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Homogeneous Palladium Catalyzed Oxidations: A Novel, Highly Effective Bimetallic Palladium Lead Acetate Complex Useful in Benzylic Acyloxylation of Alkyl Aromatics

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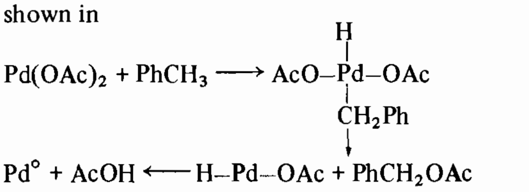
The partial oxidation of alkyl aromatics into the corresponding alcohols is economically a very interesting, but up to this time, an unresolved problem of petrochemical research. Generally, the direct oxidation results in low yields of alcohols, the considerable amounts of undesired side products, especially CO and CO_2 along with aldehydes and carboxylic acids which cannot be avoided, are caused by the fact that alcohols are generally more reactive toward oxygen than hydrocarbons [1]. For these reasons, instead of the direct conversion of an alkyl aromatic to the corresponding alcohol, an intermediate compound must first be produced which is relatively more stable under the reaction conditions and can easily be converted into the alcohol. Benzyl acetate has been shown to fulfill these requisites for the conversion of toluene into benzyl alcohol. We have been involved in developing a new toluene-based process for styrene where conversion of toluene to benzyl carboxylate is one of the key steps (eqn. (1)).

$$PhCH_3 + RCOOH + [O] \xrightarrow{\text{catalyst}} PhCH_2OCOR + H_2O \qquad (1)$$

Literature reveals that under oxidation conditions, palladium(II) acetate catalyzed liquid phase reaction of toluene can proceed in different ways such as (i) benzylic acetoxylation to give benzyl acetate [2], (ii) nuclear acetoxylation to give methylphenyl acetate [3] and (iii) coupling to give dimethyl biphenyl [4]. Among the various reports on benzylic acetoxylation, the catalytic process by Bryant and co-workers [1] using a catalyst system comprised of $Pd(OAc)_2/Sn(OAc)_2/KOAc$ appears to give the best results, however, it requires a high amount of KOAc and the rates are still not to the point that a commercial process can be developed. Working in this area with an aim to develop a successful commercial process for benzyl alcohol, we have developed new and very effective mixed palladium/lead catalyst systems for the acyloxylation of toluene or other alkyl aromatics. Here we wish to present for the first time the isolation of this novel mixed palladium(II) lead(II) tetraacetate complex, $PdPb(OAc)_4$, and its application as an excellent catalyst for the selective acyloxylation of toluene.

During our development studies for an efficient, liquid phase, catalytic process for benzylic oxidation, we have found that the palladium(II) acetate catalyzed acyloxylation of toluene can significantly be affected by various factors including (a) use of a suitable co-metal acetate salt in conjunction with $Pd(OAc)_2$, (b) temperature of the reaction, (c) rate of water removal from the reaction mixture, (d) availability of oxygen. It has been noticed that the reactions carried out in the temperature range of 160–180 °C function most effectively and an efficient removal of the water produced in the reaction results in faster reaction rates giving selectively the benzylic acyloxation product. Earlier reported [2] use of acetic acid as reaction medium has been found to be inadequate since under atmospheric pressure, the reaction temperature cannot be maintained at 160 °C and also the water separation from acetic acid is not conveniently possible. We discovered that a high boiling carboxylic acid such as lauric acid or dodecanedioic acid works quite efficiently in the above respects. It has further been found that the use of lead(II) acetate in conjunction with $Pd(OAc)_2$ in the benzylic acyloxylation of toluene in higher boiling carboxylic acid medium at ~170 °C under continuous oxygen stream and azeotropic water removal with toluene, results in the most efficient catalytic production of benzyl carboxylate. The role of a co-metal (usually a redox-metal) in the palladium catalyzed oxidation processes of organic substrates has most commonly been considered to be that of an agent to re-oxidize the reduced palladium produced in the course of reaction [5] (eqn. (2)). We strongly feel that although, the role of a co-metal such as $Pb(OAc)_2$ is certainly to help regenerate the $Pd(OAc)_2$, however, not by undergoing a Wacker-type redox-cycle as shown in



$$Pd(OAc)_2 + PhCH_3 \longrightarrow AcO{-}\overset{\displaystyle H}{\underset{\displaystyle CH_2Ph}{Pd}}{-}OAc$$

$$\downarrow \qquad (2)$$

$$Pd^\circ + AcOH \longleftarrow H{-}Pd{-}OAc + PhCH_2OAc$$

$$Pd^\circ + M(OAc)_n \longrightarrow Pd(OAc)_2 + M(OAc)_{n-2}$$

$$M(OAc)_{n-2} + 2AcOH + [O] \longrightarrow M(OAc)_n + H_2O$$

eqn. (2), but in some other ways. One of the possible ways is by forming a bimetallic complex (eqns. (3) and (4)) which might be useful in (a) making palladium more electrophilic thus providing better interaction

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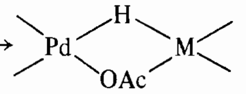
of toluene or other organic substrates and (b) stabilization of the intermediate palladium hydride complex.

$$Pd(OAc)_2 + M(OAc)_n \longrightarrow PdM(OAc)_{2+n} \qquad (3)$$

$HPd(OAc) + M(OAc)_n \longrightarrow$



(4)

This postulated role of the co-metal as complexing agent rather than in redox-cycle can be supported by the fact that the use of alkali metal acetate salts with $Pd(OAc)_2$ also results in significant improvement of its catalytic activity [6]. Details of other supporting evidence and the most probable mechanism for palladium catalyzed acyloxylation reactions is a subject of a future report.

The first conclusive evidence obtained concerning the existence of a mixed palladium lead acetate complex, $PdPb(OAc)_4$, was the result of UV–Vis studies on the solutions of the reactions of $Pd(OAc)_2$ and $Pb(OAc)_2$ in acetic acid. Incremental addition of $Pb(OAc)_2$ to the acetic acid solution of $Pd(OAc)_2$ at 60 °C resulted in color change from orange–red to yellow–orange to yellow and also formation of a new absorption band at 335 nm with disappearance of band at 400 nm characteristic of $Pd(OAc)_2$ (Fig. 1). The intensity of this new band at 335 nm was found to be maximum at the point when equimolar amount of $Pb(OAc)_2$ was allowed to react with $Pd(OAc)_2$ and no change was noticed on further addition of $Pb(OAc)_2$ to this solution. In order to determine the exact stoichiometry of the complex, a systematic experiment was carried out where the concentration of Pd(II), as $Pd(OAc)_2$, was held constant while varying the concentration of Pb(II), as $Pb(OAc)_2$. The absorbance data were plotted *versus* the mole fraction of Pd(II) (Fig. 2) and the intersection of the straight lines constructed from the data points clearly demonstrated the formation of 1:1 complex between $Pd(OAc)_2$ and $Pb(OAc)_2$. In another experiment using the reverse addition, *i.e.*, adding $Pd(OAc)_2$ to the solution of $Pb(OAc)_2$ showed the formation of only one band at 335 above 300 nm until more than one equivalent of $Pd(OAc)_2$ per lead was added, at which point the characteristic band of $Pd(OAc)_2$ at 400 nm begins to show up.

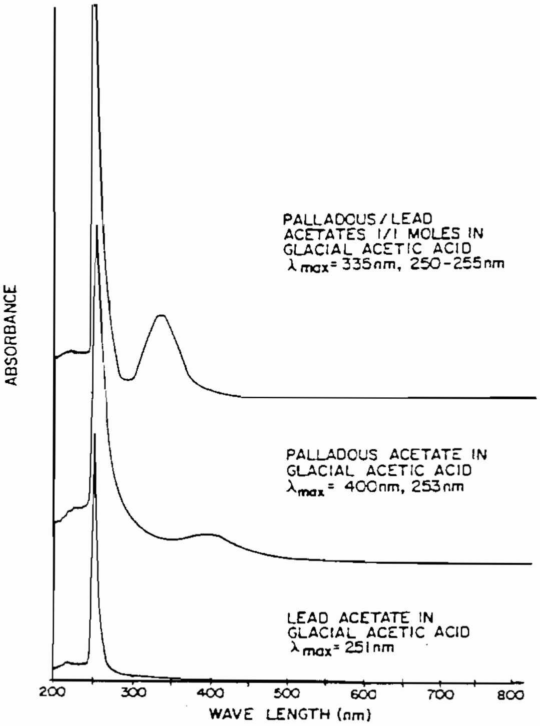


Fig. 1. UV–Vis spectra at 25 °C of (a) $Pb(OAc)_2$, (b) $Pd(OAc)_2$ and (c) 1:1 mixture of $Pd(OAc)_2/Pb(OAc)_2$ heated at 60 °C for 1 h or $PdPb(OAc)_4$ crystals dissolved in acetic acid.

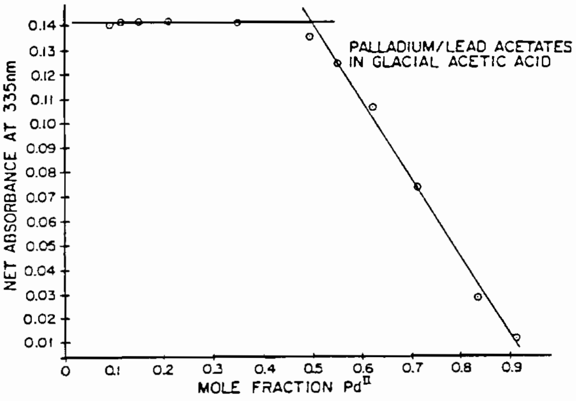


Fig. 2. Determination of the stoichiometry of the complex between $Pd(OAc)_2$ and $Pb(OAc)_2$ utilizing the UV–Vis spectroscopic method by keeping the concentration of $Pd(OAc)_2$ constant while varying $Pb(OAc)_2$ amounts and plotting the net absorbance of 335 band *vs.* mole fraction of Pd(II).

From the concentrated solution of an equimolar reaction of $Pd(OAc)_2$ with $Pb(OAc)_2$ in acetic acid at 60 °C, a bright yellow crystalline solid was isolated which was analyzed as $PdPb(OAc)_4 \cdot AcOH$ (**I**). UV–Vis spectrum of this complex (**I**) in acetic acid showed the expected absorption bands at 251 and 335 nm and IR spectrum showed bands at 1680(m) and 1595(vs) cm^{-1} due to complexed acetic acid and acetate groups. Our initial attempt to grow crystals suitable for single X-ray crystal structure have been unsuccessful however; the X-ray powder diffraction pattern was found to be different than that of the starting $Pd(OAc)_2$ and $Pb(OAc)_2$. Contrary to the starting materials which were found to be insoluble in water individually, the complex **I** was found to be fairly soluble, thus further supporting its integrity.

The mixed palladium lead acetate complex (I) has been found to catalyze the benzylic acyloxylation of toluene very effectively and the results have been found to be comparable to that using a mixture of $Pd(OAc)_2$ with $Pb(OAc)_2$. In a typical reaction, 6 mmol of complex (I) was mixed in a mixture of 550 mmol of lauric acid, 50 mmol of toluene and the reaction mixture was heated to 165–70 °C with vigorous stirring and bubbling oxygen at a rate of 50–100 cm^3/min. Additional toluene was introduced continuously by a feed pump to the reaction mixture at a range of approximately 50 mmol/h and the water formed in the reaction was removed azeotropically with toluene. This way the reaction was carried out for 5 h during which time approximately 85% of the total toluene subjected to oxidation was converted to give benzyl laurate in greater than 98% selectively. The minor by-products of the reaction were found to be benzaldehyde and benzoic acid along with a small amount of CO_2. In another experiment, following the procedure and the charge of the above reaction except the catalyst amount which was reduced to 1.2 mmol, about 215 mmol of benzyllaurate were produced in 5 h reaction period, thus showing the higher efficiency of the catalyst at lower catalyst level. This may indicate that the rate may be limited by the mass transfer of oxygen partial pressure.

In short, the isolated bimetallic complex, $PdPb(OAc)_4$, has been found to be an excellent catalyst for the benzylic acyloxylation process. Efforts are being made to expand its application in various other catalytic systems.

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