Unexpectedly high stability of benzaldehyde in the presence of Pd-561 giant cluster

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Benzyl alcohol is readily oxidized by O_2 to benzaldehyde in the presence of catalytic amounts of the $Pd_{561}phen_{60}(OAc)_{180}$ giant cluster. Unlike aliphatic aldehydes, benzaldehyde is resistant toward further transformations in this system.

Key words: palladium, clusters, benzaldehyde, oxidation, catalysis.

Giant clusters of the $Pd_{561}phen_{60}(OAc)_{180}$ type (**1**) catalyze the nonradical oxidation of alcohols with dioxygen under mild conditions (1 atm O_2, 20—50 °C). In the case of lower aliphatic alcohols, the aldehyde that formed is further transformed rapidly into carboxylic acid, anhydride, and ester; acetal is formed in parallel from the aldehyde and starting alcohol.[1,2]

We found that, unlike transformations of aliphatic alcohols catalyzed by cluster **1**, benzyl alcohol is oxidized to benzaldehyde with a high selectivity close to 100%.

In the absence of catalysts or initiators, benzyl alcohol is quite stable in air. In a solution of Pr^iOH containing cluster **1** ($3.70 \cdot 10^{-5}$ mol L^{-1}) and benzyl alcohol (0.77 mol L^{-1}), the latter is rapidly oxidized with O_2: at 60 °C the initial rate of transformation of benzyl alcohol into benzaldehyde is $1.1 \cdot 10^{-3}$ mol L^{-1} min^{-1}.

As our experiments showed, the rate of benzaldehyde accumulation in the presence of the cluster in a closed system remains unchanged for several hours, and neither benzoic acid nor its derivatives or benzaldehyde acetal are virtually formed.

The noninitiated autooxidation of benzaldehyde with dioxygen usually occurs with a noticeable rate already at 20 °C. According to our experimental data, benzaldehyde (0.77 *M* solution in MeCN) is completely oxidized into benzoic acid on contact with O_2 (1 atm) for 1 h at 60 °C (the initial autooxidation rate is $4.3 \cdot 10^{-2}$ mol L^{-1} min^{-1}). Under the same conditions but in the presence of the cluster ($7.0 \cdot 10^{-5}$ mol L^{-1}), the concentration of benzaldehyde remains almost unchanged for ~6 h, and O_2 is not almost absorbed.

In a medium of Pr^iOH, the noninitiated autooxidation of benzaldehyde occurs more slowly: at 60 °C the steady-state reaction rate is $0.78 \cdot 10^{-3}$ mol L^{-1} min^{-1}, and Pr^iOH is not almost oxidized under these conditions. After cluster **1** was added, the absorption rate of O_2 increased noticeably, but the benzaldehyde concentration remained unchanged and O_2 was absorbed only due to the cluster-catalyzed oxidation of Pr^iOH to Me_2CO. In a solution containing benzaldehyde (0.77 mol L^{-1}) and cluster **1** ($5.65 \cdot 10^{-5}$ mol L^{-1}), the oxidation rate of Pr^iOH at 60 °C is equal to $1.7 \cdot 10^{-4}$ mol L^{-1} min^{-1}, whereas pure isopropyl alcohol is oxidized, under these conditions, to Me_2CO with an initial rate of $1.2 \cdot 10^{-3}$ mol L^{-1} min^{-1}. In a solution of Pr^iOH containing *n*-butanal (0.54 mol L^{-1}) instead of benzaldehyde, the initial rate of alcohol oxidation in the presence of cluster **1** ($5.65 \cdot 10^{-5}$ mol L^{-1}) is $1.4 \cdot 10^{-4}$ mol L^{-1} min^{-1}. A similar effect of retardation of alcohol oxidation with acetaldehyde has been observed previously for the oxidation of EtOH.[3] Thus, additives of both aromatic and aliphatic aldehydes retard substantially the cluster-catalyzed oxidation of aliphatic alcohols.

The results obtained indicate that both free radical oxidation and catalytic oxidation of benzaldehyde are suppressed in the presence of the giant cluster. It is most likely that the metal core of the cluster can terminate free radical oxidation chains similarly to other metallocomplex inhibitors.[4] This can explain the found effect of retardation of benzaldehyde autooxidation by benzaldehyde, which occurs readily in the absence of **1**.

Against the background of the ready oxidation of benzyl alcohol and aliphatic aldehydes by dioxygen in the presence of cluster **1**, the stability of benzaldehyde seems to be an unusual phenomenon under conditions of this reaction. It is known[5] that the giant palladium clusters catalyze efficiently the reactions of aliphatic aldehydes in an O_2 atmosphere. The hypothetical mecha-

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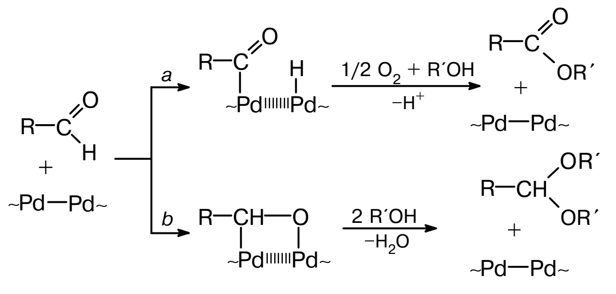
nism of the process (Scheme 1) includes the oxidative addition of the aldehyde molecule to the metal atoms of the cluster either due to the C—H bond cleavage (route *a*) or by the C=O bond opening (route *b*). Further transformations of the intermediate complex can afford either ester or carboxylic acid, or acetal, respectively.

Scheme 1



R,R′ is alkyl

The results obtained suggest that, in the case of benzaldehyde, similar intermediates (R = Ph) are quite stable and do not undergo any fast transformations into the final products.

Experimental

Benzyl alcohol and benzaldehyde (reagent grade) were prepurified by distillation *in vacuo* in an Ar flow at 20 Torr and stored in a refrigerator in an Ar atmosphere. Cluster **1** was synthesized by a described method[6] from palladium(II) acetate (pure grade), which was pre-purified by refluxing in glacial AcOH with an additive of Pd black followed by recrystallization.

Experiments were carried out by a previously published procedure[2,3] in a 20-cm^3 glass reactor equipped with a sampler, a thermostat, a vibrational stirrer, which provided intense stirring with a frequency of 200—450 min^{-1}, and a gas burette to detect a change in the gas volume with an accuracy to 0.1 cm^3. Cluster **1** (0.020 g) and the working solution (5.0 cm^3) were loaded in the reactor. The contents were shaken in an O_2 atmosphere at 60 °C. The content of the starting reactants and reaction products in the taken samples of the reaction solution was analyzed by GLC (Chrom-5, (Czechia), htd, carrier gas helium) using in parallel two glass columns (2 m × 3 mm): Polysorb-1 (0.315—0.5 mm) and 7% poly(ethylene sebacate) on Polychrom-1 (0.25—0.5 mm). The reaction rate was determined both volumetrically from O_2 absorption in time and by GLC data from benzaldehyde accumulation and benzyl alcohol consumption.

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