different for both substrates. The greater O–O bond distance (Table 2) for the O2 molecule adsorbed on Pt(100) agrees with the larger π orbital Mulliken population (Table 3), showing the relevance of the antibonding interactions.

Repulsion energy values become sufficiently large to destabilize hollow adsorption, particularly when a Pt atom and adsorbed O2 are aligned with the z axis, i.e., hollow Pt(100) and hollow (3–3) in Pt(111) (Table 2, Figure 4c,h). The adsorption bond which results from bonding interactions with a Pt atom in the second layer is similar to that previously described for linear coordination. The most stable configuration on both Pt surfaces implies a nearly dissociated state, which can be simply described as an ionic pair with the positive end closer to the Pt surface. Together with a charge transfer from the O atom closer to the surface, the π Mulliken population in the second O atom increases. Besides, the π contribution on Pt(100) also increases (Table 3).

On-top side-on adsorbate coordination is characterized by a large stabilization of the π* O2 molecule orbital through bonding interaction with dπ Pt atom orbitals, as a consequence of the O2 adsorbed structure parallel to the surface (Figure 4d,i). The σ and π O2 molecule bonding orbitals are also involved in this interaction, their relative weights being determined by the specific Pt surface geometry, that is, the O–O bond length. The larger O–O bond length in Pt(111) weakens the σ bond in the O2 molecule and diminishes the importance of the O–Pt interaction as compared to Pt(100). Otherwise, the greater O2 bond length results from a larger π* orbital population due to a charge transfer from the most densely packed Pt(111) structure. This effect does not reflect in the energy level resulting from the molecular orbital interactions depicted in Figure 4e,f for the bridge side-on geometry, as these interactions involve optimized geometries where interatomic distances are already stabilized, yielding a greater rO–O on Pt(111) resulting from the larger population of the π* orbitals. As previously discussed for hollow coordination, the rO–O equilibrium value for the on-top side-on adsorbate coordination almost corresponds to a dissociated O2 adsorbate, where the O atoms are bridge coordinated to adjacent Pt sites. Nevertheless, for equilibrium interatomic distances, the O2 molecular orbitals are still defined. Similar calculations22 without adsorbed O2 geometry optimization result in a greater contribution of σ, π O2 molecular orbitals which, for a shorter O–O interatomic distance, become closer to the Pt atom just below.

The stabilization of the bridge side-on geometry implies the interaction of the σ and π O atom orbitals with d orbitals in the two closest symmetrically equivalent Pt atoms (Figure 4e,j). This O2 adsorbate configuration is characterized by the stabilization of the π* molecular orbitals of O2 with dπ Pt atom orbitals. The Mulliken population analysis indicates an oxygen to metal charge transfer without back-bonding. The particular geometry of the Pt site facilitates the simultaneous interactions of both O atoms with adjacent Pt atoms, leading to a greater stabilization of the PtσO2 structure on Pt(100), where the charge transfer is favored because of the lower electronic density of Pt(100) as compared with Pt(111). Despite the similarity of adsorption sites, the local

Figure 4. Molecular orbital interaction for different [Pt(100)]nO2 and [Pt(111)]mO2 adsorbate configurations, as depicted in Figure 2: (a,f) on-top end-on, (b,g) bridge end-on, (c,h) hollow, (d,i) on-top side-on, and (e,j) bridge side-on.
adjustment of the equilibrium potential (VSIP) to minimize the electronegativity difference resulting from Pauling's ionicity relationship results, for this system, in a downward shift of the d band with the simultaneous increase in the VSIP absolute value in O atoms. This means a softening of the back-bonding effect.

Although no experimental data about the Pt(100)O2 adsorbate geometry has been found, NEXAFS measurements of Pt(111)O2 yield a r_{0-O} = 0.132 nm and a distance of 0.175 nm from the adsorbed O2 to the first Pt atom layer. These figures agree reasonably well with those resulting from the calculations of this work (Table 2). Furthermore, O-O vibration frequencies of peroxo compounds were detected for the same system by high-resolution EELS spectra (HREELS).\(^{26,27}\) Likewise, from other semiempirical calculations it has been concluded that σ\(_{xy}\) and σ\(_{xz}\) orbitals are the most important ones in the stabilization of the adsorption bond.\(^{22}\) Nevertheless, the molecular orbital analysis made in this work indicates that the interaction between the \(\pi\) O2 molecular orbitals and \(\delta_n\) Pt atomic orbitals also contributes to the adsorption bonds (Figure 4d,e,i). On the basis of the previous discussion, it has to be emphasized that not the coincidence of our results with those already known for O2 interaction with Pt(111) but the larger stability of the O2 molecule on Pt(100) toward dissociation is the main topic of this work.

### 3.2. Molecular vs Dissociative O2 Adsorption on Pt

Dissociation of the adsorbed O2 molecule implies the elongation of the O-O bond until the O-Pt interactions prevail. For the adsorption geometries presented in section 3.1 above, two different adsorbed states can be produced depending on the orientation of the O-O bond relative to the Pt surface. Thus, perpendicular coordination (on-top, bridge, hollow) would result in a single O atom adsorbed on the surface and the second O atom infinitely distant, whereas parallel coordination would lead to a final state of two O atoms coordinated in adjacent positions. The parallel coordination is of particular interest in this work, since O2 electroreduction first involves a simultaneous H\(^+\) ion and electron transfer prior to dissociation.\(^{5,7}\) The possibility of O2 dissociation depends not only on the energy difference between the initial and the final adsorbed states but also on the energy related to the geometry of the intermediates that defines the transition from one to the other.

To analyze the energy associated with the transitions for parallel coordination, r_{0-O} has been varied in 0.005-nm steps from 0.08 to 0.260 nm, and the energy of each ensemble has been evaluated after a full coordinate optimization. The results plotted in Figure 5a,b show a clear stabilization of molecular O2 for bridge end-on and on-top end-on coordinations. Conversely, O2 dissociative adsorption appears to be favored for bridge side-on, on-top side-on, and hollow coordinations on both Pt(111) and Pt(100), as the real minima appear for this adsorbed state.

Let us focus our attention on bridge side-on coordination because this structure is associated with the greatest Pt(100) stability and it can also explain the different trends of the O2 adsorption versus dissociation, depending on the Pt topology.

A clear minimum is defined for Pt(100)O2 with r_{0-O} = 0.119 nm and a 0.161-nm value for the perpendicular distance of O2 to the surface (b in Table 2). Although the energy is lower (0.61 eV) for the dissociated system, an activation energy equal to 0.56 eV is required for the O2 dissociation on Pt(100)O2. Besides, the lowest energy value is also related to O-atoms bonded to Pt(111), with no other local energy minima except for an inflection in the energy vs r_{0-O} curve. Then, the dissociation of O2 on Pt(111) involves O2 dissociation.

The O2 π* population is larger on Pt(111)O2 than on Pt(100)-O2 for bridge side-on coordination (Table 3). The filling of antibonding orbitals, which is favored on Pt(111), weakens the O-O bond strength and becomes the main reason why O2 dissociative adsorption on the most densely packed Pt(111) surface is favored.

---

**Figure 5.** Total energy change (eV) of the Pt10O2 ensembles as a function of r_{0-O}. (a) [Pt(111)]12O2. (b) [Pt(100)]13O2. (●) bridge side-on, (○) bridge end-on, (▼) on-top end-on, (◇) hollow, (□) on-top side-on.

Geometry, defined by two Pt atoms with r_{Pt-Pt} = 0.277 nm on both Pt(100) and Pt(111), leads to an adsorbate geometry with a greater r_{0-O} value on Pt(111). The electronic characteristics of Pt(100) and Pt(111) determine specific charge-transfer contributions and the O2 molecular orbital occupation. In particular, a greater occupation of O2 σ orbitals on Pt(111) favors (Table 3) larger r_{0-O} values and the O2 dissociation. Again, no real local minima can be defined, the adsorbate geometry and electronic characteristics have also been evaluated at the inflection point resulting from the energy vs r_{0-O} plot.

Summing up, data assembled in Table 2 show that the most stable Pt1O2 structure corresponds to bridge side-on adsorbate geometry on both Pt(111) and Pt(100), although a larger adsorbate stabilization appears on Pt(100). This difference results from the more efficient overlap of both O atoms with the nearest neighbor Pt atoms on Pt(100). For bridge side-on coordination, the adsorption bond results from a charge transfer from O2 to the Pt surface and a partial back-bonding to the O2 σ* orbital. This leads to an increase in r_{0-O} and, then, O2 dissociation when back-bonding becomes sufficiently large. Negative charge densities in O atoms of the adsorbed O2 molecule have occasionally been reported, especially when no full optimization was considered. Results from this work indicate that the large σ* O2 population in the O atoms is relaxed when the atomic overlaps are redefined after the geometry optimization routine. On the other hand, the
Molecular orbital calculations allow us to conclude that the relative contribution of dissociative and molecular O₂ adsorption on Pt is determined by the relative position of the Pt d band with respect to π* O₂ orbital energy levels. Because the Pt d band position changes with the applied potential, the characteristics of the O₂ adsorption become potential dependent, as it is expected for the OERR. Thus, positive potentials shift the Pt d band downward, decreasing the π* O₂ orbital population and favoring molecular adsorption. On the other hand, upward shifting for negatively charged Pt would promote dissociative O₂ adsorption through the filling of the π* orbitals. The energy vs r_O-O plots for bridge side-on adsorption on Pt(100), referred to the dissociated state at different applied potentials (Figure 6), show that no stable molecular O₂ adsorption results on negatively charged surfaces, whereas positive charging results in a Pt(100)/O₂ ensemble. Similar potential shifts applied to Pt(111) are insufficient to stabilize molecular Pt(111)/O₂ adsorbate ensembles.

Hence, the influence of the applied electric potential becomes extremely important to determine the stability of O₂ adsorbates on Pt(111) and Pt(100) clusters, which may appear as intermediate surface species in the OERR.

3.3. Possible Species Involved in the Mechanism of OERR on Pt(111) and Pt(100) Surfaces. The preceding structural stability study of O₂ adsorbates on Pt provides the possibility of exploring further mechanistic aspects of the OERR, particularly in relation to possible species involved in the reaction, which may account for the different behavior of Pt(111) and Pt(100) electrode surfaces.

Several mechanisms have been postulated to interpret OERR kinetic data. Following O₂ dissociative adsorption on Pt-(111), the OERR in aqueous acids would imply a possible coordination of H⁺ ions from the solution to O atoms, which further desorb as H₂O at negative potentials. The fact that only H₂O molecules desorb from Pt(111) in the course of the OERR is consistent with the dissociative O₂ adsorption on this Pt surface. In contrast, molecular O₂ adsorption would produce a peroxo-like adsorbate structure on Pt(100) which would give rise to H₂O₂ desorption at negative potentials. Peroxo intermediates and H₂O₂ were experimentally detected mostly on Pt(100) electrodes. Therefore, a tentative explanation for the peroxo intermediate species formation on Pt(100) can be advanced.

As discussed in section 3.2, peroxo O₂ adsorbates (bridge side-on coordination) would dissociate as the applied potential is shifted negatively (Figure 6) leading to H₂O as the final product as it was also found in Pt(111). However, it should be borne in mind that at potentials where O₂ adsorption on Pt occurs, other species resulting from the H₂O electrochemical and chemical decomposition, such as OH and O adatoms, would also participate in the adsorbate structure, yielding, for instance, a [Pt(100)]₁₋₂ OH ensemble at the equilibrium potential.

Following the same theoretical procedure, the geometry of the [Pt(100)]₁₋₂ OH ensemble was fully optimized for both the O₂ and OH adsorbates. The adsorption of OH results in a linear (on-top) configuration adjacent to the peroxo-group bridge side-on adsorbed species, rendering a structure that is 0.84 and 2.04 eV more stable than those associated with an OH bridge and an OH hollow coordination, respectively. Stability calculations of these ensembles showed that a H atom transfer from the hydroxo to the peroxo group is favored. This H atom transfer implies an initial tilting of the Pt–O–H bond until it becomes parallel to the Pt–O bond in the peroxo group, with a simultaneous elongation of the Pt–O bond from 0.168 to 0.182 nm. Besides, the energy increases slightly while the OH bond is bent toward the peroxo group to be finally transferred with a net gain of 0.41 eV in stability (Figure 7). Then, in the OERR potential range, the H atom transfer takes place and the adsorbate ensemble can be better described as a hydrogenated peroxo group plus an O atom coadsorbed on Pt(100). The geometry of this adsorbed ensemble, a possible reaction intermediate in the OERR on Pt(100), has also been fully optimized in bond lengths and angles, as it is shown in Figure 8.

The H atom transfer implies an activation energy equal to 0.26 eV (Figure 7). We are aware that the level of these calculations does not allow us to infer that the proposed intermediate is the one that has the lowest energy. Accordingly, a lower activation energy barrier should not be precluded. The energy required for the Pt(100)/O₂ OH to Pt(100)/H₂O transition might be provided by other simultaneous reactions, such as the underpotential deposition, upd, H₂O discharge, or the O₂ adsorption on Pt.

The stability of the O₂H–O coadsorbate on Pt(100) was also calculated as a function of the applied potential. Changes in the
adsorbed structure due to the upward shifting of the d band, i.e., potential negatively increased, have been studied, after a full optimization of the geometry for each set of the defined conditions. Thus, the activation energy barrier for the H atom displacement from oxygen 6 to oxygen 5 (Figure 8) depends on the potential, and it decreases almost to zero for a $-1$ eV potential assisting the OERR in the forward direction. Accordingly, it is reasonable to admit that the larger the cathodic overpotential the lower the activation energy.

Changes in the Mulliken atomic overlaps with the applied potential (Table 4) show that, although they both decrease for negative potentials, the destabilization of the Pt–O bond becomes more pronounced than that of the O–O bond for a given potential change. Hence, although a competition between the dissociation of the peroxo adsorbate and the formation of a hydroperoxo intermediate ensemble takes place, it is likely that the hydroperoxo intermediate ensemble preferentially desorbs as H$_2$O$_2$ prior to dissociation. On the other hand, negative applied potentials stabilize the large negative charge density in the O atom at the peroxo group not bonded to H atom (oxygen 4 in Figure 8) which becomes a center for the H$^+$ ion coordination, followed by H$_2$O$_2$ desorptive formation.

The hydroperoxide formation on Pt(100) implies that at negative potentials, the remaining oxo species (Figure 7) would be negatively charged (Table 4), and after the H$^+$ ion coordination, H$_2$O$_2$ desorption would occur. The mechanism for this reaction is similar to that proposed on Pt(111), and it justifies the simultaneous desorption of H$_2$O from Pt(100) and the detection of H$_2$O$_2$ as the only OERR product on Pt(111).

4. Conclusions

The interaction of a single O$_2$ molecule on Pt(111) and Pt(100) structures was studied. On both surfaces, bridge side-on is the most stable coordination geometry for PtO$_2$. However, a dissociative O$_2$ interaction on Pt(111) and a molecular O$_2$ interaction on Pt(100) are favored. The different characteristics of the O$_2$ adsorption on both surfaces are reflected in the OERR, leading to the preferential desorption of H$_2$O from Pt(111) and H$_2$O$_2$ from Pt(100).

H$_2$O desorption results from the coordination of H$^+$ ions from the media to O adatoms in the adsorbate ensemble, which become negatively charged for negative applied potentials due to the upward shift of the Pt d band. On the other hand, H$_2$O$_2$ results from the coordination of an H$^+$ ion to peroxo intermediates adsorbed on Pt(100), which are more likely to desorb than to dissociate, according to the larger decrease in the Pt−O than the O−O overlaps, at negative potentials.

Results from this quantum chemical approach justify the detection of peroxo and oxo intermediates on Pt(100) structures in the course of the OERR, rather than the structure of the oxo intermediates on Pt(111).

Acknowledgment. This work was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and Fundación Antorchas de Argentina. C.F.Z. thanks the Universidad de la República, Montevideo (Uruguay), for the fellowship granted.

References and Notes

(1) Tarasievich, M. R.; Sedkowski, A.; Yeager, E. B. Oxygen Electrochemistry. In Comprehensive Treatise of Electrochemistry, Vol. 7: Kinetics and Mechanisms of Electrode Processes; Conway, B. E., Bockris, J. O’M., Yeager, E. B., Kahn, S., White, R. W., Eds.; Plenum Press: New York, 1983; Chapter 6, pp 301−398.

(2) Hoare, J. P. The Electrochemistry of Oxygen; J. Wiley and Sons: New York, 1968.

(3) Appleby, A. J. In Modern Aspects of Electrochemistry; Bockris, J. O’M., Conway, B. E., Eds.; Plenum Press: New York, 1974; Vol. 9, Chapter 5.

(4) Damjanovic, A.; Brusic, V. Electrochim. Acta 1967, 12, 615.

(5) Huang, J. C.; Sen, R. K.; Yeager, E. J. B. Electrochem. Soc. 1979, 126, 736.

(6) Yeager, E. B. Electrochim. Acta 1984, 29, 1527.

(7) Zinola, C. F.; Castro Luna, A. M.; Tricà, W. E.; Arvia, A. J. Appl. Electrochem. 1994, 24, 119.

(8) El Kadiri, F.; Faure, R.; Durand, R. J. Electroanal. Chem. 1991, 301, 777.

(9) Zinola, C. F.; Castro Luna, A. M.; Tricà, W. E.; Arvia, A. J. Appl. Electrochem., in press.

(10) (a) Appleby, A. J. J. Electroanal. Chem. 1970, 24, 97. (b) Parthasarathy, A.; Srinivasan, S.; Appleby, J.; Martin, C. R. J. Electroanal. Chem. 1992, 339, 101. (c) Parthasarathy, A.; Srinivasan, S.; Appleby, J.; Martin, C. R. J. Electrochem Soc. 1992, 139, 2856. (d) Parthasarathy, A.; Srinivasan, S.; Appleby, J.; Martin, C. R. J. Electroch Soc. 1991, 138, 916.

(11) Hush, K. L.; Gonzalez, E.; Srinivasan, S.; Chiu, D.-T. J. Electrochem. Soc. 1984, 131, 822.

(12) Damjanovic, A.; Genschaw, M. A.; Bockris, J. O’M. J. Chem. Phys. 1964, 45, 4057.

(13) Ross, P. N.; Andriacon, P. C. J. Electroanal. Chem. 1983, 154, 205.

(14) Glass, J. T.; Cahn, G. L., Jr.; Stoner, G. E. J. Electrochem. Soc. 1989, 136, 566.

(15) Guo, X.-C.; Bradley, J. M.; Hopkins, A.; King, D. A. Surf. Sci. Lett. 1991, 292, L786.

(16) Poehlmann, E.; Schmitt, M.; Hoinkes, H.; Wilseh, H. Surf. Sci. 1993, 291, 317.

(17) de Meijere, A.; Hiriyama, H.; Hasselbrink, E. Phys. Rev. Lett. 1993, 70, 1147.

(18) Ohno, Y.; Matsushima, T.; Tanaka, S.; Yagasaki, E.; Kamada, M. Surf. Sci. 1992, 275, 281.

(19) Bennet, G. A.; Lingane, L. S. G. Surf. Sci. 1992, 261, 207.

(20) Heiling, B. Surf. Sci. 1993, 281, 216.

(21) Nakatsuji, H.; Nakai, H. J. Chem. Phys. 1993, 98, 2423.

(22) Chan, A. E. W.; Hoffmann, R.; Ho, W. Langmuir 1992, 8, 1111.

(23) Panas, I.; Siegbahn, P. Chem. Phys. Lett. 1988, 458.

(24) Selman, A.; Andzelm, J.; Salaphu, D. R. Int. J. Quantum Chem. 1986, 29, 829.

(25) Barreau, M. A.; Ko, E. I.; Maddix, R. J. Surf. Sci. 1981, 102, 99.

(26) Steininger, H.; Lohwald, S.; Ibach, H. Surf. Sci. 1982, 125, 1.

(27) Vaska, L. Acc. Chem. Res. 1976, 9, 175.

(28) Otuka, D. A.; Stöhr, J.; Jark, W. Phys. Rev. B 1987, 35, 4119.

(29) Wurtz, W.; Stöhr, J.; Peilner, P.; Pan, X.; Bauchspiess, K. P.; Baba, Y.; Hidai, E.; Rocker, G.; Mentel, D. Phys. Rev. Lett. 1990, 65, 2426.

(30) Stöhr, J.; Gland, J. L.; Bierhardt, W.; Otuka, D.; Madix, R. J.; Seete, F.; Koestner, R. J.; Doebeler, U. Phys. Rev. Lett. 1983, 51, 2414.

(31) Sexton, B.; Madix, R. J. Chem. Phys. Lett. 1986, 70, 294.

(32) Gland, J. L.; Sexton, B.; Fischer, G. B. Surf. Sci. 1980, 95, 587.

(33) Nakatsuji, H.; Nakai, H.; Hada, M. Metal-Ligand Interactions: from Atoms, to Clusters, to Surfaces; Salabur, D. R., Usno, N.; Eds.; Kluwer Academic Publishers: Dordrecht, 1992; pp 251−285.

(34) Przybylak, K.; Koutecy, J.; Bonacic-Koutecky, V.; Schleyer, P. V. R.; Guest, M. F. J. Chem. Phys. 1991, 94, 5533.
(35) Goursot, A.; Papai, I.; Salabub, D. R. J. Am. Chem. Soc. 1992, 114, 7452.
(36) Bagus, P. S.; Pacchioni, G. Surf. Sci. 1990, 236, 233.
(37) Hoffmann, R. J. Chem. Phys. 1963, 39, 1397.
(38) Anderson, A. B.; Hoffmann, R. J. Phys. Chem. 1974, 60, 4271.
(39) Anderson, A. B. J. Phys. Chem. 1975, 62, 1187.
(40) (a) Head, J. D.; Zerner, M. C. Chem. Phys. Lett. 1985, 122, 264. (b) Head, J. D.; Zerner, M. C. Chem. Phys. Lett. 1986, 131, 359.
(41) Anders, L. W.; Hansen, R. S.; Bartell, L. S. J. Chem. Phys. 1973, 59, 5277.
(42) Calzaferri, G.; Forss, L.; Kamber, I. J. Phys. Chem. 1989, 93, 5566.
(43) Savary, F.; Weber, J.; Calzaferri, G. J. Phys. Chem. 1993, 97, 3722.
(44) Calzaferri, G.; Hoffmann, R. J. Chem. Soc., Dalton Trans. 1991, 917.
(45) Amouyal, E.; Mouallem-Bahout, M.; Calzaferri, G. J. Chem. Phys. 1991, 95, 7641.
(46) Brändle, M.; Calzaferri, G. Helv. Chim. Acta 1993, 76, 924.
(47) (a) Vázquez, L.; Gómez Rodríguez, J. M.; Gómez Herrero, J.; Baró, A. M.; García, N.; Canullo, J. C.; Arvia, A. J. Surf. Sci. 1987, 181, 98. (b) Gómez, J.; Vázquez, L.; Baró, A. M.; Garcia, N.; Perdrich, C. L.; Tráca, W. E.; Arvia, A. J. Nature 1986, 322, 612. (c) Cerviño, R. M.; Arvia, A. J.; Vielstich, W. E. Surf. Sci. 1985, 154, 623.
(48) Tarasevich, M. R. Elektrokhimiya 1973, 9, 599.
(49) Villas-kaya, V. S.; Tarasevich, M. R. Elektrokhimiya 1973, 9, 1187.
(50) Villambi, N. R. K.; Taylor, E. J. Electrochim. Acta 1989, 34, 1449.
(51) Park, S.-M.; Ho, S.; Aruliah, S.; Weber, M. F.; Ward, C. A.; Venter, R. D.; Srinivasan, S. J. Electrochem. Soc. 1986, 133, 1641.
(52) Anastasijević, N. A.; Vesovic, V.; Adžić, R. J. Electroanal. Chem. 1987, 229, 305.
(53) Pauling, L. The Nature of the Chemical Bond, 3rd ed.; Cornell University Press: Ithaca, NY, 1992, p 45.
(54) Calzaferri, G.; Brändle, M. QCMP 116. QCPE Bull 1992, 12, No. 4.
(55) Esti, G. L.; Mauleds, S. A.; Castro, E. A.; Arvia, A. J. J. Electroanal. Chem. 1990, 284, 289.
(56) Esti, G. L.; Mauleds, S. A.; Castro, E. A.; Arvia, A. J. J. Phys. Chem. 1988, 92, 2512.
(57) Lide, D. R., Ed. CRC Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 1990–91.
(58) Levine, I. N. Quantum Chemistry; Editorial A.C.: Madrid, 1977.
(59) Taube, H. J. Gen. Phys. 1965, 49, 29.
(60) Greenwood, N. N.; Earnshaw, A. In Chemistry of the Elements; Pergamon Press: Oxford, 1984.
(61) Calzaferri, G.; Marcoli, C. To be published.
(62) Anastasijević, N. A.; Vesovic, V.; Adžić, R. R. J. Electroanal. Chem. 1987, 229, 317.
(63) Zurilla, R. W.; Yeager, E. B. Technical Report No. 23, Case Western University, 1969.
(64) Wroblowa, H. S.; Pan, Y-Chi; Razumney, G. J. Electroanal. Chem. 1976, 69, 195.
(65) Bagotski, V. S.; Tarasevich, M. R.; Filinovskii, V. Yo; Elektrokhimiya 1969, 5, 1218.
(66) Bagotski, V. S.; Tarasevich, M. R.; Filinovskii, V. Yo; Elektrokhimiya 1972, 6, 84.
(67) Hauch, K. L.; Chin, D. T.; Srinivasan, S. J. Electroanal. Chem. 1983, 152, 79.
(68) O'Grady, W. E.; Taylor, E. J.; Srinivasan, S. J. Electroanal. Chem. 1982, 132, 137.
(69) Gnanamuthu, D. S.; Petrocelli, V. J. J. Electrochem. Soc. 1971, 114, 1036.