

Palladium(II) Catalysed Aromatic Acetoxylation. IX. * An Insoluble Poly-4-vinylpyridinepalladium(II) Complex as Catalyst for the Acetoxylation of Aromatic Compounds

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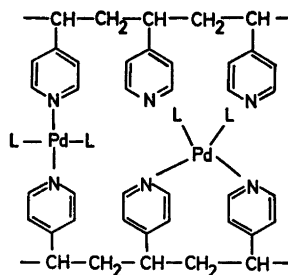


Fig. 1. Poly-4-vinylpyridinepalladium(II) complex.

The palladium(II) catalyzed acetoxylation of aromatic compounds is of synthetic interest due to its anomalous *meta* selectivity.¹⁻⁴ The problem of catalyst separation and recovery, common to many metal ion catalyzed reactions in the homogeneous phase, however, limits its usefulness to small-scale laboratory runs.

One way to achieve a better catalyst function is to anchor the metal complex to an insoluble polymeric support.^{5,6} We now report results on the acetoxylation of aromatic compounds by a Pd(II) complex with poly-4-vinylpyridine occupying two of the available ligand sites (Fig. 1). Nitrate ion is used as a cooxidant and oxygen as the primary oxidant. The reaction is thus analogous to the previously reported homogeneous acetoxylation with amine acetatonitratopalladium(II) complexes as catalysts.¹

The results are shown in Table 1. The *meta* selectivity was retained with the heterogeneous catalyst and the reaction gave yields of the

same magnitude as the corresponding homogeneous process using acetatonitrato-(2,2'-bipyridine)palladium(II) as a catalyst. The yield increases to a limiting value with increasing amounts of catalyst in the system. Compounds with activating substituents gave nitration products predominantly, as was also found in the homogeneous reaction.^{7,8} Experiment No. 9, in which a homogeneous solution obtained by extracting the polymer-anchored complex was used as the acetoxylation medium, shows that the experiments with the supported complex must have both a homogeneous and a heterogeneous component. The polymer complex could be used several times with little loss of catalytic activity in each run.

The reaction rate was determined as a function of total volume, *V*, of the reacting system in order to confirm the heterogeneity of the process. For a heterogeneous system eqn. 1 can be applied,⁹ in which *S* is the area of the catalyst interface (assumed to be constant within a given batch of catalyst), *c* concentrations of dissolved reaction components, and α and

* Part VIII, see Ref. 4.

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Table 1. Acetoxylation of some aromatic compounds catalyzed by polymer-anchored Pd(II) complex.^a

Compound (Exp. No.)	Catalyst	Acetoxy derivatives Yield, % ^b	Isomer distribution			Byproducts, % ^b
			<i>ortho</i>	<i>meta</i>	<i>para</i>	
Anisole (1) ^c	Het.	24	21	13	66	Nitroanisoles, 76
Anisole (2) ^d	Hom.	low	10	41	49	Nitroanisoles, main products
Toluene (3) ^e	Het.	60	43	28	29	Nitrotoluenes, 44
<i>p</i> -Xylene (4)	Het.	33 ^f	—	—	—	Different products
Chlorobenzene (5) ^d	Hom.	70	2	60	38	
Chlorobenzene (6)	Het.	25	19	42	39	
Chlorobenzene (7)	Het.	38	19	42	39	
Chlorobenzene (8)	Het.	44	19	42	39	
Chlorobenzene (9)	Hom.	13	19	42	39	

^a Reaction conditions, see the Experimental part. ^b GLC yield based on Pd(II). ^c Trace of acetoxy-methyl phenyl ether. ^d See Ref. 1. ^e Nuclear 90 %, α -acetate 10 %. ^f α -Acetate.

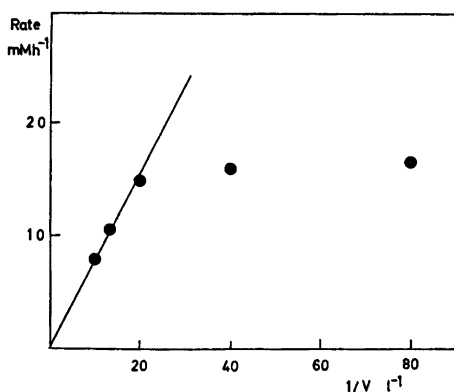


Fig. 2. Rate of reaction versus $1/V$.

β constants. For constant S and c , eqn. 1 transforms into eqn. 2. Fig. 2 shows a plot of rate vs. $1/V$, which at least for high total

$$-dc/dt = k'(S/V)c_a^\alpha c_b^\beta \quad \text{eqn. (1)}$$

$$-dc/dt = k''(1/V) \quad \text{eqn. (2)}$$

volumes is a straight line through the coordinates origin. The large deviations at low V values are presumably due to the fact that further oxidation of products (formation of diacetates) takes place in these experiments. Thus we have shown in this report that the Pd(II) catalyzed acetoxylation of aromatic compounds is possible with polymer-supported Pd(II) catalysts.

Experimental. Most chemicals used were of the quality and origin described in earlier work.¹⁻³ Solutions of nitrogen dioxide were prepared by heating a known amount of lead(II) nitrate and dissolving the gas in glacial acetic acid. 4-Vinylpyridine was purchased from Aldrich Europe and polymerized according to a literature method.¹⁰

Preparation of the polymer-anchored complex. Poly-4-vinylpyridine (2.0 mmol based on monomer) was dissolved in ethanol (25 ml) and mixed with a benzene (25 ml) solution of palladium(II) acetate (1.0 mmol). The precipitate formed was stirred for 15 min and then collected by filtration and washed with ether.

Acetoxylation procedure for expts. 1-9. A mixture of substrate (10 mmol), NO_2 (10 mmol), $\text{Pd}(\text{OAc})_2$ -poly-4-vinylpyridine (1 mmol) in glacial acetic acid (50 ml) was stirred for 4 h at 110 °C under oxygen atmosphere. In expts. 5 and 6, 2 and 4 mmol, respectively, were used of Pd(II)-PVP. In exp. 7, 50 ml catalyst solution was prepared by extraction of 1 mmol of Pd(II)-PVP in 50 ml of glacial acetic acid at 110 °C for 2 h.

Kinetic experiments. A 0.2 M glacial acetic acid solution (V ml) of chlorobenzene was stirred with NO_2 (10 mmol), $\text{Pd}(\text{OAc})_2$ -poly-4-vinylpyridine (1 mmol) for 4 h at 110 °C under oxygen atmosphere. Samples were taken at 30 min intervals and analyzed by GLC. Yield and isomer distribution were determined using a Varian 1400 gas chromatograph, equipped with a disc integrator (2 m \times 3 mm neopentylglycol succinate, 5% on Chromosorb W column). The yield was determined using an internal standard calibrated against authentic samples.

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