MECHANISM OF REACTION OF PALLADIUM(II) CARBOXYLATES WITH CARBON MONOXIDE IN NONAQUEOUS MEDIA

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Summary

The reduction of Pd^{II} carboxylates by carbon monoxide in benzene and AcOH solutions has been studied. In the case of Pd^{II} acetate the reaction is found to proceed through an intermediate complex with a $Pd-CO-CH_3$ group and the Pd^{I} carbonylacetate $[Pd(CO)(OAc)]_4$ (PCA). A reductive condensation type of mechanism is suggested for the PCA decomposition on the base of kinetic data. The metal cluster skeleton is proposed to increase stepwise as the oxidation state of Pd decreases. A number of Pd^{I} complexes, PCA analogs having composition $[Pd(CO)(OCOR)]_4$, where $R = C_2H_5$, C_6H_5, CF_3, CCl_3, CH_2Cl, have been prepared.

Introduction

Reduction of $Pd(OAc)_2$ by carbon monoxide in acetic acid solution containing alkali metal acetates yields acetic anhydride, metallic palladium and CO_2 [1]:

$$Pd(OAc)_2 + CO \rightarrow Pd^0 + CO_2 + Ac_2O \tag{1}$$

In the absence of NaOAc the reaction provides the palladium(I) carbonylacetate (PCA). X-Ray study [2] showed that PCA is a tetranuclear cluster $[Pd(CO)(OAc)]_4$ with a planar rectangular metallic skeleton.

Metallic Pd and acetic anhydride are the products of both reaction 1 and PCA decomposition in the presence of NaOAc:

$$[Pd(CO)(OAc)]_4 \xrightarrow{\text{NaOAc}} 4Pd + 2CO + 2CO_2 + 2Ac_2O \tag{2}$$
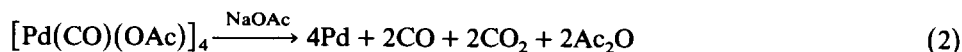
The stoichiometry and kinetics of the reduction of Pd^{II} carboxylates by CO have been studied both in the presence and in the absence of NaOAc to elucidate the mechanism of reactions 1 and 2.

Results and discussion

The reduction of Pd^{II} carboxylates by CO in AcOH solution in the absence of alkali metal carboxylates resulted in formation of Pd^I carbonylcarboxylate. The reaction of Pd^{II} propionate with CO in propionic acid gave a PCA analogue, palladium carbonylpropionate $Pd(CO)(OCOC_2H_5)$; Pd^{II} benzoate reacted with CO in benzoic acidic benzene solution to yield $Pd(CO)(OCOC_6H_5)$.

The coordinated OAc groups in PCA are rather readily substituted by other acid anions. For example, PCA was recrystallized from CF_3COOH solution to give a crystalline complex of composition $Pd(CO)(OCOCF_3)$. The complexes of compositions $Pd(CO)(OCOCCl_3)$ and $Pd(CO)(OCOCH_2Cl)$ were obtained by recrystallization of PCA from benzene solutions containing CCl_3COOH and $CH_3ClCOOH$, respectively. The main IR frequencies of the CO and COO groups in the spectra of the above carbonylcarboxylates are very similar to ones of PCA. The similarity of the IR spectra, chemical composition and chemical behavior of these complexes suggests that all of them contain tetranuclear clusters analogous to PCA [3].

The accumulation of PCA in the $Pd(OAc)_2$ + CO reaction in acetic acid may be studied readily by observing the time dependence of the maximum of PCA absorption at 330 nm in the UV spectrum. A kinetic study showed that the rate of PCA accumulation obeys a total second order equation (Figs. 1 and 2):

$$W = k\left[Pd(OAc)_2\right][CO]$$

Palladium(II) acetate is a trimer in AcOH solutions at 25°C and dissociates slowly, even at higher temperature. Therefore, Pd^{II} acetate in the freshly prepared solution is assumed to be completely in the form of the trimer. For the reaction of CO with monomeric $Pd(OAc)_2$ one would expect the rate of PCA formation to be proportional to the Pd^{II} concentration to the power of $1/3$. The observed first order dependence on Pd^{II} and CO concentration shows that CO is coordinated to the $Pd_3(OAc)_6$ trimer.

The reaction of Pd^{II} acetate with CO was carried out in anhydrous benzene to identify intermediates of this complicated reaction. Benzene is known to be an inert solvent towards Pd^{II} [4], although its molecules able to coordinate to Pd in lower
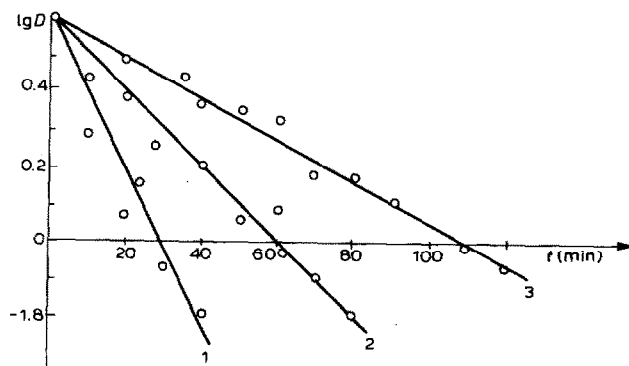

Fig. 1. $D^{(330)}$ vs. time in synthesis of PCA, $[Pd(OAc)_2] = 10^{-4}M$, 1 - $P(CO) = 0.70$ MPa, 2 - $P(CO) = 0.50$ MPa, 3 - $P(CO) = 0.25$ MPa, 40°C.

oxidation states [5]. Addition of benzene to $Pd(OAc)_2$ in acetic acid solution does not retard the PCA formation.

We found that CO absorption by benzene solutions of $Pd(OAc)_2$ at 60°C resulted
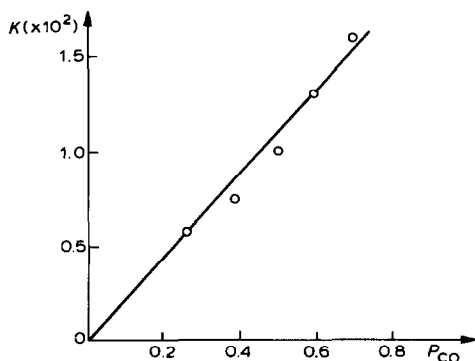

Fig. 2. Rate constant of PCA formation vs. partial pressure of CO, 40°C.

in no precipitation of metallic Pd, but that CO_2 appeared in the gaseous phase simultaneously with absorption of CO ($\geqslant 0.5$ mol/mol CO). Accordingly to reported data [6,7], Pd^{II} acetate under these conditions exists mainly in the monomeric form.

After treatment of $Pd(OAc)_2$ in benzene with carbon monoxide and low-temperature vacuum evaporation of the solvent, the IR spectrum of the dry (light brown) residue showed the band specific of a bridged CO group (1950 cm^{-1}) and the band at 1810 cm^{-1} due to the CO acetyl stretching modes. Thus one may conclude that after CO coordination to Pd^{II} CO is inserted into the Pd–O bond:

$$Pd(OAc)_2 + CO \rightleftarrows CO \cdot Pd(OAc)_2 \qquad (3)$$

$$CO \cdot Pd(OAc)_2 \rightarrow AcO-CO-Pd-OAc \qquad (4)$$
$$(I)$$

CO_2 is eliminated from complex I rapidly and irreversibly to give a σ-bonded acylpalladium derivative:

$$AcO-CO-Pd-OAc \rightarrow CO_2 + Ac-Pd-OAc \qquad (5)$$
$$(II)$$
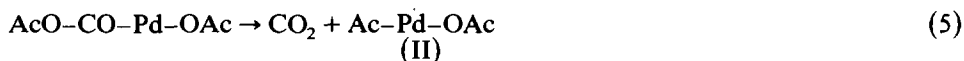
The value of $\nu(CO)$ (1810 cm^{-1}) for complex II is close to that observed for acetyl bound to a strongly electronegative group, e.g. in acetic anhydride (1810 cm^{-1}), or acetyl chloride (1815 cm^{-1}). This may be evidence for the strong electron attracting character of the Pd(OAc) group enhancing the carbonium ionic character of the CH_3CO group.

The formation of the acyl complex II was also confirmed by its in situ reactions with H_2O, ethanol, H_2, and alkali metal acetates. Equimolar quantities of acetic acid and metallic Pd were observed when H_2O was added to a benzene solution of II, prepared by reactions 3–5:

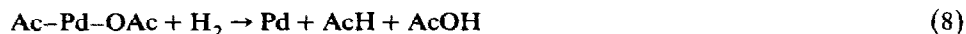$$Ac-Pd-OAc + H_2O \rightarrow Pd + 2AcOH \qquad (6)$$

A solution of complex II does not react with acetic acid (0.1–0.5 M in benzene).

Treatment of complex II with NaOAc in benzene yields an acetic anhydride in stoicheiometric quantity to the Pd metal formed:

$$Ac-Pd-OAc \xrightarrow{\text{NaOAc}} Pd + Ac_2O \tag{7}$$

A benzene solution of II treated with H_2 gives acetic acid and acetic aldehyde:

$$Ac-Pd-OAc + H_2 \rightarrow Pd + AcH + AcOH \tag{8}$$

The reaction of ethanol with a solution of II produced ethylacetate and acetic acid in equimolar quantities:

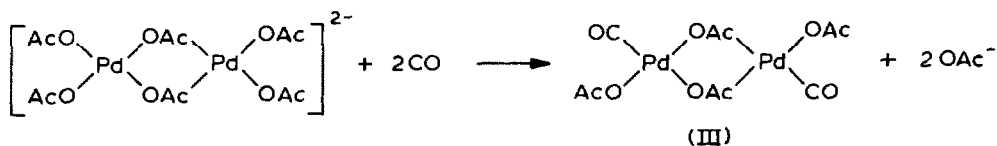$$Ac-Pd-OAc + C_2H_5OH \rightarrow Pd + AcOC_2H_5 + AcOH \tag{9}$$
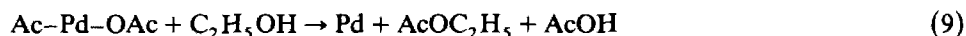
The products from reactions 6–9 were identified by GLC.

The stoichiometric and kinetic data shown above confirm that the reaction of trimeric Pd^{II} acetate with CO in AcOH proceeds via an acylic Pd complex. CO coordination to $Pd_3(OAc)_6$, resulting in cleavage of one acetate bridge in the trimeric Pd^{II} acetate, is suggested to be the rate limiting step. Cleavage of acetate bridges is proposed to have a high activation barrier. The subsequent fast reactions of the Pd^{II} carbonyl complex yielding a palladium acetyl complex are presumed to proceed retaining the trimeric structure. Volumetric and IR spectroscopy data show that the acyl complex also contains a bridging CO group.

A scheme of the formation of PCA is proposed to be as follows.

⌒ = bridging acetate group
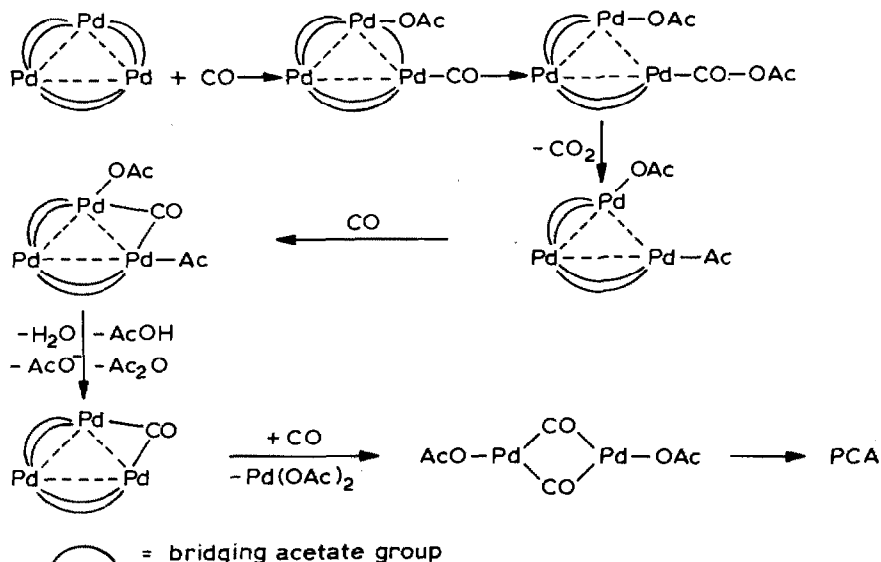
CO absorption by solutions of Pd^{II} acetate in AcOH is accelerated by alkali metal acetates due to depolymerization of the trimeric $Pd_3(OAc)_6$. The $Pd_2(OAc)_6^{2-}$ dimers with terminal OAc groups are the main forms of Pd^{II} in these solutions [6]. 1.0 mol CO per 1 g-at Pd is absorbed by these solutions at 40–60°C in 5–10 min. The maximum at 380 nm specific to the initial Pd^{II} acetate disappears upon CO absorption. Absorption due to complex III is negligable in the 300–700 nm region. After 10–15 min a peak appear at 330 nm due to formation of PCA. The optical

$$\begin{bmatrix} AcO & OAc & OAc \\ & Pd & Pd \\ AcO & OAc & OAc \end{bmatrix}^{2-} + 2CO \longrightarrow \begin{matrix} OC & OAc & OAc \\ & Pd & Pd \\ AcO & OAc & CO \end{matrix} + 2OAc^-$$
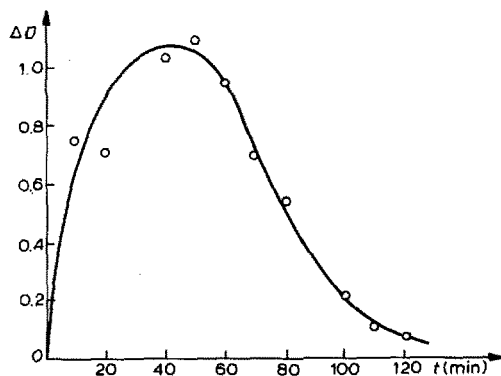
(III)

density at 330 nm vs. time has a maximum (Fig. 3).

Fig. 3. Kinetic curve for reaction of Pd^{II} acetate with CO in AcOH, $[Pd_3(OAc)_6]_0 = 0.3 \times 10^{-4}$ M, $[NaOAc] = 1$ M, 40°C.

The same products are formed both by decomposition of PCA and reduction of Pd(OAc)$_2$ by CO in the presence of NaOAc or H$_2$O:
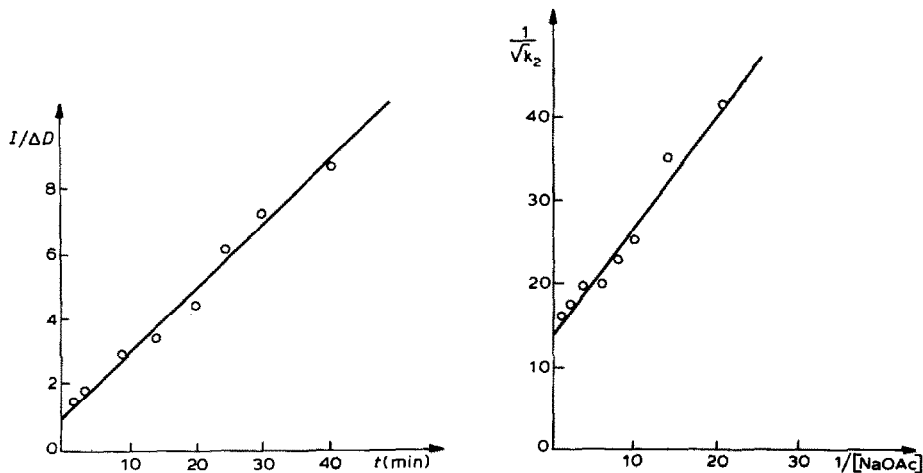
$$Pd(OAc)_2 + CO \xrightarrow{NaOAc} Pd + CO_2 + Ac_2O \tag{10}$$

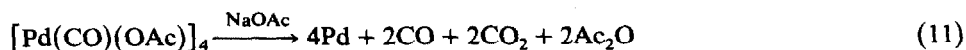$$[Pd(CO)(OAc)]_4 \xrightarrow{NaOAc} 4Pd + 2CO + 2CO_2 + 2Ac_2O \tag{11}$$

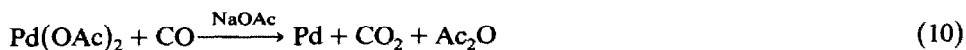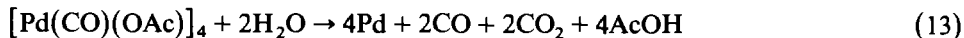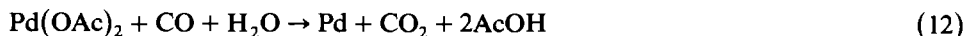
Fig. 4. Kinetics of PCA decomposition in the presence of NaOAc in AcOH, $[PCA]_0 = 10^{-4}$ M, $[NaOAc] = 1$ M, 60°C.
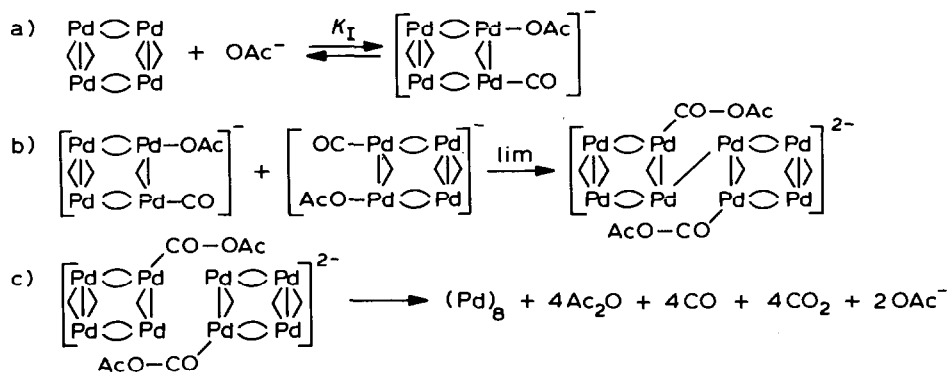
Fig. 5. The second order rate constant vs. NaOAc concentration in PCA decomposition in AcOH. $[PCA]_0 = 10^{-4}$ M, 60°C.

$$\text{Pd(OAc)}_2 + \text{CO} + \text{H}_2\text{O} \rightarrow \text{Pd} + \text{CO}_2 + 2\text{AcOH} \tag{12}$$

$$[\text{Pd(CO)(OAc)}]_4 + 2\text{H}_2\text{O} \rightarrow 4\text{Pd} + 2\text{CO} + 2\text{CO}_2 + 4\text{AcOH} \tag{13}$$

Thus, PCA may be proposed as an intermediate in the reaction of Pd[II] acetate with carbon monoxide.

The kinetic data on PCA decomposition in acetic acid solution in the presence of 0.1 to 1.0 M NaOAc showed (Figs. 4,5) that the rate of PCA decomposition at 60°C

Scheme 1

a) Pd◯Pd ⟨|⟩ ⟨|⟩ + OAc⁻ $\xrightarrow{K_I}$ [Pd◯Pd—OAc ⟨|⟩ ⟨| Pd◯Pd—CO]⁻
Pd◯Pd

b) [Pd◯Pd—OAc ⟨|⟩ ⟨| Pd◯Pd—CO]⁻ + [OC—Pd◯Pd |⟩ ⟨|⟩ AcO—Pd◯Pd]⁻ $\xrightarrow{\text{lim}}$ [Pd◯Pd ͵CO—OAc Pd◯Pd ⟨|⟩ ⟨|∕ |⟩ ⟨|⟩ Pd◯Pd Pd◯Pd AcO—CO͵]²⁻

c) [Pd◯Pd ͵CO—OAc Pd◯Pd ⟨|⟩ ⟨| |⟩ ⟨|⟩ Pd◯Pd Pd◯Pd AcO—CO͵]²⁻ $\longrightarrow$ (Pd)₈ + 4Ac₂O + 4CO + 4CO₂ + 2OAc⁻

Scheme 2

a) Pd◯Pd ⟨|⟩ ⟨|⟩ + OAc⁻ $\xrightarrow{K_I}$ [Pd⇔Pd—OAc () (Pd⇔Pd—OAc]⁻
Pd◯Pd

b) [Pd⇔Pd—OAc () (Pd⇔Pd—OAc]⁻ $\xrightarrow{K_{II}}$ [Pd⌢Pd—CO—OAc () (Pd⌣Pd—CO—OAc]⁻

c) [Pd⇔Pd—OAc () (Pd⇔Pd—OAc]⁻ + [AcO—CO—Pd⌢Pd) () AcO—CO—Pd⌣Pd]⁻ $\xrightarrow{\text{lim}}$ [Pd⇔Pd—Pd⌢Pd () () Pd⇔Pd—Pd⌣Pd] +

+ 2 Ac₂O + 2 CO₂⁻ + 2 OAc⁻

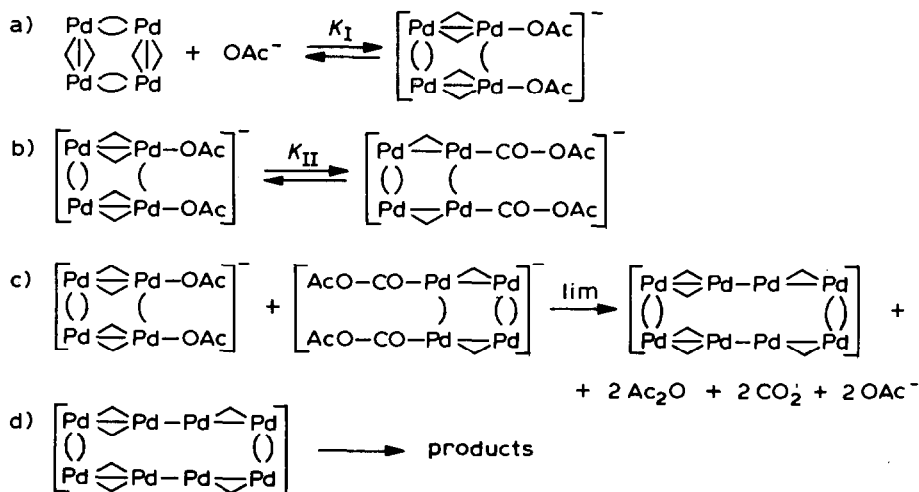d) [Pd⇔Pd—Pd⌢Pd () () Pd⇔Pd—Pd⌣Pd] $\longrightarrow$ products

Fig. 6. Mechanism of PCA decomposition in the presence of NaOAc. "◯"- bridged acetate groups, "⌢⌣"- bridged carbonyls.

obeys the following kinetic equation:

$$W = k_{eff.} [PCA]^2 \frac{[NaOAc]^2}{(1 + K[NaOAc])^2},$$ (14)

where $k_{eff.} = 78.4$ mol^3 l^{-3} sec; $K = 13.2$ mol^{-1} l.

Analysis of eq. 14 suggests a reaction mechanism in which PCA reacts with AcO$^-$ rapidly and reversibly in the first step. There are two variants possible of this step including cleavage of a carbonyl or acetate bridge under OAc$^-$ attack on the PCA molecule. In the first version (Fig. 6, Scheme 1) the limiting step is an insertion of one cluster in the Pd–O bond of another cluster giving rise to an octanuclear complex. In the other version (Fig. 6, Scheme 2) the reaction of two clusters with evolution of Ac$_2$O and CO$_2$ and formation of the same octanuclear cluster is the limiting step. The difference between Schemes 1 and 2 is in the type of the bridge (carbonyl or acetate) cleaved by OAc$^-$ attack on the PCA molecule. The formal oxidation state of Pd is decreased in both versions gradually as a result of a sequence of reactions: 1) CO coordination to Pd atom; 2) CO insertion via the Pd–terminal OAc group bond; 3) CO$_2$ elimination giving Pd–CO–CH$_3$; 4) elimination of Ac$_2$O and Pd–Pd bond formation.

The same sequence of reactions may also be true for the reduction of Pd^{II} to Pd^0 by carbon monoxide.

Experimental

The solvents were purified by described methods [8]. The complexes Pd(OAc)$_2$, Pd(OCOC$_2$H$_5$)$_2$, Pd(OCOC$_6$H$_5$)$_2$ and [Pd(CO)(OCOCH$_3$)]$_4$ were prepared by previously described methods [7,3]. IR spectra were obtained on a Specord IR-75 spectrophotometer.

Reaction of Pd(OAc)$_2$ with CO in benzene

A solution of 0.12 g (5×10^{-4} mol) of Pd(OAc)$_2$ in 10 ml of C$_6$H$_6$ was treated with CO at 1 atm in thermostated (60 ± 0.1°C) magnetically stirrer reactor equipped with a gas burette and a gas probe extractor. 2.0×10^{-4} mol CO was absorbed in 6 hours, and 1.0×10^{-4} mol CO$_2$ was detected by GLC. The solvent was removed under vacuo and 2 ml Nujol was added to the residue under CO. The suspension was smeared onto a KBr plate and the IR spectrum was recorded.

In other experiments the benzene solutions obtained as above was treated with H$_2$O, NaOAc, EtOH or H$_2$. The products were analysed by GLC.

Kinetic measurements

The preparation of PCA in AcOH was carried out in a thermostated (± 0.1°C) vessel with a magnetic stirrer and a gas burette and the optical density at 330 nm followed (λ_{max} for PCA) with a Specord UV-VIS spectrophotometer. Special experiments showed that the gas-liquid reaction proceeded in the kinetic regime at $\alpha < 0.5$ ($\alpha = V_1/V_0$, where V$_1$ is the volume of liquid phase, V_0 is total reactor volume), and n (number of revolutions of stirrer) $\geqslant 100$ min^{-1}.

The decomposition of PCA in AcOH was studied at 60°C in a thermostated reactor equipped with a magnetic stirrer, a probe extractor with a Schott filter, and a gas burette. The PCA concentration was followed by optical density at 330 nm.

Synthesis of complexes

[Pd(CO)(OCOC₂H₅)]₄. A solution of 1.26 g (5×10^{-3} mol) $Pd(OCOC_2H_5)_2$ in 100 ml C_2H_5COOH was treated with CO for three hours at 50°C. After cooling the solution, the precipitated $[Pd(CO)(OCOC_2H_5)]_4$ was filtered off and dried in vacuo. Yield 0.98 g. Found: C,23.60; H,2.50. $C_4H_5O_3Pd$ calcd.: C,23,19; H,2.42. ν(CO) 1935, 1968 cm^{-1}.

[Pd(CO)(OCOC₆H₅)]₄·2C₆H₅COOH. A solution of 1.00 g (3.4×10^{-3} mol) $Pd(OCOC_6H_5)_2$ and 5 g C_6H_5COOH in 100 ml benzene was treated with CO for 18–20 hours at 50°C. The solvent was removed under vacuo to one third of the initial volume and 50 ml of ether was added. After 3 days at 0°C a light brown precipitate was separated and dried in vacuo. Yield 0.25 g. Found: C,41.82; H,2.50. $C_{23}H_{16}O_8Pd_2$ calcd. C,42.67; H,2.21%. ν(CO) 1958, 1980 cm^{-1}.

[Pd(CO)(OCOCCl₃)]₄·2C₆H₆. 0.6 g (3×10^{-3} g-at Pd) of PCA was added to a solution of 1.2 g of CCl_3COOH in 500 ml of dry benzene. After 2 hours the solvent was evaporated in vacuo to one fifth of the initial volume. The fine yellow crystals were separated and dried in vacuo. Yield 0.35 g. Found: C,20.91; H,1.06; Cl,31.75. $C_{12}H_6Cl_6O_6Pd_2$ calcd.: C,21,42; H,0.90; Cl,31.69%. ν(CO) 1940, 1975 cm^{-1}.

$[Pd(CO)(OCOCH_2Cl)]_4 \cdot 2C_6H_6$ was prepared analogously to $[Pd(CO)-(OCOCCl_3)]_4$ from 0.6 g of PCA and 1.5 g of $CH_2ClCOOH$. Yield 0.31 g. Found: C,24.00; H,2.00; Cl,13.49; Pd,40.57. $C_{12}H_{10}Cl_2O_6Pd_2$ calcd.: C,22.96; H,1.87; Cl,13.29; Pd,39.88%. ν(CO) 1940, 1980 cm^{-1}.

[Pd(CO)(OCOCF₃)]₄. 0.2 g (1×10^{-3} g-at Pd) of PCA which was dissolved with slight heating in 20 ml of CF_3COOH contained 3% of $(CF_3CO)_2O$. The solvent was evaporated to 10 ml and the pale brown fine crystals were separated and dried in vacuo. Yield 0.06 g. Found: F,23.0; Pd,43.00. $C_3F_3O_3Pd$ calcd.: F,23.0; Pd,42.48%. ν(CO) 1970, 2005 cm^{-1}.

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