A Density Functional Study of the Acetoxylation of Ethylene to Vinyl Acetate Catalyzed by Palladium Acetate

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Vinyl acetate can be formed in the homogeneous reaction of ethylene with palladium acetate in glacial acetic acid. We propose a Wacker-like mechanism, which has been studied using density functional theory computational methods. The palladium acetate dimer, which is presumably the active catalyst, has been modeled by clusters of two palladium ions coordinated by acetate ligands. The active site is formed by a single palladium ion which is part of the dimer. In this mechanism, ethylene coordinates to palladium by substitution of a terminal acetate. Next, the ligand couples with an acetate ion, and consecutive β-hydrogen transfer forms the product vinyl acetate. The coupling probably takes place via an outer sphere attack by acetate. Theory suggests that the rate-determining step is the β-hydrogen transfer, and the activation energy is predicted to be 67 kJ/mol. Molecules from the solvent act as a catalyst in this step. However, at high acetate concentration, formation of a vacancy at a terminal acetate site is inhibited, which results in a negative reaction order with respect to acetate. Solvent effects are explicitly taken into account in all steps as a correction to the energies obtained in a vacuum.

I. Introduction

Vinyl acetate (VAc) is an important (co-) monomer in the production of various polymers. It is used for paints, adhesives, coatings, and fibers. In addition, it is important as a raw material of poly(vinyl alcohol), which is also used on a large scale for fibers. The process involves the selective acetoxylation of ethylene. A gaseous mixture of ethylene, acetic acid, and oxygen is allowed to react over a palladium-based silica-supported catalyst in a multitube reactor to form vinyl acetate.[1]

$$C_2H_4 + CH_3COOH + 1/2\ O_2 \rightarrow CH_2CHOOCCH_3 + H_2O \qquad (1)$$

The applied conditions are 130−200 °C and 5−10 atm pressure. The main byproduct is carbon dioxide, which originates from the combustion of ethylene and acetic acid.[1,2] In addition, small amounts of acetaldehyde and a number of other hydrocarbons are formed.[1,3] Commercially used catalysts are based on a silica-supported palladium−gold or palladium−cadmium alloy, with excess alkali metal acetate, and give a yield of 96% or higher of vinyl acetate, based on ethylene.[1,4] In the alloy, palladium is in excess.

Although the reaction is known to be catalyzed by a supported palladium alloy catalyst, the active phase is still unclear. Condensation of acetic acid, and water to a lesser extent, takes place on the support under reaction conditions.[5] Palladium is known to solvate in glacial acetic acid under oxidizing conditions as palladium acetate complexes.[6] These complexes are able to react homogeneously with ethylene to form vinyl acetate.[7] Palladium is thereby reduced to palladium black. The strong decrease in selectivity of homogeneous palladium acetate systems toward vinyl acetate formation by the presence of water makes it unlikely that these species are the most active species on the catalyst.[3] As a first step in a study to compare theoretically the homogeneous and heterogeneous routes, we focus here on the elementary reaction steps of the homogeneous reaction of ethylene with palladium acetate to vinyl acetate.

Solvated palladium acetate exists as three different species that are related by equilibria.[8−10] Palladium acetate solvates in glacial acetic acid in the same trimeric structure as the crystal,[10] of which the structure has been determined.[11] Decomposition toward dimers and monomers occurs when alkali metal acetates are added.[8,10] On increasing the acetate concentration, trimers convert completely to dimers. The dimer−monomer equilibrium lies, however, strongly to the side of the dimer, even when alkali metal acetate is added in large excess. Terminal acetates coordinate to these monomer and dimer complexes; bridging acetates serve to link the palladium ions in the dimers and trimers. The exact structures of dimers and monomers are still unknown. By changing the alkali metal acetate concentration, the activity and the selectivity toward vinyl acetate formation is affected.[8,9] On increasing the concentration, the reaction rate increases and goes through a maximum when the solution contains mainly dimers, as in a volcano curve. A decrease in activity by excess acetate is probably due to the blocking of vacancies by acetate.

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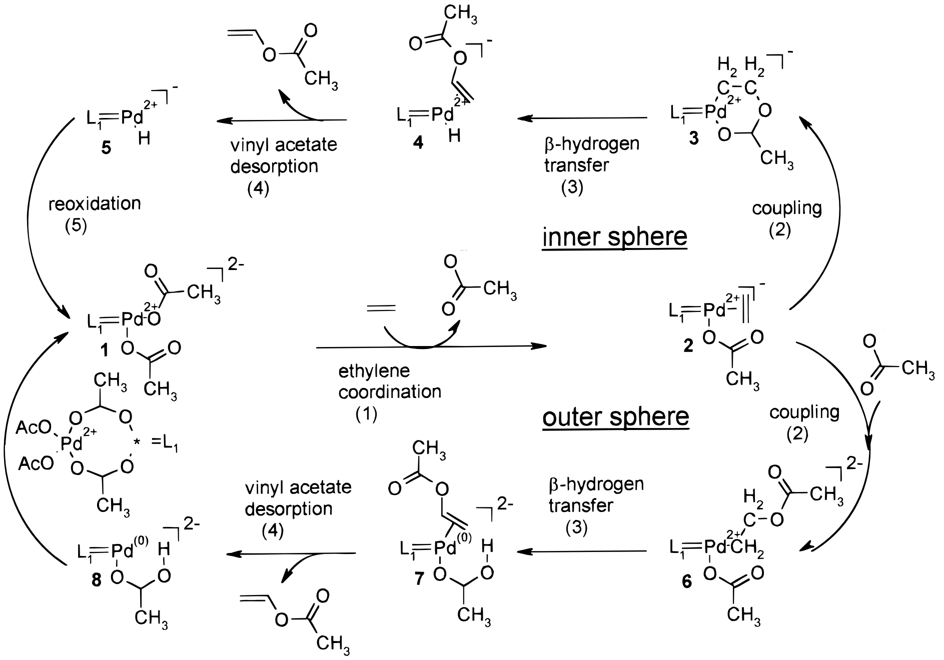


Figure 1. Proposed catalytic cycles of the inner- and the outer sphere Wacker-like mechanism for the acetoxylation of ethylene to vinyl acetate.

The homogeneous reaction mechanism is analogous to that of the Wacker process.[9] The Wacker process involves the homogeneous reaction of ethylene with water to form acetaldehyde over a palladium chloride catalyst.[9] The formation of both acetaldehyde and vinyl acetate is catalyzed by palladium(II) complexes and involves the coupling of ethylene with a base. We propose in this paper an analogous mechanism for the vinyl acetate formation, and we call it the Wacker-like mechanism (see Figure 1). In this reaction mechanism, ethylene coordinates first to palladium at a terminal acetate site[12] (step 1). Next, coupling takes place via either an inner- or an outersphere attack of acetate on coordinated ethylene (step 2). These two options will be indicated as the inner- and the outersphere mechanisms. In the literature, these two ways of coupling are also indicated by cis- and trans-nucleophilic addition, respectively. A σ-ethyl acetate ligand is formed, which reacts readily to yield vinyl acetate.[13] The conversion involves a β-hydrogen transfer (step 3). It is unlikely that a solvent-assisted 1,2-hydride shift followed by loss of a proton takes place, since protons of the solvent are not incorporated in the product.[14] In the innersphere mechanism, hydrogen is transferred to palladium, whereas it is transferred to the neighbor terminal acetate in the outersphere mechanism. Vinyl acetate desorbs in the next step (step 4). To close the catalytic cycle, palladium has to be reoxidized by oxygen (step 5).

A number of aspects of the mechanism are of interest. Key questions concern the nature of the rate-determining step and the way in which ethylene is attacked by acetate. Both issues will be discussed in this paper for the vinyl acetate formation. These questions have also been the subject of interest for the Wacker process. Recently, it has been shown for the Wacker process that coupling proceeds via an outersphere attack and that the rate-determining step involves the conversion of a σ-hydroxyethyl ligand to the acetaldehyde product.[15] Slipping of ethylene from an η^2- to an η^1-coordination complex with palladium activates ethylene in the coupling reaction.[16] However, some experimental results indicate that innersphere attack of water on the coordinated ethylene is rate determining.[17] The mechanism could well be affected by the experimental conditions, explaining differences in observations. For the homogeneous reaction of palladium acetate with ethylene, it has been suggested that acetate attack on ethylene could involve either an inner- or an outersphere mechanism,[18,8] and that the rate-determining step involves the β-hydrogen transfer.[8] As far as we know, only one study reports the activation energy of the homogeneous reaction of palladium acetate with ethylene.[19] The apparent activation energy is reported to be 71 kJ/mol.

These catalytic systems are very complicated to study with experimental methods, due to the complex relationships between many equilibria. Some steps of the Wacker process were therefore quite extensively studied by quantum chemical computational methods, as recently reviewed by Dedieu.[20] Most of the studies were performed at the semiempirical and extended Hückel levels. Furthermore, only the nucleophilic addition of hydroxyl has been studied extensively. In the review, the β-hydrogen transfer is discussed by referring to studies on analogous systems. A detailed high-level theoretical study on the mechanism gives more insight into a number of observations and has been performed by the group of Siegbahn.[21] They studied the most important steps of the Wacker mechanism: the nucleophilic addition of hydroxyl and the β-hydrogen transfer. The nucleophilic addition is demonstrated to involve a trans attack of hydroxyl. In Siegbahn's approach, the nucleophilic attack is modeled by using a chain of water molecules and embedding in a reaction field. Models that take these solvation effects adequately into account are essential. Neither of the steps studied by Siegbahn was thought to be the rate-determining step.

Another study related to the study we present here has been performed by Neurock et al.[22] Density functional theoretical methods were used to study the reaction of acetate with ethylene to form vinyl acetate. Models representing an oxidized palladium surface were used; solvent effects were not included. A very similar mechanism to our proposed Wacker-type mechanism was studied. This study involves a possible heterogeneous route for the catalyzed vinyl acetate reaction over palladium oxide. Calculations suggest that the β-hydrogen transfer is the rate-determining step, but activation barriers have not been determined.

In this paper, we present a density functional theoretical study of the Wacker-like mechanism of the acetoxylation of ethylene to vinyl acetate. We have studied all steps of the mechanism, except for the oxidation of palladium that would close the catalytic cycle. To account for solvent effects, we have used a model approach for the first coordination sphere around the solute. In addition, reaction field theory has been used to estimate the effect of the solvent outside the coordination sphere. Furthermore, the cavity formation has been considered.

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,[23] 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[24] with self-consistently incorporated gradient corrections due to Becke[25] and Perdew.[26] 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).[27] A second set of basis functions, the auxiliary basis set,[28] 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 3−4° for bond angles. Predictions for the energies were within 20−25 kJ/mol of the expected values.

B. Modeling Solvent Effects. In homogeneously catalyzed reactions, the solvent affects the chemistry and therefore has to be taken into account in theoretical studies. We have studied all reactions of the mechanism in a vacuum and have estimated the solvent effects by applying classical theories.

A solute is coordinated by solvent molecules; their intermolecular interactions are responsible for the solvation. From neutron diffraction experiments, it is seen that only the first one or two coordination spheres show an ordered structure.[29] Outside these coordination spheres, the solvent could be seen as a phase with bulk properties. To estimate the solvent−solute interactions, the suggested method would be studies with self-consistent treatment of the solute coordinated by solvent molecules and subsequently embedded in an induced potential field or a dielectric continuum.[30,31] However, we did not use this approach, as it is not implemented in the version of DGauss we have used. This approach is also computationally very demanding. A different method must be used, and so we explain our approach in the following.

TABLE 1: Dimer Interactions. Energies Are Given in kJ/mol

interaction	-$\Delta E_{\mathrm{formation}}$	dimer energy (lit.)
$H_2O\cdots H_2O$	26	23 (19.8[a])[32]
AcOH···HOAc	70	63.0[33]
AcOH···H_2O	50	

[a] Value obtained with computational theoretical methods.

To study the solute and the first coordination sphere, we have used a model approach. The solute itself is modeled by a cluster in which the charge is balanced. As will be discussed later, this has been performed by coordination of protons to the cluster. As for the solvent, acetic acid forms mainly dimer structures, since hydrogen bonds are very strong. In Table 1, a compilation of calculated and measured dimer energies is given. A good agreement between theory and experiment is found. Because of the high dimer energy, the number of monomeric acetic acid molecules is low, and the solute molecules are essentially coordinated by acetic acid dimers. This is also seen from a calculation we performed on a monomeric acetic acid molecule that was coordinated to a palladium acetate cluster. For this optimized structure, the acetic acid molecule−palladium acetate cluster bond was found to be slightly repulsive (by 4 kJ/mol). When the high energy of the acetic acid dimer is considered, binding of the acetic acid molecule to the solute seems to be precluded according to our model. In the first coordination sphere, the binding with acetic acid is therefore negligible. In our estimation of activation barriers, however, we have used acetic acid monomers to study the involvement of the solvent.

To model the rest of the solvent outside the first coordination sphere, classical theories can be used. In our version of the DGauss program, we do not have access to any embedding technique. Therefore, we calculate these contributions after the structure optimization in a vacuum, using equations given by the reaction field theory.[34] An extensive discussion of this theory can be found in textbooks.[35] Studies of the molecular interactions in solutions, whereby the solvent is treated as a continuum, are reviewed by Tomasi et al.[30]

The theory used to estimate the solvation effects is summarized below. The free energy of solvation can be partitioned as follows:

$$\Delta E_{\mathrm{solvation}} = \Delta E_{\mathrm{electrostatic}} + \Delta E_{\mathrm{cavity}} + \Delta E_{\mathrm{dispersion}} + \Delta E_{\mathrm{repulsion}} \qquad (2)$$

The electrostatic interaction is calculated by summation over the products of the reaction field (R_l^m), with the charge distribution (M_l^m) as follows:

$$E_{\mathrm{electrostatic}} = -1/2\Sigma_{l=0}^{\infty}\Sigma_{m=-l}^{l} R_l^{m} M_l^{m} \qquad (3)$$

The explicit expressions for the contributions of the ion, dipole, and quadrupole moments are given by

$$E_{\mathrm{ion}} = -(\epsilon - 1)/2\epsilon q^2/a \qquad (4)$$

$$E_{\mathrm{dipole}} = -(\epsilon - 1)/(2\epsilon + 1)\mu^2/a^3 \qquad (5)$$

$$E_{\mathrm{quad}} = -3(\epsilon - 1)/2(2 + 3\epsilon)Q^2/a^5 \qquad (6)$$

For the dielectric constant (ϵ), we used the value of acetic acid at room temperature of 6.20.[38] The dipole (μ) and quadrupole (Q) moments have been calculated. However, the quadrupole strength that should be used in formula 6 has to be evaluated from the diagonalized tensor according to

$$Q = Q_{zz} - Q_{xx} \qquad (7)$$

where $Q_{xx} = Q_{yy}$. In our cluster, the charge (q) is counterbalanced to equal zero by using water and hydroxyl ligands that are coordinated to the cluster. Therefore, we do not take the charge into account in the optimization of the cluster. This approach gives only the electrostatic contribution to the solvation energy. Further, we consider the cavity formation by using the approach suggested by Tuñón et al.[36]

TABLE 2: Energy Contributions to Steps in the Mechanism

	ΔE(kJ/mol)[a]					
reaction	total	vacuum	solvation	electrostatic	cavity	cavity radius (Å)[b]
1 ethylene coordination	−17	−3	−13	−11	−3	6.14
innersphere						
2 coupling	24	20	5	0	4	6.32
3 β-H transfer	75	68	7	2	5	6.52
4 VAc desorption	99	85	13	2	12	6.52
outersphere						
2 coupling	11	−11	21	15	7	6.79
3 β-H transfer	68	78	−11	0	−10	6.42
4 VAc desorption	−45	−66	20	1	19	6.66

[a] $\Delta E_{\text{total}} = \Delta E_{\text{vacuum}} + \Delta E_{\text{solvation}}$; $\Delta E_{\text{solvation}} = \Delta E_{\text{electrostatic}} + \Delta E_{\text{cavity}}$. [b] The cavity radii are values calculated for the palladium acetate intermediates formed in the respective step. The radius calculated for the initial palladium acetate dimer species (structure **11**) is 6.17 Å.

$$\Delta E_{\text{cavity}} = \gamma S - RT \ln(1 - V_s n_s) \qquad (8)$$

The first term accounts for the formation of the solute's surface, whereas the second term accounts for the cavitation work for a zero-surface solute. This formulation has proven to work very accurately for the solvation of hydrocarbons in water.[36] For the first term, we used the approach suggested by Uhlig:[37]

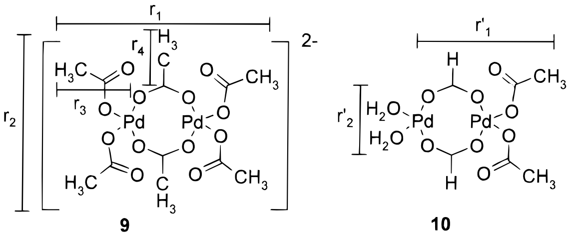
$$\Delta E_{\text{cavity}} = 4\pi a^2 \gamma \qquad (9)$$

where γ is the surface tension of the solvent, which is 27.10 mN/m for acetic acid at room temperature.[38] The volume V_s and numeral density n_s are that of the solvent; values at room temperature are used.[38] For acetic acid at room temperature, we estimated a negligible contribution of about 2 kJ/mol to the cavity formation via the second part of formula 8. Only these contributions are taken into account. The dispersion and the repulsion contributions are thought to be low when calculating the energy differences between products and reactants, and are therefore neglected. Moreover, entropy contributions of the solutes in a vacuum are neglected as well; since all chemistry takes place in solution, only small entropy effects would be expected.

The radius of the cavity a is a parameter that is difficult to determine and is extensively debated.[30] 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 in the cluster optimized in a vacuum. The largest possible perpendicular radii have 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 radius thus obtained has been used in the calculation of both the electrostatic and the cavity contributions. The volume of the solvent molecule V_s, which is used in the calculation of the cavity energy, was calculated similarly. The values of radii that we evaluated with our method for a number of the same molecules used by Tuñón et al.[36] are in agreement with that study. For the ethylene, the acetic acid dimer, and the vinyl acetate molecules, we calculated cavity radii of 2.23, 3.01, and 3.16 Å, respectively. The evaluation of the radii of palladium acetate dimer species is not straightforward and will be discussed in the following section; their values are given in Table 2.

III. Computational Results

A. Modeling Palladium Acetate. The most active palladium acetate species is thought to be the dimer. It can be made the predominant species by selecting the right conditions. It is thought that, in the dimer, palladium ions are coordinated by two acetate bridges and two terminal acetates at each palladium ion. Alkenes exchange with terminal acetates readily and thereby show that the active site of the palladium dimer is formed by a single palladium ion. A schematic representation of the dimer is shown as structure **9** in Figure 2.



9 **10**

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

Models of palladium acetate should satisfy the characteristics of the actual dimer as thought to exist in solution. Palladium is a 2+ ion, and is therefore square-planar coordinated. Furthermore, the active center, or palladium ion on which the catalytic cycle takes place, should be coordinated by two bridging and two terminal acetates. In the actual system, palladium acetate is an ion and therefore its charge has to be balanced by counterions, both in the actual system and in the model. In our studies, we used a model (see Figure 2, structure **10**) in which two palladium ions are bridged by two formate ligands, and two acetate ligands are present on the active center. To saturate the coordination of the second palladium ion, we have used water and hydroxyl ligands to save on the computational resources. Depending on the reaction studied, we have used one water and one hydroxyl, or two water ligands. The charge of the palladium acetate cluster is thereby balanced to equal zero.

The optimized palladium acetate cluster resembles the structure proposed, as is shown in Figure 3. The palladium ions are almost perfectly square-planar coordinated. The two metal ions do not form a metal bond, as can be seen from the Mulliken overlap population. The distance ranges from 2.75 to 3.10 Å, which compares reasonably well with the distance of 3.11−3.20 Å obtained experimentally for the palladium acetate trimer.[11] The bridging formate ligands and palladium ions form a puckered eight-membered ring structure in which the terminal ligands come out of the plane. Palladium−oxygen bonds of bridging formates are calculated to be slightly shorter than those measured for the trimer, *A* of 1.97−2.10 Å. The angles of the carboxyl groups compare well with those measured in the trimer, 124.8−128.7°. The acetates at terminal sites bind in a monodentate fashion, whereby the palladium−oxygen bonds differ

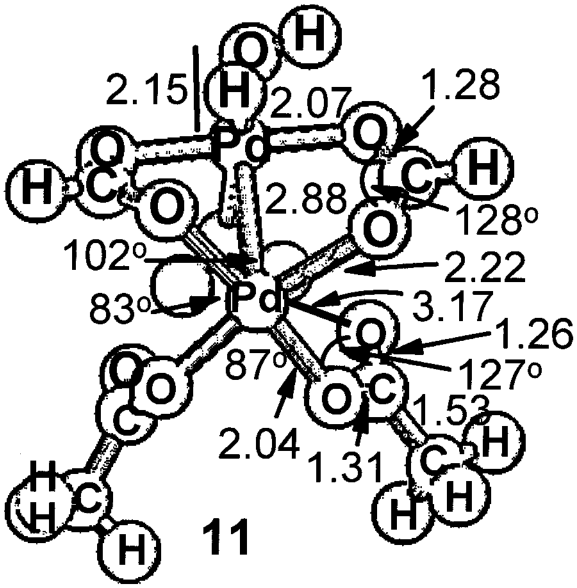


Figure 3. Optimized model for the palladium acetate dimer. Typical bond lengths (Å) and angles are given.

in length, especially when a ligand other than acetate is coordinated next to the acetate. The ligands that participate in the mechanism tend to form intramolecular hydrogen bridges and to back-bond to ring structures if possible, whereby six-membered rings are especially favorable. The water and hydroxyl ligands on the second palladium ion are orientated perpendicular to the plane formed by palladium ions and formates. In the various steps of the mechanism, their positions do not change significantly. The palladium acetate clusters have singlet spin states, unless otherwise mentioned.

As for the solvent effect, a number of aspects are of importance. Palladium acetate complexes are relatively large and therefore give rise to large cavity radii. Due both to the dependence of the electrostatic interactions on the cavity radii and to the compensation of the charge in the cluster, the contributions of the charge, dipole, and higher order multipole moments to the solvation energy are found to be negligible. The total of all these interactions is less than 4 kJ/mol. However, the contribution of the cavity formation is important. To estimate the radius of the cavity, a comparison with the actual complex has to be made. From the schematic representations in Figure 2, it is clear that the model cluster would lead to a radius that was too small, since formates are used instead of acetates to bridge the palladium ions. Moreover, terminal acetates that do not participate in the mechanism are simplified by replacing with water and hydroxyl ligands in the model. The radii used are therefore the sum of the calculated radii (as shown on the right in Figure 2) and the difference in radii between the model and the actual complexes (so $r_1 = r_1' + r_3$ and $r_2 = r_2' + 2r_4$). The radius is taken as the geometrical mean of the radii that span the ellipsoid, whereby half of each the diameters r_1 and r_2 are taken one and two times, respectively. van der Waals radii of the atoms at the shell have been added. Due to the large radii of the palladium acetate clusters, about 6−6.5 Å (see Table 2), the solvation energy contribution to the reaction enthalpy is not very sensitive to systematic errors in the radii used. 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-Like Mechanism. In the following, the Wacker-like mechanism will be discussed. First, ethylene coordinates to palladium acetate (Figure 4). Next, coupling takes place, followed by a *β*-hydrogen transfer, and finally vinyl acetate desorption. Coupling could take place via an inner- (Figure 6) or an outersphere (Figure 8) reaction. These reaction paths are very different and are discussed separately. A compilation of the thermodynamics found for all steps in the mechanism is given in Table 2. The energy contributions are separated into components obtained for the reaction in a vacuum and for the solvent effect. Moreover, the solvent effect is divided into the electrostatic and the cavity contributions. In addition,

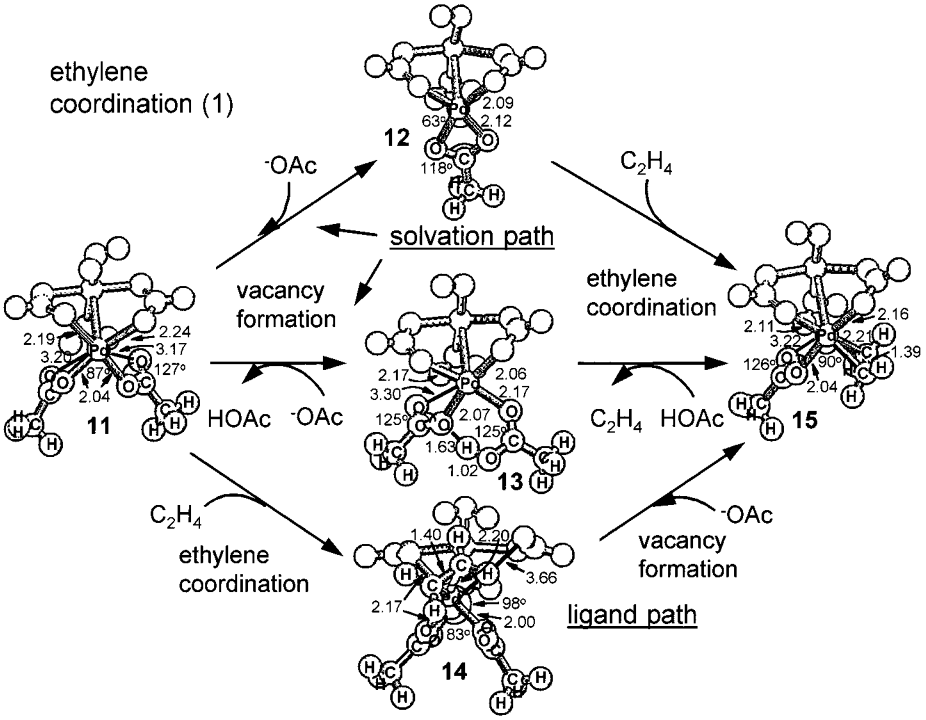


Figure 4. Reaction scheme of the coordination of ethylene to palladium acetate. Given paths involve true vacancy formation and coordinated solvent substitution (solvation path) and direct ligand substitution (ligand path). Calculated bond lengths (Å) and angles are given.

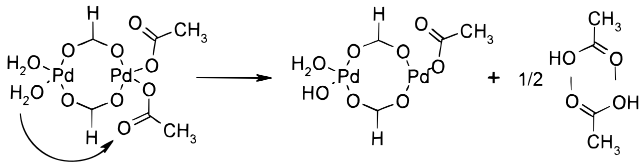


Figure 5. The approach to model the formation of a vacancy: the change in charge is counterbalanced by the transfer of a proton.

activation barriers have been estimated for some of the steps that could be rate determining.

a. Coordination of Ethylene to Palladium Acetate. To perform the acetoxylation reaction, ethylene has to coordinate to palladium (step 1). It is seen from experiments that ethylene exchanges readily with one of the terminal acetates.[12] Ethylene coordinates η^2 to palladium and is overall electron-donating, according to the Dewar−Chatt model. In principle, ethylene could coordinate to palladium via two paths: a vacancy is formed first, followed by the coordination of ethylene (solvation path); or ethylene is coordinated to palladium first, and then followed by the formation of an acetate vacancy (ligand path). In the solvation path, the vacancy (structure **12**) could be formed directly by the loss of an acetate ligand, designated as “true vacancy formation”; alternatively, the vacancy could be filled up with acetic acid (structure **13**), referred to as “coordinated solvent substitution”. In the ligand path, on the other hand, the initial step is ethylene coordination on top of the palladium (structure **14**), specified as “direct ligand substitution”. Actually, this complex shows similarity with the trigonal bipyramidal structure that is generally the activated complex in square planar substitutions of palladium and platinum.[39] These different paths are shown in Figure 4, and their reaction enthalpies are compiled in Table 3.

To model the formation of a vacancy, an approach has been used in which the changes in charges are counterbalanced. The terminal acetate that leaves the coordination sphere simultaneously removes a proton from the palladium acetate cluster (see Figure 5). Acetic acid is thereby formed, compensating for all changes in charge. Actually, it is feasible that the negatively charged palladium acetate complex is coordinated by positive ions, and thus that changes in the charge of the complex by removal of an acetate should be accompanied by removal of a positive ion. The simplest model would be a proton binding to the complex. Here, water coordinated to the second palladium in order to saturate the coordination is used to accommodate the proton.

TABLE 3: Ethylene Coordination via Two Different Solvation Paths and via a Ligand Path

reaction[a]	DE(kJ/mol)[b] total	vacuum	solvation
true vacancy formation			
vacancy generation			
PdOAcOAc* → PdOAc + 1/2 HOAc$_2$*	78	81	−3
ethylene coordination			
PdOAc + C_2H_4 → PdOAcC_2H_4	−95	−84	−11
coordinated solvent substitution			
vacancy generation			
PdOAcOAc* + 1/2 HOAc$_2$ → PdOAcHOAc + 1/2 HOAc$_2$*	47	48	−1
ethylene coordination			
PdOAcHOAc + C_2H_4 → PdOAcC_2H_4 + 1/2 HOAc$_2$	−64	−52	−12
direct ligand substitution			
ethylene coordination			
PdOAcOAc + C_2H_4 → PdOAcOAc(C_2H_4)	−8	−8	0
acetate dissociation			
PdOAcOAc*(C_2H_4) → PdOAcC_2H_4 + 1/2 HOAc$_2$*	−9	5	−13

[a] Charges of clusters are counterbalanced by addition of protons. Acetic acid which forms from acetate and the proton used to counterbalance the charge is indicated with an asterisk. Furthermore, only the group that undergoes the reactions is given in the reaction equation (see Figure 4). [b] $\Delta E_{\mathrm{total}} = \Delta E_{\mathrm{vacuum}} + \Delta E_{\mathrm{solvation}}$.

The exchange of terminal acetate with ethylene is calculated to be exothermic, with an energy of −17 kJ/mol. This agrees with the experimental result that the exchange does take place.[12] In a vacuum, the exchange is calculated to be exothermic, with −3 kJ/mol only. The solvent effect is mainly due to the high quadrupole contribution of the acetic acid molecule which solvates.

When comparing the different paths to exchanging terminal acetate with ethylene, large differences have been found (see Table 3). In the ligand path, ethylene coordinates to palladium, which is already square-planar coordinated by acetate ligands, with a slightly exothermic enthalpy of −8 kJ/mol. In a vacuum, the ethylene binds with −8 kJ/mol. The successive vacancy formation is exothermic, with an energy of −9 kJ/mol. The trigonal bipyramidal structure of the complex formed as intermediate (structure **14**) is similar to the activated complex in typical square planar substitutions. The gradual substitution reaction of acetate with coordinated ethylene therefore has to be expected to involve only a very low activation barrier, if this barrier exists at all. Solvent effects are important for the

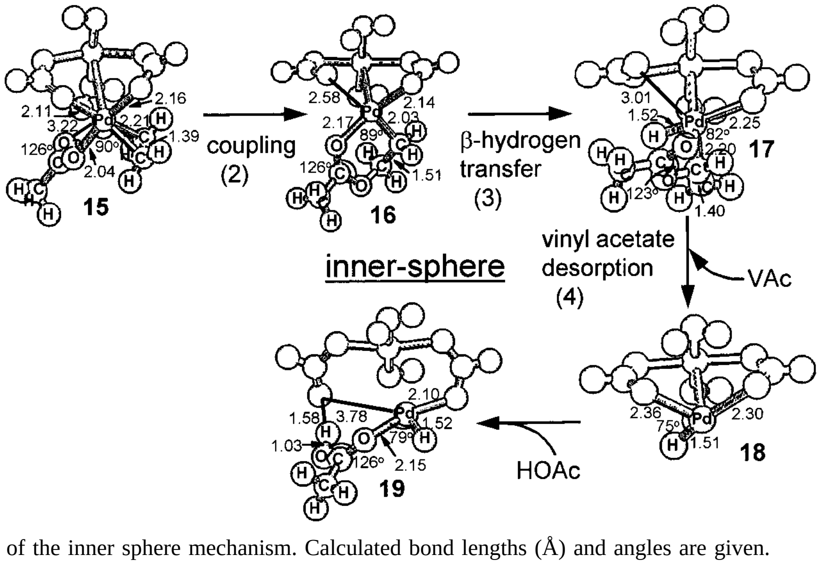


Figure 6. Reaction scheme of the inner sphere mechanism. Calculated bond lengths (Å) and angles are given.

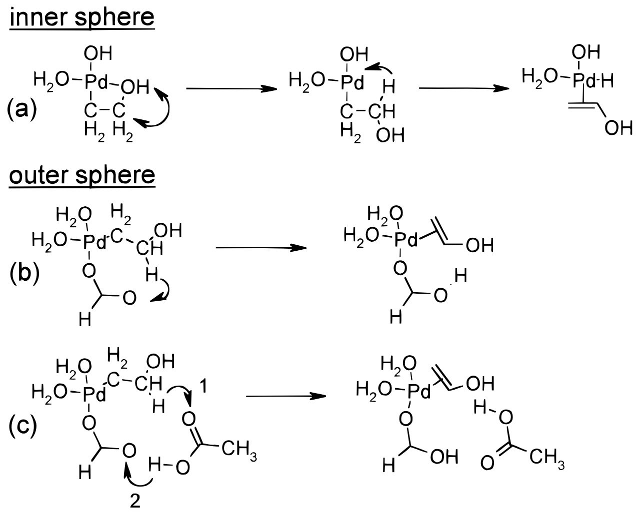


Figure 7. The modeling of the β-hydrogen transfer in the inner- (top) and the outer sphere (bottom) mechanisms.

acetate dissociation only. As for the solvation path, a vacancy has to form first. This step is endothermic, with an energy of about 78 kJ/mol, in the "true vacancy formation" route. In the resulting intermediate, acetate binds in a perfect bidentate mode to palladium (structure **12**). Saturation of the coordination by addition of acetic acid from the solvent (structure **13**), as takes place in the "coordinated solvent substitution" path, lowers the reaction energy to about 31 kJ/mol. In the solvation path, solvent effects are important for the coordination of ethylene only. It is clear that a vacancy will be filled up by the solvent. However, the ligand path, involving the initial coordination of ethylene, is the favorable path to exchanging acetate with ethylene. At high acetate concentrations, vacancy formation is inhibited in all paths, which is reflected by a negative reaction order in acetate.

b. Innersphere Mechanism. Ethylene coordination is followed successively by the coupling of acetate with ethylene (step 2), β-hydrogen transfer (step 3), and vinyl acetate desorption (step 4). Characteristic of the innersphere 2mechanism is the coupling of acetate with ethylene, both of which are coordinated to palladium. Furthermore, hydrogen is transferred to palladium in the β-hydrogen transfer. A compilation of the energies calculated for these steps is given in Table 2, and the optimized structures are shown in Figure 6.

In the coupling reaction, ethylene and terminal acetate, which are both coordinated to palladium, react to form an ethyl acetate ligand (step 2). The resulting ligand forms a back-bonding six-membered ring (structure **16**). The reaction is calculated to be endothermic, with energies of 20 kJ/mol in a vacuum and 24 kJ/mol in solution. In this reaction, slipping of the ethylene from η^2- to η^1-coordination and opening of the neighbor acetate ligand take place simultaneously. Coupling is therefore not expected to involve an activated complex.

The coupling reaction is followed by β-hydrogen transfer, which forms the vinyl acetate (step 3). Hydrogen is thereby transferred to the palladium ion. The β-hydrogen transfer costs 68 kJ/mol in a vacuum and 75 kJ/mol in solution. These energies are comparable with the generation of a vacancy at a terminal site. The resulting vinyl acetate is η^2-coordinated to palladium, similar to the coordination of ethylene. Coordinated alkenes have a strong trans-effect, causing destabilization of the ligand at the trans position. This is also seen in the optimized structure, as the bridging formate ligand shows a largely elongated palladium−oxygen bond.

In the innersphere's β-hydrogen transfer, hydrogen is transferred to palladium. In this step, the back-bonding ethyl acetate ligand has to open first. Hydrogen is transferred to palladium in a successive reaction by a slipping mechanism. We have modeled this slipping mechanism by using a single palladium ion coordinated by a hydroxyethyl ligand (see Figure 7a). The coordination has been finished with water and hydroxyl ligands, making the oxidation state and the coordination the same as in the actual palladium dimer cluster. Slipping was modeled by gradual shortening of the β-hydrogen−palladium distance with small steps of about one tenth of a bond length and then by optimizing the rest of the structure. For the actual slipping reaction, we have not found an activation barrier. The observed activation barrier, which we have found to be 20 kJ/mol relative to the product, is due to the opening of the back-bonding ethyl acetate. Therefore, the transition state is energetically and structurally closer to the product than to the reactant. Moreover, the energy of opening of the back-bonding ligand has been calculated to be the same for the model cluster of a single palladium ion and for the cluster of two palladium ions. For the palladium acetate dimer, the same activation barrier of about 20 kJ/mol is expected for the reverse reaction, thus giving an activation barrier of about 95 kJ/mol. We have modeled the hydrogen transfer in a vacuum, but it has to be expected that the solvent effect for the transition state is about the same as for the product. The barrier in a vacuum is slightly lower, with 88 kJ/mol.

Finally, vinyl acetate desorbs and acetic acid from the solvent adsorbs to complete the coordination (step 4). Calculated in a vacuum, the desorption of vinyl acetate costs 104 kJ/mol. Saturation of the vacancy by the solvent decreases the reaction enthalpy to 85 kJ/mol. In solution, the energy is 100 kJ/mol, whether the vacancy is saturated with a molecule from the solvent. These energies are again comparable with the formation of a vacancy and with the β-hydrogen transfer. The palladium acetate cluster is largely destabilized by the coordination of solvent, as the acetic acid molecule opens the formate bridge that binds the palladium ions (see structure **19**). This could lead to palladium black formation, as observed experimentally.

c. Outersphere Mechanism. The formation of vinyl acetate could also involve an outersphere mechanism. The characteristic step is the outersphere coupling (step 2), involving the reaction of acetate from the solution with coordinated ethylene. Since palladium is coordinatively saturated, hydrogen should transfer to the basic acetate ligand at the neighbor site (step 3). The reduction of palladium to palladium(0) by the β-hydrogen transfer is another difference from the innersphere mechanism, in which palladium maintains the same oxidation state. Finally, vinyl acetate desorbs (step 4). A compilation of the energies of these steps is given in Table 2, and the optimized structures are shown in Figure 8.

By the coupling of acetate from the solution with coordinated ethylene, an ethyl acetate ligand is formed (step 2). Back-bonding is sterically prohibited by the neighboring acetate. The ethyl acetate ligand is therefore linear in the outersphere mechanism, whereby palladium and acetate are trans to one another (structure **20**). Moreover, the formation of a bond by itself does not require the activation of bonds. Ethylene is activated by slipping, but that is not a difficult step energetically. A significant activation barrier is therefore not expected.

For the outersphere coupling, the same approach has been used to model the reaction as was taken for the vacancy formation. Actually, these two reactions are each other's counterpart. We have modeled the reaction by the simultaneous addition of the acetate and the proton to the palladium acetate cluster. An endothermic reaction enthalpy of about 11 kJ/mol is found. In a vacuum, the reaction is calculated to be exothermic, with −11 kJ/mol. This is the only reaction in which the solvent effects change the thermodynamics from exothermic to endothermic. Similar to the ethylene coordination, the solvent effect is mainly due to quadrupole contributions of the acetic acid from the solvent.

Coupling is followed by β-hydrogen transfer, forming the vinyl acetate (step 3). Hydrogen is thereby transferred to the neighboring terminal acetate. The reaction energy found is 78 kJ/mol in a vacuum and 68 kJ/mol in solution. The reaction energy is comparable with that of the generation of a vacancy. The acetic acid ligand formed by the β-hydrogen transfer actually desorbs (structure **21**). Vinyl acetate is thereby η^2-coordinated to palladium. Again, the palladium−oxygen bond of the formate bridge is elongated by the trans-effect of the coordinated vinyl acetate.

In the outer-sphere mechanism, the β-hydrogen of ethyl acetate is transferred to the adjacent terminal acetate. In principle, this transfer could proceed directly (see Figure 7b). We have modeled this reaction using a cluster of a single palladium ion. The palladium has been coordinated by the ethyl acetate ligand, the terminal formate, and two water molecules to saturate the coordination. The reaction has been studied by gradually shortening the oxygen−hydrogen bond, while the rest of the cluster has been completely optimized. A very high activation barrier of about 200 kJ/mol has been found this way, which is much higher than should be expected. However, a different path also exists. An acetic acid molecule from the solution could coordinate as a bridge between the ethyl acetate and the acetate, thus catalyzing the β-hydrogen transfer. As can be seen from Figure 7c, acetic acid could assist in the hydrogen transfer via two paths. The first option is to subtract the β-hydrogen first, whereby acetic acid acts as base (step 1), and then to donate a proton to the terminal acetate (step 2). In the second option, proton donation to acetic acid that acts as an acid is followed by β-hydrogen subtraction (first step 2, then step 1). We have modeled these reactions in the same manner as we have modeled the direct transfer. By subtraction of the β-hydrogen first, a barrier of 77 kJ/mol relative to the product has been found. For the other way around, the activation barrier relative to the product is completely removed. The β-hydrogen transfer therefore has an activation barrier as high as the reaction energy. This is so even if the high formation energy of dimeric acetic acid is taken into account, because the reaction energy itself is higher than the energy needed to break the acetic acid dimer. Moreover, acetic acid monomers are present in acetic acid, though their concentration is low.

Finally, vinyl acetate desorbs; subsequent adsorption of an acetic acid molecule from the solvent completes the coordination (step 4). Calculated in a vacuum, the desorption itself is energetically neutral, but becomes endothermic, with an energy of 11 kJ/mol, when solvent effects are considered. When the desorption is followed by the adsorption of acetic acid to saturate the coordination, the overall reaction energy is exothermic, with energies of −66 kJ/mol in a vacuum, and −45 kJ/mol when taking the solvent effects into account. Similar to the innersphere mechanism, the bond of the formate bridge with palladium breaks on coordination of acetic acid molecules (structure **23**). This could lead to decomposition to palladium black, as observed experimentally.

IV. Discussion

The major features of the Wacker-like acetoxylation mechanism are best shown in an energy diagram. In this diagram shown in Figure 9, the values including the solvent effects are given; in a vacuum, a very similar diagram is obtained (see Table 2). The major difference is the coupling reaction in the outersphere mechanism, which is exothermic in a vacuum, but endothermic after the correction for the solvent effect. From Figure 9, it is clear that the outersphere mechanism is the more favorable mechanism. When comparing the inner- and the outersphere mechanisms, their energy diagrams show that the overall energy of the outersphere mechanism is far less endothermic. The energetics of the β-hydrogen transfers show a small difference; these are the most difficult steps in both mechanisms. However, only in the innersphere reaction has an activation barrier relative to the product been found for this step. In the outersphere reaction, this barrier is lifted by the involvement of the solvent: The hydrogen transfer is catalyzed by an acid−base reaction of acetic acid from the solution. Because of this difference in activation barriers, the β-hydrogen transfer is less unfavorable in the outersphere mechanism than in the innersphere mechanism.

The overall reaction energy in both mechanisms seems to be unfavorable. However, the reaction is driven toward product

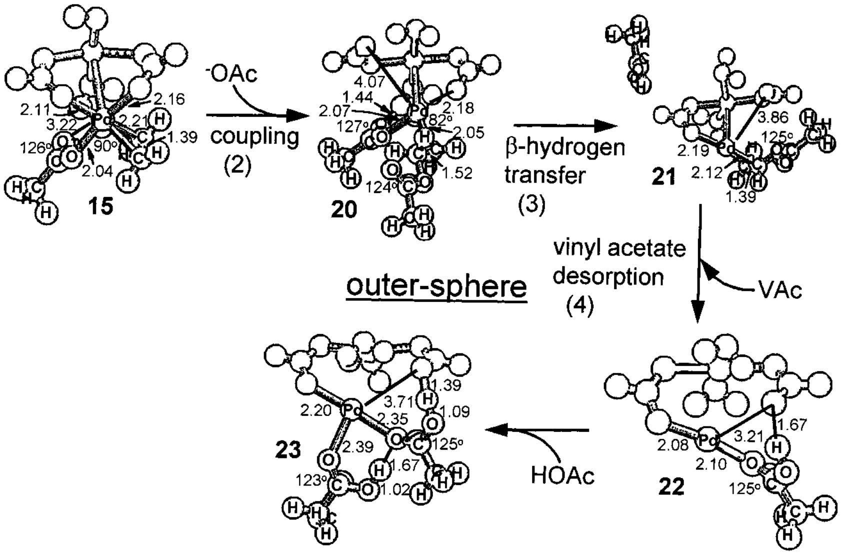


Figure 8. Reaction scheme of the outer sphere mechanism. Calculated bond lengths (Å) and angles are given.

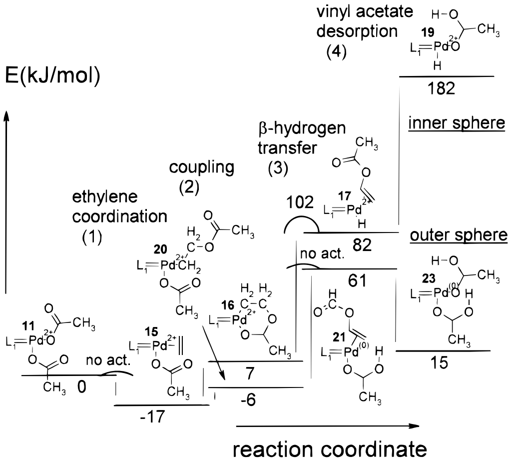


Figure 9. Energy diagrams of the inner- and the outer sphere mechanisms, including solvent effects. Activation barriers are indicated by a little arc; a barrier as low as the reaction energy is designated by “no act.” The structure numbers refer to models shown in Figures 6 and 8.

formation by removal of the products. Both the removal of vinyl acetate and the precipitation of palladium black by decomposition of the solvated palladium acetate complex take place. The destabilization of the palladium acetate by the formation of vinyl acetate is seen from our studies: the acetate bridges open on coordination of acetic acid from the solvent as vinyl acetate desorbs.

It has been proposed in the literature that the homogeneous vinyl acetate formation could involve either an inner- or an outersphere mechanism[8,9] and that the β-hydrogen transfer is rate-determining.[8,9,18] This step is proposed as the rate-determining step to account for the negative reaction order in acetate, as it is assumed that a vacancy on palladium is essential to perform the transfer. In our study, we have seen that the β-hydrogen transfer is indeed the rate-determining step. The β-hydrogen does not have to transfer to a vacancy on palladium, however. Instead, it could transfer to the neighbor terminal acetate, whereby acetic acid from the solvent acts as catalyst. The homogeneous acetoxylation involves an outer-sphere mechanism, as has been found for the Wacker process.[15,20,21] The negative reaction order in acetate has to result from inhibition of the formation of an acetate vacancy as needed to coordinate ethylene.

In both the homogeneous Wacker process and the vinyl acetate formation, solvent effects are important. This was already addressed in Siegbahn’s studies of the Wacker process.[21] Only electrostatic contributions were taken into account, of which the dipole and especially the quadrupole moments gave rise to important contributions. Charges were completely counterbalanced by the model approach of chains of water molecules coordinating to the solute. In our studies, the charge, dipole, and quadrupole contributions are negligible for the palladium acetate clusters, due to the large cavity radii. However, the quadrupole contributions of the acetic acid from the solvent are important in the ethylene coordination and in the outer-sphere coupling. We have not used chains of water molecules, as our solvent is acetic acid rather than water. Instead, we have counterbalanced the charge by the addition of protons to our palladium acetate clusters. Furthermore, the solvent is found to play a role in the activated complex. In both Siegbahn’s and our studies, the direct involvement of molecules from the solvent lowers the activation barrier significantly. However, the mechanisms differ largely in detail.

The formation of vinyl acetate as catalyzed by small palladium oxide clusters has also been studied in the literature.[22] The β-hydrogen transfer is suggested to be a candidate rate-determining step, though the activation barrier is not determined. The palladium oxide clusters in this study differ too much from our palladium acetate clusters to make possible a direct comparison of the results. The mechanisms differ in detail as well. However, for both systems the same rate-determining step is suggested. In the case of the palladium oxide clusters, hydrogen transfers to a palladium, as we discussed above regarding the inner-sphere mechanism.

Direct comparison of theoretical studies with experimental observations has to be done with care. From our studies, we are able to account for the negative reaction order in acetate. However, the activation barrier has been estimated to be lower than that observed experimentally. We have calculated a barrier of 67 kJ/mol, and thereby have estimated an upper limit of the apparent activation barrier. The 71 kJ/mol determined by Tamura and Yasui[19] is in good agreement with the value predicted by our studies. It has to be noticed that the results of experimental studies depend highly on the actual reaction conditions.

V. Summary and Conclusions

The homogeneous acetoxylation reaction of ethylene to form vinyl acetate as catalyzed by palladium acetate dimers has been studied. This reaction takes place in glacial acetic acid. We propose a Wacker-like mechanism for this reaction. Ethylene is thereby coordinated to palladium at a terminal acetate vacancy and then coupled to acetate, and successively vinyl acetate is formed by β-hydrogen transfer. Coupling could take place via two different reactions. First, coordinated ethylene could couple with the adjacent terminal acetate. This would result in the formation of ethyl acetate in a six-membered ring structure. β-Hydrogen transfer could be catalyzed by scission of the hydrogen−carbon bond over the palladium ion, whereby hydrogen is transferred to palladium, and vinyl acetate is formed. Second, 2-coordinated ethylene could couple to acetate from the solvent. The β-hydrogen could then be transferred to the neighbor acetate to form the vinyl acetate. These different coupling reactions are indicated as the inner- and the outersphere mechanisms, respectively. All steps of these mechanisms have been studied and activation barriers have been estimated. We have used palladium acetate dimer clusters that closely model the putative catalytically active species.

Solvent effects are important and have been explicitly taken into account. We have used the reaction field theory to estimate the dielectric contribution. Furthermore, the formation of the cavity has been accounted for as well. The dielectric contributions of dipoles and quadrupoles of the palladium acetate cluster are negligible. Due to our choice of models, the same applies for the ion contributions. The most difficult steps to model are the coordination of ethylene to palladium and the outersphere coupling of coordinated ethylene with acetate from the solvent. To model these reactions, we have used an approach where the counterion of acetate, which is a proton, is transferred to a base coordinated to the palladium acetate cluster. Solvent effects for these reactions are due to the quadrupole contributions of acetic acid from the solvent.

In summary, we have studied the homogeneously catalyzed formation of vinyl acetate by palladium acetate. We have proposed a Wacker-like mechanism for this reaction and have studied all steps, taking solvent effects explicitly into account. From our studies, we conclude that vinyl acetate is formed by an outersphere mechanism. This is due both to the less unfavorable β-hydrogen transfer and to the overall thermodynamics. The β-hydrogen transfer is found to be rate-determining. An activation barrier of 67 kJ/mol is estimated, whereby solvent acts as a catalyst in the transfer. At high acetate concentration, the formation of a vacancy at a terminal site, and thereby the ethylene coordination, is inhibited. This implies a negative reaction order with respect to acetate.

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