

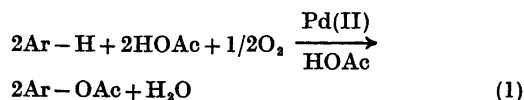
## Palladium(II) Catalyzed Aromatic Acetoxylation. IV. Nuclear Acetoxylation in the Gas Phase: Reversal of the Usual Isomer Distribution Pattern in Aromatic Substitution

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The acetoxylation of aromatic compounds in the gas phase using different palladium based catalysts has been studied. Low yields (of the order of 1 % per pass) of acetoxylation products were obtained on catalysts in which promoters, such as bismuth or silver-bismuth, had been added to the palladium. For monofunctional benzenes the isomer distributions observed were close to the statistically expected ones. However, when a cooxidant (*e.g.* potassium dichromate) was incorporated in the catalyst, the *meta* isomer became predominant, as has earlier been observed in homogeneous palladium acetate catalyzed acetoxylation reactions. ESCA studies on two of the catalysts indicated that the catalyst favoring *meta* orientation has a relatively high surface concentration of Pd(II) species.

Previous work from this laboratory<sup>1-4</sup> has shown that the homogeneous palladium(II) acetate catalyzed acetoxylation of monofunctional benzene derivatives that takes place in acetic acid in the presence of oxygen (eqn. 1) shows a reversal of the normal substituent effect, *i.e.*,



*ortho,para*-directing substituents give predominantly *meta* acetoxylation and *meta*-directing ones *ortho,para* acetoxylation. Similar findings have been reported by other investigators.<sup>5,6</sup>

Under the conditions referred to above, the reaction is, however, very slow, the degree of

conversion being typically of the order of 100 % per 24 h, based on the amount of palladium used. We have therefore initiated a study of the factors influencing the rate and selectivity of this acetoxylation process with the goal of attaining practically useful reaction rates while retaining the selectivity for *meta* substitution. Since it was known that aromatic acetoxylation is also feasible in the gas phase over solid palladium based catalyst,<sup>7-9</sup> we decided to investigate this type of reaction first. This paper shows that it is indeed possible to achieve a modest degree of *meta* selectivity in the gas phase process too, and that possibly the presence of Pd(II) species on the catalyst surface is necessary for the *meta* selectivity.

### RESULTS AND DISCUSSION

*Product studies.* A number of palladium catalysts for the gas phase acetoxylation of benzene have already been described by Arpe and Hörnig.<sup>9</sup> It was shown that gold is an efficient promoter for the formation of phenyl acetate, and that impregnation with activators like potassium and cadmium acetate—alone or in combination—was necessary to suppress the formation of phenol and concomitant resinification of the catalyst. The catalyst carrier in all these cases was silica (Davison, grade 62).

We have repeated these experiments with benzene as the substrate using the apparatus and conditions described in the experimental section with essentially the same results as those

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Table 1. Catalysts used for gas phase acetoxylation of aromatic compounds; palladium content = 1.0 %; impregnated with KOAc and Cd(OAc)<sub>2</sub><sup>a</sup>.

Designation	Promotor(s) atom-% of Pd	Carrier <sup>b</sup>
A	Bi 30	Alumina pellets
B	Bi 30	Alumina granules
C	Bi 30	Glass wool
D	Au 55, Bi 20	Alumina pellets
E	Ag 40, Bi 10	Alumina pellets
F	Ag 20, Bi 10, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , 36 <sup>c</sup>	Alumina pellets
G	Bi 30, K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , 36 <sup>c</sup>	Alumina pellets

<sup>a</sup> Without these activators the yield of acetoxy compounds was considerably lower. <sup>b</sup> With activated carbon or silica as carrier, no acetoxy compounds were formed. <sup>c</sup> Before reduction.

Table 2. Gas phase acetoxylation of benzene at 185 ± 5 °C over different palladium based catalysts with air as oxidant.

Catalyst (see Table 1)	Yield of phenyl acetate per pass, %	Space-time yield g l <sup>-1</sup> h <sup>-1</sup>	Other products, %
A	1.5	1.0	Phenol, trace
B	1.0	1.0	Phenol, 0.2
D	3.5	3.0 <sup>a</sup>	Phenol, 0.5
F	1.0	1.0	Phenol, trace
H <sup>b</sup>	trace	—	—
I <sup>c</sup>	0	0	—

<sup>a</sup> Reported <sup>o</sup> STY: 2.9 g l<sup>-1</sup> h<sup>-1</sup> with 0.75 % Pd and 0.75 % Au on silica, and 7.9 g l<sup>-1</sup> h<sup>-1</sup> with 2 % Pd and 2 % Au on silica. <sup>b</sup> Catalyst D with activated silica gel (0–1 mm) as carrier. <sup>c</sup> Catalyst D with activated carbon (3–5 mm) as carrier.

Table 3. Gas phase acetoxylation of anisole at 185 ± 5 °C over different palladium based catalysts (see Table 1) with air as oxidant.

Catalyst	Yield of nuclear acetate per pass, %	Space time yield, g l <sup>-1</sup> h <sup>-1</sup>	Nuclear acetates Isomer distribution			Relative yield, %	Phenyl methoxy-methyl ether, %	Other products, %
			<i>o</i>	<i>m</i>	<i>p</i>			
A	1.5	0.42	44	30	26	84	16	
B	1.0	0.28	38	33	29	67	16	Phenol, 17
C	0.1	0.03	38	32	30	87	13	
D	0.5	0.14	48	24	28	42	9	Phenol, 17; <i>m</i> -methoxyphenol, 6; PhOAc, 26
E	0.5	0.14	39	32	29	40	10	PhOH, 16; <i>m</i> -methoxyphenol, 11; PhOAc, 23
F	1.0	0.28	24	52	24	87	13	
G	0		—	—	—	—	—	

obtained by Arpe and Hörnig<sup>9</sup> (see Tables 1 and 2). We found, however, alumina in the form of pellets or granules to be superior to silica as a catalyst support and have therefore consistently used this material in this investigation. The yield of phenol and resulting resinification was especially less pronounced with this carrier. Also, it was found advantageous to use lower concentrations of palladium on the catalyst (1 % instead of 2–3 %). The optimum temperature was found to be in the range of 180–190 °C; at lower temperatures vaporization was not sufficiently fast and at higher temperatures side-reactions often occurred, sometimes with almost complete combustion of acetic acid and substrate and a spontaneous increase of reactor temperature to above 300 °C.

Next anisole was used as a substrate with a number of catalyst compositions modelled after those used by Arpe and Hörnig (Table 1, catalyst A–E). In this case bismuth or the combination silver-bismuth were found to be better promoters than gold, at least with respect to the yield of nuclear acetate obtained per pass (see Table 3). Alumina as pellets or granules and glass wool could be used as carriers, whereas silica or activated carbon did not support the acetoxylation process. As seen from the results given in Table 3, none of the catalysts A–E show any selectivity toward *meta* substitution. The isomer distribution in all five cases is close to the statistically expected one, 40:40:20.

It has been shown that the presence of co-oxidants, such as potassium dichromate<sup>5</sup> or nitric acid and derivatives thereof,<sup>5,6,10,11</sup> has a favorable effect on the homogeneous acetoxylation process and that *meta* selectivity is obtainable under such conditions.<sup>6,12</sup> We have suggested<sup>1,3,4</sup> that the *meta* selectivity of the homogeneous Pd(II) catalyzed reaction can be explained by electrophilic attack of a Pd(II) species on the aromatic substrate with formation of an oxypalladation adduct. The role of the cooxidant would then be to assist in the decomposition of the oxypalladation intermediate. Another possible role of the cooxidant in the homogeneous process would be to reoxidize Pd(0) to Pd(II) species.

Translating these ideas to the heterogeneous system, it was expected that impregnation of the catalyst with potassium dichromate would increase the *meta* selectivity. Firstly, the redox system Cr(III)/Cr(VI) would act as a mediator between O<sub>2</sub> and Pd(0) (it is known<sup>13</sup> that O<sub>2</sub> oxidizes Cr(III) to Cr(VI) on alumina) and hence possibly increase the concentration of Pd(II) on the catalyst surface. Secondly, Cr(VI) would assist in decomposing any oxypalladation adduct formed. As can be seen from Table 3, catalyst F, designed along these lines, does increase the *meta* selectivity for anisole acetoxylation compared to the others, even though the effect is fairly small. The possible correctness of the idea behind the incorporation of the

Table 4. Gas phase acetoxylation of aromatic compounds at 185 ± 5 °C over catalyst F (see Table 1).

Compound	Atmosphere	Yield of acetate per pass, %	Nuclear acetates Isomer distribution			Relative yield, %	Other products, %
			<i>o</i>	<i>m</i>	<i>p</i>		
Anisole	Air	1.0	24	52	24	87	PhOCH <sub>2</sub> OAc, 13
Chlorobenzene <sup>a</sup>	O <sub>2</sub>	0.1	30	70	<1	70	PhOAc, 30
Toluene	Air	2–3	—	—	—	0	PhCH <sub>2</sub> OAc, 99; PhCHO and PhCH(OAc) <sub>2</sub> , traces
<i>p</i> -Xylene	O <sub>2</sub>	1.5	—	—	—	25	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OAc, 75
Mesitylene	O <sub>2</sub>	1.2	—	—	—	0	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> OAc, 100
<i>t</i> -Butylbenzene	O <sub>2</sub>	0.5	trace	66	34	100	PhOAc, trace
Isopropylbenzene	O <sub>2</sub>	0.2	12	65	23	65	PhC(OAc)Me <sub>2</sub> , 35
Ethylbenzene	O <sub>2</sub>	0	—	—	—	—	Styrene
Naphthalene <sup>b</sup>	O <sub>2</sub>	0	—	—	—	—	
Methyl benzoate <sup>b</sup>	O <sub>2</sub>	0	—	—	—	—	

<sup>a</sup> Fluoro-, bromo-, and iodobenzene did not react under the reaction conditions employed. <sup>b</sup> At 245 ± 5 °C.

Cr(III)/Cr(VI) redox system in the catalyst was, however, further substantiated by the following experiment: The catalyst (F) bed was first oxidized by air at 300 °C (10 l/h for 10 h), and then the acetic acid/anisole solution introduced at 185 °C using a slow stream of *nitrogen*. The product from this run consisted of methoxy-methyl phenyl ether (19 %) and nuclear acetates (81 %) in the *o:m:p* ratio of 17:62:21. Since the preoxidized catalyst is expected to contain a relatively high concentration of Pd(II) and Cr(VI) sites, it is obvious that the presence of these oxidation states favors *meta* orientation. Further evidence in this direction is provided by the ESCA results discussed below.

Catalyst F was then used for the acetoxylation of a number of aromatic substrates. It can be seen by inspection of Table 4 that nuclear acetoxylation is by no means a general reaction under these conditions, but that four mono-substituted benzenes (anisole, chlorobenzene, *t*-butylbenzene, and isopropylbenzene) do undergo acetoxylation with predominant *meta* orientation. For *p*-xylene, a substrate that previously has been shown<sup>7</sup> to undergo only side-chain acetoxylation in the gas phase, we were able to secure a 25 % relative yield of the nuclear acetate on catalyst F. Mesitylene gave side-chain acetate only.

While it has been shown above that it is possible to achieve *meta* selectivity in the gas phase process, it is not as high as in the homogeneous Pd(OAc)<sub>2</sub>/CH<sub>3</sub>COOH/O<sub>2</sub> reaction described by us earlier. On the other hand, later

experience by us<sup>13</sup> and others<sup>6</sup> has revealed that attempts to increase the reaction rate, e.g., by addition of nitrate ion, result in a decrease in *meta* selectivity. What appears to be a greater disadvantage of the gas phase reaction is the low space-time yield and the relatively fast inactivation of the catalyst due to resin formation. In spite of a great deal of experimentation with the catalyst composition, we have not been able to overcome these difficulties.

*ESCA studies.* Since the ESCA technique<sup>14</sup> is a sensitive method for the analysis of surface species, an ESCA investigation of two of the catalysts used in this investigation was performed in the hope that it would be possible to decide if the palladium metal of the reduced catalyst—the final step in the preparation of the catalyst is reduction by methanol—is transformed to Pd(II) during the reaction.

ESCA spectra of catalysts A and F, recorded before and after the catalytic reaction, revealed that charging of the samples made the exact external energy calibration impossible. It was, however, established from a reference spectrum<sup>15</sup> of a mixture of Pd(II) acetate and Pd metal that there is a shift between Pd(0) and Pd(OAc)<sub>2</sub> of 2.7 ± 0.5 eV (Fig. 1). A spectrum of the same mixture, applied on the carrier used in the catalysts, showed a shift of 2.9 ± 0.5 eV. In this experiment, it was noticed that Pd(II) acetate was partially transformed into Pd metal under the conditions prevailing during the recording of the spectrum.

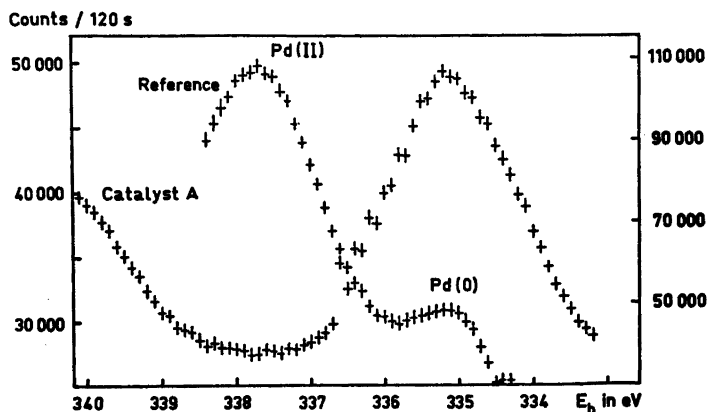


Fig. 1. ESCA spectra of (1) a reference mixture of Pd(II) acetate and Pd metal ( $3d_{5/2}$  level) and (2) catalyst A.

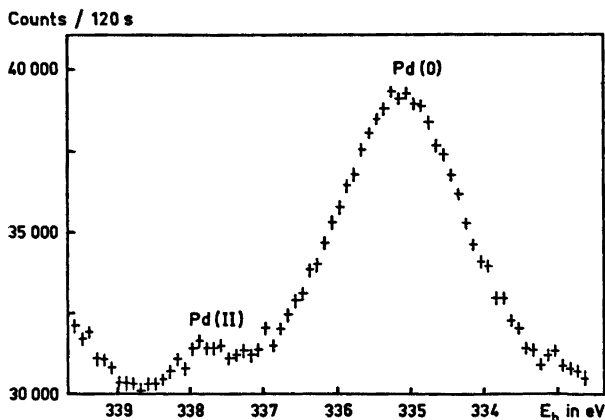


Fig. 2. ESCA spectrum of catalyst F.

Fig. 1 and 2 show printout spectra of catalysts A and F, respectively, after the reaction. In both cases the catalysts have been prepared in a way which excludes the presence of any Pd(II) on the catalyst before the reaction. Yet the spectrum of catalyst F, one which has been shown to give predominantly *meta* substitution and designed to do so by incorporation of a feature favoring formation of Pd(II), shows a signal shifted 2.8 eV from that of Pd(0). This signal must originate from Pd(II) generated in the course of the reaction. We thus conclude that the presence of Pd(II) species is a necessary requirement for the oxypalladation mechanism leading to anomalous substitution patterns both in the homogeneous and heterogeneous process. It also appears probable that there is another, more efficient acetoxylation mechanism possible in these systems, mediated *via* Pd(0) and leading to a statistical isomer distribution in nuclear acetoxylation or, if possible, to side-chain substitution. We have previously noticed<sup>2</sup> and commented<sup>4</sup> upon the fact that the appearance of Pd metal in the homogeneous process seems to be connected with the commencement of side-chain acetoxylation and would like to suggest that some type of dehydrogenation mechanism catalyzed by Pd(0) does occur both in side-chain and nuclear acetoxylation.

In a recent paper,<sup>16</sup> Evnin, Rabo, and Kasai have shown that it is possible to effect the vapor-phase oxidation of ethylene to acetaldehyde over a heterogeneous catalyst system. In the design of this catalyst, the same principle as

that described above was used, *i.e.*, palladium metal was combined with an oxidizing agent, capable of reoxidizing Pd(0) to Pd(II) with high efficiency. In this particular case, vanadium pentoxide was used as the oxidizing agent.

## EXPERIMENTAL PART

**Materials.** All chemicals used in this investigation were either purchased in the highest commercial quality available or prepared according to known procedures (see Parts I–III of this series). Carriers for catalysts were alumina pellets (1/8 in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, activated), alumina granules (from Kebo, Stockholm, Sweden), silica (activated, 0–1 mm), carbon (activated 3–5 mm) and glass wool.

**Preparation of catalysts.** Catalysts A–G were prepared as follows: Alumina in the form of pellets or any of the other carriers used (100 g) was impregnated with *ca.* 100 ml of an HNO<sub>3</sub>/H<sub>2</sub>O (50:50) solution containing palladium acetate (2.1 g, corresponding to a Pd content of 1% in the final catalyst) and the different compounds added as promoters. These were for A–C, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (1.4 g); D, Au(NO<sub>3</sub>)<sub>3</sub> (1.9 g) + Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.9 g); E, AgNO<sub>3</sub> (0.6 g) + Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.5 g); F, AgNO<sub>3</sub> (0.3 g) + Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.5 g) + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1.0 g); G, Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (1.4 g) + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1.0 g). The catalyst was first dried in a rotating film evaporator and then in the reactor tube at 200°C for 30 min. Reduction of the catalyst was achieved by passing nitrogen, saturated with methanol at 25°C, through the reactor for 2 h at 200°C and 2 h at 400°C at a flow rate of 5 l/h. The reduced catalyst was allowed to cool under nitrogen. Finally, the catalyst was impregnated with 50 ml of a water solution of

potassium acetate (1.5 g) and cadmium acetate (2.0 g) and dried in an oven at 150 °C.

**Acetoxylation reactions.** The catalytical reactions were carried out in a conventional flow reactor, consisting of a Pyrex tube (700 × 25 mm) which contained catalyst (100 g) and carrier (ca. 25 g) in the part (150 mm) adjacent to the inlet tube. This part of the reactor served to vaporize the liquid reactants before entering the catalyst zone. The tube was heated in an electrical oven, the temperature of which was controlled to within  $\pm 5$  °C.

The reaction was carried out in the following way: A solution of the substrate (0.05 mol) and a small amount of acetic anhydride (2 g) in acetic acid (20 g; molar ratio substrate/acetic acid = 1:6) was introduced into the reactor during 3 h via a fine dosage dropping funnel. Air (7–7.5 l/h) or oxygen (3–3.5 l/h) was flowing through the reactor at the same time. The product was condensed at  $-20$  °C and worked up by treatment with sodium bicarbonate solution and subsequent ether extraction (three times). The combined ether extracts were washed with water and dried with anhydrous magnesium sulfate and analyzed by GLC (Varian 1400 gas chromatograph, equipped with a disc integrator; column 2 m × 3 mm 5% neopentylglycol succinate on Chromosorb W or 2 m × 3 mm 10% Apiezon L on Chromosorb P). Internal standard was *m*-*t*-butylphenyl acetate, pentamethylbenzene, durene, or benzal diacetate. Products were identified by comparison with authentic specimens (GLC or GLC/MS).

**ESCA studies.** The ESCA measurements were carried out with an ES 100 electron spectrometer from AEI Scientific Apparatus Ltd., England. The pressure of the sample compartment was  $10^{-6}$ – $10^{-7}$  Torr and the temperature 25 °C. The energy of the X-ray radiation was 1486.6 eV ( $\text{AlK}_{\alpha 1,2}$ ) and the apparatus constant of the spectrometer 9.5 eV. The samples were deposited on nonconducting tape.

The spectra were recorded using both recorder and printer. The printout spectra (Fig. 1 and 2) were plotted from a printout giving the number of counts per 120 s in intervals of 0.1 eV.

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