

FORMATION OF ACETALS FROM CARBONYL COMPOUNDS AND ALCOHOLS  
IN THE PRESENCE OF GIGANTIC PALLADIUM CLUSTERS AND PALLADIUM  
BLACK

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Gigantic Pd clusters having idealized formulas of  $\text{Pd}_{561}\text{Phen}_{60}(\text{OAc})_{180}$  (I) [1] and  $\text{Pd}_{561}\text{Phen}_{60}\text{O}_{60}(\text{PF}_6)_{60}$  (II) [2] (Phen = 1,10-phenanthroline) catalyze the oxidation by oxygen of primary alcohols into esters; at the same time aldehydes and the corresponding acetals are also formed [3]. It can be assumed that the formation of the latter in the presence of clusters (I) and (II) is a result not of the oxidative transformations of the starting alcohols, but of a nontypical acetalization by these catalysts of the carbonyl compounds, the reaction of which is usually catalyzed by acids [4, 5].

To verify this hypothesis, we studied the reaction of aldehydes and ketones with alcohols under anaerobic conditions in the presence of (I) and (II), and also Pd-black having a nature similar to these clusters.

#### EXPERIMENTAL

Clusters (I) and (II) were synthesized by methods described in [2, 3]. Samples of Pd-black were prepared by reduction of  $\text{PdCl}_2$  by three methods.

A. A 5 g portion of  $\text{PdCl}_2$  in 150 ml of 5% hydrochloric acid was neutralized by aqueous KOH to pH 8, and  $\text{NaBH}_4$  was added with stirring to the complete precipitation of Pd black, which was separated and washed by decantation with  $10 \times 500$  ml of water to a negative reaction for the  $\text{Cl}^-$  ions, filtered, and dried in vacuo over  $\text{P}_2\text{O}_5$  at  $20^\circ\text{C}$ .

B. A 10 ml portion of an 80% hydrazine hydrate was added to a suspension obtained after the neutralization by alkali according to method A, and the mixture was held for 10 min at  $60^\circ\text{C}$ . Subsequent operations were carried out as in method A.

C. A 20 g portion of potassium formate in 50 ml of water was added to a suspension obtained by the neutralization by alkali according to method A, and the mixture was stirred for 10 min at  $60^\circ\text{C}$ . Subsequent operations were according to method A.

The experiments on the acetalization of the carbonyl compounds were carried out in a thermostated reactor of "catalytic long-necked hydrogenation flask" type at  $25$ - $50^\circ\text{C}$ , in an Ar atmosphere. The rate of the reaction was monitored according to the formation of the acetal or ketal, the content of which was determined by GLC on a "Biochrom 1" chromatograph ( $70^\circ\text{C}$ , a  $500 \times 0.3$  cm column, 10% dinonyl phthalate on chromatone, catharometer, carrier gas helium). In inhibition experiments, the suspension of Pd-black was allowed to stand before the experiment for 30 min at  $50^\circ\text{C}$  in an alcoholic solution of pyridine.

During the potentiometric titration, the pH value was measured by means of a pH-340 potentiometer (an ESL-41G-05 glass electrode and an EVL-1M3 silver chloride electrode).

#### RESULTS AND DISCUSSION

The experiments showed that (I) and (II) effectively catalyze the formation of acetals and ketals in neutral alcoholic solutions of acetaldehyde and acetone (Table 1). Unlike (I), cluster (II) is insoluble in the reaction medium, but nevertheless in its presence, both the initial rates (Table 1) and the degree of conversion are, for the same time of reaction, markedly higher than for (I).

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TABLE 1. Initial Specific Rates ( $W_0$ , mole/liter·min·g Pd) of the Formation of Acetals in the Presence of Clusters (I), (II) and Pd-Black Obtained by Methods A, B, C

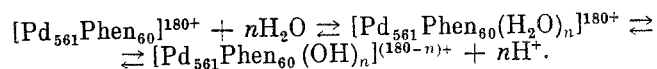
Catalyst	Carbonyl compound	Alcohol	$T_s$ , °C	$W_0$
(I)	CH <sub>3</sub> CHO	C <sub>2</sub> H <sub>5</sub> OH	25	0.052
(II)	»	»	25	0.63
(II) (neutral KOH)	»	»	25	0.77
(I)	»	»	50	0.21
(II)	(CH <sub>3</sub> ) <sub>2</sub> CO	CH <sub>3</sub> OH	25	3.3
(I)	»	»	25	0.068
(II)	CH <sub>3</sub> CHO	»	25	12.3
Pd-black (A)	»	C <sub>2</sub> H <sub>5</sub> OH	50	0.24
Pd-black (B)	»	»	50	0.054
Pd-black (C)	»	»	50	0.12

A close to equilibrium yield (90-95%) of the acetalization products is achieved at 25-50°C in the course of 10-120 min not only for the reagents shown in Table 1, but also when propionaldehyde and benzaldehyde are used as the carbonyl compounds, and benzyl alcohol and ethylene glycol as alcohols. This indicates the general character of the reaction, catalyzed by clusters (I) and (II).

The conventional catalysts for the acetalization of carbonyl compounds by alcohols are protonic and aprotic acids, including transition metal compounds [4, 5]. In this connection, it was of interest to study the acidic properties of (I) and (II).

The experiments have shown that after a sample of (I) or (II) is introduced into distilled water (pH 6.1), the pH value sharply decreases to 5.5 and 3.9, respectively. The  $pK_a$  values: 4.2 for (I) and 3.8 for (II), were found by potentiometric titration with a KOH solution; the number of proton-donor centers, calculated per molecule of the two clusters is equal to  $10 \pm 3$ .

The Bronsted acidity may possibly be determined by reactions of (I) and (II) with water, substituting a part of the acido ligands by OH<sup>-</sup> anions



The molecules of Phen are coordinated by the metal skeleton of clusters (I) and (II) [1, 2]. On vigorous stirring of (II) with water, in which the cluster is insoluble, in the pH range of 2 to 12 (HCl, KOH) for at least 1 h, even trace amounts of Phen or its hydrochloride, which could be detected spectrophotometrically at 280-360 nm, did not separate out into the aqueous phase. Thus, the Phen molecules remain strongly bound with the metal skeleton of the cluster. Under these conditions, (II) retains not less than 99% of the ligands, and the molecule of Phen does not participate in the observed protolytic transformations.

From these data it would appear that the catalytic activity of (I) and (II) could be related to their Bronsted acidity, which is manifested not only in aqueous, but also in alcoholic solutions. However, further experiments have shown that after treatment of (II) with an aqueous solution of KOH until pH 10 is reached, i.e., after complete neutralization of all the protonic centers, followed by removal of water and drying at 20°C in vacuum, the cluster which had passed into a basic form, displayed practically the same catalytic activity with respect to the acetalization of acetaldehyde by ethanol as the initial sample (Table 1). The time to reach the equilibrium composition of the reaction medium also did not change.

It was shown that also Pd-black can be successfully used as a catalyst for the synthesis of acetals. The three samples of Pd-black obtained by different methods (see the experimental part), exhibited a catalytic activity in the acetalization of acetaldehyde, which approached the activity of the clusters (Table 1).

In contrast to (I) and (II), the Pd-black samples studied almost do not change the value of pH on contact with distilled water, while the curves of the potentiometric titration by a KOH solution for these Pd-blacks almost coincide with the pH changes for pure water. A small deviation in the curve, only slightly exceeding the error in the determination of pH, was detected for the Pd-black A only.

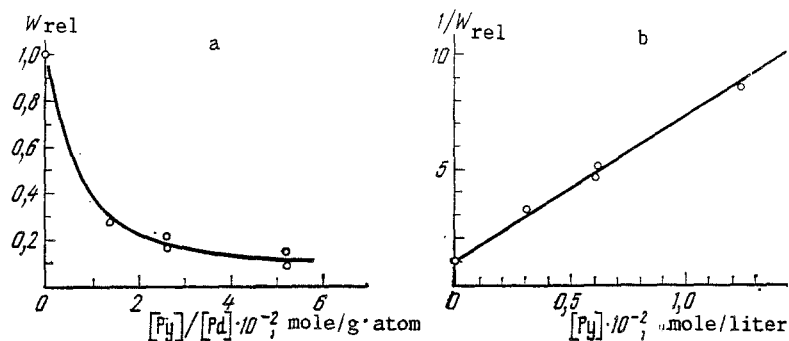


Fig. 1. Dependence of relative initial rate of formation of an acetal from acetaldehyde and ethanol in the presence of Pd-black, obtained by method A, on the concentration of pyridine added at 50°C (a), the same data in the  $1/W_{rel}$  vs.  $[Py]$  coordinates (b).

The acetalization that we observed in the presence of Pd-black agrees well with the previous observation [6] that metallic catalysts Rh, Ir, Pd and Pt on carbon, for which manifestation of protonic acidity is not characteristic, catalyze the formation of cyclic acetals from carbonyl compounds and diols.

In contrast to the "rigid"  $\text{OH}^-$  base, the relatively "mild" pyridine (Py) base markedly inhibits the formation of acetals. Thus, after holding the Pd-black A in alcohol containing 0.01-0.05 mole/liter of Py, the initial rate of accumulation of the acetal substantially decreases, whereby the dependence of the relative rate  $W_{rel} = W_0/W_0'$  ( $W_0$  is the reaction rate in the presence of Py;  $W_0'$  is the reaction rate in the absence of Py) rectifies in the  $1/W_{rel}$  vs.  $[Py]$  coordinates (Fig. 1). The equilibrium constant of the coordination of the active centers of Pd-black with Py, calculated from these data, is equal to  $K = [\text{Pd}_s \cdot \text{Py}] / [\text{Pd}_s] \cdot [\text{Py}] = 6.2 \cdot 10^2 \text{ liter} \cdot \text{mole}^{-1}$ .

Despite the fact that in the experiments using the potentiometric titration no protolytic reactions with the participation of Pd-black and water could be observed, the data obtained for the inhibition of the acetalization by pyridine in the presence of Pd-black indicate that the surface of the Pd-black particles has a highly appreciable aprotic acidity.

The acidic properties of aquacomplexes of transition metals usually increase with increase in the formal degree of oxidation of the metal atom [7]. A mean formal degree of oxidation of the Pd atoms, equal to +1/3, corresponds to the idealized formulas (I) and (II). However, because of electrostatic reasons, the positive charge of the massive cluster of (I) and (II) should be mainly concentrated on the Pd atoms of the surface layer of the metal skeleton: in the model under consideration, there is a charge of +180 e per 252 metal atoms of the external layer of the cluster skeleton, and thus, the formal charge of these Pd atoms is only a little lower than +1.

The  $\text{pK}_a$  values found for (I) and (II) correlate well with this evaluation of the charge of the Pd atoms, if it is considered that the proton donor ability of the aquaion  $\text{Pd}(\text{H}_2\text{O})_4^{2+}$  is so high that  $\geq 3 \text{ M HClO}_4$  is needed for its suppression [8]. It should be noted, however, that aquaions of Pd(II), such as for example,  $\text{PdCl}_3(\text{H}_2\text{O})^+$ ,  $\text{PdCl}_2(\text{H}_2\text{O})_2$ ,  $\text{PdCl}(\text{H}_2\text{O})^-$ , at an overall Pd concentration close to those used in our experiments, do not catalyze the formation of an acetal from acetaldehyde and ethanol [9], despite the higher formal charge of the Pd atoms, as compared with the case of the surface atoms of (I) and (II), and the higher proton-donor ability in aqueous and alcoholic media.

The acetalization experiments in the presence of Py showed that the base, the action of which is related to Lewis acidity, rather than protonic acidity, inhibits the process, which indicates the role of the aprotic centers in the reaction studied. Comparison of the acidic properties of the clusters with the properties of mononuclear Pd(II) complexes also supports this conclusion.

For the formation of the acetal, the molecule of the substrate (the carbonyl compound or its semiacetal) must replace the donor ligand in the coordination sphere of the Pd atom. The high effective charge of the central atom in mononuclear Pd(II) compounds and the in-

creased strength of the bond with the donor ligands – the "rigid" bases caused by it, possibly hinder their substitution by the weaker donor molecule of the substrate. In contrast to this, in clusters and Pd-black particles, because of the lower charge, the bond of the potentially accessible Pd atoms (not blocked by Phen or Py molecules) with the donor ligands (molecules and anions of alcohol or water) is weaker, and this facilitates the coordination of the substrate molecule.

Since the carbonyl compounds studied rapidly convert into semiacetals in alcoholic solutions also without the participation of the catalyst [4], it can be assumed that in the presence of (I) and (II), and also of Pd-black, the key stage in the reaction is the substitution of the OH group in the coordinated molecule of the semiacetal by an OR group as a result of attack of a free molecule of the alcohol.

The Pd atoms of the surface layer of the cluster or Pd-black function as aprotic acid centers, accepting the substituted OH group. Coordination of these centers with a "mild" base inhibits the reaction.

#### CONCLUSIONS

1. Gigantic palladium clusters and palladium black effectively catalyze the formation of acetals from carbonyl compounds and alcohols.

2. Comparison of the acid properties of the clusters, Pd-black and mononuclear complexes of palladium(II) indicates that aprotic acid centers of the catalyst participate in the reaction.

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