

## CARBONYLATION OF ETHANOL PROMOTED BY PALLADIUM CHLORIDE

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### SUMMARY

The reaction of ethanol with carbon monoxide at atmospheric pressure and mild temperatures in the presence of palladium chloride and lithium chloride produces ethyl chlorocarbonate, ethyl acetate, palladium metal, and an unidentified compound. Only diethyl carbonate is produced along with palladium metal in the absence of lithium chloride when sodium carbonate is added to the ethanol solution of palladium chloride saturated with carbon monoxide. A very labile palladium carbonyl intermediate complex can be isolated. A reaction mechanism is proposed.

### INTRODUCTION

To the best of our knowledge, only one example of carbonylation of alcohols under mild conditions has been previously, reported, and that is in a patent<sup>1</sup>, which describes the formation of diethyl carbonate along with diethyl ether and ethyl chloride. There are examples of palladium chloride catalysis of the oxidation of alcohols to produce aldehydes, ketones, or esters (*e.g.* ethyl acetate from ethanol)<sup>2</sup>.

Recently it has been reported that bubbling carbon monoxide through a solution of palladium chloride in 2-methoxyethanol or ethanol in the presence of bulky cations produces salts of the unstable hydrido carbonyl complex<sup>3</sup>,  $[\text{HPd}(\text{CO})\text{Cl}_2]^- \nu(\text{CO}) 1900 \text{ cm}^{-1}$ . The reaction products, which might indicate the role and fate of the alcohol were not reported.

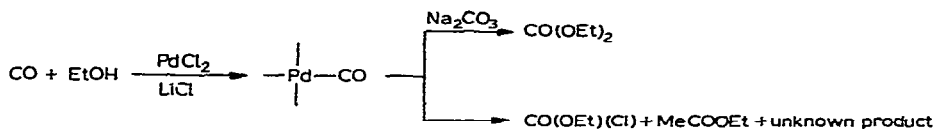
As a part of a general investigation on carbonylation reactions catalyzed by palladium salts, we have studied the interaction of ethanol with carbon monoxide under ambient conditions in the presence of palladium chloride, and we describe the results below.

### RESULTS AND DISCUSSION

On treating an ethanol solution of  $\text{PdCl}_2$  and  $\text{LiCl}$  with carbon monoxide at atmospheric pressure at 20–40° a yellow-green, insoluble compound is obtained which appears to be a palladium carbonyl complex  $[\nu(\text{CO}) 1980 \text{ cm}^{-1}]$ . This decomposes rapidly to palladium metal on exposure to air, and was too unstable to

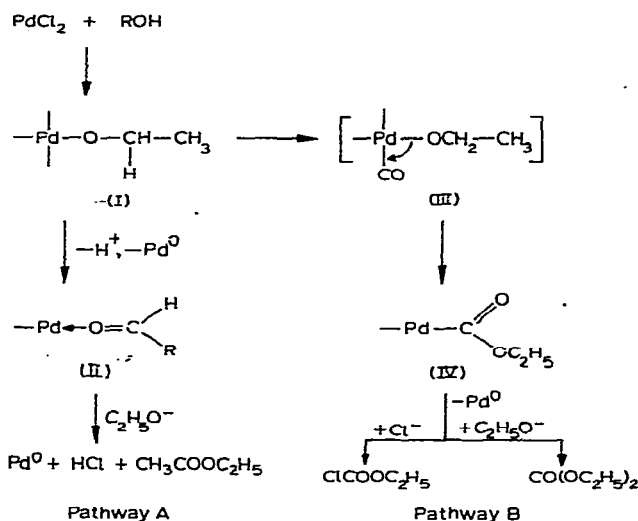
permit full characterization. Clearly it is not a salt of the anion  $[\text{HPd}(\text{CO})\text{Cl}_2]^-$ .

The carbonyl complex also decomposes to palladium metal when suspended in the reaction solution, at a rate which increases with temperature. The resulting ethanol solution, analyzed by GLC, contains mainly ethyl chlorocarbonate, ethyl acetate, and an unidentified product, all in almost equal amounts. If the reaction of  $\text{PdCl}_2$  with carbon monoxide is carried out without  $\text{LiCl}$  and then a small amount of sodium carbonate is added, precipitation of palladium metal is again observed and a single product is obtained; this has been shown by GLC to be diethyl carbonate:



A mechanism accounting for the nature and composition of the identified reaction products is proposed in Scheme 1 (For simplicity not all the ligands are shown).

Scheme 1



Pathway A accounts for the formation of ethyl acetate in the absence of  $\text{Na}_2\text{CO}_3$ , via the already known oxidation of ethanol to acetaldehyde and eventually to ethyl acetate by  $\text{PdCl}_2$ , perhaps involving the aldehyde species (II):



The resultant hydrido-palladium species is unstable and decomposes to palladium metal, as does the analogous complex produced in the oxidation of ethanol

to aldehyde. (It may possibly contain CO and be the same as the labile [HPd(CO)Cl<sub>2</sub>]<sup>-</sup> which has been isolated as a salt of precipitating cations.) The formation of esters has been shown<sup>2</sup> to be an undesired side reaction in the oxidation of alcohols to aldehydes catalyzed by PdCl<sub>2</sub>, although it may become predominant in some cases<sup>4</sup>.

Pathway B accounts for the formation of carbonylation products of ethanol. According to this scheme, the carbonyl-alkoxy-palladium species (III) undergoes internal rearrangement with insertion of carbon monoxide across the metal-oxygen bond. The resulting (alkoxycarbonyl)palladium species (IV) undergoes cleavage of the Pd-C bond via competitive attack by either RO<sup>-</sup> or Cl<sup>-</sup> to give diethyl carbonate or ethyl chlorocarbonate, depending on whether Na<sub>2</sub>CO<sub>3</sub> is added or not. In any case, such cleavage involves reduction of Pd<sup>II</sup> to palladium metal. It can be expected that other nucleophiles will be able to compete with the solvent in cleaving the Pd-C bond of (IV) to give a variety of products, thereby expanding the scope of this reaction.

The formation of (IV) might also be thought of as a nucleophilic attack of alkoxide on the coordinated carbon monoxide, since attacks of hard bases at the carbonyl carbon in metal carbonyls have been shown to occur in other systems<sup>5,6</sup>. Whatever the mode of formation of (IV) (whether carbon monoxide insertion or nucleophilic attack by alkoxide), such a carbonylation of a Pd-O bond is a reasonable postulate. Carbon monoxide is known to insert into a Hg-O bond<sup>7</sup> and more recently it has been suggested that the formation of palladium-allyl complexes catalyzed by carbon monoxide involves conversion of a carbonylhydroxypalladium species (HO-Pd-CO) into a carboxypalladium compound, Pd-COOH<sup>8</sup>.

At present we are extending this study to other primary and secondary alcohols in order to find out how the nature of the alcohol affects the nature and relative composition of the reaction products.

## EXPERIMENTAL

Anhydrous ethanol was prepared by refluxing 95% ethanol over magnesium ethoxide and distilling. All other chemicals were reagent grade materials.

Infrared spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer as Nujol mulls. GLC analyses were carried out with a "Porapak" column on a Hewlett-Packard gas chromatograph.

### *Carbonylation of ethanol in the presence of lithium chloride*

A well-stirred suspension of PdCl<sub>2</sub> (1 g) and LiCl (1 g) in anhydrous ethanol (150 ml) was kept under carbon monoxide at a pressure of 1 atm at 20–40° for ca. 1 h. A yellow-green precipitate soon appeared, a portion of which was filtered off, washed with ethanol, and dried. The solid decomposed rapidly to palladium metal on exposure to air. Its infrared spectrum, recorded as soon as possible, showed a strong band at  $\nu(\text{CO})$  1980 cm<sup>-1</sup>.

The original suspension darkened in the course of ca. 1 h owing to decomposition of the precipitate to palladium metal. After filtration, the solution was distilled and the collected liquid analyzed by GLC on a "Porapak" column. This ethanol solution was shown to contain nearly equal amounts of ethyl chlorocarbonate, ethyl acetate, and an unidentified product, in addition to solvent.

*Carbonylation of ethanol in the presence of sodium carbonate*

The reaction was carried out as described above, in the absence of lithium chloride. After the yellow-green precipitate had appeared, a small amount of sodium carbonate was added. The suspended solid was converted to palladium metal in ca. 1 h. After filtration, the ethanol solution was shown by GLC to contain only diethyl carbonate, beside the solvent.

## ACKNOWLEDGEMENTS

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