New Perspectives on the Nucleophilic Addition Step in the Wacker Process

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The Wacker process for producing acetaldehyde by oxidation of ethylene consists of many steps. One of these steps is the nucleophilic addition of a hydroxyl group to an olefin coordinated to a Pd(II) center. The first quantum chemical study of this step was made by Eisenstein and Hoffmann[1] in the framework of extended Hückel theory. This study was followed by several *ab inito* self-consistent field studies which yielded more quantitative results. Theoretical studies of the Wacker process were very recently reviewed,[2] and it was concluded that these studies "provide us now with a quite deep understanding of the nucleophilic addition of the coordinated ethylene in square planar Pd(II) complexes". It is the purpose of this Communication to present new results which show that the previous understanding of the nucleophilic addition step was, in fact, far from satisfactory in contrast to the conclusion made in the review.

A typical model for the nucleophilic addition step in the Wacker process has consisted of a square-planar Pd(II) complex, for example $PdCl_2(H_2O)(C_2H_4)$, and a nucleophile represented by OH^-. Similar types of anionic models are commonly used for other nucleophilic addition reactions also. In reality, of course, the Wacker process occurs in a water solution, but it has been assumed that the effect of the surrounding water should be relatively small. As usual, the model chosen was designed to cover only the main aspects of the reaction being studied. One of the main questions regarding the nucleophilic addition step in the Wacker process has been that of whether the nucleophile attacks ethylene directly from the outside or if it attacks the Pd(II) center and then migrates to the olefin. This question has been answered experimentally. Bäckvall et al.[3] and Stille et al.[4] have demonstrated by stereochemical work that the hydroxyl group attacks the olefin directly from the outside and does not migrate from the palladium atom, which was previously believed to be the case. This does not mean that the nucleophile energetically prefers to attack the olefin rather than the metal, but if it attacks the metal, there will be no migration from this point to the olefin. The question of whether the hydroxyl attack on the metal is energetically favorable compared to the attack on the olefin is still not answered, and this is therefore one of the main points of interest in the present study. The experimental indications are that the nucleophile actually energetically prefers to attack the Pd(II) center.[5]

The present calculations were carried out using GAUSSIAN92/DFT[6] and double-ζ plus polarization basis sets.[7] All the structures were fully geometry optimized without constraints. Density functional theory) (DFT) calculations using the three-parameter Becke functional (B3LYP)[8] were carried out for geometries optimized at this level using standard double-ζ basis sets in most cases. Some comparative calculations at the parametrized configuration interaction with parameter 80 (PCI-80) level[7] were also performed. The effects of the surrounding water solvent were investigated using reaction field theory[9] with a dielectric constant of 80.4 and optimal spherical cavities.

In a recent study of several steps of the Wacker process,[10] the nucleophilic addition was also investigated. The model complex was $PdCl_2(C_2H_4)$ with OH^-. The results were quite surprising. First, the outside attack of OH^- on the olefin,

$$PdCl_2(C_2H_4) + OH^- \rightarrow [PdCl_2(C_2H_4OH)]^- \quad (1)$$

was found to be exothermic by 108.7 kcal/mol at the PCI-80 level. Second, the outside attack on the olefin was preferred by as much as 50.0 kcal/mol compared to the attack on the Pd(II) center,

$$PdCl_2(C_2H_4) + OH^- \rightarrow [Pd(OH)Cl_2(C_2H_4)]^- \quad (2)$$

(Reoptimization of the geometry with the C−C axis of ethylene perpendicular to the coordination plane reduces these energies slightly to 100.5 and 41.8 kcal/mol, respectively.) These results are quite unrealistic, and it is clear at this point that the model used is unchemical. It must be noted in this context that the computational methods are very reliable, so the accuracy of the calculations cannot be questioned. This is also confirmed here, where the result at the present DFT level is an energy difference between the two positions of attack of 43.1 kcal/mol, only 1.3 kcal/mol different from the PCI-80 result. The first question investigated about the model used was whether completion of the coordination shell of palladium by adding a water molecule would change the results significantly. The answer to this question was found to be no. The large exothermicity decreases, but only marginally, and the large energy difference between the two sites of attack actually increases. The origin of the large exothermicity of the nucleophilic attack was also analyzed in the previous study. The main reason for the large energy gain is that an electron from OH^- can be transferred to the Pd(II) center, which has a very large electron affinity. In the attack on the olefin, two strong σ-bonds, the Pd−C and the C−O bonds, can then be formed, while the C−C π-bond is lost.

An obvious deficiency of the above simple model of the nucleophilic addition step is that the water solvent is not included. The effect of a surrounding solvent can be modeled in a qualitative way by using reaction field theory,[9] where the molecule is placed in a spherical cavity in a dielectric medium. The results using this model are quite disappointing in terms of correcting the unchemical results of the gas phase model. In particular, the energy difference between the two sites of attack is reduced by only 3.0 kcal/mol, from the previous difference of 43.1 down to 40.1 kcal/mol, obtained at the same computational level. It should be kept in mind that the correct energy difference should probably be in the opposite direction with a reversal of the optimal site of attack. The effect of the surrounding solvent on the exothermicity is somewhat larger but not at all large enough. Due to the small size of the hydroxyl anion, the monopole polarization energy is 25 kcal/mol larger than that for the complexes formed after the attack. The

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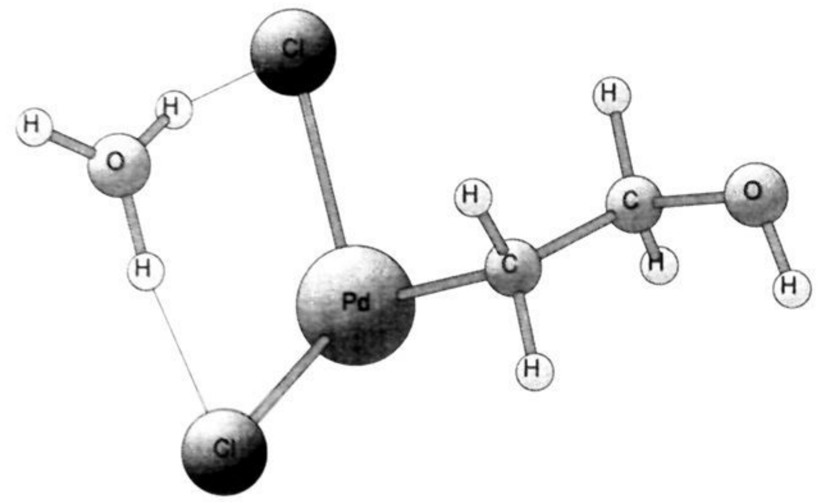

Figure 1. Product of the hydroxyl anion attack on the olefin for a complex including a coordinating H_3O^+.

exothermicity is thus reduced to about 75 kcal/mol. The actual value is expected to be less than 20 kcal/mol.

Even though some small deficiencies of the model used have been noted in the above investigations, the main part of the problem remains. From the results discussed above, it is clear that the solvent must play a more direct role which cannot be described so simply as a dielectric effect. The central metal complex, therefore, has to be extended in some way by explicitly adding part of the solvent. In this case, where an anion has been added to the metal complex, the first choice must be to add also the corresponding cation. For a complex in water, the simplest choice of a cation is a proton. DFT calculations were therefore performed for $Pd(OH^-)(H^+)Cl_2(C_2H_4)$ and $Pd(H^+)Cl_2(C_2H_4OH^-)$ to investigate the energy difference between hydroxyl anion attack on the olefin and that on the metal. Without the proton, the energy difference was found to be 43.1 kcal/mol (see above). When the proton was added, the energy difference decreased significantly, but only down to 24.6 kcal/mol. Embedding these complexes in a dielectric medium reduces the energy difference further by about 3 kcal/mol. The final energy difference for this model is thus about 20 kcal/mol. As noted above, the experimental evidence points toward a reversed stability. The reaction between water and $PdCl_2(C_2H_4)$ with the hydroxyl attack on the olefin is endothermic by 17.4 kcal/mol. A problem with the protonated model is rather obvious. Even though adding an OH^- and a H^+ to the palladium complex formally does not change the oxidation state, in reality covalent bonding is possible, leading to Pd(IV) complexes. This is also what happens in the geometry optimization with short Pd−H bond distances of 1.50 Å and with rather small charges on OH and H, indicative of strong covalent bonding. Even this model is thus not satisfactory for the nucleophilic attack.

The final model tried for the nucleophilic attack is the one shown in Figures 1 and 2. In this model, the added cation is H_3O^+. This cation has the advantage over a proton in that it cannot form a covalent bond to the metal even if it accepts an electron from the metal. H_3O^+ must therefore coordinate electrostatically to the complex and will not change the Pd(II) oxidation state. The addition of H_3O^+ has a dramatic influence on the relative energetics. The energy difference between the two structures in Figures 1 and 2 is now 11.6 kcal/mol in favor of the hydroxyl attack on the metal. This energy difference includes the dielectric reaction field, which increases this energy difference by 2.7 kcal/mol. The small relative effect of the dielectric medium on these two neutral structures is partly expected. The leading energy term from the dielectric medium on a neutral system is proportional to the square of the dipole moment and inversely proportional to the radius of the cavity to the third power. With a radius of 4−5 Å, as in the present case, this can only lead to relative energy effects on different isomers of at most a few kcal/mol. Finally, the reaction between two water molecules and $PdCl_2(C_2H_4)$ with the hydroxyl attack on the metal (as in Figure 2) is exothermic by 11.0 kcal/mol.

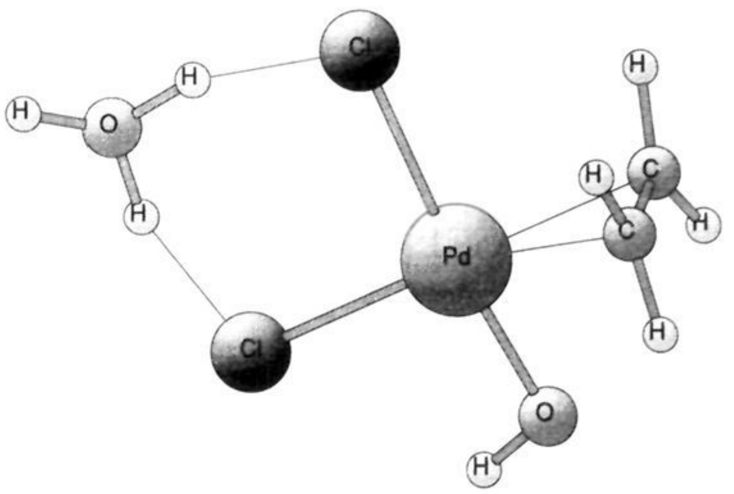

Figure 2. Product of the hydroxyl anion attack on the Pd(II) center for a complex including a coordinating H_3O^+.

The explanation for the dramatic effect on the relative stability of adding H_3O^+ to the two different Pd(II) complexes is quite simple. In $Pd(OH^-)Cl_2(C_2H_4)$, the negative charge is located at one end of the molecule at the chlorides and the hydroxyl group. Adding H_3O^+ at this end of the molecule will therefore lead to a large electrostatic energy gain. In $PdCl_2(C_2H_4OH^-)$, on the other hand, the negative charge is spread out in both ends of the molecule at the chlorides and at the OH group on the alcohol, leading to a much smaller electrostatic energy gain for this isomer.

In summary, the present model calculations have shown that a positive counterion is definitely needed in the simplest possible model of nucleophilic addition. The importance of the addition of H_3O^+ is best illustrated by its effect on the relative stability of the two complexes formed after a hydroxyl attack on the olefin and on the metal for $PdCl_2(C_2H_4)$. By addition of H_3O^+, the relative stability is changed from 40.1 kcal/mol in favor of the attack on the olefin to 11.6 kcal/mol in favor of the attack on the metal. This ligand is thus similar in importance to, for example, the chlorides in the complexes in Figures 1 and 2. The calculations have also shown that H_3O^+ is a much better model of the positive counterion than H^+, since H_3O^+ cannot form covalent bonds to the metal by accepting electrons. The presence of the H_3O^+ ligand is thus a minimal requirement for a qualitative model. The question of whether this requirement is enough for quantitative purposes in all cases remains to be investigated. As a beginning of such an investigation, the optimal position of H_3O^+ was studied. It turns out that there is a tendency for H_3O^+ to react with the OH groups of the metal complex to form water molecules if the distance between these ligands becomes too short. It is therefore possible that a few additional water molecules are needed around H_3O^+ to stabilize the positive charge on this ligand. Investigations of this type are in progress.

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