KINETICS OF THE REDUCTIONAL DECOMPOSITION OF PALLADIUM (I) CLUSTERS UNDER THE ACTION OF SODIUM ACETATE

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The carbonylacetate of Pd(I), $[Pd(CO)(OAc)]_4$ (I), undergoes oxidation-reduction decomposition in the presence of nucleophilic reagents such as the alkali metal acetates [1]

$$[Pd(CO)(OAc)]_4 = Pd(0) + 2CO + 2CO_2 + 2Ac_2O. \quad (1)$$

Acetic anhydride and CO_2 are also formed in the reduction of Pd(II) acetate by carbon monoxide in the presence of the alkali metal acetates [2]

$$Pd(OAc)_2 + CO = Pd\,(0) + CO_2 + Ac_2O \quad (2)$$

We have attempted to bring out the role played by compound (I) as an intermediate in the oxidation of CO by Pd(II) acetate by studying reactions (1) and (2) in acetic acid solutions containing AcONa.

EXPERIMENTAL

The $Pd(OAc)_2$ (II) used here had been prepared by oxidizing Pd-black (itself obtained from $PdCl_2$ and $NaBH_4$) with a concentrated solution of HNO_3 in glacial AcOH, following the procedure of [3]. The CO was prepared by dehydrating HCOOH with concentrated H_2SO_4, the product so obtained being purified by passage through a trap cooled to −70°C. The AcOH was a cp product which had been purified by the method of [4].

Mass balance experiments were carried out in a thermostatted reactor equipped with a magnetic stirrer which was loaded with the NaOAc and AcOH and heated to 60°C, compound (I) being added once the NaOAc had passed into solution. The evolution of CO and CO_2 was followed by measuring volumes in a gas buret, using benzene as the sealing fluid. The gaseous mixtures were analyzed by LG chromatographic methods (LKhM-8MD chromatograph, 2-m column, Polysorb-1, He carrier gas, katharometer), samples being withdrawn from the reactor through a rubber membrane. The liquid reaction products were also analyzed chromatographically (LKhM-8MD chromatograph, 3-m column, Carbowax 20M on Chromaton, He carrier gas, katharometer).

The kinetics of the reaction of compound (I) with CO in the presence of NaOAc, and the kinetics of the decomposition of (I), were studied at 60°C, working in a system consisting of a thermostatted reactor equipped with a magnetic stirrer, a liquid sampler equipped with a Shott filter, and a gas buret. Solutions of compound (I) and NaOAc in AcOH were prepared gravimetrically immediately before use. The alteration in the concentration of compound (I) with the passage of time was followed by measuring the optical density at 330 nm, the adsorption maximum in the spectrum of acetic acid solutions of the compound. The electronic spectra were obtained with a Specord UV-VIS spectrometer.

DISCUSSION OF RESULTS

Carbon monoxide is slowly absorbed by AcOH solutions of Pd(II) acetate containing the $Pd_3(OAc)_6$ trimer [5]. According to [6], depolymerization of the trimer with formation of the acetocomplex takes place in AcOH solutions containing NaOAc at 0.1-1.0 M concentration, almost all of the Pd(II) existing as $Pd_2(OAc)_6^{2-}$ when $[Pd]_\Sigma = 0.01\text{-}0.1$ M.

The presence of NaOAc markedly increases the rate of CO absorption in these solutions. Experiment shows that 0.025-0.1 M solution of Pd(II) acetate containing NaOAc at 1 M concentration will take up 1 mole of CO for

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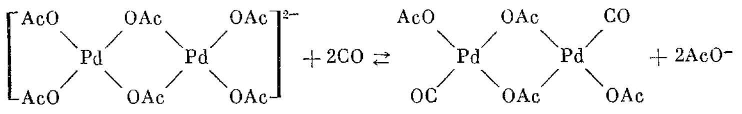
each 1 g-atom of Pd in the course of 5-10 min. The fact that neither CO_2 nor metallic Pd are formed here suggests that reaction proceeds according to the following scheme



(3)

Carbon dioxide begins to appear in the gaseous phase as soon as the absorption of CO is completed but no metallic Pd is formed. The characteristic Pd(II) maximum at 360 nm does not appear in the electronic spectrum of the transparent solution at this stage of the reaction. A maximum at 330 nm does appear, however, as soon as the evolution of CO_2 begins, its intensity increasing for 40-50 min, and then diminishing (Fig. 1). The position of the maximum in this spectrum is the same as that of the maximum in the electronic spectrum of compound (I) in AcOH solution. Metallic Pd begins to form, and the reaction mass darkens, 20-30 min after the absorption of CO ceases.

These facts suggest that formation of the CO-Pd(II) acetate complex through reaction (3) leads to the reduction of Pd(II) to Pd(I) and the formation of compound (I), the latter eventually breaking down to metallic Pd. This would be consistent with the fact that the same product is formed in the breakdown of compound (I) under the action of NaOAc as is formed in the reduction of $Pd(OAc)_2$ by carbon monoxide in the presence of NaOAc [reactions (1) and (2)].

Study of the kinetics of the reductional decomposition of compound (I) under the action of NaOAc according to reaction (1) gave information concerning the mechanism of the reduction of the Pd(I) carboxylate complex by carbon monoxide. This work showed that at 60°C the breakdown of (I) according to Eq. (1) is a second-order process with respect to the compound itself (Fig. 2)

$$W = -d\,[(\mathrm{I})]/dt = k_2\,[(\mathrm{I})]^2 \tag{4}$$

The observed second-order rate constant, k_2, increases linearly with an increase in the NaOAc concentration but becomes essentially constant at $[\mathrm{NaOAc}] \geq 0.4$ M. The relation in question here can be linearized by plotting in $k_2^{-1/2} - 1/[\mathrm{NaOAc}]$ coordinates (Fig. 3). The rate of breakdown of compound (I) satisfies a kinetic equation of the form

$$W = k_{\mathrm{ef}}\,[\mathrm{I}]^2 \frac{[\mathrm{NaOAc}]^2}{(1 + K\,[\mathrm{NaOAc}])^2} \tag{5}$$

with k_{ef} = 78.4 mole^3/(liter^3 · sec) and K = 13.2 liter/mole.

It could have been expected that the cluster containing four metal atoms would undergo intramolecular breakdown after attack by a OAc^- ion. However, the fact that the rate of breakdown of compound (I) was proportional to the concentration suggested that breakdown proceeds through breakdown of the carbonyl, or acetate, bridges in a process involving either two of the cluster molecules or the products resulting from cluster interaction with the OAc^- ions. Scheme A shows penetration of the terminal group of one cluster along a Pd–O bond of another cluster with formation of an eight-membered complex as the limiting step in the decomposition. Here the expression for the reaction rate takes the form

$$W = k_2 K_{\mathrm{I}}^2\,[\mathrm{I}]_\Sigma^2\,\frac{[\mathrm{NaOAc}]^2}{(1 + K_{\mathrm{I}}\,[\mathrm{NaOAc}])^2} \tag{6}$$

in which k_2 is the rate constant for the limiting step of reaction (2) and K_I is the equilibrium constant for step (I) in Scheme A.

Scheme B, a second variant of the decomposition process shows the reaction rate as limited by the interaction of two clusters with the production of Ac_2O and CO_2 and formation of an eight-membered complex, just as in Scheme A. Here the mass balance equation takes the form

$$[(\mathrm{I})]_\Sigma = [(\mathrm{I})] + [(\mathrm{I})\cdot\mathrm{OAc}] + [(\mathrm{I})\cdot\mathrm{OAc}^*] \tag{7}$$

It was reasonable to assume that the values of

$$K_{\mathrm{I}} = \frac{[(\mathrm{I})\cdot\mathrm{OAc}]}{[(\mathrm{I})]\,[\mathrm{OAc}^-]}, \quad K_{\mathrm{II}} = \frac{[(\mathrm{I})\cdot\mathrm{OAc}^*]}{[(\mathrm{I})\cdot\mathrm{OAc}]}$$

the equilibrium constants for the first and second stage of the reaction, would be such that $K_{II} \ll K_I$, the equilibrium concentration $[(I) \cdot OAc^*]$ being negligibly low in comparison with the equilibrium concentrations of the

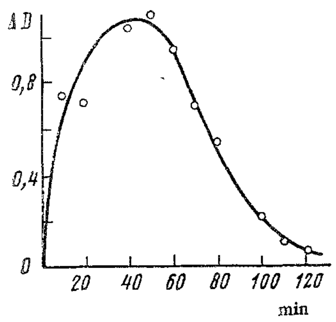


Fig. 1

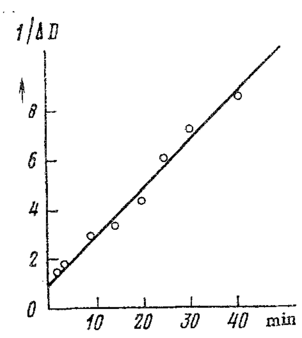


Fig. 2

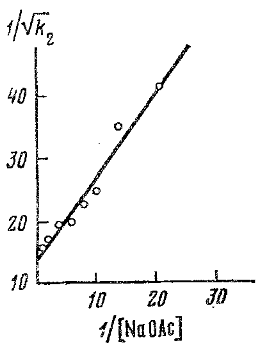


Fig. 3

Fig. 1. Time variation of optical density at 330 nm resulting from the absorption of compound (I) during reaction of Pd(II) acetate ($[Pd(OAc)_2] = 10^{-4}$ M) with CO in AcOH solution containing NaOAc at 1 M concentration, at 60°C and a CO pressure of 0.1 MPa.

Fig. 2. Time variation of the reciprocal of optical density at 330 nm during reductional decomposition of compound (I) by NaOAc in AcOH. $[I]_0 = 10^{-4}$ M, [NaOAc] = 1 M, 60°C.

Fig. 3. Second-order breakdown of compound (I) by NaOAc in AcOH vs. NaOAc concentration in the coordinates of Eq. 5.

other two forms appearing in the mass balance equation. On this basis, the concentrations [(I) · OAc] and [(I) · OAc*] could be expressed as

$$[(I)\cdot OAc] = \frac{K_I[(I)]_\Sigma[OAc^-]}{1+K_I[OAc^-]}\,;\ [(I)\cdot OAc^*] = K_{II}[(I)\cdot OAc]$$

with the rate equation taking the form

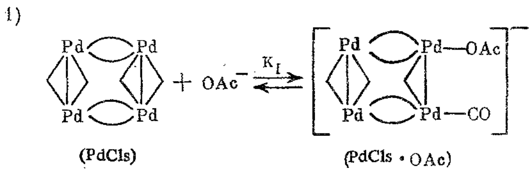
$$W = k_2K_I{}^2K_2\,[(I)]_\Sigma{}^2\,\frac{[NaOAc]^2}{(1+K_I\,[NaOAc])^2}\,. \tag{8}$$

The kinetic equations (6) and (8), of the respective variant schemes are formally identical with (5), the experimentally developed relation. For Scheme A, $k_{ef} = k_2K_I^2$, while for Scheme B $k_{ef} = k_2K_I^2K_{II}$.

The difference between Scheme A and Scheme B is determined by the type of bridging, the carbonyl or the acetate, broken down in OAc^- attack on the Pd(I) carbonylacetate. In turn, CO penetration along the Pd-OAc bond can proceed intermolecularly, in the limiting state of the reaction, or intramolecularly, in the rapid reversible step proceeding the limiting stage.

It seems unlikely that subsequent steps in the reduction to Pd(O) would lead to the degradation of the polynuclear system. It is more reasonable to assume that the oxidation state of the Pd atoms would decrease gradually, while the metallic skeleton of the complex was being extended through repeated cycling of the type: 1) penetration of CO along the bond between the Pd atom and the terminal OAc group; 2) elimination of CO_2 with the formation of a $Pd-CO-CH_3$ fragment; 3) formation of Ac_2O with establishment of a Pd−Pd bond. So considered, this is a reductional condensation of the palladium clusters. It is likely that a similar sequence of reactions of type 1-3 is involved in the reduction of Pd(II) to Pd(0) by carbon monoxide. The polynuclear palladium complexes formed in these systems seem to be promising catalysts [7-9].

Scheme A †



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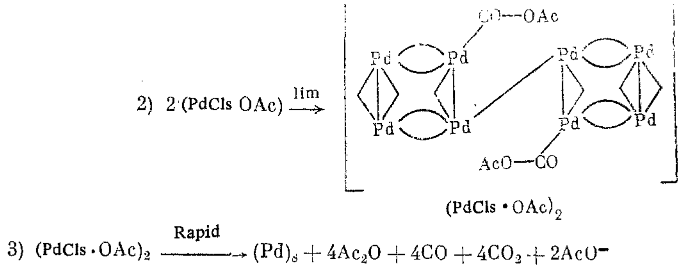
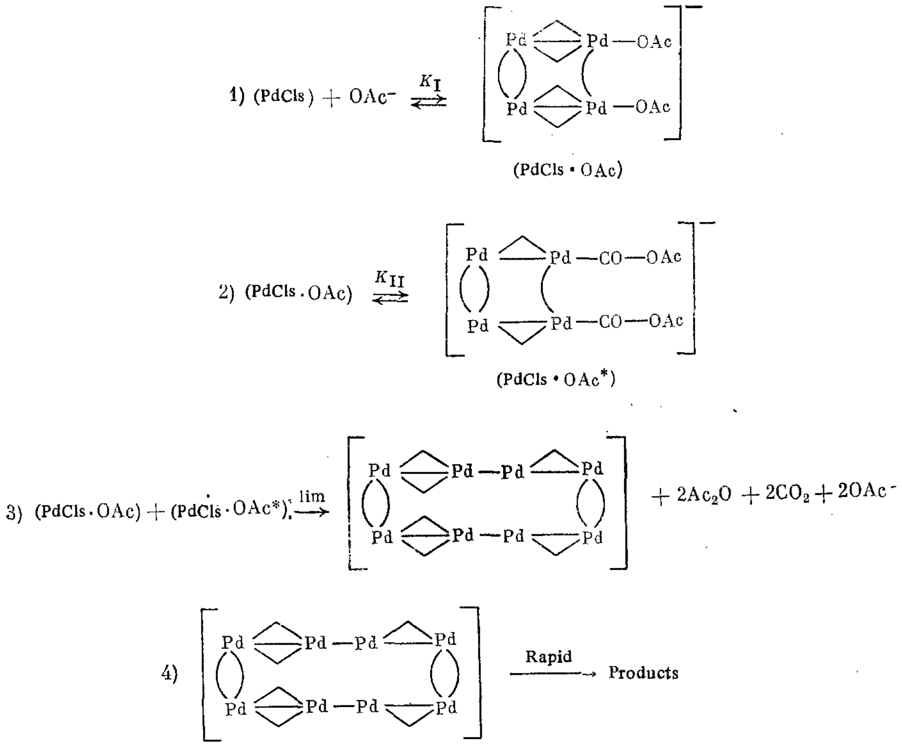
†The asterisk designates a bridging acetate group, the angle sign a bridging carbonyl group.



Scheme B



CONCLUSIONS

1. The carbonylacetate of Pd(I) is an intermediate product in the reduction of Pd(II) acetate by carbon monoxide in acetic acid solutions containing sodium acetate.

2. The kinetic data indicate that reductional decomposition of Pd(I) clusters is a reductional condensation process, in which a decrease in the oxidation state of the atomic palladium and stepwise growth of the metallic cluster skeleton proceed simultaneously.

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