Homogeneous Palladium Catalyzed Oxidations.
Part II: Isolation of K₂Pd(OAc)₄ and Its Application in Benzylic Acyloxylation of Alkyl Aromatics

ANIL B. GOEL

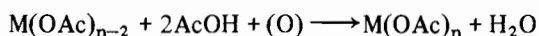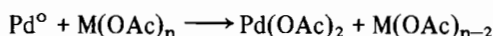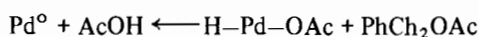*Ventures Research and Development, Ashland Chemical Company, P.O. Box 2219, Columbus, Ohio 43216, U.S.A.*
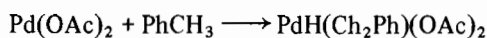
The partial oxidation of alkyl aromatics into the corresponding alcohols is economically a very attractive problem of petrochemical research. Generally, the direct oxidation results in low yields of alcohols and considerable amounts of side products such as CO_2, aldehydes and carboxylic acids due to the fact that alcohols are 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. We have been involved in developing a liquid-phase process for the conversion of toluene to benzyl alcohol via benzyl carboxylate, catalyzed by palladium complexes. Literature reveals that under oxidation conditions, palladium(II) acetate catalyzed liquid phase reaction of toluene in carboxylic acid medium 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].

During the development studies for an efficient, liquid phase, catalytic process for benzylic oxidation, it has been found that the Pd(OAc)₂ catalyzed acyloxylation of toluene can significantly be affected by various reaction parameters including (a) temperature of the reaction, (b) rate of water removal from thee reaction mixture, (c) availability of oxygen, (d) use of a suitable co-metal acetate salt [2, 5] in conjunction with Pd(OAc)₂. We have found that the reactions carried out in the temperature range of 160–180 °C in high boiling carboxylic acids (*e.g.* lauric acid or dodecanedioic acid) under oxygen atmosphere 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 further been found that the use of KOAc in conjunction with Pd(OAc)₂ results in much higher catalytic reactivity compared to that of Pd(OAc)₂ alone. Thus, when a catalyst system comprising Pd(OAc)₂ (6 mmol)/n KOAc (where n = 2 or higher) was used in the benzylic acyloxylation of toluene (320 mmol) in lauric acid (550 mmol)

at ~168 °C under continuous oxygen stream (100 ml/min) and azeotropic water removal with toluene, formation of approximately 107 mmol of benzyllaurate along with benzaldehyde (~3 mmol) and benzoic acid (~4 mmol) was observed in ~5 hours reaction period.

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 re-oxidize the reduced palladium produced in the course of reaction [6] (Scheme 1):

$$Pd(OAc)_2 + PhCH_3 \longrightarrow PdH(Ch_2Ph)(OAc)_2$$

$$Pd^\circ + AcOH \longleftarrow H-Pd-OAc + PhCh_2OAc$$

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

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

Scheme 1.

Since the co-metal, potassium, used in the present studies is not a redox metal, its role cannot be to re-oxidize the reduced palladium. We strongly feel that although the role of a co-metal is certainly to help regenerate the Pd(OAc)₂, however, not by undergoing a Wacker-type redox cycle as shown in Scheme 1, but in some other ways. One of the possible ways is by forming a bimetallic complex (*e.g.* **2** and **3**) which might be useful in (a) making palladium more electrophilic thus providing better interaction of toluene, and (b) stabilization of the intermediate palladium hydride complex [7].

$$Pd(OAc)_2 + 2KOAc \longrightarrow K_2Pd(OAc)_4 \quad \mathbf{2}$$
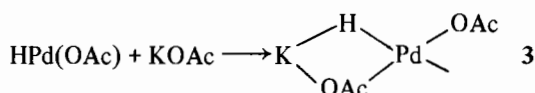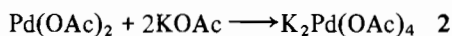
Formation of a bimetalic acetate complex between palladium and potassium of the type KPd(μ-OAC)₂(OAc) has been proposed by Eberson *et al.* [3]. However, in the UV–visible studies on the solutions of Pd(OAc)₂ and KOAc in 1:1 molar ratio, we did not observe the disappearance of the original maximum due to Pd(OAc)₂ at 397 nm and formation of only a weak shoulder at ~368 nm could be observed. Addition of an excess (4 fold) of KOAc resulted in the increase of the intensity of the shoulder at 368 nm; however, the band at 397 nm due to Pd(OAc)₂ was still observable. In view of this, reaction between Pd(OAc)₂ and KOAc appears to be reversible in solution. From the concentrated

TABLE I. Benzylic Acyloxylation of Alkyl Aromatics in Carboxylic Acid Medium.[a]

E. No.	Reactants (mmol)			Products (mmol)
	Catalyst	Carboxylic Acid	Substrate	
1	Pd(OAc)$_2$/KOAc (6)/(12)	L.A. (550)	Toluene (320)	B.L. (107); Bld. (3); B.A. (4)
2	K$_2$Pd(OAc)$_4$ (3)	(280)	(180)	B.L. (54); Bld. (2); B.A. (2)
3	(3)	O.A. (350)	(180)	B.O. (51); Bld. (2); B.A. (2)
4	(3)	DDA (270)	(185)	MBDD (37); DBDD (7); Bld. (2); B.A. (2)
5	K$_2$Pd(OAc)$_4$/C (3)/2g	O.A. (350)	(186)	B.O. (65); Bld. (3); B.A. (3)
6	K$_2$Pd(OAc)$_4$/PPh$_3$ (3)/(6)	L.A. (280)	(184)	B.L. (59); Bld. (3); B.A. (3); Ph$_3$PO (5.6)
7	K$_2$Pd(OAc)$_4$/Ph$_3$PO (3)/(6)	(280)	(180)	B.L. (57); Bld. (2); B.A. (3)
8	K$_2$Pd(OAc)$_4$/(EtO)$_3$P (3)/(6)	(280)	(185)	B.L. (63); Bld. (3); B.A. (3)
9	K$_2$Pd(OAc)$_4$ (3)	(280)	o-Xylene (160)	OMBL (21); OXDL (3)
10	(3)	(280)	m-Xylene (165)	MMBL (40); MXDL (7)
11	(3)	(280)	p-Xylene (164)	PMBL (36); PXDL (6)
12	(3)	(280)	p-Methyl-anisole (145)	p-Methoxybenzyllaurate (51)

[a]Reactions were carried out at 165 ± 3 °C under oxygen atmosphere (30–50 ml/min). Products were analyzed by GLC (internal standard method). L.A. = Lauric Acid; O.A. = Octanoic Acid; DDA = Dodecane Dioic Acid; B.L. = Benzyllaurate; Bld. = Benz-aldehyde; B.A. = Benzoic Acid; B.O. = Benzyloctanoate; MBDD = Monobenzyl Dodecanedioate; DBDD = Dibenzyl Dodecane-dioate; 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.

solution of the reaction of Pd(OAc)$_2$ with three mole equivalent of KOAc per palladium in acetic acid at ~50 °C, a bright red crystalline solid (rock-like crystals) was isolated which analyzed* as K$_2$Pd(OAc)$_4$·AcOH (1) (eqn. 2). The UV–visible spectrum of this complex (1) in acetic acid was similar to that of the reaction between Pd(OAc)$_2$ and KOAc showing the strong band at 397 nm with a shoulder at ~368 nm. Contrary to the starting Pd(OAc)$_2$ which is insoluble in water, complex 1 has been found to be readily soluble.

The mixed palladium potassium acetate complex (1) has been found to catalyze the benzylic acyloxylation of toluene very effectively and results have been found to be comparable to that using the mixture of Pd(OAc)$_2$ with KOAc. In a typical reaction, 3 mmol of complex (1) was mixed in a mixture of 280 mmol of lauric acid and 50 mmol of toluene. The reaction mixture was heated to 165–170 °C

with vigorous stirring and bubbling oxygen at a rate of 50–100 cc/min. Additional toluene was introduced at a constant rate of approximately 30 mmol/hr by a feed pump and the water produced in the reaction was removed azeotropically with toluene. The reaction carried this way for ~5 hours resulted in the formation of approximately 54 mmol of benzyllaurate. The minor by-products of the reaction were found to be benzaldehyde and benzoic acid along with a small amount of CO$_2$. Results of the oxidation of various alkylaromatics in mono- and dicarboxylic acids are given in Table I. Water solution of complex (1) was also found to catalyze the oxidation of styrene under mild conditions (40 °C and atmospheric pressure) to give aceto-phenone with catalytic turn-over number (TON) ~5/hr (4).

$$PhCH{=}CH_2 + [O] \xrightarrow{\text{Cat. 1}} PhC\overset{\displaystyle O}{\overset{\|}{C}}CH_3 \quad \textbf{4}$$
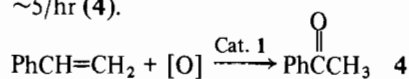
In short, palladium(II) acetate has been found to interact with potassium acetate to yield a bimetallic complex, K$_2$Pd(OAc)$_4$, which has been found to

*Atomic absorption analysis of complex 1 indicated the presence of two equivalent of K per Pd.

be an effective catalyst for the benzylic acyloxylation process. Presence of potassium resulting in the improvement of catalytic activity of $Pd(OAc)_2$ perhaps indicates the role of a co-metal in the palladium catalyzed oxidation processes is to provide the stability to $Pd(OAc)_2$ by complexation and not to regenerate the $Pd(OAc)_2$ by undergoing a Wacker-type redox cycle. Efforts are being made to provide further evidence in support of this and to expand the application of $K_2Pd(OAc)_4$ in various other catalytic systems.

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