

# Mechanism and Kinetics of the Wacker Process: A Quantum Mechanical Approach

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Study of the mechanism of the Wacker oxidation is of great importance for many reasons. Thus far, from a theoretical point of view, particularly in connection with the rate-determining step, no mechanism has been presented which includes all experimental evidence, notably the isotopic effect, the energy barrier, and the rate constant of the reaction. In this work, we proposed a mechanism for nucleophilic addition which quantitatively and qualitatively will be in good agreement with the experimental evidence. The mechanism study of the Wacker process has been performed using a density functional method in the gas and solution (Onsager and PCM models) phases. The internal nucleophilic addition of the OH group on the coordinated alkene has been investigated as a direct attack or water chain attack. The reaction progress in both routes of syn and anti attack yields two different products for this step; therefore, modeling of attacks has been performed for both routes. The results obtained in the gas and solution phases showed that the direct attacks in both routes have a high energy barrier and applying water chains highly reduces the energy barrier. The anti attack of the three-water-chain model has the lowest energy barrier. Applying this model leads to results which have good consistency with the experimental evidence.

## 1. Introduction

Study of the mechanism of palladium chloride (PdCl<sub>2</sub>) oxidation of acyclic alkenes in aqueous solution (Wacker oxidation<sup>1</sup>) is of great importance from different aspects, the most significant of which are as follows: (1) The technological<sup>1–3</sup> and biological<sup>4</sup> importance of the reaction in the synthesis of carbonyl compounds from corresponding alkenes is well known. (2) The palladium(II) complex is one of the most valuable metal complexes in various catalytic reactions and organic syntheses<sup>5</sup> such as aminopalladation of olefins,<sup>6</sup> oxidative alkylation of

olefins,<sup>7</sup> etc.,<sup>8,9</sup> in which nucleophilic attack on an olefin is implicated as a key step. (3) Many of the organic reactions such as deactivation of the Brookhart catalyst in emulsion polymerization of ethylene<sup>10</sup> and aerobic oxidation of alcohols by palladium complexes<sup>11</sup> follow the mechanism of the Wacker-type reaction. Hence, clarification of the mechanism of the Wacker reaction should provide important informations on such reactions. (4) Theoretical modeling on the role of the solvent–water molecules for the reactions is especially appropriate in helping us gain a deeper understanding about reactions that take place in aqueous medium, such as the Heck reaction.<sup>12</sup> However, the modeling of these reactions can be quite difficult. (5) Much experimental data is available in connection with the Wacker process, which makes it possible to test the various models and to obtain a suitable model.

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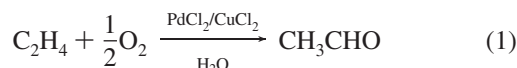
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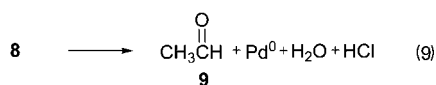
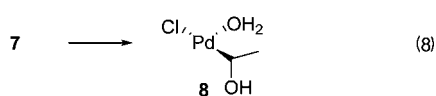
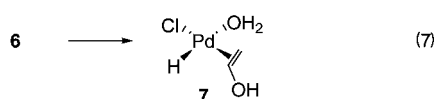
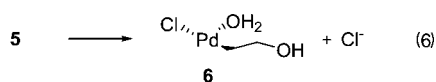
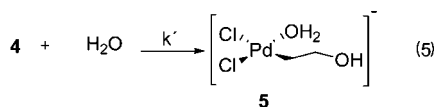
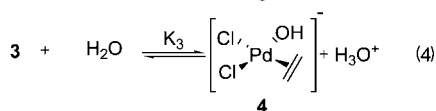
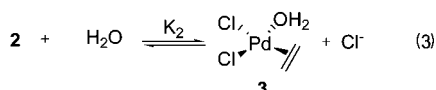
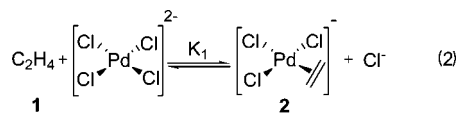
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The overall reaction of the Wacker process is equal to direct oxidation of ethylene by  $O_2$ .<sup>1a,13</sup>



Presently, it is widely believed that the main steps of the Wacker process are those that are shown below (eqs 2–9).<sup>2,9a,10b,14</sup>

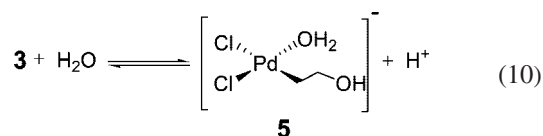


Under the usual Wacker process conditions ( $[Cl^-] < 1$  M), Pd(II) ethylene  $\pi$ -complex species **2**, which exists in solution, has been assumed to be the first intermediate formed.<sup>15,16</sup> Since the net initial ethylene uptake decreases with increasing chloride ion, it is rational to suppose that the initial reaction can be represented by eq 2, which is consistent with the first-order dependence of reaction rate on ethylene and palladium ion concentrations.<sup>17</sup> Second-order chloride ion inhibition on the rate of reaction is consistent with the prior formation of an aquated palladium dichloride  $\pi$ -complex intermediate **3** and separation of the chloride ion corresponding to the eq 3. In the next step, the alkene complex **3** deprotonates first to a negative hydroxymetal complex ion **4** (eq 4), pursued by a rate-determining step during which, through an intramolecular attack of coordinated hydroxide upon one of the double bond carbon atoms, a Pd(II) alkene  $\pi$ -complex **4** convert into a Pd(II)  $\sigma$ -hydroxyalkyl **5** (eq 5). The isotope effects with deuterated

ethylene also demonstrate that the hydroxo complex **4** does not decompose directly to final product but progresses via another intermediate such as a  $\sigma$ -bonded complex **5**.<sup>17</sup> Then in a fast step, intermediate **5** is converted into  $\beta$ -hydroxyalkyl intermediate **6** through loss of the chloride ion (eq 6). According to eq 7,  $\beta$ -hydrogen elimination of the intermediate **6** gives a palladium enol  $\pi$ -complex **7**, which then undergoes  $\beta$ -hydrogen addition to give the palladium  $\alpha$ -hydroxyalkyl **8** (eq 8). Finally, the species **8** decomposes to yield the carbonyl compound **9**, Pd(0), and HCl (eq 9).

The alternative proposed mechanism,<sup>8,18</sup> instead of slow internal nucleophilic attack of OH, includes the external nucleophilic attack in a rapid and equilibrium step, in which a  $H_2O$  molecule attacks the carbon atom of the ethylene double bond directly to give the intermediate **5** (eq 10). In this mechanism, species **5** loses a  $Cl^-$  ion in the rate-determining step (eq 6) following to yield intermediate **6**.

Kinetic studies indicate that for the ethylene oxidation, the



reaction is first order with respect to Pd(II) and ethylene concentrations. The reaction is inhibited by proton (first order), and the rate depends on the inverse square of the chloride ion concentration.<sup>17</sup> The  $O_2$  concentration does not play any role in the rate of reaction.<sup>19</sup> The experimental rate expression can be written as<sup>17,8b</sup>

$$-\frac{d[C_2H_4]}{dt} = k \frac{[C_2H_4][PdCl_4^{2-}]}{[H^+][Cl^-]^2} \quad (11)$$

where  $k$  is the overall rate constant of the reaction. Both proposed mechanisms (internal and external nucleophilic attack) are consistent with the experimental rate expression.

Experimental evidence confirms the internal nucleophilic attack mechanism: (i) The large isotope effect  $k_H/k_D$ , going from a  $H_2O$  to a  $D_2O$  solution, might be used to infer that the rate-determining step should be due to the O–D bond breaking occurring during the nucleophilic attack.<sup>20</sup> (ii) Other interesting information about the mechanism of the Wacker process is related to the effect of structure on the rate of reaction, indicating that in the rate-determining step the  $\pi$ -complex converts to the oxypalladation adduct, which rapidly decomposes to the aldehyde or ketone product.<sup>2a</sup> Another experimental study showed that both steric and electronic effects of olefins are responsible for the reaction rate and the rate-determining step of the reaction is a nucleophilic attack upon the coordinated alkene, leading from the  $\pi$ -complex.<sup>14c</sup> This result is consistent with the proposed hydroxypalladation (eq 5) as the rate-determining step by Henry.<sup>2</sup> (iii) The formation of oxythallation intermediate has also been suggested in the rate-determining step of the thallic ion oxidation of olefins.<sup>21</sup>

Since in the external attack mechanism nucleophilic addition occurs in a rapid equilibrium step and the rate-determining step neither involves  $\pi$  electrons nor is ac-

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accompanied by break up of the O–H bond, this mechanism is not consistent with all experimental evidence. In a theoretical study, Siegbahn<sup>22</sup> used from two to four water molecules in the water-chain model for the external nucleophilic attack. Using the exothermicity calculations and the proton affinity values for chains of water, the three-water-chain model was selected as the best model. He considered the trans isomer for intermediates **3** and **4**. In this model, chain of water was located between the negative chloride ligand and ethylene. This model predicts the low energy barrier for the nucleophilic addition. Such a conclusion is reasonable because, in the external attack mechanism, the nucleophilic addition step is rapid and the subsequent step is the rate-determining step (for consistency with the experimental rate expression). As stated previously, due to inconsistencies with the experimental evidence, the loss of a chloride ion from the palladium could not be the rate-determining step. He also investigated the  $\beta$ -elimination step and predicted a high energy barrier for this step. Isotope effects with deuterated ethylene indicate that in the rate-determining step the C–H bond does not break.<sup>17</sup> In addition, other experimental evidence indicates that the  $\beta$ -elimination step could not be the rate-determining step.<sup>14a,23</sup>

Another probable pathway for carbonyl generation has been proposed, on the basis of which intermediate **8** directly converts to final products by the chloride-mediated reductive elimination.<sup>17,24</sup> A new theoretical study predicted the high energy barrier for this step.<sup>25</sup> Since this step does not involve  $\pi$  electrons, it could not be considered as the rate-determining step.

So far, from a theoretical point of view, particularly in connection with the rate-determining step, no mechanism has been presented which includes all experimental evidence, notably the isotopic effects, the energy barrier, and the rate constant of the reaction. In this work, using water chains, we proposed a mechanism for the nucleophilic addition which quantitatively and qualitatively will be in good agreement with the experimental evidence.

## 2. Computational Details

All of the present calculations have been performed with the B3LYP<sup>26</sup> hybrid density functional level using the Gaussian 98 package.<sup>27</sup> The 6-311+g(d,p) basis sets were employed except for Pd and Cl, where the LANL2DZ basis set was used with effective core potential (ECP) functions. For increasing accuracy of calculations, one sp diffuse function and two d and one f polarization functions were added to Cl atoms.

The solvent has an important role in chemical reactions. One group of approaches to study the solute–solvent interactions is referenced to as self-consistent reaction field (SCRF) methods. In this work, we use two of these methods: the simplest one, the Onsager model,<sup>28</sup> and the more sophisticated polarized continuum model (PCM).<sup>29</sup> In the Onsager method, the solute occupies a fixed spherical cavity of radius within the solvent field. A dipole in the solute will interact with the medium to

create a reflection dipole, which will lead to a net stabilization of solute. This model has the advantage of simplicity and low computing times; its principal deficiency is that a system having a zero dipole moment will exhibit no solvent effects at all and the calculations will thus give the same results as for the gas phase. In the PCM method, the molecular cavity is made up of the union of interlocking atomic spheres. This model has the deficiency of much longer computing times and an arbitrary choice of the van der Waals radii to construct the cavity.

First, all degrees of freedom for all geometries were optimized. The transition states obtained were confirmed to have only one imaginary frequency of the Hessian. Then, the gas-phase-optimized geometries were used to apply the solvent effects. However, for the comparison of stability of the cis and trans isomers of species **3**, the optimization and frequency calculations of these isomers have been performed by using the Onsager model. The dielectric constant of water and the temperature used were 78.93 and 298.15 K, respectively. All cavity radii were taken to be values obtained from standard procedures in the program.

In the gas phase and Onsager model, thermal corrections to enthalpy derived from the frequency calculations were included to obtain relative enthalpies. The zero-point corrections were also considered to obtain activation energies.

The PCM model calculates the molecular free energy in solution as the sum over three terms:<sup>30</sup>

$$G_{\text{sol}} = G_{\text{es}} + G_{\text{dr}} + G_{\text{cav}} \quad (12)$$

These components represent the electrostatic free energy,  $G_{\text{es}}$ , dispersion-repulsion free energy,  $G_{\text{dr}}$ , and cavitation free energy,  $G_{\text{cav}}$ , respectively. The PCM energies were evaluated by neglecting the thermal corrections.

## 3. Results and Discussion

Regarding the issues put forward in the Introduction, the experimental evidence indicates that the nucleophilic hydroxy-palladation (eq 5) is the most possible mechanism for the rate-determining step of the Wacker process. In this work, this mechanism will be studied theoretically.

For internal attack, a cis arrangement of the H<sub>2</sub>O (or OH) and C<sub>2</sub>H<sub>4</sub> in the intermediates **3** (or **4**) would appear necessary while the trans effect of the ethylene group would lead to a trans arrangement. However, even with the corresponding platinum complex of **3**, where the trans effect is stronger, there is evidence that as much as 10% of the complex is present as the cis isomer.<sup>31</sup> Thus, in the case of **3** or **4** it is quite reasonable that kinetically considerable amounts of the cis isomer are present.

Cis and trans arrangements, first appear for species **3**. Therefore, it is logical that the stability comparison should be done between the cis and trans isomers of species **3**. Considering the equilibrium between the cis and trans isomers, the value of the equilibrium constant ( $K$ ) is calculated by using

$$K = \exp\left(-\frac{\Delta G}{RT}\right) \quad (13)$$

where  $\Delta G$ ,  $R$ , and  $T$  are the Gibbs free energy difference between two isomers, the gas constant and temperature, respectively. Optimization and frequency calculations of the cis

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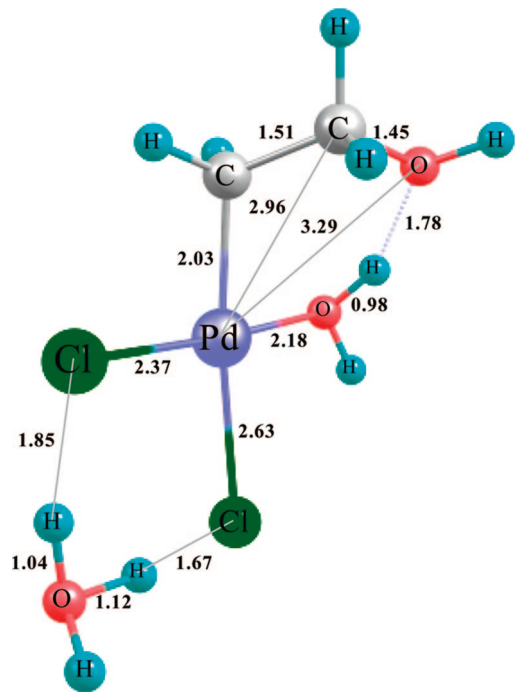
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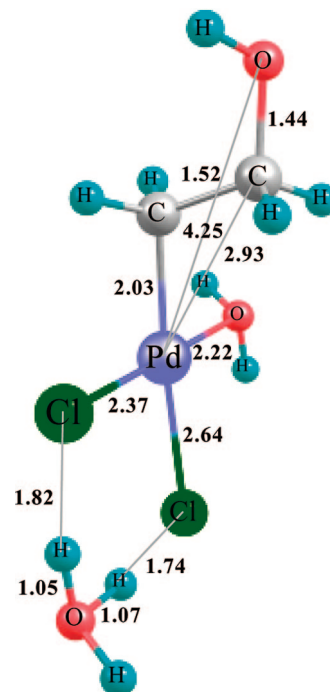
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**Figure 1.** Optimized structure of the cis  $\sigma$ -complex obtained after the syn direct attack of OH.

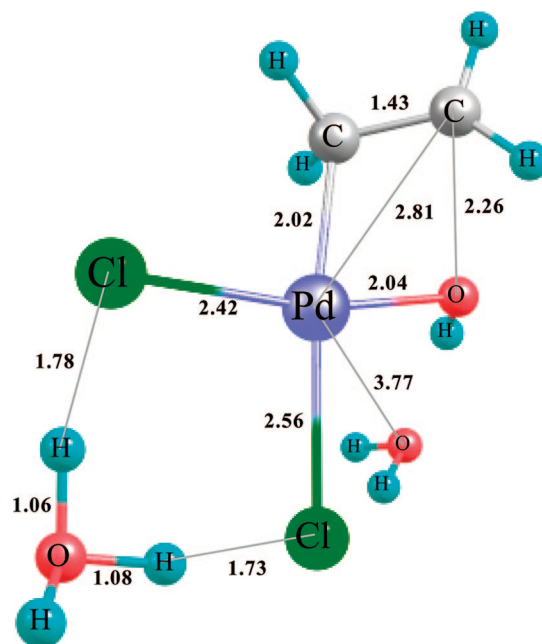


**Figure 2.** Optimized structure of the trans  $\sigma$ -complex obtained after the anti direct attack of OH.

and trans forms of **3** have been performed using the Onsager model. Cavity radii for the cis and trans forms were 4.17 and 4.32 Å, respectively. The Gibbs free energy difference between them is 0.76 kcal/mol. Consequently, the amount of the cis form is predicted to be 21.7%, which makes the progress of the reaction possible through internal attack mechanism. Calculations showed that for species **4**, the cis isomer is more stable than trans isomer, 1.74 kcal/mol for the gas phase and 4.19 kcal/mol for the Onsager model, respectively. Onsager cavity radii for the cis and trans forms of species **4** were 4.25 and 4.27 Å, respectively.

The product of the nucleophilic addition step is the  $\sigma$ -complex **5**, which could exist as two cis and trans isomers. These two isomers result from syn attack (cis form) or anti attack (trans form), where syn implies an attack of the actual nucleophile between the Pd(II) and two carbons of the double bond while anti means attack of the actual nucleophile on the other side of the olefin. Their structures are shown in Figures 1 and 2, respectively. These figures present optimized structures of the  $\sigma$ -complex, obtained after the syn and anti direct attack of the OH nucleophile on the complexed alkene in the cis form of species **4**. It should be noted that the cis and trans isomers of  $\sigma$ -complex **5** are related to the orientation of Pd-C $_{\alpha}$  and C $_{\beta}$ -O bonds relative to each other and are different from cis and trans isomerism, which are related to space arrangement of Cl atoms relative to each other. From now on, our intention in referring to the cis and trans isomerism is the first definition (the orientation of Pd-C $_{\alpha}$  and C $_{\beta}$ -O bonds relative to each other).

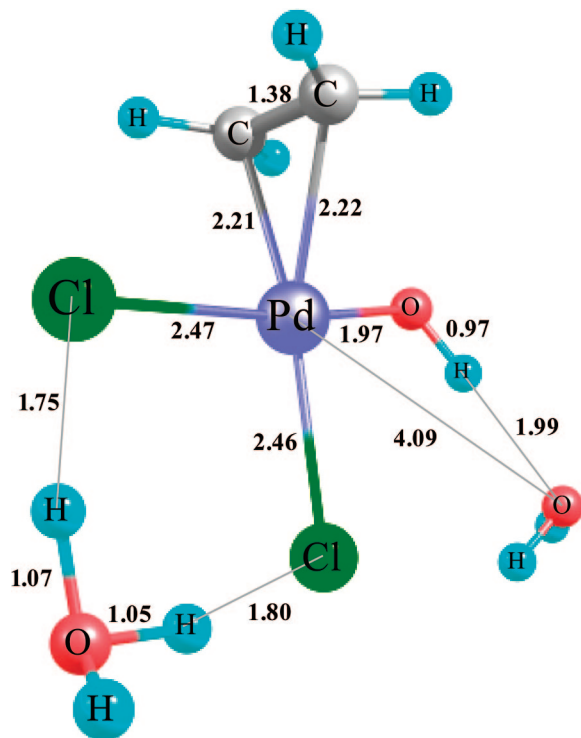
The main important difference between the structures of the cis and trans forms of the  $\sigma$ -complex is the distance between the Pd central atom and O atom of the hydroxyl group, which varies from 3.29 Å for the cis form to 4.25 Å for the trans form. Also, for the cis form, there is a hydrogen bond with an O-H distance of 1.78 Å between the O atom of the  $\sigma$ -ligand and the H atom of the coordinated H $_2$ O molecule. Now, considering



**Figure 3.** Optimized transition-state structure for the anti direct attack of OH.

both paths of anti and syn attacks, leading to the cis and trans forms of the  $\sigma$ -complex, respectively, we concentrated on the rate-determining step.

**3.1. Anti Attack of the Nucleophile on the Olefin.** The simplest possible model that can be used to study the anti nucleophilic addition is a direct attack of the coordinated OH nucleophile upon the double-bond carbon atom. The resulting structures for the trans form of the  $\sigma$ -complex, the transition state, and the reactant are shown in Figures 2–4. As shown in these figures, H $_3$ O $^+$  should coordinate electrostatically to



**Figure 4.** Optimized reactant structure for direct attack of OH.

**Table 1.** Activation Energies (kcal/mol) for the Anti Nucleophilic Attack of OH and Water Chain (H<sub>2</sub>O)<sub>n</sub> Model

form of attack	gas phase	Onsager model	PCM model
direct OH attack	46.95	47.21	47.20
H <sub>2</sub> O	34.76	37.09	32.79
(H <sub>2</sub> O) <sub>2</sub>	20.50	20.64	19.18
(H <sub>2</sub> O) <sub>3</sub>	14.72	13.02	12.66
(H <sub>2</sub> O) <sub>4</sub>	14.88	12.08	13.42

the complexes, according to proposal made by Siegbahn.<sup>32</sup> The H–Cl distances in the range of 1.67 to 1.85 Å show the hydrogen bonds between negative chloride ligands and H<sub>3</sub>O<sup>+</sup> ion. Subsequently, we will see this model leads to results that are consistent with the experimental evidence.

The activation energies ( $E_a$ ) for direct attack in the gas phase and the Onsager and PCM models are 46.95, 47.21, and 47.20 kcal/mol, respectively. Due to the high value of the force constant for the Pd–OH bond, the direct attack of the OH nucleophile has a very high energy barrier.<sup>33</sup> The use of the direct attack of the hydroxyl anion leads to quite unsatisfactory results. Therefore, a more suitable model for the nucleophilic attack is required. The nucleophilic attack could be modeled by a chain of water molecules which was formerly used by Siegbahn.<sup>22</sup> Of course, he studied the possibility of an external attack instead of an internal attack mechanism.

In this work, chains with one, two, three, and four water molecules were used for the anti nucleophilic attack. The activation energies related to each case have been calculated in the gas phase and the Onsager and PCM models. The results are shown in Table 1. These results show that using one water molecule for the anti attack of the nucleophile,  $E_a$  related to the gas phase and the Onsager and PCM models is reduced by 12.19, 10.12, and 14.41 kcal/mol, respectively, in comparison

**Table 2.** Relative Enthalpies (kcal/mol) for the Reaction between [(H<sub>3</sub>O)PdCl<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(OH)] and Chains of One, Two, Three, and Four Water Molecules

system	energy		
	gas phase	Onsager model	PCM model <sup>a</sup>
reactant			
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(OH)](H <sub>2</sub> O)	0.00	0.00	0.00
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(OH)](H <sub>2</sub> O) <sub>2</sub>	0.00	0.00	0.00
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(OH)](H <sub>2</sub> O) <sub>3</sub>	0.00	0.00	0.00
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(OH)](H <sub>2</sub> O) <sub>4</sub>	0.00	0.00	0.00
$\sigma$ -complex, anti attack			
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)]	-1.74	-1.55	-8.02
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)](H <sub>2</sub> O)	-7.29	-5.84	-10.16
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)](H <sub>2</sub> O) <sub>2</sub>	-10.56	-10.57	-12.40
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)](H <sub>2</sub> O) <sub>3</sub>	-9.84	-10.66	-11.35
$\sigma$ -complex, syn attack			
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)]	-8.65	-7.54	-10.89
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)](H <sub>2</sub> O)	-10.91	-9.14	-11.98
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)](H <sub>2</sub> O) <sub>2</sub>	-11.94	-12.06	-9.69
[(H <sub>3</sub> O)PdCl <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)(H <sub>2</sub> O)](H <sub>2</sub> O) <sub>3</sub>	-13.24	-14.24	-10.71

<sup>a</sup> Relative enthalpies are without thermal correction.

with direct attack, a considerable decrease in the energy barrier of the reaction.

The second water-chain model tried was the one with two water molecules (H<sub>2</sub>O)<sub>2</sub>. This model reduces  $E_a$  in the gas phase and the Onsager and PCM models by 14.26, 16.45, and 13.61 kcal/mol compared to the one-water-chain model, respectively.

The most important model used in the present study is a chain of *three* water molecules model (H<sub>2</sub>O)<sub>3</sub>. The results in Table 1 indicate that the addition of a single water molecule in the two water molecule chain model reduces  $E_a$  in the gas phase and the Onsager and PCM models by 5.78, 7.62, and 6.52 kcal/mol, respectively.

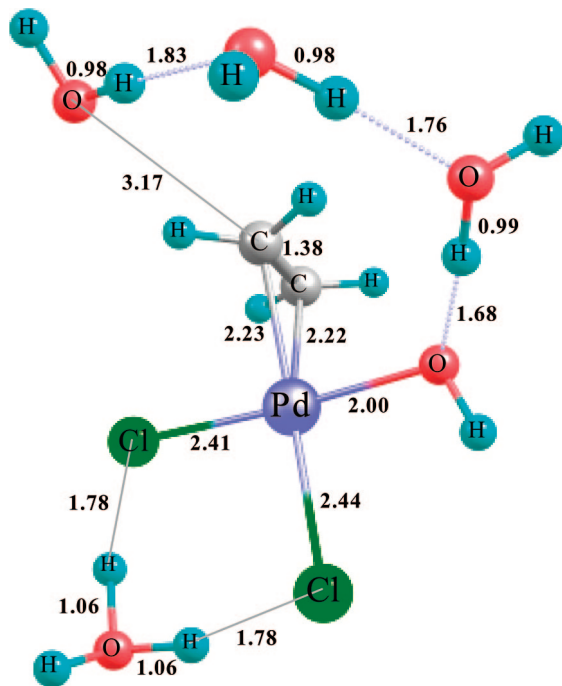
Going from three to four water molecules in the water-chain model increases  $E_a$  in the gas phase and PCM model from 14.72 to 14.88 kcal/mol and from 12.66 to 13.42 kcal/mol, respectively. In the Onsager model,  $E_a$  decreases less than 1 kcal/mol, which is small in comparison with the corresponding values for the addition of one water molecule to the chains with one to two water molecules. Regarding the higher accuracy of the PCM relative to the Onsager model and lack of considerable reduction of energy barrier in the Onsager model, it is clear that the three-water-chain model is the best model for the anti nucleophilic attack.

The calculated exothermicity of the reactions is another reason for the selection of the three-water-chain model. Table 2 lists the calculated relative enthalpies of the reactant and the trans and cis forms of the  $\sigma$ -complex calculated in the gas phase and the Onsager and PCM models for one to four water molecules in the water-chain model. Cavity radii of the reactant, the transition state, and the  $\sigma$ -complex for anti three-water-chain attack were 5.04, 4.70, and 4.68 Å, respectively. Corresponding values for syn three-water-chain attack were 5.04, 4.95, and 4.88 Å, respectively. The results of anti attack show that in the gas phase and PCM method, the largest exothermicity is related to the three-water-chain model. In the Onsager model, exothermicity is favorable for the four-water-chain model at a very trivial level (0.09 kcal/mol).

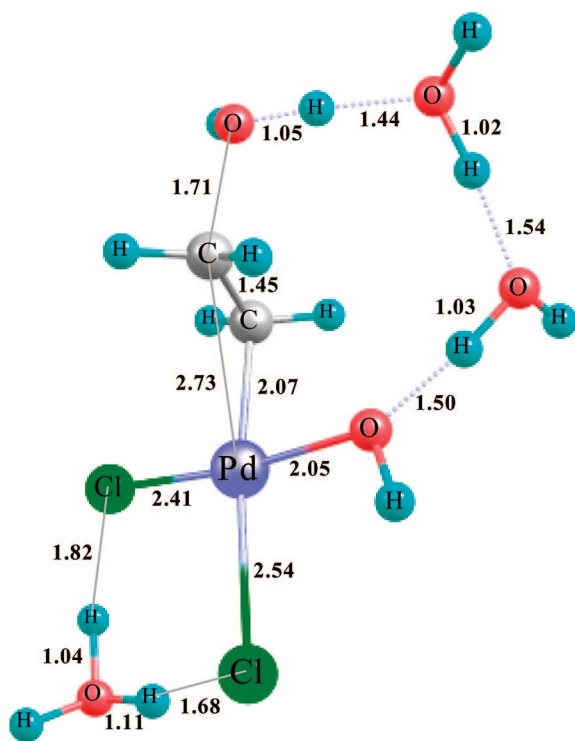
The optimized structures of the reactant, the transition state, and the  $\sigma$ -complex for the anti attack of the three-water-chain model are shown in Figures 5–7. In these figures, between H<sub>3</sub>O<sup>+</sup> and chloride ligands there are hydrogen bonds with H–Cl distances within the range of 1.66–1.85 Å. Also, the reactant and product structures contain hydrogen bonds with the H–O distances in the range of 1.44–1.83 Å.

(32) Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 5409–5410.

(33) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369–4373.

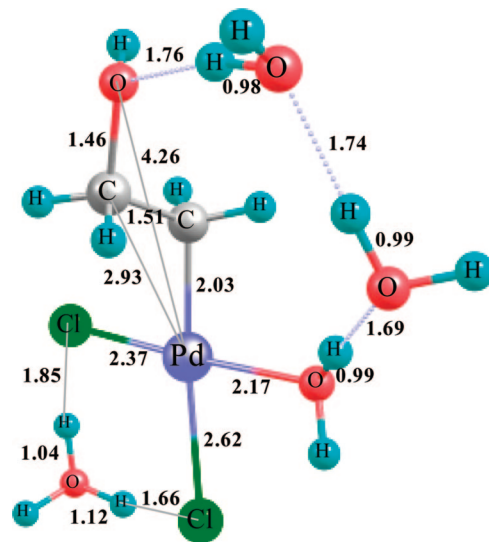


**Figure 5.** Optimized reactant structure for the anti and syn attack of a  $(\text{H}_2\text{O})_3$  chain on  $[(\text{H}_3\text{O})\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})]$ .



**Figure 6.** Optimized transition-state structure for the anti attack of a  $(\text{H}_2\text{O})_3$  chain on  $[(\text{H}_3\text{O})\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})]$ .

Comparison between the reactant and transition-state structures of the anti attack (see Figures 5 and 6) shows that the C–C and Pd–C $_{\beta}$  distances increase from 1.38 to 1.45 Å and from 2.23 to 2.73 Å, respectively. The region around the attacking  $\text{H}_2\text{O}$  molecule of the water chain is another important part of these structures. The distance between C $_{\beta}$  and the O atom of the attacking  $\text{H}_2\text{O}$  molecule decreases from 3.17 to 1.71 Å, which shows C $_{\beta}$ –O bond formation. The O–H bond length increases from 0.98 Å for the reactant to 1.05 Å for the transition



**Figure 7.** Optimized structure of the  $\sigma$ -complex obtained after the anti attack of a  $(\text{H}_2\text{O})_3$  chain on  $[(\text{H}_3\text{O})\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})]$ .

**Table 3.** Activation Energies (kcal/mol) for the Syn Nucleophilic Attack of OH and Water Chain  $(\text{H}_2\text{O})_n$  Model

form of attack	gas phase	Onsager model	PCM model
direct OH attack	46.95	47.03	47.21
$\text{H}_2\text{O}$	24.01	26.11	23.63
$(\text{H}_2\text{O})_2$	22.60	23.37	24.48
$(\text{H}_2\text{O})_3$	21.50	21.40	22.90
$(\text{H}_2\text{O})_4$	21.50	21.50	23.93

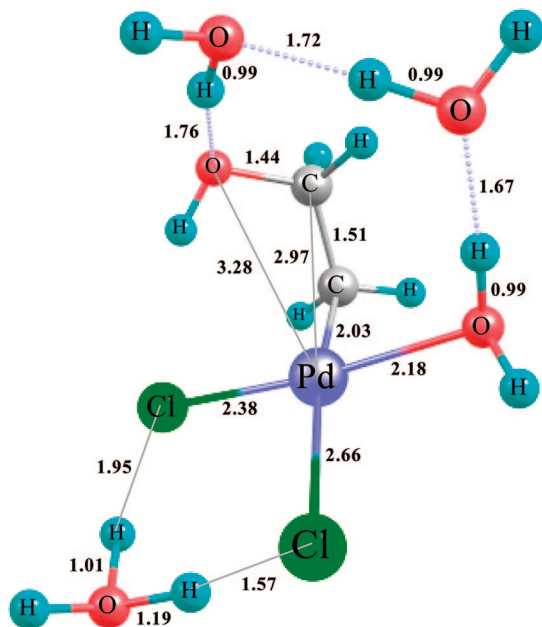
state, but the distance between H atom of this  $\text{H}_2\text{O}$  molecule and O atom of adjacent  $\text{H}_2\text{O}$  molecule decreases from 1.83 to 1.44 Å. These changes show the O–H bond breaking during the nucleophilic addition step, which is consistent with experimental results.<sup>20</sup>

The structure of the trans form of the  $\sigma$ -complex, Figure 7, has a long C–C distance of 1.51 Å, a short C–O distance of 1.46 Å, and a long distance between Pd and the  $\beta$ -carbon of 2.93 Å, which indicates that it is a proper  $\sigma$ -complex.

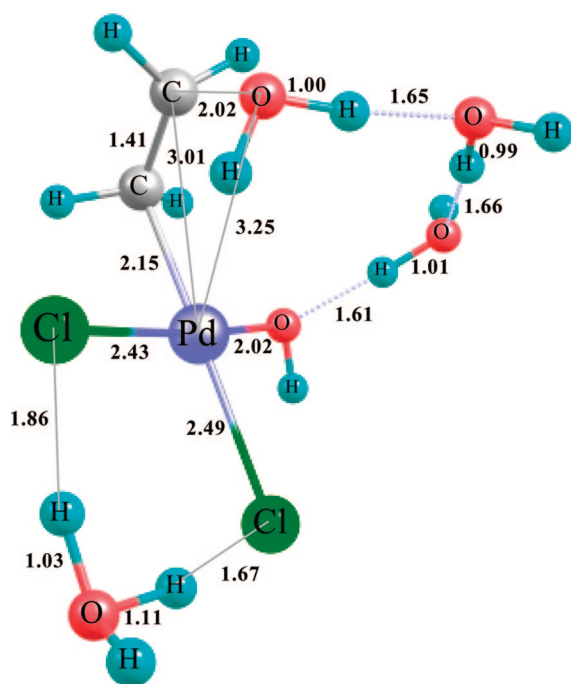
**3.2. Syn Attack of the Nucleophile on the Olefin.** Table 3 contains the computed energies of activation for the syn attack of the nucleophile on the complexed olefin. With respect to the given values, in all cases in the gas phase and the Onsager and PCM models, the lowest  $E_a$  is related to the three-water chain model, i.e. 21.50, 21.40, and 22.90 kcal/mol, respectively. However, these quantities are larger in comparison with those of the anti attack of the three-water-chain model in the gas phase and the Onsager and PCM models, and the differences are 6.78, 8.38, and 10.24 kcal/mol, respectively. Thus, the anti attack of the three-water chain is more appropriate than the syn attack.

In addition, the exothermicity values obtained using the PCM method given in Table 2 confirm this conclusion. In this method, the exothermicity of the anti attack of a chain with three water molecules is 2.71 kcal/mol larger than the syn attack. For comparison purposes of the syn and anti attacks, optimized structures for transition state and product of the syn attacks are presented in Figures 8 and 9, respectively. The structure of the trans form of the  $\sigma$ -complex (Figure 7) very much resembles the cis form of the  $\sigma$ -complex (Figure 8) when compared, including the C $_{\beta}$ –O, C–C, and Pd–C $_{\alpha}$  bond lengths. A notable difference in these two structures is that the distance between





**Figure 8.** Optimized structure of the  $\sigma$ -complex obtained after the syn attack of a  $(\text{H}_2\text{O})_3$  chain on  $[(\text{H}_3\text{O})\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})]$ .



**Figure 9.** Optimized transition-state structure for the syn attack of a  $(\text{H}_2\text{O})_3$  chain on  $[(\text{H}_3\text{O})\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})]$ .

the Pd and O atom of the hydroxyl group of the  $\sigma$ -ligand for the cis complex (3.28 Å) is shorter than that of the trans complex (4.26 Å).

**3.3. Kinetics of the Wacker Process.** Regarding eqs 2–5, assuming eq 5 is the rate-determining step, then the overall rate constant of the reaction is

$$k = K_2 K_3 K_4 k' \quad (14)$$

where  $K_2$ ,  $K_3$ , and  $K_4$  are the equilibrium constants of eqs 2–4, respectively, and  $k'$  is the rate constant of eq 5.

Henry<sup>17</sup> investigated kinetic of the reaction experimentally. His studies showed that for the Wacker process at 25 °C, the following equation holds

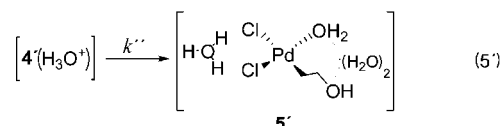
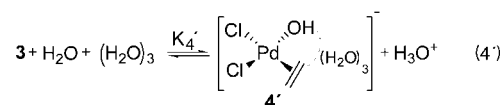
$$\frac{K_3 K_4 k'}{[\text{H}^+][\text{Cl}^-]} = \frac{(2 \pm 0.2) \times 10^{-4}}{[\text{H}^+][\text{Cl}^-]} \text{S}^{-1} \quad (15)$$

and  $\Delta H^\ddagger$  is 19.8 kcal/mol, where  $\Delta H^\ddagger$  is the slope of the plot of  $\ln(k_3 k_4 k')$  versus  $1/T$ . Hence,

$$\Delta H^\ddagger = \Delta H_3 + \Delta H_4 + E_a \quad (16)$$

where  $\Delta H_3$  and  $\Delta H_4$  are the enthalpy changes related to eqs 3 and 4, respectively, and  $E_a$  is the activation energy of the rate-determining step (eq 5).

Regarding the selection of the three-water model, eqs 4 and 5 are converted as follows where  $(\text{H}_2\text{O})_3$ ,  $K'_4$ , and  $k''$  are the



chain with three water molecules, the equilibrium constant of eq 4', and the rate constant of the rate-determining step (eq 5').  $(\text{H}_2\text{O})_3$  does not convert into chain arrangement in gas phases, rather water molecules congregate around each other; therefore, the configuration of  $(\text{H}_2\text{O})_3$  in species 4' has been accepted as the  $(\text{H}_2\text{O})_3$  configuration in the solution phase.

Therefore, eqs 15 and 16 are changed into

$$\frac{K_3 K'_4 k''}{[\text{H}^+][\text{Cl}^-]} = \frac{(2 \pm 0.2) \times 10^{-4}}{[\text{H}^+][\text{Cl}^-]} \text{S}^{-1} \quad (17)$$

and

$$\Delta H^\ddagger = \Delta H_3 + \Delta H'_4 + E''_a \quad (18)$$

where  $\Delta H'_4$  and  $E''_a$  are the enthalpy change related to eq 4' and the activation energy of the anti nucleophilic attack of a three-water-chain model (eq 5'), respectively.

We have performed here detailed kinetic study of the Wacker process in the PCM model. The calculated Gibbs free energy differences between reactants and products at 25 °C, relating to eq 3 ( $\Delta G_3$ ) and eq 4' ( $\Delta G'_4$ ), are 4.41 and 7.81 kcal/mol, respectively. These quantities lead to  $K_3$  and  $(K'_4)$  are equal to  $5.89 \times 10^{-4}$  and  $1.91 \times 10^{-6}$ , respectively.

The change in Gibbs free energy for the formation of the activated complex for the rate-determining step ( $\Delta G^\ddagger$ ) is 10.35 kcal/mol. Using traditional transition state theory:

$$k'' = \frac{k_b T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (19)$$

the value of  $1.63 \times 10^5 \text{S}^{-1}$  was obtained for  $k''$ , where  $k_b$  and  $h$  are Boltzmann and Plank constants, respectively.

Using the calculated values related to  $K_3$ ,  $K'_4$ , and  $k''$ , we have

$$\frac{K_3 K'_4 k''}{[\text{H}^+][\text{Cl}^-]} = \frac{1.84 \times 10^{-4}}{[\text{H}^+][\text{Cl}^-]} \text{S}^{-1} \quad (20)$$

which is in good agreement with experimental data.

The calculated values for  $\Delta H_3$ ,  $\Delta H'_4$ , and  $E''_a$  are 5.25, 5.94, and 12.66 kcal/mol, respectively. Hence,  $\Delta H^\ddagger$  is equal to 23.85 kcal/mol, which is consistent with experimental value (19.8 kcal/mol). These results show that the anti nucleophilic attack of a

three-water-chain model is a suitable model quantitatively for the kinetic study of the Wacker process. Therefore, the solvent molecules of water have an important role in the rate-determining step of the reaction.

#### 4. Conclusion

The mechanism of the rate-determining step and kinetics of the Wacker process have been studied in detail in the gas phase and solvent environment, using the Onsager and PCM models. The comparison of stability of the cis and trans isomers showed that 21.7% of the species **3** exist as the cis isomer in solution. This amount is kinetically sufficient for the progress of the reaction through the internal nucleophilic attack mechanism.

The possibility of both syn and anti attacks for the realization of the internal nucleophilic attack as the rate-determining step has been investigated. Also,  $\text{H}_3\text{O}^+$  was included in the structures of reactants, transition states, and products. The direct attack of coordinated OH on coordinated ethylene results in a very high energy barrier in both syn and anti attack within the range of 46.95–47.21 kcal/mol. These values are far too high to be consistent with experiment. Using the water-chain model for nucleophilic attack has a considerable effect on reducing the barrier energy. The lowest energy barrier is related to the anti nucleophilic attack of a three-water-chain model. The activation energies of this model in the gas phase and the Onsager and PCM models are 14.72, 13.02, and 12.66 kcal/mol, respectively. In addition, the calculated exothermicity values of the reactions

in both gas and solution phases confirm the suitability of this model as a rate-determining step. The exothermicity values of the gas phase and the Onsager and PCM models are –10.56, –10.57, and –12.40 kcal/mol, respectively.

The increase of the length of O–H bond from 0.98 to 1.05 Å is consistent with the large isotopic effects when the reaction is run in  $\text{D}_2\text{O}$  solvent because O–D bond breaks up in this step. These results are consistent with the experimental evidence which has shown that the rate-determining step is a nucleophilic addition. Choosing the anti nucleophilic attack of three water chain model, the calculated values for ( $K_3K'_4k''$ ) and  $\Delta H^\ddagger$  are  $1.84 \times 10^{-4} \text{ M}^2 \text{ S}^{-1}$  and 23.85 kcal/mol, respectively, which are well in agreement with experimental values of  $(2 \pm 0.2) \times 10^{-4} \text{ M}^2 \text{ S}^{-1}$  and 19.8 kcal/mol, respectively.

Thus, we conclude that *the anti nucleophilic attack of a three-water-chain model* is the dominate mechanism for the rate-determining step of the Wacker process. The theoretical description of this route is consistent with experimental observations.

**Supporting Information Available:** Complete ref 27 and tables giving Cartesian coordinates, electronic energies ( $E$ ), sum of electronic and zero-point energies ( $E + \text{ZPE}$ ), sum of electronic and thermal enthalpies ( $H$ ), and Gibbs free energies ( $G$ ) for the calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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