

PALLADIUM CATALYSED AEROBIC  
OXIDATION OF ALCOHOLS

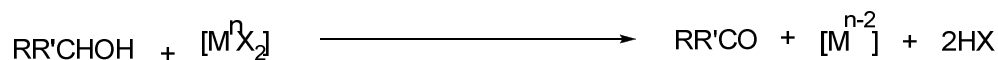
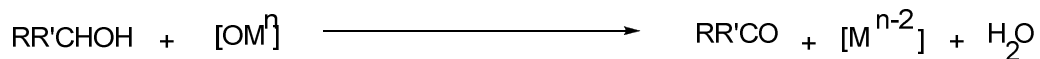
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## **INTRODUCTION:**

Transformation of alcohols to aldehydes or ketones is one of the most important reactions in organic synthesis. These usually use large amount of metal salts. A new method is to use heavy metals like Palladium, platinum, Copper, Rhodium in small amounts as catalysts. This method is also called as “oxidative dehydrogenation”. This review is mainly about palladium catalysed reactions that involve the oxidation of alcohols in to their respective carbonyl compounds ie; aldehydes and ketones.

## **HISTORY:**

Metal catalysed oxidative dehydrogenation of alcohols gained importance with some new discoveries. In 1963 Moiseev et.al reported the production of Acetic acid in to aqueous ethanol containing catalytic amounts of palladium chloride and copperchloride. In 1969, Brown et.al reported the oxidation of Aliphatic alcohols using palladiumacetate in acidic medium, in small amounts. But these gained less attention .In 1998, Peterson and Larock reported efficient oxidation of primary and secondary allylic and benzylic alcohols to corresponding aldehydes and ketones using 5mol% of Palladiumacetate in DMSO(Dimethyl sulphoxide) at 80C temperature in presence of atmospheric pressure of Oxygen and a mineral base like sodium carbonate, Potassium carbonate.



Generally Oxidation of alcohols involve stoichiometric quantities of Palladium in which Pd gets reduced by 2 oxidative units .The catalytic cycle requires regeneration of oxidative species of palladium which can be achieved by using co-oxidants like oxygen, Hydrogenperoxide, tertiary Butyl hydroperoxide, Aromatic halides, Potassium periodate, Carbon tetrachloride; 1,2-dichloroethane, N-Halosuccinimides, Vinyl bromide and some Metal salts.

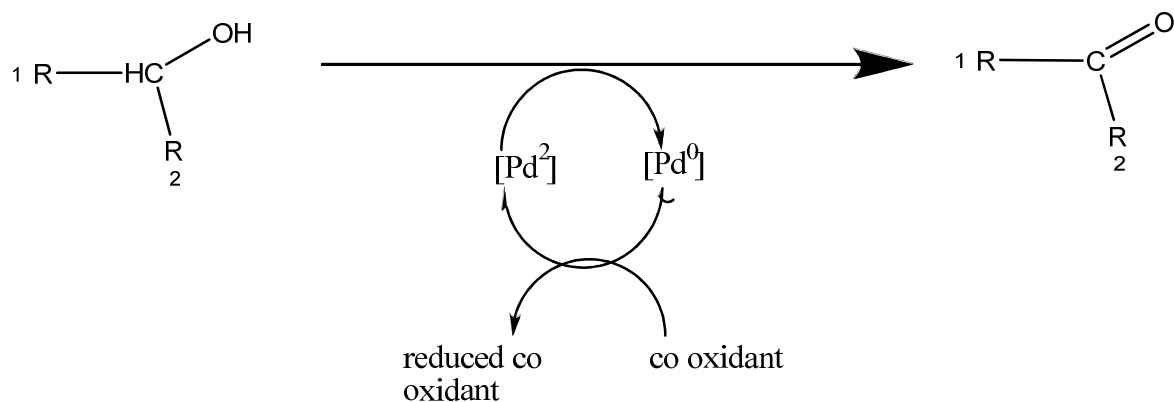


Figure 1

Most of the Oxidative reactions involving Palladium are usually Dehydrogenation reactions and form Palladium Hydride intermediates and reactivated by H Acceptors. It is rather difficult to distinguish between a co-oxidant and H acceptor. Most of the co-oxidants can also act as H acceptor like Oxygen, Allyl halogens, Compounds containing double bonds etc.

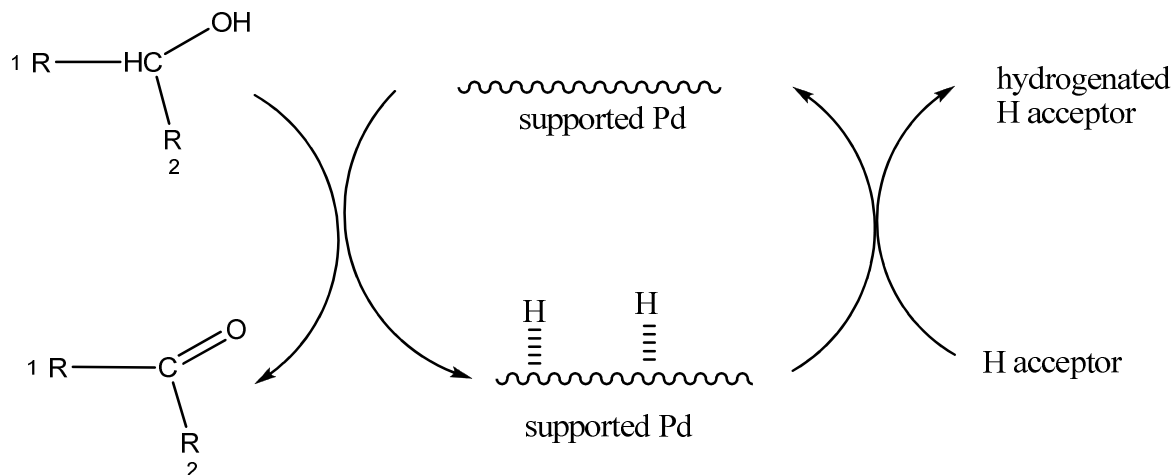


Figure 2

As with many procedures, no reaction is observed with alcohols containing functionalities that are able to co-ordinate strongly to Palladium as oxidation and subsequent reduction of metal cannot be possible or difficult.

### OXIDATION OF PRIMARY ALCOHOLS:

Primary aliphatic alcohols oxidizes to corresponding aldehydes in high yields without formation of carboxylic acids or esters using a catalyst system ie; (a) Palladium acetate(.05mmol), alcohol(1mmol), pyridine(.2mmol) toluene(10ml) and 3 Angstroms molecular Sieve(MS3A). For example 1-Octadecanol yielded 95% within 2hrs. Catalytic system showed compatibility with various Hydroxyl protecting groups such as Tetrahydropyranyl ether, tertiary Butyldimethylsilyl ether and Benzyl ether. Whereas another catalytic system, (b) Palladium acetate coordinated to disodium salt of 4,7-diphenyl-1,10-phenanthroline disulfonic acid at a

temperature of 100C under high air pressure and small amounts of sodium acetate in aqueous medium yields corresponding acid. Formation of acid has a radical character because addition of a radical scavenger stops the reaction to aldehydes.

### **OXIDATION OF SECONDARY ALCOHOLS:**

Secondary alcohols oxidizes to give corresponding ketones with same catalytic system (a) and (b) as mentioned in Oxidation of primary alcohols. Ex: Borneol oxidized to give Borneal in high yields and also Menthol oxidizes to give Menthone.

### **OXIDATION OF ALKENIC ALCOHOLS:**

Alkenic alcohols oxidizes to corresponding aldehydes with catalytic system (a) example is Cinnamyl alcohol gives Cinnamaldehyde but only to 65% with regular conditions in 12 hrs and sometimes palladium precipitates as palladium black. By increasing the concentration of pyridine for 25 times, yields 91% after 4 hrs. This is due to the strong complexation of alkene to palladium which might accelerate the reduction of Palladium(+2) could be inhibited by the coordination of excess pyridine. Whereas oxidation of terminal C-C double bond is strongly preferred with catalytic system (b) to form diols Ex: 10-Undecen-1-ol oxidizes to give 1,10-Undecenediol.

### **MECHANISMS OF OXIDATION REACTIONS:**

Different mechanisms have been proposed for the catalytic oxidation reactions of alcohols.(1)When a catalytic system (a)is used Pd(reduced)is stabilized with regard to Palladium Black by coordinating with DMSO and regeneration of the catalyst is achieved through a peroxy-palladacycle intermediate, the addition of the acetic acid to this latter complex regenerates

the oxidized Palladium catalyst and leads to the concomitant formation of Hydrogenperoxide under these reaction conditions, Hydrogen peroxide disproportionates rapidly to give water.

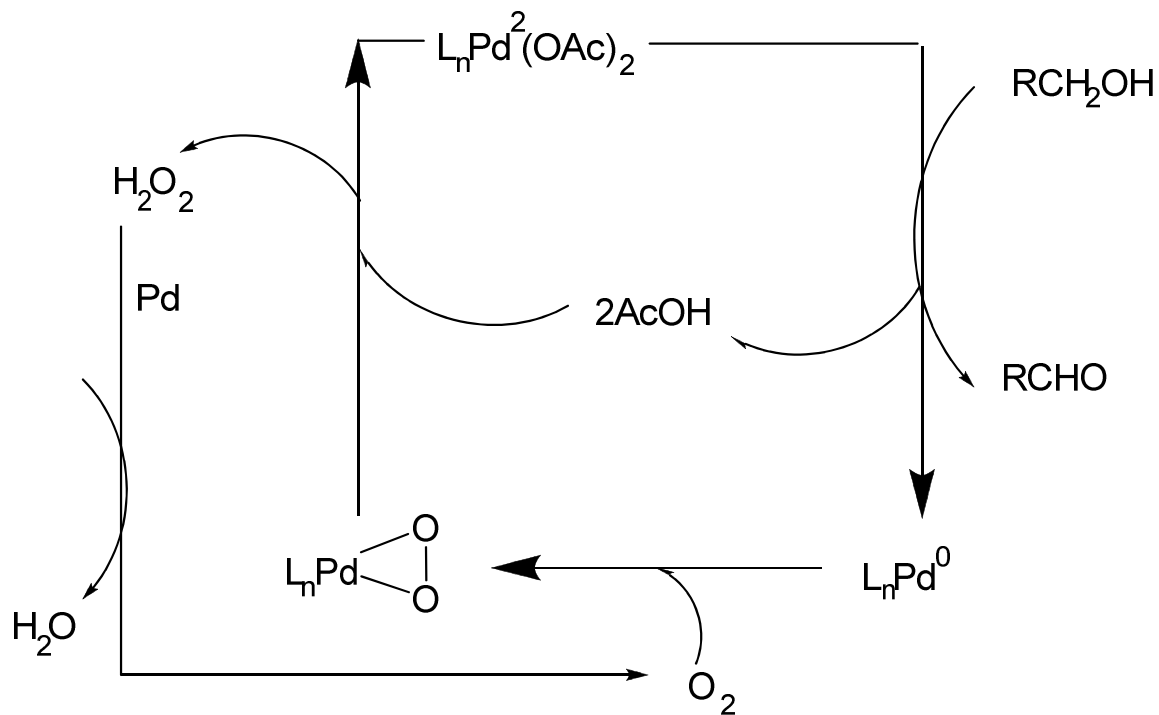


Figure 3

But this mechanism is not compatible with the reactions that are carried out in the presence of a base such as sodium carbonate because of the capture of Acetic acid.

For the reactions involving bases following mechanism seems to be appropriate in which the alcohol reacts with Hydroperoxypalladium intermediate to form a palladium alkoxide instead of regeneration of initial catalyst (path (b) of figure 4).

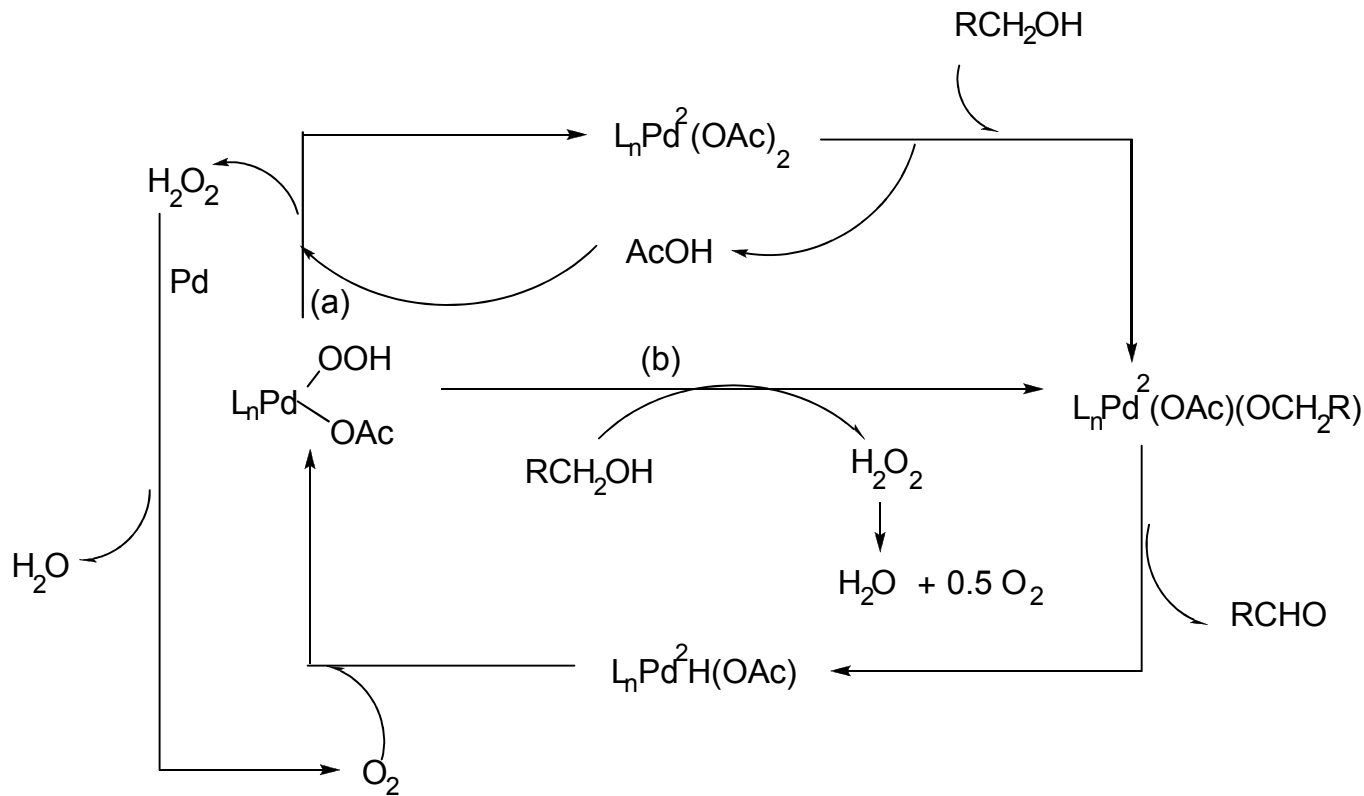
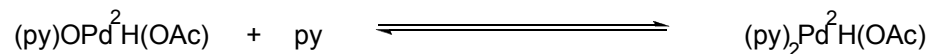
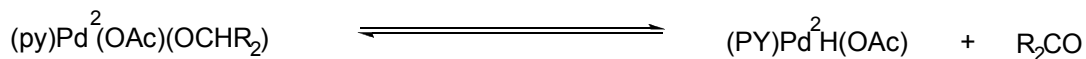
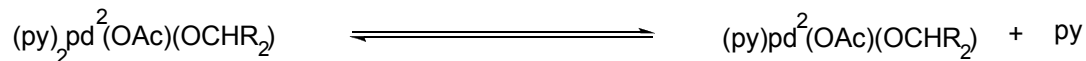


Figure 4

But from the recent investigations it was found that the turnover rate of product formation has decreased considerably when the ratio of pyridine/palladium is higher than 1, which indicates that formation of Palladium(2) hydride from Palladium(2) alkoxide requires reversible dissociation of one pyridine molecule to generate a three co-ordinated Palladium(2) species from which beta hydride elimination will proceed. In contrast they retain a catalytic cycle regenerating  $(py)_2Pd^2(OAc)_2$  from  $(py)_2Pd^0$  and hence the whole catalytic cycle would be similar to the one described in figure 3.



In both the mechanisms there is formation of hydrogenperoxide. To detect the hydrogenperoxide produced, the aqueous layer extracted from the reaction mixture is treated with starch and potassium iodide which gave rapid color change from light yellow to dark blue in the layer obtained from reaction mixture without MS3A. The test was negative for the extracts of reaction mixture with MS3A. This illustrates that hydrogen peroxide is produced and absorbed and/or decomposed to Oxygen and water by MS3A.

Another evidence is, 30% of aqueous hydrogenperoxide was confirmed immediately and decomposed to generate oxygen in toluene at a temperature of 80C in presence of pyridine & MS3A. From this it can be concluded that combination of Palladium acetate/pyridine/MS3A shows high catalytic activity for aerobic oxidation of benzylic and aliphatic alcohols using oxygen as sole oxidant. However there are some limitations reported such as lack of oxidation of 1-dimethylamino-2-propanol; 1-methoxy-1-phenyl-2-ethanol are some examples.

## DIFFERENT FORMS OF CATALYST

**Palladium(0) complexes:** Pd(dba)<sub>2</sub>/PPh<sub>3</sub> are able to catalyse the oxidation of allylic alcohols by air in Toluene at 100-110C temperature. The selectivity is improved by the addition of small amounts of bases like potassium carbonate or ammonium phosphorous hexafluoride. Although

the O-H bond of the alcohols is normally reluctant to add to Pd(0) complexes, MeOPdH and ArOPdH have been documented.

1. Palladium chloride/copper nitrate, at a temperature of 100C and Oxygen oxidizes 1-butanol to n-butyl acetate.
2. Palladium chloride/Sodium acetate in solvents like sulpholane, acetone, ethylene carbonate and oxygen.
3. Palladium acetate/DMSO, mineral bases like sodium and potassium carbonates and bicarbonates and oxygen.
4. And also the catalytic systems (a)&(b) mentioned somewhere earlier in this paper.

**Supported Palladium:** Various alcohols undergo oxidation with Palladium/charcoal, Palladium/calcium carbonate, Palladium/alumina catalysts systems in aqueous, basic solutions. With Palladium/charcoal primary alcohols lead mainly to the acids. A range of arylacetic acids have been prepared from Pd/C with selectivity enhanced by additives such as copper and lead(pb).

Another is Pd supported Hydrotalcite, oxidizes alcohols to corresponding aldehydes and ketones in presence of pyridine under atmospheric pressure of Oxygen. Palladiumhydrotalcite can be prepared by mixing Palladium acetate, pyridine and hydrotalcite in toluene at a temperature of 80C for 1hr, followed by filtration, washing and drying at room temperature and reduced pressure. This catalyst is easy for use and is recyclable. This can be deactivated by blockade of surface by strongly adsorbed molecules either impurities or reaction products or by adsorbed Oxygen. Deactivation due to adsorption of Oxygen is also called as 'Over Oxidation' or Oxygen poisoning.

## **METAL PROMOTED REACTIONS**

Metal promoters mainly Bismuth and Lead(Pb), extensively improves the rate and selectivity of Platinum and Palladium catalysts. They also suppress the deactivation of catalyst. According to Mallat et.al, the main course of catalyst deactivation during oxidation of secondary alcohols is the formation of strong irreversible adsorption of biproducts. The presence of Bi or Pb on the surface of Pd decreases the size of active site ensembles, thus suppresses the poison formation. It was also proposed that the geometry of active site ensembles depends up on the size of the metal promoter. Thus the higher the number of active sites, which the promoter occupies, the higher is its promoting effect.

## **CONCLUSION**

Palladium catalyses many of the oxidative reactions of alcohols, yielding high percentages of respective carbonyl compounds, though there are some exceptions like 1-dimethylamino-2-propanol; 1-methoxy-1-phenyl-2-ethanol which are not oxidized. Compounds that form stable complexes with Palladium by coordinating strongly to it cannot be oxidized. Main advantage of this method is recycling of catalyst and solvent which conserves a lots of money and material and also reduces the environmental pollution by decreasing the chemical wastes in large quantities. Use of readily available commercial catalysts is increasing now a days due to ease of use and reproducibility. Several projects are undertaking with production of commercial varieties of ready to use catalytic systems and is of area of great interest.

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