# REACTION BETWEEN CARBON MONOXIDE AND Pd(II) CARBOXYLATES IN NONAQUEOUS MEDIA

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Reduction of Pd(II) acetate with carbon monoxide in AcOH leads to palladium carbonyl acetate $[Pd(CO)(OAc)]_4$ (PCA) [1], and in the presence of alkali metal acetates, to metallic Pd and $Ac_2O$ [2]

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

To determine the mechanism of this reaction and the nature of the intermediate Pd complexes, we studied the kinetics of formation of PCA and also the stoichiometry of the reaction between $Pd(OAc)_2$ and CO in the presence and absence of AcOH.

## EXPERIMENTAL

Palladium acetate ($Pd(OAc)_2$) was obtained by oxidation of Pd black (from $PdCl_2$ and $NaBH_4$) with concentrated $HNO_3$ in glacial AcOH [3]. Carbon monoxide was obtained by dehydration of HCOOH by the action of concentrated $H_2SO_4$, and dried by passage through a trap, cooled to −70°C. Chemically pure benzene and AcOH were purified by standard methods [4].

The experiments were carried out in a thermostated reactor with a magnetic stirrer at 20 and 60°C; $Pd(OAc)_2$ and solvent were placed into the reactor, the system was evacuated, and CO passed in. Carbon monoxide absorption was followed from the change in the volume of the gas in a burette with benzene, used as reference liquid. The gas mixture was analyzed by gas chromatography (LKhM-8MD chromatograph, 2 m column, Polysorb-1, gas carrier He, heat conductivity detector), and probes of the gas were withdrawn from the reactor through a rubber membrane.

The products of the reaction of the acetyl complex with $H_2O$, NaOAc, $C_2H_5OH$, and hydrogen were determined by GLC (LKhM-8MD chromatograph, 3 m columns, Carbowax-20M on Chromaton and polyethylene glycol adipate on Chromaton, carrier gas He, heat conductivity detector).

To obtain the IR spectra from an acetyl complex solution, the solvent was distilled off in vacuo at 20°C, and mineral oil added to the reactor in a CO atmosphere to completely wet the precipitate. The suspension (precipitate + mineral oil) was transferred to KBr plates and the spectra were recorded on the "Specord IR-75" apparatus.

The kinetics of PCA formation was studied at 60°C on an apparatus consisting of a gasometer and a thermostatted reactor with a liquid sampler. PCA formation was followed from the change in the optical density at 330 nm, where an absorption maximum is observed of PCA dissolved in AcOH. Palladium acetate in AcOH was introduced into the reactor, which was evacuated, and gas was passed in. The gas mixtures were prepared in a gasometer by diluting CO with argon. The electronic spectra were taken on the "Specord UV-VIS" apparatus.

Since the reaction between $Pd(OAc)_2$ and CO proceeds in a two-phase gas–liquid system, to avoid diffusional retardation of the reaction, the solution was stirred with a magnetic stirrer. By varying the degree of filling of the reactor ($\alpha = 0.1$-$0.8$) and the number of rotations of the stirrer ($n = 60$-$500\ min^{-1}$), it was shown that at $\alpha \leqslant 0.5$ and $n \geqslant 100\ min^{-1}$ the reaction proceeds kinetically.

## DISCUSSION OF RESULTS

The kinetic experiments showed that the rate of PCA formation during the reaction between Pd(II) acetate and CO in AcOH solution obeys an overall second-order reaction (Figs. 1-3)

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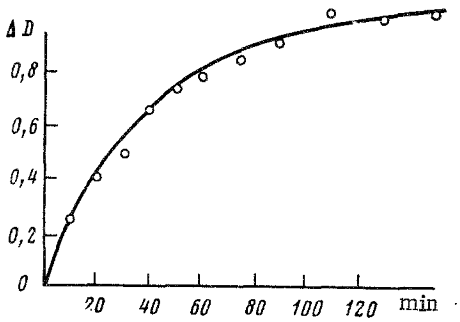


Fig. 1. Time dependent change in optical density (λ 330 nm) of $Pd_3(OAc)_6$ solutions in AcOH in reaction with CO ($[Pd_3(OAc)_6]_0 = 0.67 \cdot 10^{-3}$ M; 50°C).

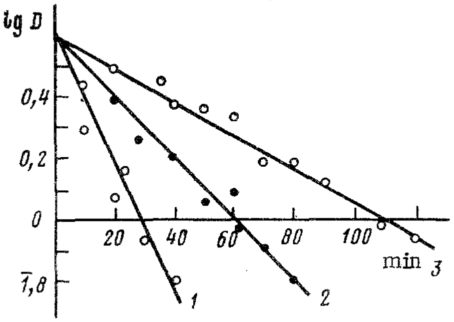


Fig. 2

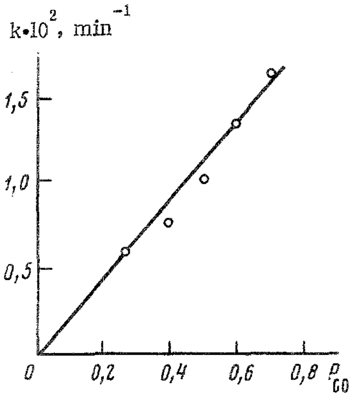


Fig. 3

Fig. 2. Dependence of the logarithm of optical density (λ 330 nm) of solutions on time at $P_{CO}$, MPa: 1) 0.07; 2) 0.05; 3) 0.025 ($[Pd_3(OAc)_6]_0 = 0.67 \cdot 10^{-3}$ M; 50°C).

Fig. 3. Dependence of first-order reaction constant on partial pressure of CO ($[Pd_3(OAc)_6]_0 = 0.67 \cdot 10^{-3}$ M; 50°C).

$$W = k\,[\mathrm{Pd\,(OAc)_2}]\,[\mathrm{CO}]$$

Since in AcOH solutions at 25°C, Pd(II) acetate is completely trimeric [5], and its autodissociation proceeds very slowly even at elevated temperatures, we can assume that in freshly prepared solutions used by us, Pd(II) acetate is completely present in the form of a trimer. If CO reacts with monomeric $Pd(OAc)_2$, then irrespective of whether a coordination takes place slowly or rapidly between CO and Pd(II) acetate, or whether this stage is limiting, a proportionality would be expected between the rate of formation of PCA and Pd(II) concentration to the extent of 1/3. The observed first orders with respect to Pd(II) and CO concentrations indicate that CO is coordinated with $Pd_3(OAc)_6$.

The study of the kinetics and mechanism of this reaction is complicated by the fact that its rate and direction are substantially affected by the $H_2O$ content in AcOH. Increasing $H_2O$ concentration from 0.05 to 0.5% ($10^{-2}$–$10^{-1}$ M) increases the rate of PCA formation, and at higher $H_2O$ concentration a considerable amount of metallic Pd is formed, although PCA solutions in AcOH containing 0.5–1% of $H_2O$ are stable toward decomposition to metal for a long time.

To find intermediate compounds in this complex reaction, we studied the reaction between Pd(II) acetate and CO in anhydrous benzene. The choice of this solvent is determined by the fact that benzene is relatively inert toward Pd(II) compounds [6], and can coordinate with Pd complexes only in lower oxidation states [7], while the addition of benzene to acetic acid solutions of $Pd(OAc)_2$ does not deter PCA formation.

It is known that at elevated temperatures, benzene slowly reduces $Pd(OAc)_2$ with the formation of metallic Pd and biphenyl [8]. We therefore chose conditions (not more than 5 h at 60°C, and not more than 30 h at 20°C) under which $Pd(OAc)_2$ is not reduced by benzene.

We found that at 20°C, 0.1–0.4 M $Pd(OAc)_2$ solutions in dry benzene at $P_{CO}$ = 0.1 MPa do not absorb CO above the physical solubility for 10–20 h. At 60°C, CO is slowly (0.04 mole

CO/mole Pd·h) absorbed by these solutions, and simultaneously with the beginning of the CO absorption, $CO_2$ appears in the gas phase ($\lesssim 0.5$ mole/mole CO), while metallic palladium does not separate.

After treating the benzene solution of $Pd_3(OAc)_6$ with CO, and low-temperature vacuum distillation of the solvent, a band at 1950 $cm^{-1}$ is observed in the IR spectrum, which is characteristic of the bridged CO group [9]; another band at 1810 $cm^{-1}$ can be related to the stretching vibrations of the acetyl CO group. Therefore, we can conclude that the coordination of CO with Pd(II)

$$Pd_3(OAc)_6 + CO \rightarrow CO \cdot Pd_3(OAc)_6 \qquad (2)$$

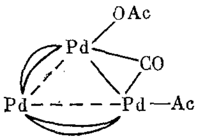
is followed by the penetration of CO into the Pd—O bonds,

$$CO \cdot Pd_3(OAc)_6 \rightarrow \underset{(I)}{AcO{-}CO{-}Pd(OAc) \cdot Pd_2(OAc)_4} \qquad (3)$$

and complex (I) rapidly and irreversibly splits off $CO_2$ with the formation of a σ-bond acyl derivative of palladium

$$AcO{-}CO{-}Pd(OAc) \cdot Pd_2(OAc)_4 \rightarrow CO_2 + Ac{-}Pd(OAc) \cdot Pd_2(OAc)_4 \qquad (4)$$

Data on the stoichiometry and kinetics of the reaction between CO and Pd(II) acetate to form PCA leads to the conclusion that this process is limited by the stage of coordination of CO with $Pd_3(OAc)_6$, accompanied by a cleavage of one acetate bridge. It is possible that the cleavage of the acetate bridges in trimeric Pd(II) acetate requires a considerable activation energy, and it can be assumed that further, more rapid transformations of the carbonyl complex with Pd(II), leading to the acetyl derivative of palladium, proceed with the retention of the trimeric structure of the complex.* Since the number of g-moles of $CO_2$ liberated during the formation of the trimeric complex is about half that of the absorbed CO, whereas coordinated CO is, according to the IR data, of the bridged type, the acetyl complex has probably the form of a trimer of type (II)†



(II)

which will be represented here by the formula Ac-Pd(OAc)X, where X = $Pd_2(\mu\text{-}CO)(\mu\text{-}OAc)_4$.

The value of νCO (1810 $cm^{-1}$ for complex (II)) is close to that observed for compounds where the acetyl group is bound to a strong electronegative grouping, for example, in $Ac_2O$ (1810 $cm^{-1}$) or AcCl (1815 $cm^{-1}$), which suggests strong electron-acceptor properties of the $Pd_3(OAc)_5$ grouping, intensifying the carbonium ion character of the $CH_3CO$ group.

The formation of the acyl complex (II) is also indicated by its reaction in situ with water, ethanol, $H_2$, and alkali metal acetates. When $H_2O$ is added to a solution of (II) obtained by reactions (2)-(4) in benzene, metallic palladium rapidly separates out, and an equimolar amount of AcOH is formed:

$$AcPd(OAc)X + H_2O \rightarrow Pd + 2AcOH \qquad (5)$$

The solution of complex (II) does not react with AcOH (0.1-0.5 M in benzene).

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*Here and below, it is assumed that all the groups in the initial trimer $Pd_3(OAc)_6$ are of the bridged type, except for two of them which directly participate in the reaction all remaining groups are bidentate-coordinated bridged.

†Here and below, the bidentate-coordinated bridged OAc groups are indicated by an arc.

The reaction with NaOAc, KOAc, or $(t\text{-}Bu)_4NOAc$ in benzene and AcOH leads to a stoichiometric amount of $Ac_2O$, based on the amount of metallic Pd formed.

$$AcPd(OAc)X + OAc^- \rightarrow Pd + Ac_2O + OAc^- \tag{6}$$

$H_2$ reacts with the benzene solution of (II) to give AcOH and acetaldehyde:

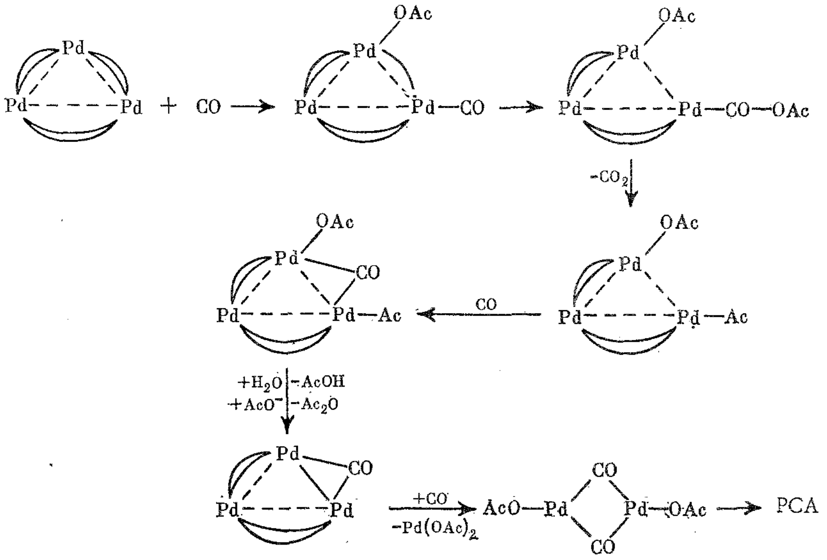
$$AcPd(OAc)X + H_2 \rightarrow Pd + AcH + AcOH \tag{7}$$

Ethanol reacts with the solution of (II) to form equimolar amounts of ethyl acetate and AcOH:

$$AcPd(OAc)X + C_2H_5OH \rightarrow Pd + AcOC_2H_5 + AcOH \tag{8}$$

During contact of CO with Pd(II) acetate solutions in AcOH containing 0.05% ($10^{-2}$ M) of $H_2O$, apart from PCA, after 2-4 h at 20°C or 1-2 h at 60°C, metallic Pd begins to separate out. Both $Ac_2O$ and other transformation products of the acetate ligands are absent in the liquid phase (except for AcOH, the change in the concentration of which cannot be measured in this case). Carbon dioxide appears in the gas phase earlier, even before the formation of trace amounts of metallic Pd could be observed.

The asynchronous character of the separation of metallic Pd and $CO_2$ shows that both in AcOH and in benzene the reaction between CO and $Pd_3(OAc)_6$ proceeds via an intermediate formation of an acyl derivative of palladium:



## CONCLUSION

1. The reduction of palladium(II) acetate by carbon monoxide is limited by the reaction between trimeric palladium acetate molecules and carbon monoxide molecules.

2. The reaction between palladium(II) acetate and carbon monoxide proceeds via the intermediate formation of an acyl complex with palladium.

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# REDUCTION OF CYANIDE AND ACETONITRILE BY PROTON NIGROGEN-FIXATION SYSTEMS

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The physiological function of the enzyme nitrogenase consists in the reduction of $N_2$ to $NH_3$ but, in the fermentation system, it is also possible to observe a number of other reduction reactions [1]. For instance, HCN or $CN^-$ which is in equilibrium with it, gives mainly six-electron reduction products, although a little methylamine is formed simultaneously

$$CN^- + 6e + 7H^+ \rightarrow CH_4 + NH_3 \qquad (1)$$

$$CN^- + 4e + 5H^+ \rightarrow CH_3NH_2 \qquad (2)$$

Acetonitrile is also reduced with the participation of six electrons to $C_2H_6$ and $NH_3$.

When the reactions of the enzyme nitrogenase and model proton nitrogen-fixation systems [2] were compared we studied the reaction of $CN^-$ and $CH_3CN$ in model systems based on V(II), Cr(II), and Ti(III).

## EXPERIMENTAL

$VSO_4 \cdot 7H_2O$ was synthesized by electric reduction of vanadium sulfate. Hydrochloric acid solutions of $TiCl_3$ and $CrCl_2 \cdot 4H_2O$ were prepared by dissolving metallic Ti and Cr in aqueous HCl. The starting solutions were prepared and stored in a box with Ar and two- or three-component Rittenberg vessels in which the experiments were carried out were filled with them. The total volume of the aqueous reaction solutions or mixtures was usually 10 ml and their content of V(II), Ti(III), or Cr(II) was 0.5 mmole. The gaseous reaction products were separated by a Tepler pump and analyzed by GC or mass spectrometrically. To record the PMR spectra, using a Bruker SXP-4-100 spectrometer, the volatile reaction products were frozen in a well-pumped system in the receiver containing 1.5 ml of 0.1 N HCl and immersed in liquid nitrogen; the resulting solution was evaporated to dryness and the dry residue was dissolved in 0.6 ml of an 0.05 M solution of acetone in $D_2O$.

## DISCUSSION

Catechol complexes with V(II) formed by mixing solutions of V(II) salts with alkaline solutions of catechol in water or methanol effeciently reduce $N_2$ and, in the absence of substrates, they react with the protons in the medium [2]

$$2V(II) + 2H^+ \rightarrow 2V(III) + H_2 \qquad (3)$$

KCN and acetonitrile, even with V(II)/substrate proportions of $\approx 2-3.5$, almost completely suppress reaction (3), which is comparatively slow at pH $\leqslant 13$. The yellow or red coloration of the complexes, generated by mixing aqueous solution of 0.5 mmole V(II), 5 mmole of pyrocatechol, and 5-8 mmole of NaOH (pH ~ 10-13), changes rapidly to green V(III) complexes when an 0.15 mmole solution of KCN or $CH_3CN$ is added. The following results confirm the formation of methylamine from cyanide and ethylamine from acetonitrile. Both products diffuse readily from the reaction solutions and are absorbed by dilute solutions of acid at about 20°C; they are also frozen out together with the water. During chromatography on paper they have the same

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