Inorganica Chimica Acta, 121 (1986) L11–L13

Homogeneous Palladium Catalyzed Oxidations: Benzylic Acyloxylation of Alkyl Aromatics Using Mixed Palladium Copper Acetate Catalyst

ANIL B. GOEL

Ashland Chemical Company, Venture Research & Development, P.O. Box 2219, Columbus, Ohio 43216, U.S.A.

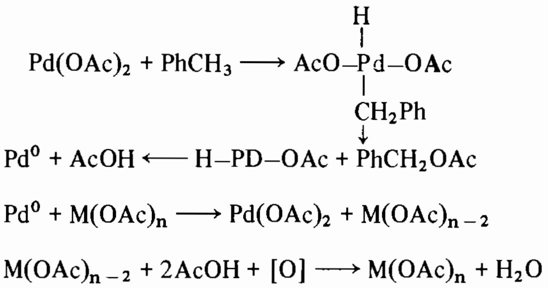
(Received July 29, 1986)

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 and considerable amounts of undesirable side products (especially CO and CO_2 along with aldehydes and carboxylic acids) due to 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 be easily converted into alcohol.

We have been involved in the development of a liquid phase catalytic air oxidation process for the conversion of toluene and other alkyl aromatics to the corresponding benzylic alcohols via benzylic carboxylate using homogeneous palladium catalysts. Literature reveals that palladium(II) acetate catalyzed liquid phase oxidation reaction of toluene in acetic acid medium can proceed in different ways including (a) benzylic acetoxylation to give benzyl acetate [2], (b) nuclear acetoxylation to give methyl phenylacetate [3] and (c) coupling to give dimethyl biphenyls [4].

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, and (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 acyloxylation product. It has now been found that the use of cupric acetate in conjunction with $Pd(OAc)_2$ in the benzylic acyloxylation of toluene in higher boiling carboxylic acid medium (e.g., octanoic, lauric or dodecanedioic acid) at ~170 °C under continuous oxygen stream and azeotropic water removal with toluene, results in an improved catalytic production of benzyl carboxylate compared to that of $Pd(OAc)_2$ alone.

Thus, when a catalyst system comprising of 6 mmols of $Pd(OAc)_2$ and 6 mmols of $Cu(OAc)_2$ was used in the benzylic acyloxylation of toluene [(220 mmols) in lauric acid (550 mmols) at 165–170 °C under continuous oxygen stream (~50 ml/min)] and water produced in the reaction was removed azeotropically with toluene using a Dean–Stark type collector, conversion of ~55% of the toluene was noticed in a 5-hour reaction period. This yielded 114 mmols of benzyllaurate, along with benzaldehyde (~2 mmols) and benzoic acid (~4 mmols). Results of benzylic acyloxylation of toluene and other alkyl aromatics in various high boiling mono and dicarboxylic acids are given in Table I. The role of copper (a redox metal) in the palladium catalyzed oxidation processes of organic substrates has most commonly been considered to be that of an agent to reoxidize the reduced palladium produced in the course of reaction [5] and to regenerate the $Pd(OAc)_2$ by undergoing a Wacker-type redox cycle as shown in Scheme 1.

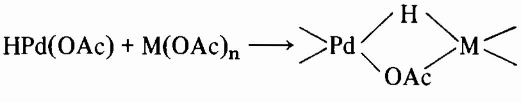


$$\mathrm{Pd(OAc)_2} + \mathrm{PhCH_3} \longrightarrow \mathrm{AcO{-}}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{CH_2Ph}}{\mathrm{Pd}}}\mathrm{{-}OAc}$$
$$\downarrow$$
$$\mathrm{Pd^0} + \mathrm{AcOH} \longleftarrow \mathrm{H{-}PD{-}OAc} + \mathrm{PhCH_2OAc}$$
$$\mathrm{Pd^0} + \mathrm{M(OAc)_n} \longrightarrow \mathrm{Pd(OAc)_2} + \mathrm{M(OAc)_{n-2}}$$
$$\mathrm{M(OAc)_{n-2}} + 2\mathrm{AcOH} + [\mathrm{O}] \longrightarrow \mathrm{M(OAc)_n} + \mathrm{H_2O} \qquad (1)$$

Scheme 1.

Alternatively, however, the role of the co-metal may be to maintain the soluble palladium by forming a bimetallic complex of type shown (eqns. 2 and 3) which might be useful in (a) making palladium more electrophilic, thus providing better interaction of toluene or other organic substrates and (b) stabilization of the intermediate palladium hydride complex.

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



$$\mathrm{HPd(OAc)} + \mathrm{M(OAc)_n} \longrightarrow {>}\mathrm{Pd}\overset{\mathrm{H}}{\underset{\mathrm{OAc}}{\lessgtr}}\mathrm{M}{<} \qquad (3)$$

Formation of mixed palladium thallium acetate complex [6] and hydrido-acetate bridged palladium/copper complex [7] has been proposed in the litera-

0020-1693/86/£3.50

TABLE I. Pd/Cu Catalyzed Benzylic Acyloxylation of Alkyl Aromatics in Carboxylic Acid Medium[a]

Experiment Number	Catalyst	Carboxylic acid	Substrate	Products (mmols)
1	$Pd(OAc)_2/Cu(OAc)_2$ (6) (6)	L.A. (550)	Toluene (220)	B.L. (114); Bld. (2); B.A. (4)
2	(3) (3)	(550)	(215)	B.L. (62); Bld. (1); B.A. (3)
3	$PdCu(OAc)_4$ (6)	(550)	(210)	B.L. (102); Bld. (2); B.A. (5)
4	$Pd(OAc)_2/Cu(OAc)_2$ (6) (6)	O.A. (700)	(232)	B.O. (110); Bld. (2); B.A. (5)
5	(6) (6)	DDA (552)	(217)	MBDD (94); DBDD (8); B.A. (4)
6	(6) (6)	(L.A.) (540)	*o*-Xylene (190)	OMBL (40); OXDL (5); B.A. (5)
7	(6) (6)	(545)	*m*-Xylene (218)	MMBL (82); MXDL (13); B.A. (4)
8	(6) (6)	(538)	*p*-Xylene	PMBL (70); PXDL (10); B.A. (4)
9	(6) (6)	(548)	*p*-Methyl Anisole	*p*-Methoxy benzyllaurate (106); B.A. (4)

[a] Reactions were carried out at 165 ± 3 °C under oxygen atmosphere (30–50 ml/min). Products were analyzed by GLC after silylation of the reaction mixture with BSTFA (internal standard method). L.A. = lauric acid; O.A. = octanoic acid; DDA = dodecane dioic acid; B.L. = benzyllaurate; Bld. = benzaldehyde; B.A. = benzoic acid; B.O. = benzyloctanoate; MBDD = monobenzyl dodecanedioate; DBDD = dibenzyl dodecanedioate; OMBL = *o*-methylbenzyllaurate; OXDL = *o*-xylene α,α'-dilaurate; MMBL = *m*-methylbenzyllaurate; MXDL = *m*-xylene α,α'-dilaurate; PMBL = *p*-methylbenzyllaurate; PXDL = *p*-xylene α,α'-dilaurate.

ture in other oxidation processes. This postulated role of the co-metal as a complexing agent rather than in the redox cycle can be supported by the fact that the use of a non-redox metal, such as alkali metal acetate salts with $Pd(OAc)_2$, also results in significant improvement of its catalytic activity [8].

The first evidence obtained concerning the existence of a mixed palladium copper acetate complex, $PdCu(OAc)_4$ (**I**) was the result of UV–Vis. studies on the solutions of the reactions of $Pd(OAc)_2$ and $Cu(OAc)_2$ 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 green and also formation of a new absorption band at 352 nm with disappearance of the band at 400 nm, characteristic of $Pd(OAc)_2$. The intensity of this new band at 352 nm was found to be maximum at the point when equimolar amount of $Cu(OAc)_2$ was allowed to react with $Pd(OAc)_2$.

From the concentrated solution of an equimolar reaction of $Pd(OAc)_2$ with $Cu(OAc)_2$ in acetic acid at 60 °C, a green crystalline solid was isolated. This was found to contain Pd and Cu in roughly 1:1 ratio by atomic absorption analysis. The UV–Vis. spectrum of this complex in acetic acid showed the expected absorption bands at 352 nm. Our initial attempt to grow crystals suitable for single X-ray crystal structure has been unsuccessful.

The mixed palladium copper 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 $Cu(OAc)_2$. In a typical reaction, 6 mmols of complex **I** were mixed in a mixture of 550 mmols of lauric acid, 60 mmols of toluene and the reaction mixture was heated to 165–170 °C with vigorous stirring and bubbling oxygen at a rate of ~50 cc/min. Additional toluene was introduced continuously to the reaction mixture, by a feed pump, at a rate of approximately ~30 mmol/h. 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 51% of the total toluene (210 mmols) subjected to oxidation was converted to give benzyllaurate in greater than 94% 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 short, the mixed palladium copper acetate catalyst system has been found to be quite efficient for the selective benzylic acyloxylation process.

References

1 M. Watanabe and K. Namikawa, 'Benzyl alcohol – its manufacturing processes and uses', *CEER: Chem. Econ. Eng. Rev.*, *9*, 50 (1970).

2 D. R. Bryant, J. E. McKeon and B. C. Ream, *Tetrahedron Lett.*, 3371 (1968; *J. Org. Chem.*, *33*, 4123 (1968); J. M. Davidson and C. Triggs, *Chem. and Ind.*, 457 (1966); J. E. McKeon and D. R. Bryant, *U.S. Pat. 3 547 982*, Dec. 15, 1970; J. Matsuda and T. Shirafuji, *Japan 52-151135*, Dec. 15, 1977; T. Okada and Y. Kamiya, *Bull. Chem. Soc.*

Jpn., 52, 3221 (1979); H. D. Holtz and L. E. Gardner, *U.S. Pat. 4 088 823,* May 9, 1978.

3 L. Eberson and L. Gomez-Gonzalez, *Acta Chem. Scand., 27,* 1162, 1249, 1255 (1973); L. Eberson and L. Jonsson, *Acta Chem. Scand., 28,* 597, 771 (1974).

4 R. Van Helden and G. Verberg, *Recueil, 84,* 1263 (1965); *U.S. Pat. 3 145 237,* Aug. 18, 1964.

5 P. M. Henry, 'Palladium Catalyzed Oxidation of Hydrocarbons', Reidel, Boston, Mass., U.S.A., 1981.

6 A. F. M. J. Van der Ploeg, G. Van Koten and K. Vrieze, *Inorg. Chim. Acta, 39,* 253 (1980).

7 T. Hosokawa, T. Uno, S. Inui and S. I. Murahashi, *J. Am. Chem. Soc., 103,* 2318 (1981).

8 A. B. Goel, *Inorg. Chim. Acta, 90,* L15 (1984).