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Oxidative and anaerobic reactions of benzyl alcohol catalysed by a Pd-561 giant cluster

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The unusual redox disproportionation of benzyl alcohol to benzaldehyde and toluene catalysed by the $Pd_{561}phen_{60}(OAc)_{180}$ giant cluster under anaerobic conditions was found, whereas in an O_2 atmosphere the Pd giant cluster catalyses benzyl alcohol oxidation to benzaldehyde and inhibits its further oxidation.

Giant cluster $Pd_{561}phen_{60}(OAc)_{180}$ **1** is known to catalyse the polar oxidation of alcohols by dioxygen to the corresponding aldehydes under mild conditions (1 atm O_2, 20–60 °C).[1,2] In the case of lower aliphatic alcohols, the aldehyde formed is further oxidised into the corresponding carboxylic acid, anhydride and ester. In a parallel route, the aldehyde and starting alcohol produce acetal.[3–5] In this work, we found that, unlike aliphatic alcohols, benzyl alcohol is transformed in a solution of cluster **1** under O_2 into benzaldehyde and toluene as the major reaction products, and the minor reaction products are benzoic acid, benzene and CO_2 (Table 1).[†]

The initial rate of $PhCH_2OH$ consumption at 60 °C and [**1**] = = 4.55×10^{-5} mol dm^{-3} was 6.3×10^{-2} mol dm^{-3} min^{-1}. After 120 min of the reaction, the conversion of benzyl alcohol reached 40%. As can be seen in Figure 1, the curves for both $PhCH_2OH$ consumption and product accumulation have no induction period.

Our experiments showed that benzaldehyde undergoes autoxidation by dioxygen with a noticeable rate already at 20 °C when neither initiators nor catalysts are present. Meanwhile, in the presence of cluster **1**, benzaldehyde is rather stable in air and even under O_2.

For instance, benzaldehyde (0.77 mol dm^{-3} solution in MeCN) was completely oxidised to benzoic acid upon stirring under O_2 (1 atm) for 1 h at 60 °C (initial autoxidation rate was 9.0×10^{-4} s^{-1}). Unlike this, under the same conditions but in the presence of the Pd-561 cluster (7.0×10^{-5} mol dm^{-3}), the concentration of benzaldehyde remained almost unchanged and O_2 was not absorbed during 600 min.

In a solution of isopropanol, the autoxidation of benzaldehyde is much slower (initial rate is 1.7×10^{-5} s^{-1} at 60 °C), and isopropanol does not undergo oxidation. Meanwhile, when cluster **1** was introduced into the solution after 200 min, the O_2 consumption rate increased and Pr^iOH oxidation to acetone and water started. Since that moment, the concentration of benzaldehyde became constant (Figure 2).

All these facts point to a parallel rather than consecutive formation of the products of $PhCH_2OH$ conversion. In order to clarify the reaction mechanism, we studied the behaviour of benzyl alcohol in the presence of cluster **1** in an Ar atmosphere. When a solution of cluster **1** (4.60×10^{-5} mol dm^{-3}) in thoroughly degassed benzyl alcohol was stored under Ar for 120 min at 60 °C, ~8% benzyl alcohol was converted into benzaldehyde and toluene. As shown in Figure 3, both of the reaction products were formed in equal amounts.

Table 1 The products of cluster **1**-catalysed benzyl alcohol reactions (neat benzyl alcohol as a solvent, 1 atm O_2, 60 °C, [**1**] = 4.55×10^{-5} mol dm^{-3} and reaction time 120 min).

Reaction product	Concentration/ mol dm^{-3}	Yield based on $PhCH_2OH$ consumed (%)
PhCHO	3.09	70.2
PhMe	0.96	21.8
PhCOOH	0.27	6.1
PhH	0.084	1.9
CO_2	0.08	1.8

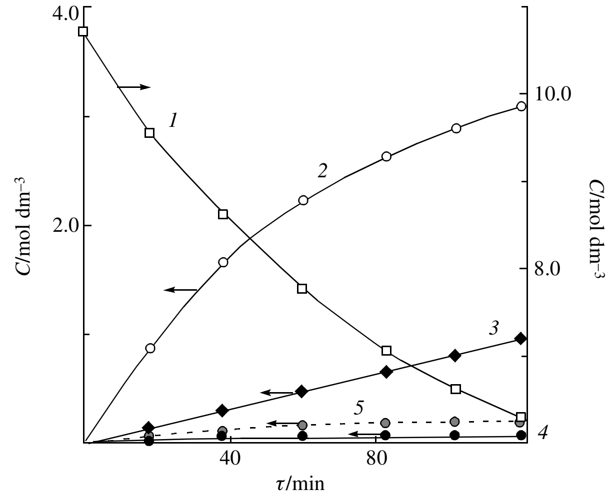

Figure 1 Curves for benzyl alcohol consumption and product accumulation in the presence of cluster **1** (4.55×10^{-5} mol dm^{-3}) under O_2 (1 atm) in neat benzyl alcohol at 60 °C: (*1*) benzyl alcohol, (*2*) benzaldehyde, (*3*) toluene, (*4*) benzene and (*5*) benzoic acid.

Hence, the Pd-561 cluster causes the redox disproportionation of benzyl alcohol to benzaldehyde and toluene under anaerobic conditions.

$$2PhCH_2OH \rightarrow PhCHO + PhMe + H_2O \qquad (1)$$

and at least a fraction of benzaldehyde and toluene that formed during the oxidation of benzyl alcohol can be due to the anaerobic conversion of the alcohol.

All these findings point to the fact that cluster **1** not only provides the catalytic polar oxidation and redox disproportionation of benzaldehyde but also retards its free-radical oxidation. It is most likely that the metal core of the cluster can terminate free-radical oxidation chains similarly to other metal complex inhibitors.[6]

The found synchronism in the accumulation of benzaldehyde and toluene during the contact of benzyl alcohol with the Pd-561 giant cluster implies two parallel reaction pathways, which are originated from two different modes of $PhCH_2OH$ coordination by the Pd atoms of the metal core of cluster **1**. The first coordination mode is the oxidative addition of the $PhCH_2OH$ molecule *via* C–H bond dissociation [Scheme 1, route (*a*)], and the second mode occurs *via* C–OH bond cleavage [Scheme 1, route (*b*)]. As a result, four coordinated (adsorbed) species occur at the surface layer of the metal core of cluster **1**: [$PhCH_2$], [PhCHOH], [H] and [OH]. The formation of benzaldehyde and

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[†] Experiments were carried out according to published procedures[1,3] in a 20 cm^3 glass reactor equipped with a sampler, a thermostat, a vibration stirrer (frequency of 200–450 min^{-1}) and a gas burette for the measurement of gas volumes to within 0.1 cm^3. Cluster **1** (0.020 g) and the working solution (5.0 cm^3) were loaded in the reactor. The reaction solution was rigorously shaken under O_2 at 60 °C. The reactants and reaction products were analysed by GLC. The reaction rates were determined by O_2 absorption and the GLC analysis of liquid reaction products.

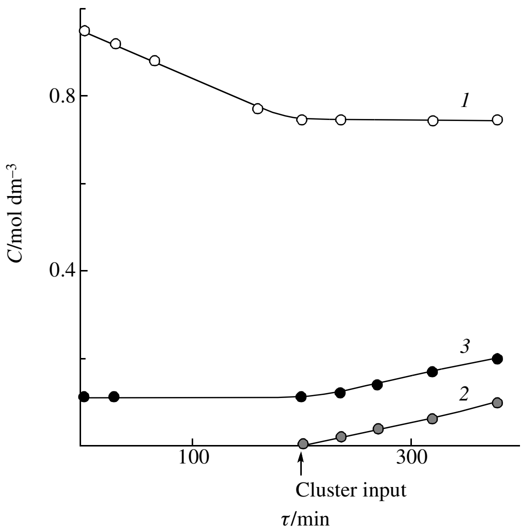
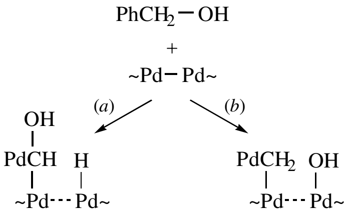


Figure 2 Curves for benzaldehyde oxidation in a solution of isopropanol. T = 60 °C, [**1**] = 5.65×10^{-5} mol dm^{-3}; (*1*) benzaldehyde, (*2*) acetone and (*3*) water.

toluene can be ascribed to the following recombinations of the adsorbed species:



Scheme 1

$$[\mathrm{PhCHOH}]_{\mathrm{ads}} + [\mathrm{OH}]_{\mathrm{ads}} = \mathrm{PhCHO} + \mathrm{H_2O}, \qquad (1)$$

$$[\mathrm{PhCH_2}]_{\mathrm{ads}} + [\mathrm{H}]_{\mathrm{ads}} = \mathrm{PhMe}. \qquad (2)$$

This mechanistic scheme allows us to explain the equal yields of benzaldehyde and toluene in the anaerobic reaction [equation (1), Figure 3]: reactions (2) and (3) involve the adsorbed species originated from different coordination routes irrespectively of which of the $PhCH_2OH$ adsorption mode, (*a*) or (*b*), prevails. Meanwhile, when benzyl alcohol is in contact with cluster **1** under O_2, the latter also forms the adsorbed species [O_2] and/or [O], switching on an additional reaction pathway such as

$$[\mathrm{PhCH_2}]_{\mathrm{ads}} + [\mathrm{O}]_{\mathrm{ads}} \rightarrow \mathrm{PhCHO}, \qquad (4)$$

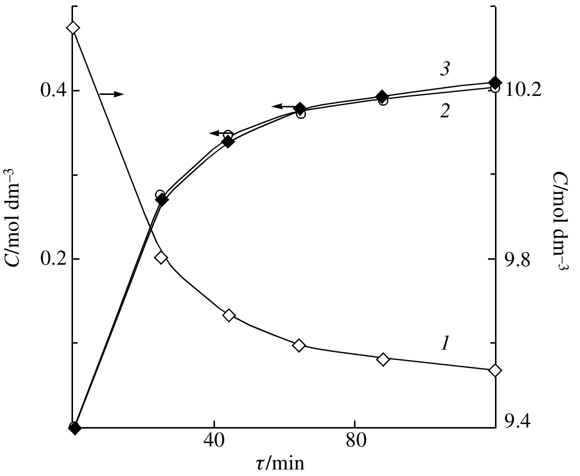


Figure 3 Curves for benzyl alcohol consumption and product accumulation in the presence of cluster **1** (4.6×10^{-5} mol dm^{-3}) under Ar (1 atm) in neat benzyl alcohol at 60 °C: (*1*) benzyl alcohol, (*2*) benzaldehyde and (*3*) toluene.

whereas the adsorbed hydride species [H], which are necessary for reaction (3) are removed

$$2[\mathrm{H}]_{\mathrm{ads}} + [\mathrm{O}]_{\mathrm{ads}} \rightarrow \mathrm{H_2O}, \qquad (5)$$

thus decreasing the PhCHO:PhMe ratio between the reaction products (Table 1, Figure 1).

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