ELECTROCHEMICAL STUDY OF THE MECHANISM OF OXIDATION OF ZEROVALENT PALLADIUM COMPLEXES

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Abstract

It is demonstrated that the electrochemical oxidation of zerovalent palladium complexes involves a two electron process at low scan rates, affording cationic palladium(II) complexes, but at high scan rates, one electron oxidation affords palladium(I) complexes. This may be interpreted by a geometrical rearrangement induced by the solvent.

Introduction

Oxidation of olefins to ketones with Pd^{2+} salts is a well-established synthetic method and the following reaction is an example:

$$RCH=CH_2 \xrightarrow[\text{Benzoquinone}]{Pd^{II}/O_2} RCCH_3$$
$$\underset{O}{\overset{\|}{}}$$
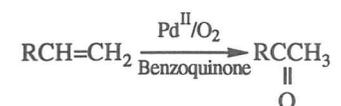
In this oxidation palladium(II) complex is reduced to palladium(0) complex and an appropriated oxidant (ex. benzoquinone) is necessary to oxidize palladium(0) to palladium(II) to make the reaction catalytic[1].

An alternative route to recycle the palladium complexes in the catalytic reactions can be the electrochemical oxidation of palladium(0) to palladium(II)[2].

Hence, the objective of this work is to present the results obtained in the study of the electrochemical mechanism of the oxidation of tetrakis(triphenylphosphine)-palladium(0), $Pd^{\circ}(PPh_3)_4$, in DMF at a gold disc electrode.

Zerovalent palladium complexes are stable under argon atmosphere but in solution they loose a triphenylphosphine ligand giving the species $Pd^{\circ}(PPh_3)_3$ which also loose another PPh_3 ligand giving rise to the species $Pd^{\circ}(PPh_3)_2$, according to the following equilibrium:

$$Pd^{\circ}(PPh_3)_4 \rightleftharpoons Pd^{\circ}(PPh_3)_3 + PPh_3$$

$$Pd^{\circ}(PPh_3)_3 \rightleftharpoons Pd^{\circ}(PPh_3)_2 + PPh_3$$

Nevertheless, the main species in solution is $Pd^{\circ}(PPh_3)_3$ and the oxidation of these species is supposed to form cationic divalent palladium complexes ligated by two or three ligands:

$$Pd^{\circ}(PPh_3)_3 \xrightarrow{-2e} Pd^{2+}(PPh_3)_n$$

This cationic divalent palladium complexes may activate aromatic or aliphatic C-H bonds.

Results

Cyclic Voltammetry Investigation at Long Time-Scales

Figure 1 represents a cyclic voltammogram recorded at low scan rate of a solution of $Pd^{\circ}(PPh_3)_4$ in DMF.

Figure 1. Cyclic voltammogram of a solution of $Pd^{\circ}(PPh_3)_4$ 1.5 mM in DMF/n-Bu$_4$NBF$_4$ 0.3M. v = 0.2 V/s.

In the oxidation range it can be seen that zerovalent palladium complex oxidises in a single irreversible wave, O_1. Determination of the absolute number of electrons showed that the oxidation involved an overall two-electron transfer per molecule of starting material.

On the reverse scan a first reduction wave, R'_1, a small second reduction peak, R_2, and other reduction waves are observed at more negative potentials which indicates that the oxidation process is complex.

Since $Pd^{\circ}(PPh_3)_4$ alone in the absence of extra phosphine is not very stable in solution 10 equivalents of PPh_3 were added to the solution and the same behaviour was noticed in the oxidation range, but in the reduction range the wave R'_1 shifted towards the positive potentials. Thus, the oxidation wave O_1 correponds to the oxidation of zerovalent palladium complex which forms divalent palladium complexes.

Since the reduction potentials of the electrogenerated palladium(II) complexes depended on the concentration of PPh_3, electrochemical investigation of then complexes $Pd(PPh_3)_2(BF_4)_2$ was undertaken in the presence of excess of PPh_3 and the following equilibrium was established:

$$Pd^{2+}(PPh_3)_2 + PPh_3 \rightleftharpoons Pd^{2+}(PPh_3)_3$$
$$\quad\quad 1 \quad\quad\quad\quad\quad\quad\quad 2$$

The species **1** gives rise to the reduction peak R'_1 and the species **2** gives rise to the reduction peak R_1.

Cyclic Voltammetry at Short Time-Scales

Figure 2 shows cyclic voltammograms of a solution of $Pd^{\circ}(PPh_3)_4$ in DMF and in the presence of 10 equivalents of PPh_3, recorded at high scan rates.

Figure 2. Cyclic voltammograms of a solution of $Pd^{\circ}(PPh_3)_4$ 1.5 mM in DMF/n-Bu$_4$NBF$_4$ 0.3M in the presence of 10 equivalents of PPh_3.

When the scan rate is increased the appearance of another reduction peak, R_0, is observed in the reduction range at more positive potentials than R_1. The height of the new peak, R_0, increases but that one of R_1 decreases as the scan rate increases. In this situation it was also observed that the number of electrons involved in the oxidation of zerovalent palladium complex was not constant but that it decreased when we increased the scan rate.

This fact can be most clearly seen by plotting the parameter $I_p/v^{1/2}$, for the oxidation wave O_1, as a function of the logarithm of the scan rate, v, as it is shown in the Figure 3. From that plot it can be concluded that at low sweep rates the oxidation process of palladium(0) corresponds to a two electron process, whereas at high scan rates the number of electrons involved in the process approaches one, due to a chemical reaction that occurs between the first and the second electron transfer.

Figure 3. Plot of the parameter $I/v^{1/2}$ as a function of log v. I: Peak current.

Thus, in order to better understand the mechanism of the oxidation of $Pd^{\circ}(PPh_3)_4$ in the presence of PPh_3, we decided to consider the influence of different concentrations of palladium(0) and PPh_3 on the oxidation process. In both cases, we observed that they had no significant influence in the process.

These results may be interpreted in the light of the mechanism:

$$A \xrightleftharpoons{k_s, a, E^0} B + 1e \qquad O_1/R_0$$

$$B \xrightleftharpoons[fast]{k_1, k_{-1}} C$$

$$C \xrightarrow{Before\ O_1} D + 1e$$
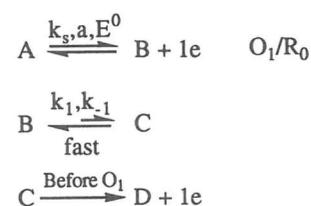
Based on this hypothesis the mechanism was simulated. A theoretical analysis indicates that three parameters are important:
- Parameters related to the system:
* μ (transfer coefficient)
$$* \ r = \frac{k_s}{(D)^{1/2}} \frac{(k_{-1})^{1/2}}{k_1}$$
- Experimental parameter:
$$* \ p = \frac{k_{-1}}{k_1^2} \frac{F}{RT} v$$

Numerical simulations of the voltammograms were carried out for several values of these three parameters. Using the data obtained from the voltammograms , that is, peak potential, peak current and peak width, the parameters were polotted as a function of log p for several values of μ and r. Comparing the theoretical curves with the experimental data a good agreement was found assuming $\mu = 0.4$ and $\log(r) = 0.5$.

Based on these facts, the mechanism of the oxidation of the zerovalent palladium complexe is:

$$Pd^0(PPh_3)_3 \xrightleftharpoons{k_s, a, E^0} Pd^I(PPh_3)_3{}^+ + 1e \qquad O_1$$

$$\underset{\substack{tetraedric \\ structure}}{Pd^I(PPh_3)_3{}^+} \xrightleftharpoons[fast]{k_1, k_{-1}} \underset{\substack{square\ planar \\ structure}}{Pd^I(PPh_3)_3{}^+}$$

$$Pd^I(PPh_3)_3{}^+ \longrightarrow Pd^{II}(PPh_3)_3{}^{2+} + 1e \qquad O_2 < O_1$$
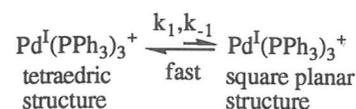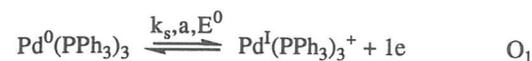
From the theoretical treatment we obtain the following data:
- First electron transfer
  * $0.09\ V/SCE < E^{\circ} < 0.12\ V/SCE$
  * $7\ s^{-1/2} < k_s/D^{1/2} < 10\ s^{-1/2}$
  * $0.4 < \mu < 0.45$
- Chemical equilibrium
  * $6 \times 10^{-4}\ s < k_{-1}/k_1^2 < 4 \times 10^{-3}\ s$

CONCLUSION

The above results suggest that the electrochemical oxidation of zerovalent palladium complexes involves a two electron process at low scan rates, affording cationic palladium(II) complexes, but at high scan rates, one electron oxidation affords palladium(I) complexes that are involved in a fast chemical equilibrium that corresponds to a geometrical rearrangement induced by the solvent.

References

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(1b) J. Tsuji, *Synthesis*, 369 (1984).
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THE EFFECTS OF MERCAPTOPYRIDINES ON MONOLAYERS DEPOSITED ON GOLD AND PLATINUM ELECTRODES.

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The present work is a voltammetric study on the behavior followed by gold and platinum electrodes covered by copper or oxide monolayers, in aqueous 0.5 M sulphuric acid solution, and in the presence of organic adsorbates containing a sulphur heteroatom. The adsorbates employed were 2-Mercaptopyridine (2-MP) and 4-Mercaptopyridine (4-MP). All experiments were made with both electrodes.

Introduction:

The use of electrochemical techniques such as cyclic voltammetry allows the characterization of the processes taking place in the electrodeposition of metals, both in the presence and absence of coadsorbed species, reflecting the interactions existing between the co-adsorbates, the electrode surface and the metal overlayer.

Strong adsorption of mercaptans to polycrystalline platinum and gold electrodes takes place through the sulfur atom[1,2]. Reductive elimination of alkyl and aryl groups from adsorbed mercaptans on platinum yields a layer of adsorbed sulfide [1].

Hubbard et al. have studied the adsorption of 4-MP and 2-MP on Ag (111) surfaces and concluded that it is potential dependent, with the adsorbed molecule forming a dimer at higher potentials [3]. The adsorbate binds to the electrode surface through the sulfur atom in a normal orientation rather than through the nitrogen site as would be anticipated.

When a Pt electrode was pretrated with a solution of 4-MP in water or H_2SO_4 0.5M , the UPD processes of copper [4] or silver [5] were inhibited and the onset of bulk deposition was shifted. These results suggested that the 4-MP or 2-MP adsorption is through the sulfur atom. Studies of silver deposition onto Pt (111) in the presence of a 2-MP adlayer reveal further evidence for a quelate adsorption model [6].

Studies of Surface Enhanced Raman Scattering (SERS) have demostrated that 4-MP adsorbs on gold through the sulfur atom in a normal orientation [7], forming a dimer at high potentials, as observed on platinum.

Results obtained in this work indicate a strong dependence of the voltammetric response on the nature of the adsorbate that is consistent with the strength of adsorption on the platinum and gold surfaces.