Density Functional Study of the Palladium Acetate Catalyzed Wacker Reaction in Acetic Acid

David D. Kragten* and Rutger A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513,
5600MB Eindhoven, The Netherlands

Jan J. Lerou

DuPont CR&D, Wilmington, Delaware 19880

Received: July 28, 1998; In Final Form: October 30, 1998

In the Wacker process, palladium acetate complexes catalyze the homogeneous reaction of ethylene and water to form acetaldehyde. We have studied the mechanism of this reaction in detail, using density functional theory computational methods. The putative most active catalyst is a dimer complex, which has been modeled by clusters of two palladium ions coordinated by acetate ligands. The active site is formed by one of the palladium ions. In the Wacker process as catalyzed by palladium acetate, ethylene coordinates to palladium. Next, coupling with hydroxyl species from the solution takes place in an outer-sphere mechanism. A series of hydrogen transfers, in which terminal acetate participates, converts the hydroxyethyl ligand into acetaldehyde. Finally, the product desorbs. The overall reaction enthalpy is exothermic. One of the hydrogen transfers, the step that results in acetaldehyde formation, is the rate-determining step. This step costs 61 kJ/mol. All reactions presumably take place within the coordination sphere, and thus hydrogen from the solvent is not incorporated into the product. Solvent effects are explicitly taken into account in all steps.

I. Introduction

An industrially important homogeneously catalyzed reaction is the selective oxidation of ethylene to acetaldehyde, generally known as the Wacker process. This process was simultaneously developed by Wacker-Chemie[1] and by the group of Moiseev[2] in the late nineteen-fifties. The Wacker reaction involves the reaction of ethylene with palladium(II) chloride in water (reaction 1). Palladium is thereby reduced to palladium black. To make the reaction catalytic, palladium is reoxidized by reaction with copper(II) chloride and oxygen (reactions 2 and 3). Commercially, the process gives about 95% yield of acetaldehyde, and applied conditions are about 120−130 °C and 4 atm pressure.[3]

$$C_2H_4 + PdCl_4^{2-} + 3H_2O \rightarrow CH_3CHO + Pd^0 + 2H_3O^+ + 4Cl^- \quad (1)$$

$$Pd^0 + 2CuCl_2 + 2Cl^- \rightarrow PdCl_4^{2-} + 2CuCl \quad (2)$$

$$CuCl + 4H_3O^+ + 4Cl^- + O_2 \rightarrow 4CuCl_2 + 6H_2O \quad (3)$$

The major features of the Wacker process are well established.[4,5] First, ethylene coordinates to palladium, replacing a chloride ion. Some of the other chlorides are replaced by water and hydroxyl ligands. Then, addition of hydroxyl to the ethylene takes place to form a hydroxyethyl ligand. It is not clear whether this step involves a trans[6] or a cis addition,[7] whereby hydroxyl originates respectively from the coordination to palladium or from the solvent. Both mechanisms are proposed, but agreement seems to be more in favor of trans addition. Differences in observations could also be due to differences in reaction conditions. Successively, a series of hydrogen migrations takes place to form acetaldehyde. All these transfers take place within the coordination sphere of the palladium, as hydrogen exchange with the solvent does not take place.[8] One of these hydrogen migrations is rate-determining.

The first steps of the Wacker process have been studied extensively by computational methods. The most important studies have been reviewed recently by Dedieu.[9] The nucleophilic coupling reaction, especially, has been studied extensively, both with semiempirical[10] and ab initio techniques.[11] Studies of the actual system are not always available, so results from analogous reactions have to be used to obtain insight into factors of importance.[9] As for the coupling reaction, the main conclusion is that it involves a trans attack of hydroxyl species or water on ethylene. This induces slipping of ethylene and further activates the ligand. For other reactions that take place in the mechanism, however, results are hard to compare, as they were obtained for other metal ions. The involvement of the metal ion is critical in the hydrogen transfers.

Recently, extensive studies of the most important steps of the Wacker process, which are the coupling reaction and β-hydrogen elimination, have been performed with ab initio and density functional theory computational methods by Siegbahn.[12] Solvent effects, which were previously neglected, are explicitly taken into account. Actually, it is not straightforward to develop models that consider solvent effects of the first coordination sphere, as can be seen from the many approaches studied. The best approach seems to involve coordination of chains of water molecules to model the coupling and the β-elimination reactions.[12a] The effect of the water solvent outside the coordination sphere is self-consistently taken into account by a reaction field. Siegbahn[12] demonstrates that the trans attack is indeed the favorable coupling reaction. It is suggested that the

10.1021/jp983192h CCC: $18.00

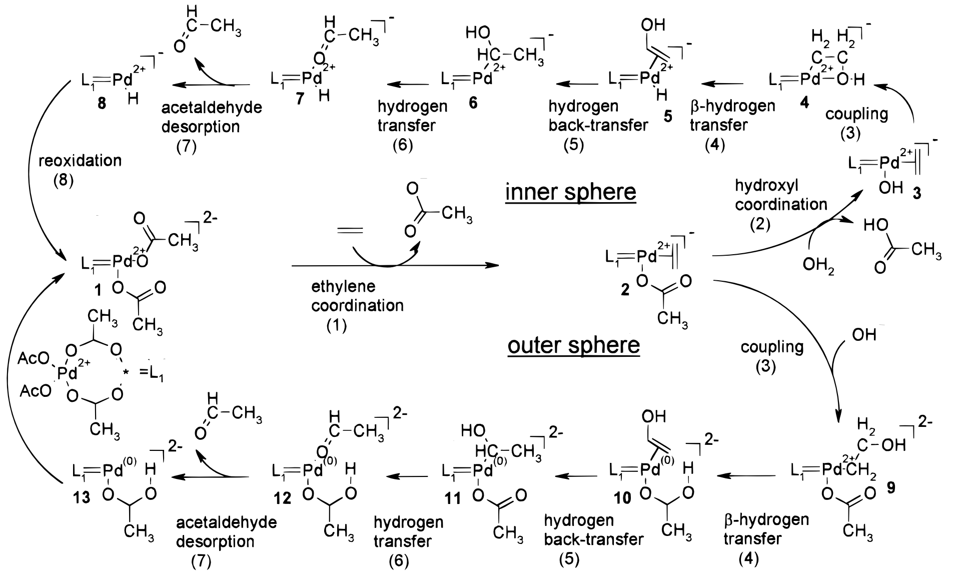

Figure 1. Proposed catalytic cycles of the inner- and the outer-sphere Wacker reaction as catalyzed by palladium acetate.

rate-determining step is not the β-hydrogen elimination, but the hydrogen transfer that finally forms the acetaldehyde.[12a]

In a reaction analogous to the Wacker process, vinyl acetate is formed by the reaction of ethylene with acetate in acetic acid solvent.[13] Higher yield and activity are obtained by using palladium acetate as catalyst with alkali acetate promoters.[13,14] In a previous paper,[15] we have presented the results of a study of a Wacker-like mechanism to form vinyl acetate as catalyzed by palladium acetate. In the presence of water, acetaldehyde is formed as a byproduct via the Wacker reaction.[14,16] Both reactions, the vinyl acetate formation and the Wacker reaction, are competitive reactions. In this paper, we present a mechanism for the palladium acetate-catalyzed Wacker process. The mechanism is schematically presented in Figure 1. This mechanism is analogous to that proposed for the vinyl acetate formation and shows close resemblance with the Wacker reaction catalyzed by palladium chloride.

We have studied both the inner- and the outer-sphere mechanisms (see Figure 1), as characterized by the coupling reaction of hydroxyl with ethylene. First, ethylene coordinates to palladium at a terminal acetate site (step 1). In the inner-sphere mechanism, hydroxyl is coordinated to palladium by exchange with a terminal acetate (step 2). Then, coupling of hydroxyl and ethylene to form hydroxyethyl takes place via an inner- or an outer-sphere reaction, whereby hydroxyl originates respectively from prior coordination to palladium or from the solvent (step 3). Successively, several hydrogen transfers take place, resulting in the formation of acetaldehyde (steps 4 through 6). Acetaldehyde desorbs (step 7), and reoxidation of palladium to palladium acetate closes the catalytic cycle (step 8). This Wacker reaction as catalyzed by palladium acetate has not been studied previously with computational methods, as far as we know. We have studied all steps apart from the reoxidation. In principle, the studies have been performed in a vacuum, but the solvent effects have also been taken into account explicitly.

The importance of this study is the comparison with the reaction that forms vinyl acetate. Both reactions are catalyzed by the same palladium acetate complexes, and are therefore competitive. The formation of acetaldehyde is the most important side reaction in the homogeneous vinyl acetate formation.[3,13,16] It is this side reaction that makes the homogeneous process to form vinyl acetate unfavorable with respect to the heterogeneous process.

II. Methods

A. Computational Details. Both the inner- and the outer-sphere Wacker-like mechanisms were studied by means of density functional theoretical (DFT) computational methods. These calculations have been performed with the DGauss program,[17] version 2.3. All structures have been completely geometry optimized at the GGA level. Optimizations have been performed spin-restricted; the ground state has been determined for all structures. We have used the local density approximation (LDA) in the form given by Vosko−Wilk−Nusair[18] with self-consistently incorporated gradient corrections due to Becke[19] and Perdew.[20] Relativistic corrections for palladium have been applied self-consistently via effective core potentials. The program represents the molecular orbitals as linear combinations of Gaussian-type orbitals. The basis sets are of double-ζ quality and include polarization functions for all non-hydrogen atoms (DZPV).[21] A second set of basis functions, the auxiliary basis set,[22] is used to expand the electron density in a set of single-particle Gaussian-type functions. Basis sets are optimized to reduce basis set superposition (BSSE) errors. The accuracy of the method is very high. Structural predictions for transition-metal containing species were found to be within 0.05 Å for bond lengths and 3 to 4° for bond angles. Predictions for the energies were within 20 to 25 kJ/mol of the expected values.

B. Solvent Effects. In homogeneous reactions, the solvent plays an important role. Energies and mechanisms are often affected. Therefore, in a detailed study of a homogeneously catalyzed reaction, the solvent effect should be taken into account explicitly. The theories to estimate the solvent effect have been studied extensively. Basically, the best methods involve accounting for the solvent effects by coordinating the solute with solvent molecules in the first coordination sphere and modeling the rest of the solvent by embedding it all in a reaction field. We do not have these embedding techniques in our computational program, and therefore use a different approach. This is explained in detail elsewhere.[15] The most important features are given below.

An important property of acetic acid is the formation of dimer structures due to the large dimer energy. A compilation of calculated and measured energies obtained for various dimer structures is given in Table 1. The agreement between theory and experiment is good. Both the bonds in acetic acid dimers

TABLE 1: Dimer Interactions[a]

interaction	$-\Delta E_{\text{formation}}$	dimer energy (lit.)
$H_2O..H_2O$	26	23 (19.8[b])[23]
AcOH..HOAc	70	63.0[24]
$AcOH..H_2O$	50	

[a] Energies are given in kJ/mol. [b] Value obtained with computational theoretical methods.

and in water that binds to acetic acid are strong; these bonds are much stronger than in water dimers. From these dimer energies, it is predicted that acetic acid forms mainly dimer structures and that water is bound to acetic acid in the acetic acid solution.

Only in reactions involving water or acetic acid is the coordination with an acetic acid molecule from the solvent modeled explicitly. For all other reactants, such as the palladium acetate clusters, bonds with acetic acid are too weak to break the acetic acid dimer structure.[15] Coordination with acetic acid monomers is therefore not considered. However, the coordination of molecules from the solvent is important in the activated complex, as the activation barrier could be lowered significantly. This will be demonstrated in the next section.

For the rest of the solvent effect, we have used an approach with continuum theories. An extensive review of the techniques to consider the solvent as a continuum is given by Tomasi and Persico.[26] We have used the approach of the reaction field theory,[27] which is reviewed in textbooks,[28] to estimate the electrostatic contribution. In addition, the cavity formation is also taken into account by using the approach suggested by Tuñón et al. [29] (see formula 6), with the formulation of Uhlig[30] to consider the formation of the cavity surface (first term of formula 6). The dispersion and the repulsion contributions to the solvent effect are neglected, as they are expected to be low. We observed in a previous study[15] that dipole and quadrupole contributions to the electrostatic energy are negligible for palladium acetate clusters, due to their large size. Moreover, ion contributions are absent due to the choice of models in which the charges are counterbalanced. However, electrostatic contributions are important in reactions involving molecules from the solvent. The solvation energy is calculated according to

$$\Delta E_{\text{solvation}} = \Delta E_{\text{electrostatic}} + \Delta E_{\text{cavity}} \tag{4}$$

with

$$E_{\text{electrostatic}} = E_{\text{dipole}} + E_{\text{quadrupole}} = -(\epsilon - 1)/(2\epsilon + 1)\mu^2/a^3 - 3(\epsilon - 1)/2(2 + 3\epsilon)Q^2/a^5 \tag{5}$$

and

$$E_{\text{cavity}} = 4\pi a^2\gamma - \text{RT}\ln(1 - V_s n_s) \tag{6}$$

For the dielectric constant (ϵ) and surface tension (γ), we have used the values of acetic acid at room temperature of 6.20 and 27.10 mN/m, respectively.[25] The volume, V_s, and numeral density, n_s, are that of the solvent; values at room temperature are used.[25] The dipole (μ) and quadrupole (Q) moments have been calculated.

The radius of the cavity (a) is difficult to estimate. In the literature, several methods are suggested.[26] We have used an approach of enclosing the cluster in an ellipsoid. The radius is taken as the geometrical mean of the radii that span the ellipsoid around the cluster optimized in a vacuum. The largest possible perpendicular radii have always been used; in the calculation of the mean, we multiplied the largest radius by the square of the second largest radius. This is done to account for the different conformations arising from those rotations in the molecules that are fastest around the axis of the largest radius. Van der Waals radii of the atoms at the shell of the ellipsoid have been added (we used: $r_O = 1.52$ Å; $r_H = 1.20$ Å). The obtained radius has been used in the calculation of both the electrostatic and the cavity contributions. The values of radii that we evaluated with our method for a number of the same molecules used by Tuñón et al. [29] are in agreement with that study.

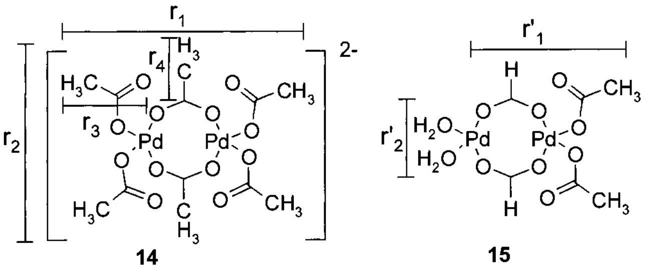

Figure 2. Schematic representation of the palladium acetate dimer. Representations of the actual complex (left) and the model used (right) are shown. Diameters used for the calculation of the cavity radius are indicated.

III. Computational Results

A. Palladium Acetate Clusters. Palladium acetate dimers are the putative catalytically most active species for vinyl acetate formation and for alkene exchange reactions.[13] Hence, it is very reasonable to assume the same level of activity for these dimers in the Wacker reaction. A schematic representation is shown as structure 14 in Figure 2. Two palladium ions are linked by bridging acetates; each palladium ion has two additional acetates coordinated in a monodentate mode at terminal sites. The palladium(II) ions are expected to be square planar coordinated.

We have modeled the palladium acetate dimer, as shown schematically as structure 15 in Figure 2. The bridging acetates are modeled by formates. At the active site, a palladium(II) ion, we used two terminal acetates. However, at the palladium ion that does not participate in the reactivity of the complex, we saturated the coordination with water and hydroxyl ligands. This simplification has a 2-fold reason. First, the cluster is smaller, thereby saving computational resources. Second, the charge of the ion can be balanced to equal zero by the addition of protons, which are then accommodated at these water and hydroxyl ligands.

The palladium acetate cluster optimized in a vacuum shows all expected features. The bridging ligands form a puckered eight-membered ring structure, whereby the terminal ligands come out of the plane. The water and hydroxyl ligands on the palladium ion that does not participate in the mechanism are oriented perpendicular to the plane formed by the bridging acetates and the palladium ions; these ligands do not change their positions during the course of the reaction. These clusters have a singlet spin state. A more elaborate description of the palladium acetate cluster used is given elsewhere.[15]

As for the solvent effect, it is important to notice the large size of the palladium acetate cluster. In our approach to estimate the solvent effect, only the cavity formation is significant. Because of the simplifications of the palladium acetate dimer structure, the estimation of the cavity radius is not straightforward. As discussed elsewhere,[15] we corrected this by addition of the differences in the radii between the model and the actual complex (so $r_1 = r_1' + r_3$ and $r_2 = r_2' + 2r_4$), as indicated in

TABLE 2: Energy Contributions to Steps in the Mechanism

	ΔE (kJ/mol)		
reaction step	total	vacuum	solvation
1. ethylene coordination	−17	−3	−14
Inner Sphere			
2. hydroxyl coordination	4	15	−11
3. coupling	−21	−24	2
4. β-H transfer	41	39	2
5. H back-transfer	−53	−55	2
6. H transfer	63	67	−4
7. AcH desorption	48	38	10
Outer Sphere			
3. coupling	−42	−43	0
4. β-H transfer	36	42	−6
5. H back-transfer	−96	−104	8
6. H transfer	60	59	2
7. AcH desorption	−43	−45	2

Figure 2. Van der Waals radii of the atoms at the shell are added. The radius is taken as the geometrical mean of the radii that span the ellipsoid, which are half the diameters r_1 and r_2. The radius of the cluster is between about 6 and 6.5 Å. The solvation energy contribution to the reaction energy is not very sensitive to systematic errors in the radii used. For instance, an error of 0.5 Å in the radii of reactants and products results in a change in the energy of up to 10 kJ/mol, which is well within the error of the DFT computational method.

B. The Wacker Process. In the following, the Wacker process as catalyzed by palladium acetate dimer structures will be discussed. First, ethylene coordinates to palladium acetate. Then, in the inner-sphere mechanism, terminal acetate is exchanged with hydroxyl. The next step is the coupling of hydroxyl with ethylene. The hydroxyl originates either from prior coordination to palladium in the inner-sphere mechanism or from the solution in the outer-sphere mechanism. After the coupling, a series of hydrogen transfers takes place, whereby hydroxyethyl is transformed into acetaldehyde. The two possible mechanisms, inner- and the outer-sphere, differ most apparently in the coupling reaction. In addition, the hydrogen transfers differ.

The inner- and the outer-sphere mechanisms are discussed separately. A compilation of the thermodynamics found for all steps in the mechanisms is given in Table 2. The energy contributions are separated into components obtained for the reaction both in a vacuum and after the correction for the solvent effect. In addition, activation barriers have been estimated for some of the steps that could be rate-determining.

The coordination of ethylene to palladium acetate has been studied previously by density functional theory.[15] In both the theoretical study and the experiment,[13] it is seen that coordination is slightly favorable. In our previous study, we calculated that ethylene binds weakly to palladium (see Table 2). We suggested in the same study that the exchange does not involve an activation barrier. Ethylene coordinates on top of the palladium ion and gradually coordinates to the terminal site as the palladium−acetate bond breaks. The mechanism involves a trigonal bipyramidal structure, which is generally the geometry adopted by the activated complex or intermediate in square planar substitutions of palladium and platinum.[31] Ethylene has an η^2-coordination to palladium (structure 16 in Figures 3 and 5).

a. The Inner-Sphere Mechanism. The coupling of ethylene with hydroxyl coordinated to palladium is characteristic of the inner-sphere mechanism. In this path, hydroxyl exchanges with terminal acetate (step 2). Then, coupling takes place (step 3), resulting in a back-bonding hydroxyethyl ligand. Successive hydrogen transfers convert the hydroxyethyl to acetaldehyde (steps 4 through 6). Acetaldehyde desorbs (step 7), and reoxidation of palladium closes the catalytic cycle (step 8). A compilation of the energies calculated for these steps is given in Table 2, and the optimized structures are shown in Figure 3.

TABLE 3: Hydroxyl Coordination via a Solvation Path

	ΔE (kJ/mol)		
reaction[a]	total	vacuum	solvation
$PdOAc^*C_2H_4 \rightarrow PdC_2H_4 + {}^1/_2HOAc_2^*$	92	98	−6
$PdC_2H_4 + AcOH..H_2O^* \rightarrow PdOH^*C_2H_4 + {}^1/_2HOAc_2$	−88	−83	−5
total	4	15	−11

[a] Charges of clusters are counterbalanced by the addition of protons in some reactions. Water and acetic acid, which form from hydroxyl, acetate, and the proton used to compensate for the charge, are indicated with an asterisk. Only the group that undergoes the reactions is given in the reaction equation.

A distinctive step in the inner-sphere mechanism is the coordination of hydroxyl to palladium (step 2). After the coordination of ethylene at a terminal site, a terminal acetate is exchanged with hydroxyl. The ethylene and the hydroxyl ligands are thereby coordinated adjacent to one another. As seen from structures 16 and 17, the changes in the square planar coordination of the palladium ion are minimal. For the exchange, we have calculated an energetically neutral reaction enthalpy, after taking solvent effects into account (see Table 2). The reaction energy in a vacuum is slightly higher, with 15 kJ/mol. The solvent effect of 11 kJ/mol is largely due to the differences in the solvation energy of water and of acetic acid in acetic acid. Dimer formation is responsible for most of the solvation energy, though also the quadrupole contributions of the solvent molecules are important.

There are actually two different paths possible to perform the substitution of hydroxyl for acetate: a solvation path or a ligand path. In the solvation path, acetate has to desorb first, and successively the vacancy is filled up by hydroxyl. In contrast, in the ligand path, hydroxyl or water is coordinated to palladium first and is then followed by desorption of acetate. Both are analogous to the two options for the coordination of ethylene to palladium. We have demonstrated in a previous study[15] that ethylene exchanges with acetate via a ligand path. The same mechanism to exchange hydroxyl with acetate has to be expected. The activated complex must have a structure that is nearly trigonal bipyramidal, and the activation barrier therefore has to be low. We did not study this mechanism in detail.

To study the option that acetate dissociates first, preceding the hydroxyl coordination, we have taken an approach in which charges are balanced (see Table 3). In this approach, the dissociation of acetate and the coordination of hydroxyl are accompanied by the transfer of a proton from and to the palladium acetate cluster, respectively. The proton is accommodated on the hydroxyl ligand coordinated to the palladium ion that does not participate in the mechanism. The same approach will be discussed in more detail later for the outer-sphere coupling reaction. We calculated an energy of about 92 kJ/mol for the vacancy formation; the addition of hydroxyl from the solvent results in an overall reaction energy of 4 kJ/mol. It is clear that the formation of a vacancy is energetically highly unfavorable. The ligand path is therefore the more likely path.

Inner-sphere coupling involves the insertion of ethylene into the palladium-hydroxyl bond. A four-membered ring structure is formed, whereby the hydroxyethyl back-bonds, e.g., binds with both the α-carbon and the oxygen to palladium (see

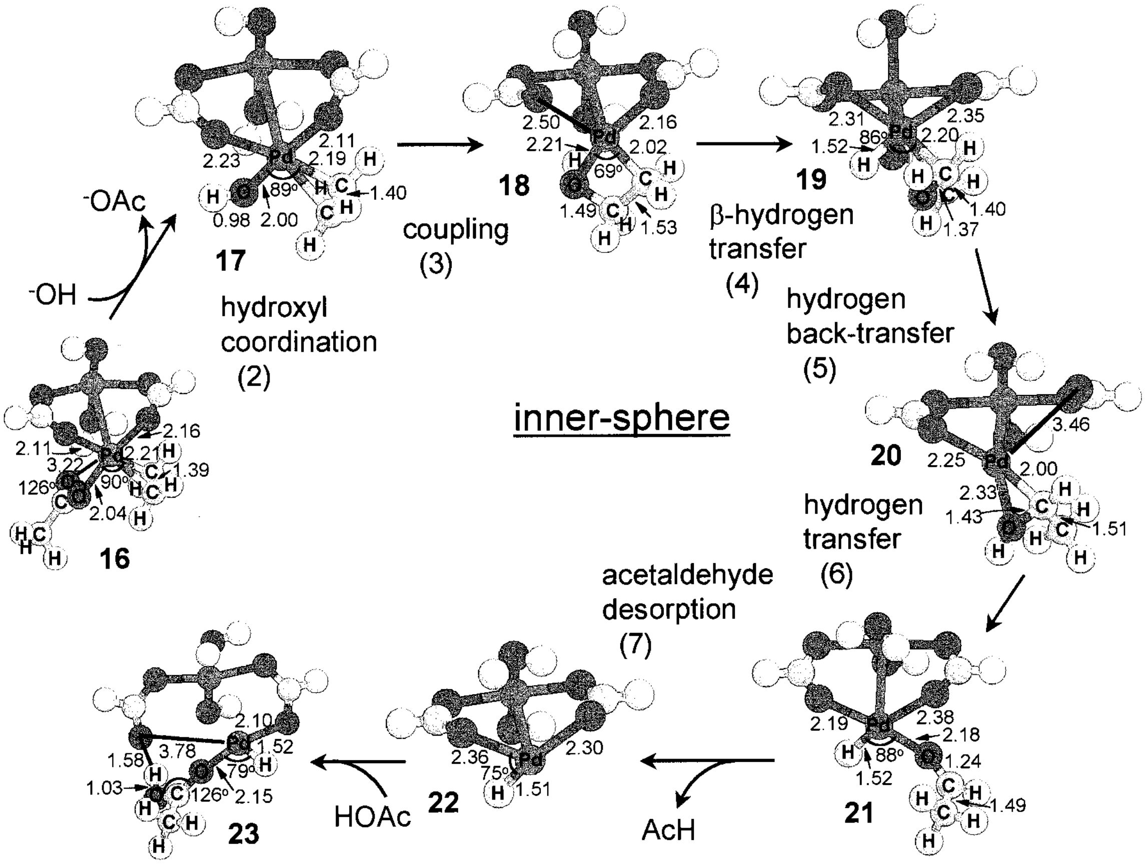

Figure 3. Reaction scheme of the inner-sphere mechanism. Calculated bond lengths (Å) and angles are given. Only the atoms that are involved in the mechanism are labeled.

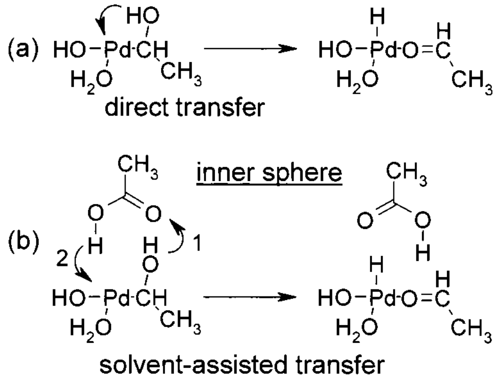

Figure 4. Models used for the inner-sphere hydrogen transfer. Both direct transfer (a) and solvent-assisted transfer (b) are shown.

structure 18, Figure 3). This step is calculated to be exothermic, with −21 kJ/mol. The reaction involves slipping of ethylene from an η^2- to an η^1-coordination, which is energetically not a difficult step.

After hydroxyethyl is formed, a series of hydrogen transfers converts the ligand to acetaldehyde. Hydrogen is thereby transferred back and forth between the ligand and the palladium ion. A β-hydrogen transfer results in hydroxyvinyl (step 4), which has an η^2-coordination (structure 19). Hydrogen is successively transferred back to the hydrocarbon ligand (see structure 20) in a step indicated as "hydrogen back-transfer" (step 5). Finally, the hydrogen from hydroxyl is transferred to palladium, designated as "hydrogen transfer," to give the coordinated acetaldehyde ligand (step 6). Both transfers of hydrogen from the hydrocarbon ligand to palladium are unfavorable; the back-transfer is favorable. The calculated energies are +41, −53, and +63 kJ/mol for the β-H transfer, H back-transfer, and H transfer, respectively. Solvent effects are relatively small. The estimation of the activation barriers of the endothermic steps will be discussed in the following.

The β-hydrogen transfer was studied in a previous work.[15] This reaction involves a slipping mechanism, for which no activation barrier is found. The only contribution to the activation barrier is the opening of the back-bonding hydroxyethyl ligand. When taking all contributions into account, we have found an activation barrier of 25 kJ/mol with respect to the hydroxyvinyl product formed. The activation barrier thus becomes 65 kJ/mol.

We have used a model approach to estimate the activation barrier of the hydrogen transfer (step 6), as will be discussed in the following. In this reaction, hydrogen from the hydroxyl is transferred to palladium, and acetaldehyde is formed. We have used a model with one palladium ion, coordinated by hydroxyethyl, hydroxyl, and water (see Figure 4). To perform the transfer, two different paths could be followed that we designate by "direct transfer" and "solvent-assisted transfer". In the solvent-assisted transfer, the transfer proceeds via an acetic acid solvent molecule that acts either as acid or as base. On the other hand, the direct transfer proceeds without solvent involvement. For both paths, the transfer has been performed by changing the fundamental reaction coordinate in small steps of about one-tenth of a bond length. At each position, the energy has been evaluated for the structure in which all other coordinates have been completely optimized. In the direct transfer, the reaction coordinate is the hydrogen−palladium bond; in the solvent-assisted transfer, this is either the hydrogen−palladium bond (step 2 in Figure 4b) or the acetic acid's oxygen−hydrogen bond (step 1 in Figure 4b). For the direct transfer, we have found a

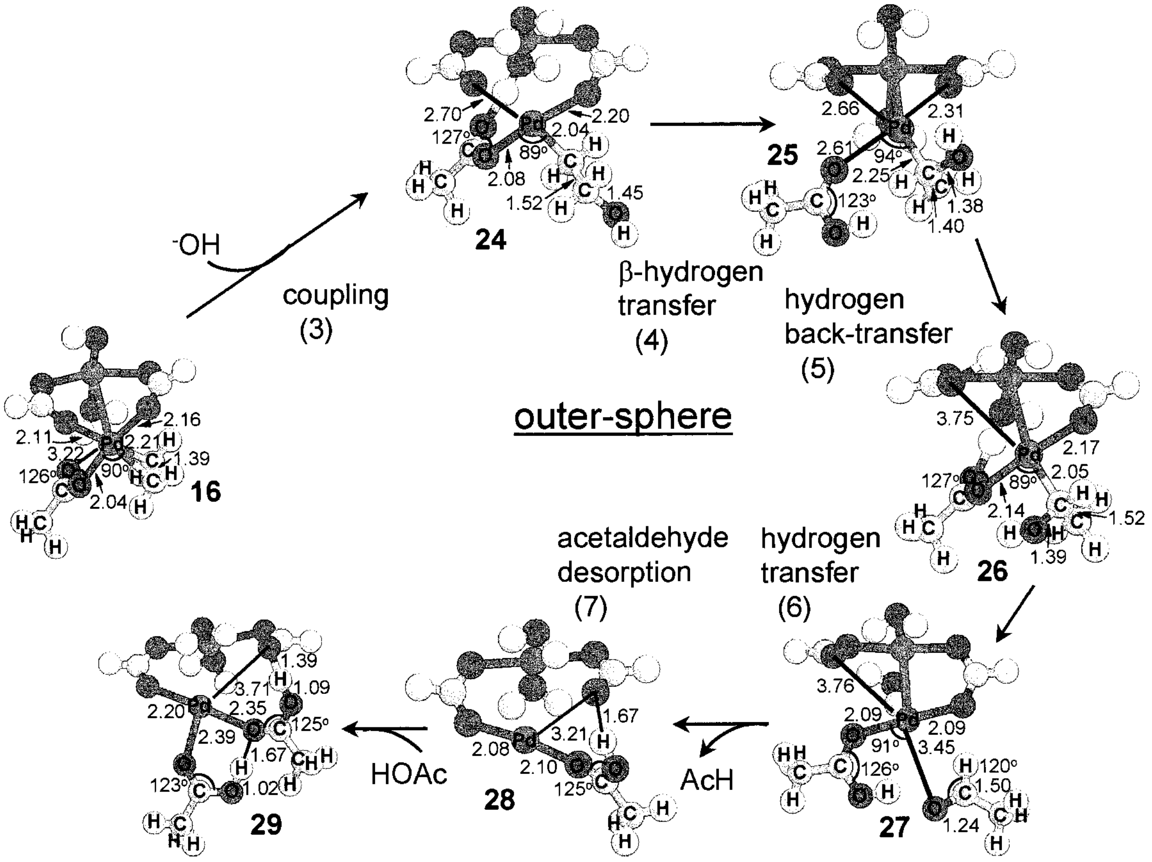

Figure 5. Reaction scheme of the outer-sphere mechanism. Calculated bond lengths (Å) and angles are given. Only the atoms that are involved in the mechanism are labeled.

high activation barrier of 160 kJ/mol. Involvement of acetic acid decreases the activation barrier significantly. In the transfer, acetic acid could act first as a base or as an acid. This is indicated in Figure 4 with steps 1 and 2, respectively. In step 1, a protonated acetic acid has been formed; this path does not give rise to an activation barrier relative to the product. On the other hand, when acetic acid acts as an acid first (step 2), the activation barrier is higher by 18 kJ/mol. The former path (first step 1, then step 2) seems to be the most favorable, and the activation barrier relative to the product is absent. Adsorption and desorption energies of acetic acid could be neglected, as both are about the same and are estimated to be about 30 kJ/mol, whereby coordination is endothermic.

The last step of the mechanism that we studied involves the acetaldehyde desorption (step 7). In a vacuum, the desorption costs 57 kJ/mol. When considering the solvent effects, the desorption is 8 kJ/mol more favorable. In this step, a vacancy is created (structure 22), which will be filled by an acetic acid molecule from the solvent (structure 23). We calculated in that case an endothermic energy of 48 kJ/mol, of which 10 kJ/mol is attributable to the solvent effect.

b. The Outer-Sphere Mechanism. In the outer-sphere mechanism, the coupling of hydroxyl from the solvent with palladium-coordinated ethylene is the most characteristic step (step 3). Since hydroxyl originates from the solvent, it does not have to be coordinated to palladium first, as in the inner-sphere mechanism. Analogous to the inner-sphere mechanism, a series of hydrogen transfers converts the hydroxyethyl to acetaldehyde (step 4 through 6). The main difference is that the hydrogen transfer involves the adjacent terminal acetate rather than the palladium metal itself. Again, acetaldehyde desorbs (step 7), and the catalytic cycle is closed by reoxidation of palladium (step 8). Another difference from the inner-sphere mechanism is the reduction of palladium to a zero oxidation state, which takes place by the β-hydrogen transfer (step 4). A compilation of the energies of these steps is given in Table 2, and the optimized structures are shown in Figure 5.

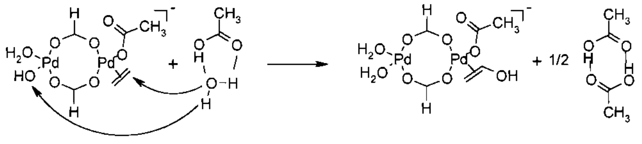

Figure 6. Approach to model the outer-sphere coupling of ethylene with hydroxyl: the change of charge is counterbalanced by transfer of a proton.

The coupling of hydroxyl from the solvent with ethylene coordinated to palladium is characteristic of the outer-sphere mechanism (step 3). A hydroxyethyl ligand is thereby formed. The adjacent site is saturated by an acetate ligand, which prevents the back-bonding of the hydroxyethyl ligand (structure 24) that is seen in the inner-sphere mechanism.

Modeling the coupling reaction is not straightforward. The charge of the palladium acetate cluster changes, and solvated hydroxyl has to be modeled in an adequate way. To study this reaction, we have used an approach that balances charges. This is schematically indicated in Figure 6. In this approach, the addition of hydroxyl is accompanied by the addition of a proton to balance the charge of the palladium acetate cluster. The addition of an ion to the complex is very likely accompanied by the coordination of an ion with an opposite charge to balance the charge. The simplest model would be a proton binding to the complex. The reaction is calculated to be exothermic, with −42 kJ/mol; the solvent effect is negligible.

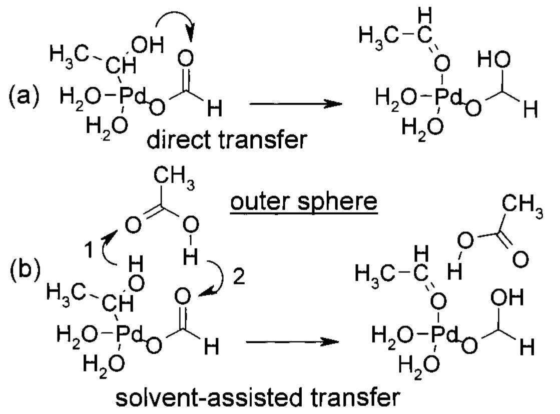

Figure 7. Models used for the outer-sphere hydrogen transfer. Both direct transfer (a) and solvent-assisted transfer (b) are shown.

Once hydroxyethyl is formed, acetaldehyde is formed by a series of hydrogen transfers (steps 4 through 6). Contrary to the inner-sphere mechanism, the hydrogen is not transferred to the palladium ion, but to the adjacent terminal acetate. Due to strong trans effects by the hydrocarbon ligand, the bridging acetate−palladium bond is elongated. In some of the steps, this bond is even almost broken. Similar to the inner-sphere mechanism, the transfer of hydrogen to the terminal acetate is endothermic, and the back-transfer of hydrogen is exothermic. The calculated reaction energies are +36, −96, and +60 kJ/mol for the β-H transfer, H back-transfer, and H transfer, respectively. Solvent effects are relatively small. The estimation of the activation barriers of the endothermic steps will be discussed in the following.

The activation barrier of the β-hydrogen transfer has been studied previously.[15] In this reaction, the activation barrier is lowered to become the same as the reaction energy by the involvement of an acetic acid molecule from the solution. The transfer of hydrogen goes via acid−base reactions between the ligands and the acetic acid of the solvent that is coordinated to the cluster.

To estimate the activation barrier of the hydrogen transfer in the outer-sphere mechanism (step 6), an approach has been used similar to that of the inner-sphere mechanism. Again, the direct transfer and the solvent-assisted transfer have been studied. Both paths are shown schematically in Figure 7. In the direct transfer, we did not find an activation barrier relative to the product. This seems to be due to the seven-membered cyclic structure that can be formed. In addition, we have studied the solvent-assisted transfer. Acetic acid could act first as a base (step 1) or as an acid (step 2). When step 1 is performed first, a protonated acetic acid molecule is formed. A mechanism via this structure does not give rise to an activation barrier relative to the product. For the reaction the other way around, thus step 2 first, the activation barrier is calculated to be higher by 164 kJ/mol. Solvent-assisted hydrogen transfer, whereby step 1 is followed by step 2, is the favorable path. Coordination of acetic acid is endothermic, with 30 kJ/mol, which is lower than the reaction energy of this step. The energy cost to coordinate acetic acid is offset by the removal of the molecule after the transfer. From our studies, it cannot be concluded whether the solvent is involved, as the activation barrier is eliminated both with and without solvent involvement. Since the concentration of acetic acid monomers in the solvent is low, direct transfer is expected to be the favorable path.

The last step of the mechanism is the acetaldehyde desorption (step 7). The desorption is endothermic, with 14 kJ/mol (structure 28), but saturation of the created vacancy by acetic acid from the solution (structure 29) makes the reaction energy exothermic, with −43 kJ/mol. The solvent effects are small.

IV. Discussion

A summary of the thermodynamics is given in an energy diagram, as shown in Figure 8. From this diagram, it is clear that the outer-sphere mechanism is energetically the more favorable mechanism. This is due to the more favorable or less unfavorable energetics of all steps of the mechanism. The outer-sphere coupling, especially, is more favorable. The rate-determining step differs between the two mechanisms. In the inner-sphere mechanism, this seems to be either the β-hydrogen transfer (step 4) or the hydrogen transfer (step 6); both have about the same barrier. On the other hand, the hydrogen transfer (step 6) is the rate-determining step in the outer-sphere mechanism. Only for the β-hydrogen transfer in the inner-sphere mechanism have we found an activated complex; we did not find an activation barrier higher than the reaction energy for any other step. Another difference is the participation of acetic acid molecules in the transfers. In the inner-sphere mechanism, this participation is important in lowering or even eliminating the activation barriers. On the other hand, in the outer-sphere mechanism, the geometry of the palladium acetate clusters does make direct transfers between the terminal ligands possible, and thereby excludes participation of the solvent. The activation barriers of the rate-determining steps both in the inner-sphere and in the outer-sphere mechanisms are about the same.

When comparing the proposed mechanisms of the Wacker reaction as catalyzed by palladium chloride and by palladium acetate, many similarities can be observed. As far as we know, the only detailed study of the Wacker reaction as catalyzed by palladium acetate is presented in this paper. The catalysts and the solvent are very different, but most of the major features are found to be similar for both systems. This is seen from the similarity of the proposed mechanisms in the literature for the palladium chloride-catalyzed reaction[4,5,13] and in our present study. Catalyzed by either catalyst, the coupling of hydroxyl with ethylene probably involves an outer-sphere reaction. For the palladium chloride-catalyzed reaction, this was demonstrated by experimental[5,6,13] and theoretical[9,12] methods. Further, in both systems the rate-determining step seems to involve one of the hydrogen transfers. In addition, in both systems all reactions take place inside the palladium coordination sphere: hydrogen from the solvent is not incorporated into the product when performing the reaction with palladium chloride in water.[8] The most apparent difference is the involvement of the adjacent terminal acetate. This ligand acts as a “storage place” for hydrogen in the hydrogen transfers that take place on the palladium acetate complex. The transfer of hydrogen to the palladium ion, which takes place for the palladium chloride catalyst, is unfavorable.

A similar detailed computational study of the Wacker reaction has been performed by Siegbahn.[12a] Both the coupling reaction and the β-hydrogen transfer, as catalyzed by palladium chloride species in water, have been studied. In contrast, we have studied palladium acetate dimer species in acetic acid. In addition to the differences in solvent and catalyst, the approach to estimate the solvent effect also differs from our studies. In Siegbahn’s studies, a chain of water molecules accounts for the first coordination sphere of the solvent. At the best level of Siegbahn’s studies,[12a] the reaction energies and the activation barriers are in fair agreement with our values; differences could be attributed to the differences in systems and the uncertainty

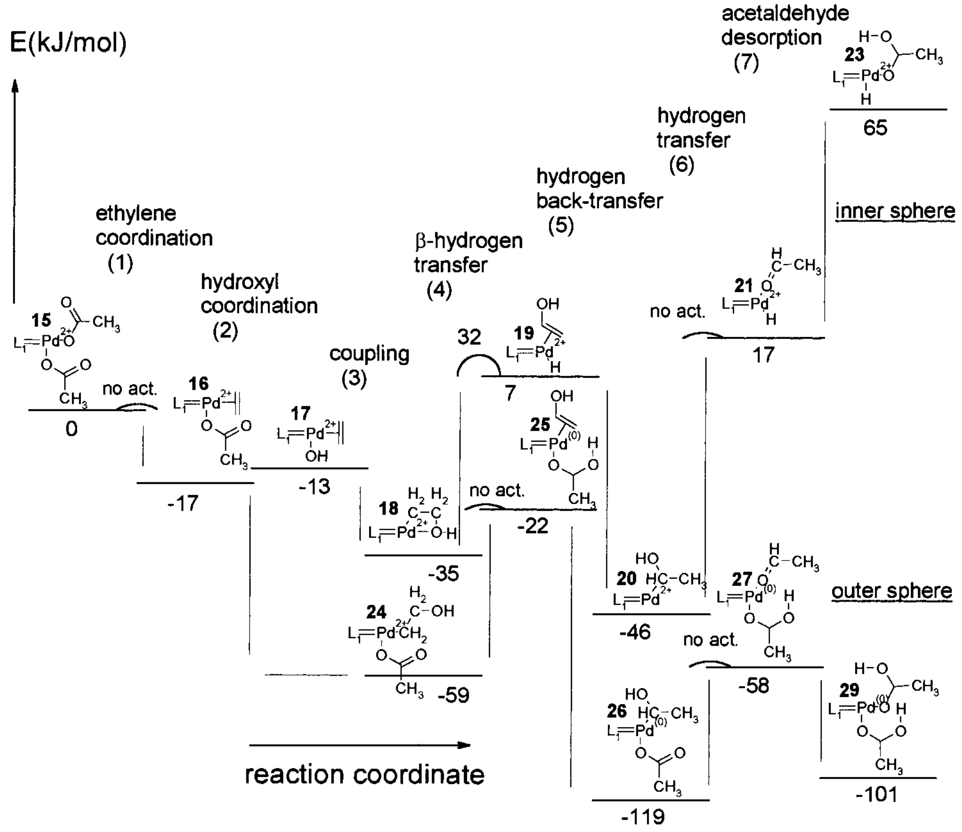

Figure 8. Energy diagrams of the inner- and the outer-sphere mechanisms, including solvent effects. Activation barriers are indicated by a little arc; a barrier as low as the reaction energy is designated by "no act.". The structure numbers refer to models shown in Figures 3 and 5.

in the computational methods. For the outer-sphere coupling, Siegbahn calculated a reaction energy of −19 kJ/mol. Our estimate is −42 kJ/mol. The β-hydrogen transfer has been performed by transferring hydrogen to the palladium ion. A reaction energy and an activation barrier of 14 and 37 kJ/mol are given, respectively. Our inner-sphere β-hydrogen transfer is similar to this reaction. We estimate 41 and 66 kJ/mol, respectively, for the reaction energy and the activation barrier. When taking the activation barrier with respect to the hydroxyvinyl complex formed, both studies agree very well, with a value of about 25 kJ/mol. Siegbahn's studies did not consider the possibility of β-hydrogen transfer to a terminal acetate, as in our outer-sphere mechanism, due to the differences in the catalyst studied. In addition, in acetic acid the hydrogen transfers could proceed via a solvent molecule, which is very different from the mechanisms studied by Siegbahn. Although the systems and the methods differ, we have obtained comparable results with those of Siegbahn. The major differences between Siegbahn's studies and our studies presented here are the catalyst and the solvent. Both give rise to significant differences in the mechanisms.

The same isotope effects as observed for the Wacker reaction catalyzed by palladium chloride in water are predicted from our studies of the palladium acetate catalyst in acetic acid. For the palladium chloride system, the following observations with respect to isotope experiments have been made. Deuterium from the solvent is not incorporated into the product.[8] Further, deuterated ethylene does not give rise to an isotope effect.[32] However, deuterated water gives rise to a strong isotope effect of 4.05.[33] In our outer-sphere mechanism for the reaction catalyzed by palladium acetate, hydrogen or deuterium from the solvent is not expected to be incorporated into the acetaldehyde product. The rate-determining step in our mechanism is the hydrogen transfer that forms the acetaldehyde (step 6). In this step, hydrogen from the hydroxyl that originates from water is transferred to the adjacent terminal acetate. This gives rise to an isotope effect for the hydroxyl scission and not for the hydrogen−carbon scission, which is exactly what is observed in the experiments for the palladium chloride system.

One of the reasons to study the Wacker reaction on palladium acetate catalysts is the comparison with the formation of vinyl acetate. Both reactions are catalyzed by the same catalysts and in the same solvent. The problem with the homogeneous formation of vinyl acetate is that the presence of water causes the Wacker reaction to become the major reaction, rather than the vinyl acetate formation.[16] When comparing the mechanisms proposed for the vinyl acetate formation[15] and for the Wacker reaction in this study, an explanation of this preference can be given. In both mechanisms, ethylene coordinates to palladium acetate at a terminal acetate site. Since high acetate concentrations inhibit the coordination of ethylene, as demonstrated by experiments[13] and theory,[15] both reactions are equally affected at this step of the mechanism. The step where the two competitive mechanisms diverge is the coupling reaction: either hydroxyl in the Wacker reaction or acetate in the vinyl acetate formation couples to the coordinated ethylene. This coupling is predicted to be far more favorable for the hydroxyl reactant. In addition, the overall thermodynamics is predicted to be far more favorable for the Wacker reaction. However, the activation barriers of both reactions are about the same, although they involve a different step.

V. Summary and Conclusions

The homogeneous Wacker reaction as catalyzed by palladium acetate dimers in acetic acid has been studied. This reaction involves the selective oxidation of ethylene with water to acetaldehyde. Although the major features of the mechanism are well established for the Wacker reaction as catalyzed by palladium chloride in water, the mechanism is previously unknown for the system we have studied. We propose a mechanism for this reaction. Initially, ethylene is coordinated to palladium at a terminal acetate vacancy. In an inner-sphere mechanism, the adjacent terminal acetate ligand is replaced by hydroxyl. Successively, coupling of hydroxyl with coordinated ethylene takes place. Hydroxyl originates from coordination to palladium, in the inner-sphere mechanism, or from the solution, in the outer-sphere mechanism. Hydroxyethyl thus formed is transformed into the acetaldehyde product by a series of hydrogen transfers. In the inner-sphere mechanism, the palladium ion is involved, but in the outer-sphere mechanism, a terminal acetate ligand accommodates the hydrogen. Acetaldehyde desorbs, and reoxidation of palladium closes the catalytic cycle. All steps, apart from the reoxidation, have been studied and activation barriers have been estimated.

Solvent effects are important and are explicitly taken into account. Dielectric contributions, as estimated by reaction field theory, are not important when considering the palladium acetate clusters due to their large size. Moreover, charges are balanced to equal zero in all our structures. However, these contributions are important for molecules from the solvent. Furthermore, the formation of the cavity has been taken into account. In several steps of the mechanism, reactions involve addition or dissociation of ions. These reactions are not straightforward to model. We have used an approach in which the changes in charge are balanced: the addition of an ion to the palladium acetate cluster is accompanied by the addition of a proton. Another consequence of the involvement of the solvent is the lowering of activation barriers. The activation barriers are lowered to become the same as the reaction energies for the hydrogen transfers in the inner-sphere mechanism by performing the transfers via a coordinated acetic acid molecule from the solvent. This is not the case for the analogous hydrogen transfer reactions in the outer-sphere mechanism: in this case, hydrogen transfers directly.

In summary, we have studied the homogeneous Wacker process as catalyzed by palladium acetate dimer complexes in acetic acid solvent. We have proposed a mechanism for this reaction and have studied all steps, considering solvent effects. From our studies, we conclude that acetaldehyde is formed by an outer-sphere mechanism. This is due to the overall thermodynamics. In addition, almost all steps of the mechanism are more favorable or less unfavorable in the outer-sphere mechanism; the coupling of hydroxyl with ethylene is more favorable. One of the hydrogen transfers, the step that forms the acetaldehyde, is found to be rate-determining. This step costs 61 kJ/mol, but does not involve an activated complex. It is predicted that all reactions take place within the coordination sphere and thus that hydrogen from the solvent is not incorporated into the product.

Acknowledgment. This work has been supported by E. I. du Pont de Nemours & Co. (Wilmington, DE). The computer resources were supplied by DuPont and by the Dutch foundation for the use of supercomputers (National Computing Facilities) under contract SC-183.

References and Notes

(1) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Rüttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71* (5), 176. (b) Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlmeier, J.; Sabel, A. *Angew. Chem.* **1962**, *74* (3), 93.

(2) Moiseev, I. I.; Vargaftic, M. N.; Syrkin, Ya. K. *Dokl. Akad. NAUK SSSR* **1960**, *133*, 377.

(3) Jira, R. In *Ethylene and its Industrial Derivatives*; Miller, S. A., Ed.; Ernest Benn Ltd.: London, 1969; p 650 (and references therein).

(4) See any textbook on inorganic chemistry, for example: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience: London, 1988.

(5) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd ed.; John Wiley & Sons: New York, 1997.

(6) (a) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Chem. Soc., Chem. Commun.* **1977**, *2*, 64. (b) Idem. *J. Am. Chem. Soc.* **1979**, *101*, 2411. (c) Stille, J. K.; Divakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1304. (d) Idem. *J. Organomet. Chem.* **1979**, *169*, 239.

(7) (a) Kosaki, M.; Isemura, M.; Kitaura, Y.; Shinoda, S.; Sarto, Y. *J. Mol. Catal.* **1977**, *2*, 351. (b) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81.

(8) (a) Moiseev, I. I.; Vargaftik, M. N. *Izv. Akad. NAUK SSSR* **1965**, 744. (b) Hafner, W.; Jira, R.; Sedlmeier, J.; Smidt, J. *Chem. Ber.* **1962**, *95*, 1575.

(9) Dedieu, A. In *Theoretical Aspects of Homogeneous Catalysis*; Leeuwen, P. W. N. M.van; Morokuma, K.; Lenthe, J. H.van, Eds.; Kluwer Academic Publishers: Dordrecht, 1995; p 167 (and references therein).

(10) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(11) (a) Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578. (b) Sakaki, S.; Maruta, K.; Ohkubo, K. *Inorg. Chem.* **1987**, *26*, 2499.

(12) (a) Siegbahn, Per E. M. *J. Phys. Chem.* **1996**, *100*, 14672. (b) Idem. *Struct. Chem.* **1995**, *6* (4/5), 271. (c) Idem. *J. Am. Chem. Soc.* **1995**, *117*, 5409.

(13) (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 2 (and references therein). (b) Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; Reidel: Dordrecht, 1980; Vol. 2 (and references therein).

(14) Helden, R.van; Kohll, C. F.; Medema, D.; Verberg, G.; Jonkhoff, T. *Recueil* **1968**, *87*, 961.

(15) Kragten, D. D.; Santen, R. A.van; Neurock, M.; Lerou, J. J. Submitted to *J. Phys. Chem. A.*

(16) Moiseev, I. I.; Vargaftik, M. N. In *Perspectives in Catalysis*; Thomas, J. M., Zamaraev, K. I., Eds.; Blackwell Scientific Publications: Oxford, U.K., 1992; p 91 (and references therein).

(17) Andzelm, J.; Wimmer, E. *J. Chem. Phys.* **1992**, *96* (2), 1280.

(18) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(19) Becke, A. D. *Phys. Rev. A* **1988**, *33*, 3098.

(20) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(21) Godbout, N.; Andzelm, J.; Wimmer, E.; Salahub, D. R. *Can. J. Chem.* **1992**, *70*, 560.

(22) Andzelm, J.; Russo, N.; Salahub, D. R. *Chem. Phys. Lett.* **1987**, *142*, 169.

(23) (a) Curtiss, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703. (b) van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *J. Chem. Phys.* **1992**, *97* (7), 5019.

(24) Weltner, W., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 3941.

(25) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, 1990.

(26) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

(27) (a) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351. (b) Onsager, L. *Electric Moments Liq.* **1936**, *58*, 1486. (c) Dillet, V.; Rinaldi, D.; Rivail, J.-L. *J. Phys. Chem.* **1994**, *98*, 5034.

(28) (a) Böttcher, C. J. F. *Theory of Electrical Polarisation*; Elsevier Publishing Company: Amsterdam, 1952 (and references therein). (b) Partington, J. R. *An Advanced Treatise on Physical Chemistry: Molecular Spectra and Structure Dielectrics and Dipole Moments*; Longmans: London, 1954; Vol. 5 (and references therein).

(29) Tuñón, I.; Silla, E.; Pascual-Ahuir, J. L. *Chem. Phys. Lett.* **1993**, *203* (2/3), 289.

(30) Uhlig, H. H. *J. Phys. Chem.* **1937**, *41*, 1215.

(31) Cross, R. J. *Adv. Inorg. Chem.* **1989**, *34*, 219.

(32) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246.

(33) Moiseev, I. I.; Vargaftik, M. N.; Syrkin, Ya. K. *Izv. Akad. NAUK SSSR* **1963**, 1144.