



## O–H bond cleavage step of the Wacker process: A DFT study

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## ABSTRACT

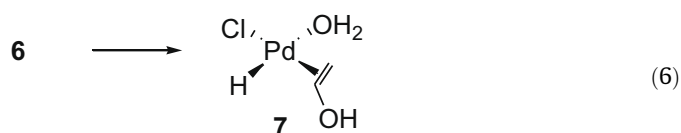
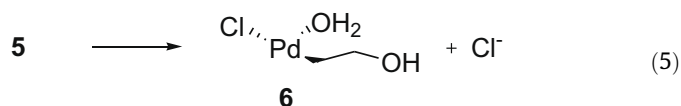
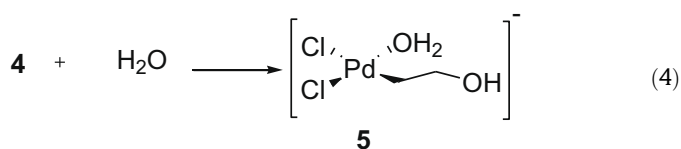
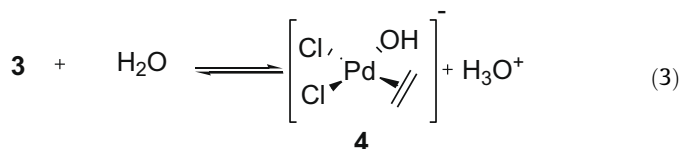
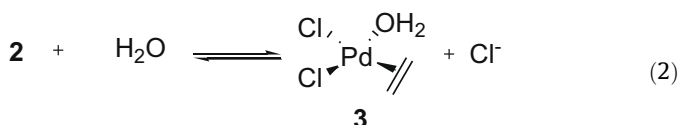
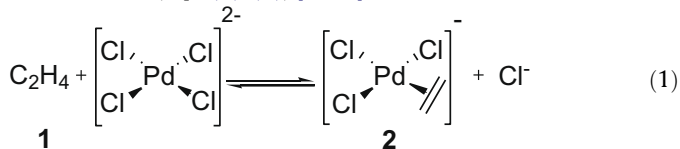
The Wacker process consists of several important organometallic reactions. The termination step of this process, i.e., the O–H bond cleavage reaction, was investigated by employing density functional theory (DFT) with modeling the solvent (water) as a polarizable continuum (PCM) and also assuming that the water molecules will directly involve in this reaction. The termination step can proceed either through  $\beta$ -hydrogen elimination from –OH group ( $\beta$ HE) or through direct reductive hydrogen elimination (RHE). As regards  $\beta$ HE, two different pathways were assumed, for both of which the test calculations showed high energy barriers. Therefore,  $\beta$ HE turns out to be implausible. As for the RHE mechanism, in which the solvent molecules have a significant effect on the reduction of the activation energies, four different pathways were assumed. Here, the lowest energy barriers ( $E_{as}$ ), which are considerably lower than the  $E_{as}$ s of rate-determining step, belong to the pathway in which a “chain” of one water molecule assists the H-transfer from –OH group to the chloride ligand, (pathway **D**). This pathway, therefore, can be accepted as the most appropriate mechanism for the O–H bond cleavage step of the Wacker process.

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## 1. Introduction

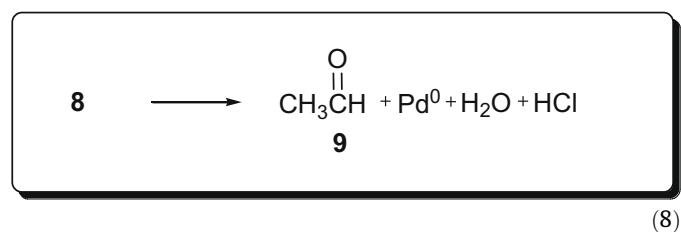
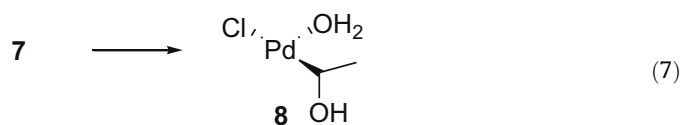
The Wacker oxidation is of great importance, especially in the synthesis of carbonyl compounds from corresponding alkenes. Also, its mechanism involves a number of fundamental kinds of organometallic reactions, such as hydroxymetallation,  $\beta$ -hydrogen elimination and 1,2-insertion [1,2].

So far there have been a great number of experimental data about the Wacker process. These data have made it possible to test any computational model. The main steps of the Wacker process are as follows (Eqs. (1)–(8)) [1–16].



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In our previous work [10] by using density functional calculations, a mechanism for the rate-determining step (RDS) of the Wacker process was proposed, which is well in agreement with the experimental evidence [7,12], especially isotopic effects [15,17] and the rate law of the reaction under usual conditions [15,18]. In this mechanism, the internal-anti-attack of a chain with three water molecules in the hydroxypalladation step (Eq. (4)), seems to be the most appropriate mechanism for the RDS of the Wacker process. The activation energies of the RDS of the Wacker process were found to be 14.72 and 12.66 kcal/mol, in the gas phase and PCM model, respectively [10]. It is clear that the energy barriers ( $E_{\text{a}}$ s) of the steps following the RDS have to be lower than these calculated  $E_{\text{a}}$ s.

By using the one water molecule-assisted pathway, involving the —OH group located next to the coordinated  $\text{H}_2\text{O}$  [16], the calculated  $E_{\text{a}}$ s for steps 6–8 were in good agreement with the experimental evidence [15,17–18]. As expected, the  $E_{\text{a}}$ s of all steps were less than those for the hydroxypalladation as the RDS of the Wacker process. In the PCM model, the energy differences between  $E_{\text{a}}$  of RDS and the  $E_{\text{a}}$ s of  $\beta$ -hydrogen elimination (Eq. (6)) and insertion (Eq. (7)) steps are 8.49 and 3.42 kcal/mol, respectively, while this difference is only 0.34 kcal/mol, for the termination step (Eq. (8)), which is a negligible value. Therefore, a more satisfactory model for the O—H bond cleavage step is to be searched out.

In the termination step (Eq. (8)) of the Wacker process, an O—H bond cleavage of the  $\alpha$ -hydroxyalkyl group will result in a Pd-acetaldehyde complex, which will be decomposed to the final products. This reaction can take place via two different mechanisms, the H-transfer from —OH group to Pd—H formation mechanism ( $\beta$ HE) or direct reductive H-elimination mechanism, where HCl and Pd(0) form directly (RHE). For a simplified system PdCl ( $\text{CH}_2\text{OH}$ ), Siegbahn [13] obtained a very high barrier, 30.1 kcal/mol, for the  $\beta$ HE. In an acetic acid medium, the O—H bond cleavage has an energy barrier that is more than 38 kcal/mol [11]. For the  $\beta$ HE from O—H, another theoretical study [12] predicted very high barrier. Using a chloride-mediated model, Keith et al. [19] predicted energy barrier of 17.2 kcal/mol, for RHE mechanism, yet this barrier is high for one step compared with the experimental activation enthalpy of the Wacker process (19.8 kcal/mol) [15]. In the present work, using water-chain model, we proposed a model for the O—H bond cleavage step of the Wacker process, which is in good agreement with the experimental evidence [15]. As expected, this model has considerably lower barriers than those for the RDS of the Wacker process.

## 2. Theoretical methods

All calculations have been performed by using the hybrid functional (B3LYP) [20,21] as implemented in the Gaussian 98 program package [22]. The 6-311+G(d,p) basis set was employed except for Pd and Cl atoms, in which the LANL2DZ [23] basis set was used

including effective core potential functions. To improve the accuracy of the calculation, one sp diffuse function, two d and one f polarization functions were added to Cl atoms.

All degrees of freedom for all geometries were optimized. The obtained transition states (TSs) were confirmed to have only one imaginary frequency of the Hessian. The structure of **TS4** was examined by the intrinsic reaction coordinate (IRC) [24] calculation to ensure that this TS is in fact the intermediate between the reactant and the product.

In the gas phase, the zero-point-energy (ZPE) corrections were made to obtain energies. Here, one of the self-consistent reaction field methods, i.e., the sophisticated polarizable continuum model (PCM) [25,26] has been used to investigate the solute–solvent interactions. The solvent effects were involved in the gas phase optimized geometries. The PCM energies were evaluated by neglecting the ZPE corrections.

## 3. Results and discussion

The O—H bond breaking (Eq. (8)) can take place via two different mechanisms:  $\beta$ HE or RHE. Previously [16] several models were proposed for both RHE and  $\beta$ HE mechanisms. In the PCM model, the lowest  $E_{\text{a}}$  belongs to the RHE mechanism (12.32 kcal/mol) [16]. In this work, in both mechanisms (RHE and  $\beta$ HE), the O—H bond cleavage step (Eq. (8)) were studied theoretically through six modeled pathways (A–F). The calculated  $E_{\text{a}}$ s and the corresponding values of the RDS [10] are given in Table 1.

### 3.1. $\beta$ HE mechanism

In the  $\beta$ HE mechanism, the central Pd atom can contribute to the reduction of the barrier height. Here, two different models (A and B) are investigated for this mechanism. Without involving any water molecule in the pathway A, production of Pd-acetaldehyde can take place via **TS1**. In the optimized structure of **TS1**, breaking of the O—H bond and the formation of Pd—H bond is clear. The O—H and Pd—H distances vary from 0.97 and 2.80 Å for reactant (**R1**) to 1.41 and 1.58 Å for **TS1**, respectively (see Fig. 1). As seen in Table 1, the  $E_{\text{a}}$ s of this model are 13.91 and 23.41 kcal/mol higher than those for the RDS of the Wacker process, in the gas phase and PCM model, respectively. Therefore, this pathway is implausible.

In the second model (pathway B), the role of addition of one water molecule in the coordination sphere of Pd was examined. The optimized structures for reactant (**R2**), transition state (**TS2**) and product (**P2**) of this pathway are presented in Fig. 2. Variation of the bond lengths from **R2** to **TS2** and to **P2** shows the O—H bond breaking and Pd—H formation. The  $E_{\text{a}}$ s of this pathway are 6.31 and 19.63 kcal/mol higher than those for the RDS of the Wacker

**Table 1**

The calculated  $E_{\text{a}}$ s of the proposed pathways (A–F) for O—H bond cleavage step together with the calculated  $E_{\text{a}}$ s of hydroxypalladation as the RDS of the Wacker process.

Proposed pathway	$E_{\text{a}}$ (kcal/mol)	
	Gas phase ( $E + \text{ZPE}$ )	PCM
$\beta$ HE mechanism		
A	28.63	36.07
B	21.03	32.29
RHE mechanism		
C	21.10	27.08
D	5.60	8.98
E	9.67	14.97
F	9.17	15.02
Hydroxypalladation as the RDS	14.72	12.66

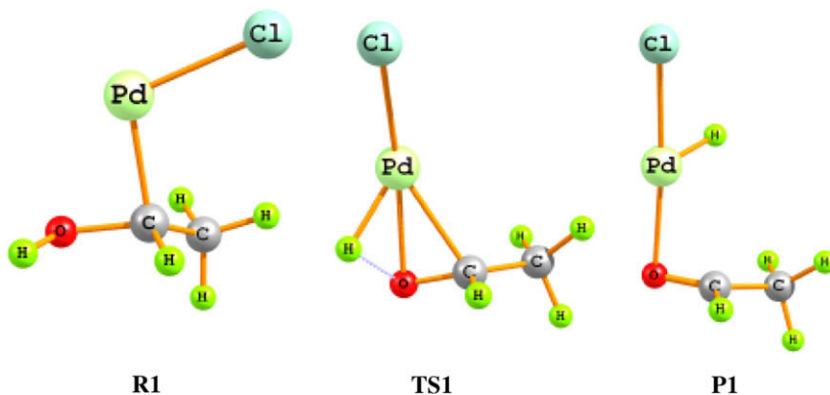


Fig. 1. Optimized structures of the reactant (R1), transition state (TS1) and product (P1) of pathway A.

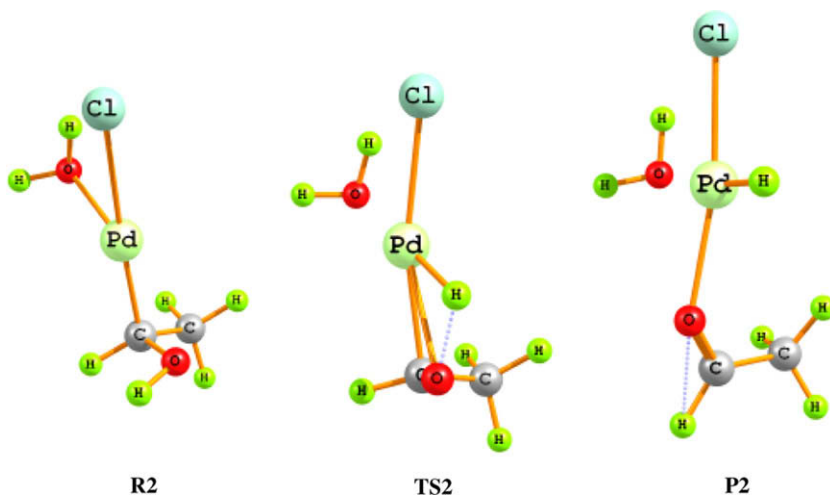


Fig. 2. Optimized structures of the reactant (R2), transition state (TS2) and product (P2) of pathway B.

process, in the gas phase and PCM model, respectively. Hence, the  $\beta$ HE mechanism leads to unsatisfactory results.

### 3.2. RHE mechanism

The first model is assumed to bear one water molecule in the first-coordination sphere of Pd (pathway C). The optimized structures for reactant (R3), transition state (TS3) and product (P3) of this pathway

are shown in Fig. 3. A comparison between the R3 and TS3 structures will indicate the O–H bond breaking and the formation of the H–Cl bond. The O–H bond length increases from 0.97 to 1.34 Å. This pathway results in a considerable decrease in the energy barrier compared with the pathways A and B, but the calculated  $E_a$ s of this model are 6.38 and 14.42 kcal/mol higher than those for the RDS of the Wacker process, in the gas phase and PCM model, respectively. Therefore a more sophisticated model is to be postulated.

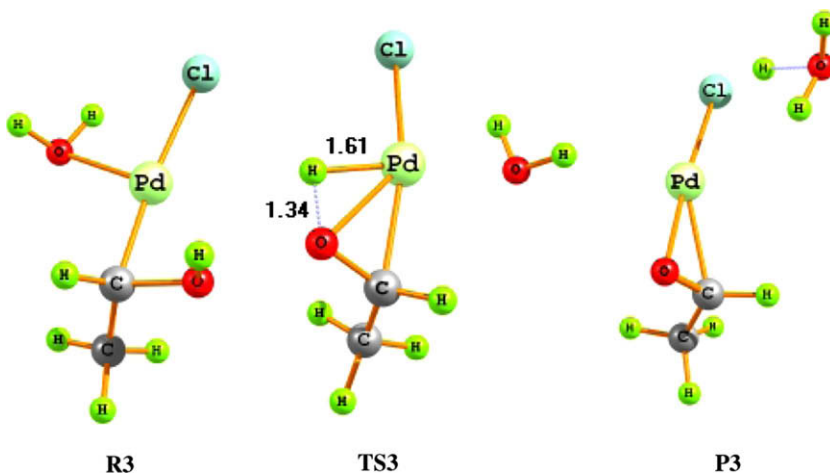


Fig. 3. Optimized structures of the reactant (R3), transition state (TS3) and product (P3) of pathway C.

The central feature of this model is the assumption that the solvent water molecules have a dominant role. In the sense that the solvent molecules (water) could play a role in assisting H-transfer from —OH group to Cl ligand, rather than being solely a dielectric medium. We [10,16] demonstrated that the  $E_a$  related to some steps of the Wacker process is significantly reduced by using the water-chains models. Also, several theoretical investigations on the mechanism of the Wacker reaction indicated that the chains of water molecules bring about a reduction in the calculated energy barriers [12,19,27,28].

First, one-water-chain model (pathway **D**) was used in a manner such that the water molecule will be located between the —OH group and the coordinated Cl. The optimized structures of reactant (**R4**) and product (**P4**) of this pathway are shown in Fig. 4. Its transition state (**TS4**) structure is given in Fig. 5. The water molecule acts as a bridge, assisting to break H atom from —OH group and then the formation of H—Cl. In comparison with the pathway **C**, the obtained results (Table 1) indicated that by using one water molecule,  $E_a$ s related to the gas phase and PCM model are reduced dramatically, from 21.10 to 5.60 kcal/mol and from 27.08 to 8.98 kcal/mol, respectively. The calculated  $E_a$ s of pathway **D** are 9.12 and 3.68 kcal/mol lower than those for the RDS of the Wacker process, in the gas phase and PCM model, respectively. Since these differences are significant, this pathway is chosen as a satisfactory model for the O—H bond cleavage step of the Wacker process.

Similar to the other obtained TSs in this work, the **TS4** has only one imaginary frequency in the frequency calculations, which confirms its validity. The IRC analysis is an important tool to ensure the suitability of the proposed TS. Therefore, the IRC calculation has performed, which confirms the suitability of **TS4**, as an intermediate stage between the **R4** and **P4** in the pathway **D**. The IRC results have been given in the supporting information file.

Comparison between **R4** and **TS4** structures (see Figs. 4 and 5) shows that the O1—H1 and O2—H2 distances increase from 0.99 to 1.56 Å and from 0.98 to 1.20 Å, respectively. In the **P4** structure, these distances are 1.78 and 1.58 Å, respectively. On the other hand, the H2—Cl distance decreases from 2.40 Å in **R4** to 1.58 and 1.36 Å, for **TS4** and **P4**, respectively. These changes indicate the H-transfer from —OH group to Cl, where the water molecule acts as a bridge. The C1—O1 bond length shortens from 1.39 Å for **R4** to 1.29 Å for **P4**, which confirms the formation of C1=O1 bond and Pd-acetaldehyde complex. The Cl ligand will separate from the Pd atom and move to the second-coordination sphere. The Pd—Cl distance increases from 2.40 Å for **R4** to 2.73 and 3.99 Å for **TS4** and **P4**, respectively.

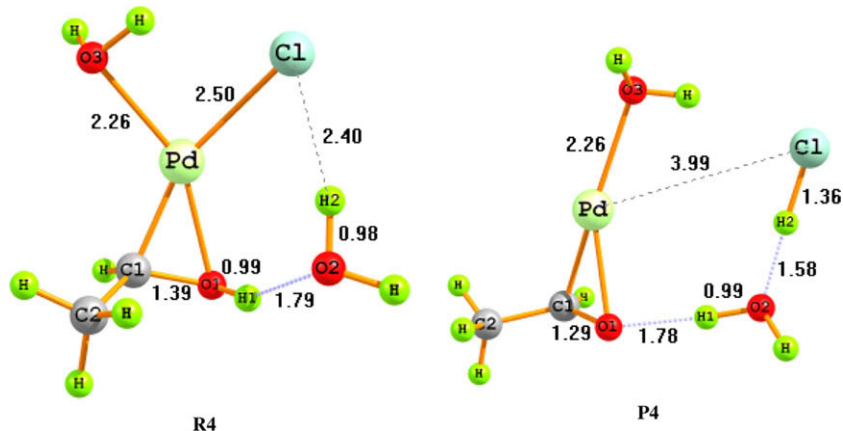


Fig. 4. Optimized structures of the reactant (**R4**) and product (**P4**) of pathway **D**.

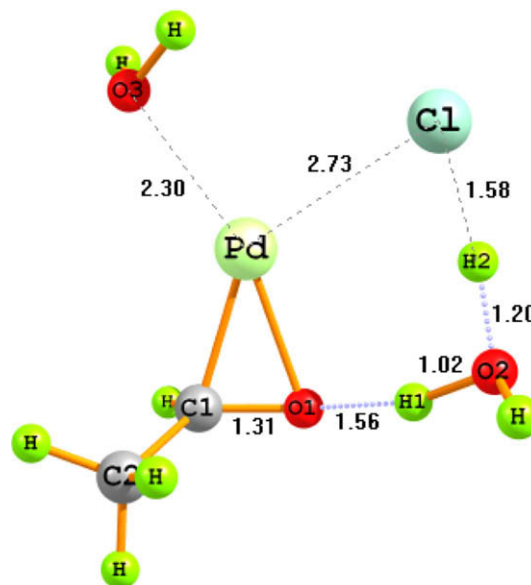


Fig. 5. Optimized transition state structure (**TS4**) of pathway **D**.

Subsequently, the effect of water-chain length on the energy barrier was investigated. For the RDS, elongation of water chain to three water molecules resulted in the reduction of energy barrier [10]. Here, going from one to two water molecules in the water-chain model (pathway **E**) increased  $E_a$  in the gas phase and PCM model from 5.60 to 9.67 kcal/mol and from 8.98 to 14.97 kcal/mol, respectively. In the PCM model, the  $E_a$  of pathway **E** is 2.31 kcal/mol more than the  $E_a$  of the RDS. This indicates that the size of one water molecule is the best length for the water chain in the O—H bond cleavage step of the Wacker process. Therefore, the one water molecule “chain” is just enough to bridge between the —OH group and the chloride ligand. Increasing the chain length by another water molecule leads to unsatisfactory results. The reactant (**R5**), transition state (**TS5**) and product (**P5**) structures of this pathway are shown in Fig. 6.

Calculations showed that the incorporation of one water molecule in the first-coordination sphere has a significant role. The omission of this water molecule as in pathway **F**, leads to higher activation energies. The optimized structures for reactant (**R6**), transition state (**TS6**) and product (**P6**) are shown in Fig. 7. For this model,  $E_a$  in the gas phase is 9.17 kcal/mol. The solvent effects raise  $E_a$  value to 15.02 kcal/mol. These barriers are 3.57 and 6.04 kcal/

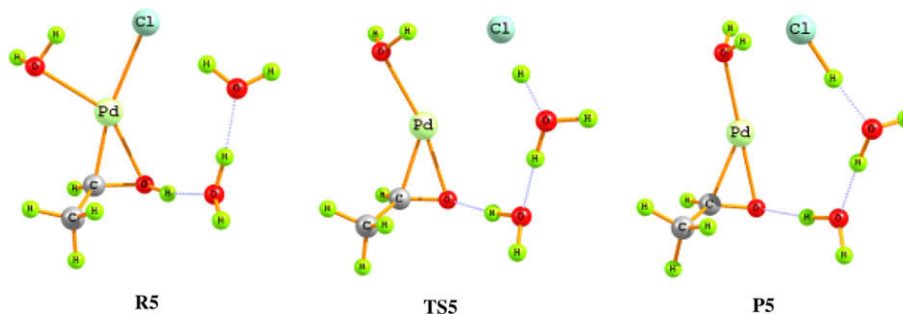


Fig. 6. Optimized structures of the reactant (R5), transition state (TS5) and product (P5) of pathway E.

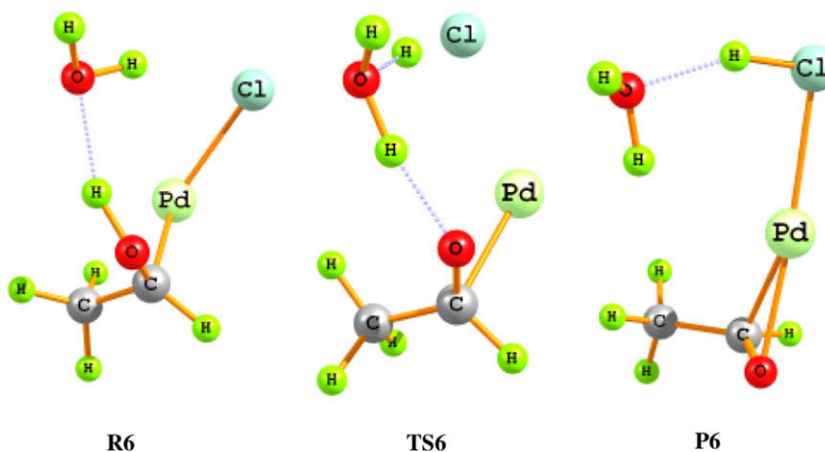


Fig. 7. Optimized structures of the reactant (R6), transition state (TS6) and product (P6) of pathway F.

mol higher than  $E_a$ s of the one water-chain model (pathway D), in the gas and PCM model, respectively. Also, the obtained  $E_a$  is 2.36 kcal/mol higher than  $E_a$  of the RDS in the solution phase.

#### 4. Conclusions

The O–H bond cleavage step of the Wacker process (Eq. (8)) was studied in both gas phase and the PCM model, which could proceed via two  $\beta$ HE and RHE mechanisms. Both mechanisms were studied theoretically. The suggested pathway A for  $\beta$ HE mechanism results in very high energy barriers. Considering one water molecule in the first-coordination sphere of Pd (pathway B) had no considerable effect on the reduction of activation energies compared with the pathway A. The barriers of the pathways A and B are very much higher than the  $E_a$ s of the RDS, causing the rejection of the  $\beta$ HE mechanism.

The RHE mechanism has lower  $E_a$ s than those of  $\beta$ HE one. In the simplest model of RHE mechanism (pathway C), one water molecule was located in the first-coordination sphere of Pd. The calculated  $E_a$ s of this model are quite higher than the  $E_a$ s of RDS.

The solvent molecules of water can play an important effect on reducing the energy barriers. A chain of water molecule(s) could assist the H-transfer from –OH group to chloride ligand. The obtained results show that the lowest  $E_a$  is related to the one-water-chain model (pathway D). The  $E_a$ s of this model are considerably lower than the  $E_a$ s of RDS, 9.12 and 3.68 kcal/mol in the gas phase and PCM model, respectively. In addition, the IRC calculations confirm the suitability of this pathway as a model for the O–H bond cleavage step of the Wacker process.

Both paths of going from one to two water molecule in the water-chain model (pathway E) and the omission of the water

molecule located in the first-coordination sphere (pathway F) lead to increasing  $E_a$ s in the gas phase and PCM model. Thus, using the one-water-chain model in the pathway D, we proposed a proper mechanism for the O–H bond cleavage step of the Wacker process. As expected, this model has a considerably lower energy barrier than the calculated  $E_a$ s of RDS of the Wacker process [10].

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2009.11.019.

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