Oxidation, Redox Disproportionation and Chain Termination Reactions Catalysed by the Pd-561 Giant Cluster

Grigory Kovtun,[a] Tatiana Kameneva,[a] Serhy Hladyi,[b] Mykhailo Starchevsky,[b] Yury Pazdersky,[b] Igor Stolarov,[c] Michael Vargaftik,[c,*] Ilya Moiseev[c]

[a] Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences
of Ukraine, Murmanskaya str. 1, 02094 Kiev, Ukraine
Fax: (+8)-44-573-25-52, e-mail: echoc@mail.kar.net
[b] "Sintez" Research Institute, Truskavetska str. 125, 82300 Borislav, Ukraine
Fax: (+8)-380-3248 41369, e-mail: main@insyntez.com.ua
[c] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky prospect 31,
117907 Moscow, Russian Federation
Fax: (+7)-95-954-1279, e-mail: mvar@igic.ras.ru

Received: April 22, 2002; Accepted: July 23, 2002

Dedicated to Professor Roger Arthur Sheldon in recognition of his inspiring leadership and many seminal achievements in homogeneous catalysis

Abstract: Redox disproportionation of benzyl alcohol to benzaldehyde and toluene catalysed by the $Pd_{561}phen_{60}(OAc)_{180}$ (phen = 1,10-phenanthroline) giant cluster **1** under anaerobic conditions was found, whereas in an O_2 atmosphere cluster **1** catalyses the oxidation of benzyl alcohol to benzaldehyde and inhibits further oxidation of the latter. A study of the AIBN-initiated and non-initiated oxidation of benzyl alcohol, *sec*-butyl alcohol and styrene in the presence of cluster **1** revealed that cluster **1** performs three functions in the oxidation reactions: 1) catalysis of polar oxidation of the substrates with O_2, 2) termination of the chains of radical oxidation, and 3) catalysis of redox disproportionation.

Keywords: benzaldehyde; benzyl alcohol; catalysis; clusters; oxidation; palladium

Introduction

Oxidation of alcohols and related compounds constitutes one of the main bodies of homogeneous catalysis.[1] Palladium compounds have been known as alcohol oxidants since Berzelius found that Pd metal precipitates from a solution of a Pd(II) salt in ethanol.[2] A more detailed study with a series of alcohols (*viz*., MeOH, EtOH, *i*-PrOH, *n*-BuOH, isoamyl alcohol and $PhCH_2OH$) showed that the reaction with $PdCl_2$ produces the corresponding carbonyl compounds (aldehydes in the case of primary alcohols and ketones for secondary alcohols) along with Pd metal and HCl (Eq. 1).[3]

$$\text{R-}\overset{\text{OH}}{\text{CH}}\text{-R'} + PdCl_2 = \text{R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-R'} + 2\,HCl + Pd^{o}, \quad (1)$$

R = H, Me, Et ... Ph; R' = H, Me

Aldehydes that are formed can be further oxidised to the carboxylic acids. Benzyl alcohol is the most readily oxidised by Pd(II) among the above-mentioned alcohols.[4,5] Recently,[6] the Ru/TEMPO-catalysed aerobic oxidation of alcohols, involving benzyl alcohol was thoroughly studied. Highly selective oxidation of benzyl alcohol with dioxygen to benzaldehyde in the $Pd(OAc)_2$/1,10-phenanthroline system has been found.[7]

In our earlier studies[8–11] we have found that not only divalent palladium but also low-valent Pd clusters can provide aerobic oxidation of alcohols. The palladium giant cluster $Pd_{561}phen_{60}(OAc)_{180}$ **1** (see below) efficiently catalyses the polar oxidation of alcohols by dioxygen under mild conditions (0.2–1 atm O_2, 20–60 °C).[9,10] In the case of lower aliphatic alcohols, besides aldehydes the corresponding carboxylic acids, anhydrides and esters were found among the reaction products. In a parallel route, the aldehydes and starting alcohols produce acetals.[9–11]

Recently we found that the behaviour of benzyl alcohol in the presence of cluster **1** differs from that of aliphatic alcohols (see Refs.[12,13] for preliminary communications). Redox disproportionation and inhibition of autooxidation were observed along with the cluster **1**-catalysed oxidation of benzyl alcohol to benzaldehyde.

1615-4150/02/34409-957–964 $ 17.50+.50/0

In this work we studied the reactions of benzyl alcohol, *sec*-butyl alcohol and styrene occurring in the presence of cluster **1** both under O_2 and in anaerobic conditions.

Results and Discussion

Palladium Giant Cluster

The giant cluster $Pd_{561}phen_{60}(OAc)_{180}$ **1** was synthesised by reduction of palladium(II) acetate $Pd_3(OAc)_6$ by gaseous H_2 in an AcOH solution containing small amount of the phen ligand (initial phen:Pd ratio is $\leq 1{:}2$).[5]

Modest-sized palladium clusters containing from 3–6 to 30–40 metal atoms can normally be prepared as crystalline samples, and their structures have been established by X-ray diffraction analysis. Larger palladium clusters are much less accessible in the crystalline form. Only recently was the unprecedented crystalline cluster $Pd_{145}(CO)_{\sim 60}(PEt_3)_{39}$ synthesised and structurally characterised by X-ray diffraction.[14]

Meanwhile, many high-nuclearity, low-valent palladium complexes that display remarkable catalytic performance were prepared during last decades as non-crystalline, highly dispersed powders.[5,8] Such species, close in size to colloidal metal particles (metal skeleton of at least 20–30 Å size and ≥50 Å with coordinated ligands), barely could form stable crystalline lattices. For this reason, indirect techniques, such as high resolution electron microscopy (HREM), electron diffraction (ED), scanning tunnel microscopy (STM), EXAFS, NMR and magnetic susceptibility measurements, were used for the structural characterisation of these species. These studies, combined with elemental analysis data, have revealed the main structural features of Pd giant clusters, including cluster **1**.[5]

The concept of giant clusters goes back to the hypothesis of P. Chini[15] that the arrangement of metal atoms in large clusters can be similar to the atom packing in the bulk metal. In this arrangement, the most stable clusters were expected to contain the "magic number" (*viz*., 55, 147, 309, 561, 923...) of the metal atoms.[15]

Based on the data of HREM, ED, STM, EXAFS and NMR studies combined with the magnetic susceptibility measurements and thorough elemental analysis data, the molecule of **1** has been formulated[5,8] as containing a positively charged metal core of ~25 Å in diameter, densely packed with 570 ± 30 Pd atoms (idealised five-shell icosahedron or cuboctahedron built of $1 + 12 + 42 + 92 + 162 + 252 = 561$ Pd atoms). The Pd metal core is surrounded by ~60 phen molecules as covalently bound ligands and ~180 outer-sphere OAc^- anions, the last counterbalancing the positive charge ($+180$) of the metal core. The idealised structure of palladium cluster **1** is shown in Figure 1.

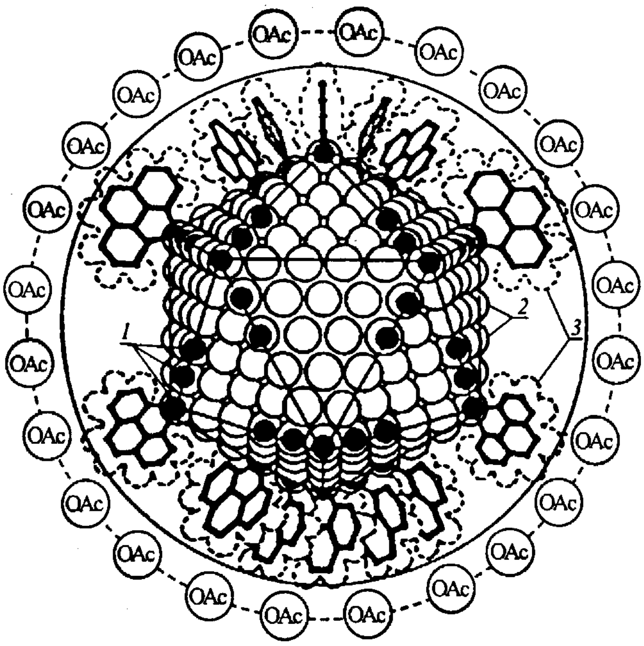


Figure 1. Idealised structure of the cluster $Pd_{561}phen_{60}(OAc)_{180}$ **1**. 1: Pd atoms bound covalently with phen ligands; 2: Pd atoms accessible for coordination of the substrate molecules; 3: van der Waals shapes of the coordinated phen ligands on the cluster core surface.

As seen in Figure 1, the accessible surface of the cluster core is sufficiently screened by the phen and OAc^- ligands. Kinetic studies of the alkenes oxidation inhibited with extra ligands of different sizes (*viz*., I^-, C_2H_5SH, SCN^-, PPh_3 and phen)[5] showed that among 252 metal atoms located in the outer layer of the Pd metal core only ~25 (~10%) of them are accessible for the substrate molecules and can participate in the catalytic reaction.

Note that the idealised formula corresponds to the most abundant size, shape and chemical composition of the cluster rather than a certain fixed structure. In practice, there is some (rather narrow) distribution in these parameters, and the real cluster samples consist of nearly continuous set of species, whose most abundant portion differs negligibly from the idealised structure.

The Pd giant clusters have been found to exhibit catalytic activity in diverse reactions under mild conditions, e.g., oxidation of alkenes, CO and alcohols, oxidative acetoxylation of alkenes and alkylarenes, displacement of C=C and C=O double bonds, reduction of nitriles and nitroaromatics, acetal formation and oxidative carbonylation of phenol.[5,8]

Polar Catalytic Oxidation

We found that unlike aliphatic alcohols, neat benzyl alcohol in the presence of cluster **1** under O_2 gives rise not only to benzaldehyde but also toluene as the major

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

Reaction products	PhCHO	$PhCH_3$	PhCOOH	PhH	CO_2
Concentration [mol dm^{-3}]	3.09	0.96	0.27	0.084	0.08
Yield based on $PhCH_2OH$ consumed [%]	70.2	21.8	6.1	1.9	1.8

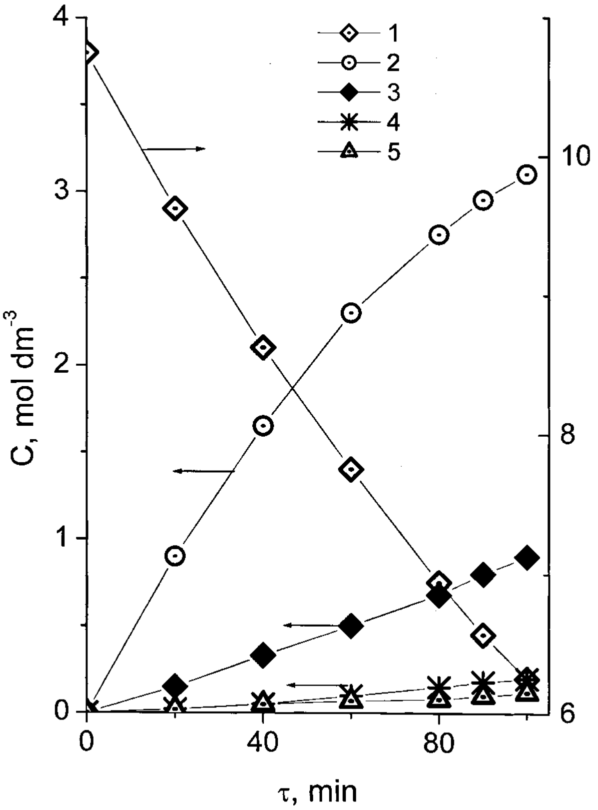


Figure 2. Curves for benzyl alcohol consumption and the products accumulation in the presence of cluster **1** (4.55×10^{-5} mol dm^{-3}) under O_2 (1 atm) in neat benzyl alcohol at 60 °C: 1: benzyl alcohol, 2: benzaldehyde, 3: toluene,4: benzene, 5: benzoic acid.

reaction products, along with benzoic acid, benzene and CO_2 as the minor reaction products (Table 1).

The initial rate of $PhCH_2OH$ consumption at 60 °C and [**1**] = 4.55×10^{-5} mol dm^{-3} is 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 2, the curves for both $PhCH_2OH$ consumption and the products accumulation have no induction period.

Meanwhile, benzaldehyde is known to undergo autooxidation by dioxygen with a noticeable rate already at 20 °C when neither initiators nor catalysts are present.[16] Surprisingly, benzaldehyde was rather stable both in air and under 0.1 MPa of O_2 when cluster **1** was added. In our experiments, benzaldehyde (0.77 mol dm^{-3} solution in MeCN) was completely oxidised into benzoic acid upon stirring under O_2 (0.1 MPa) for 1 h at 60 °C (initial autooxidation rate in the absence of cluster **1** was 9.0×10^{-4} s^{-1}). Unlike this, under the same conditions but in the presence of cluster **1** (7.0×10^{-5} mol dm^{-3}), the concentration of benzaldehyde remained almost unchanged and O_2 was not absorbed during at least 6 h.

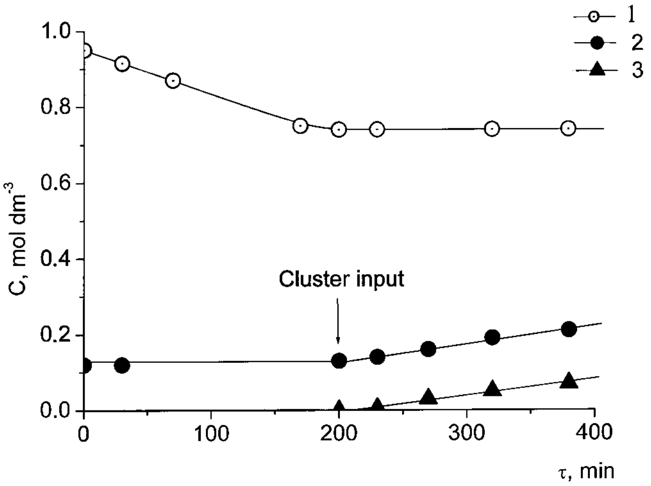


Figure 3. Curves for benzaldehyde oxidation in a solution of isopropyl alcohol. T = 60 °C, P_{O2} = 0.1 MPa, [**1**] = 5.65×10^{-5} mol dm^{-3}; 1: benzaldehyde, 2: acetone, 3: water.

In a solution of isopropyl alcohol non-catalytic oxidation of benzaldehyde was much slower (initial rate is 1.7×10^{-5} s^{-1} at 60 °C) and isopropyl alcohol did not undergo oxidation. After 200 min of storage under O_2 (0.1 MPa) cluster **1** was added to the solution. Immediately after this the O_2 consumption rate increased and *i*-PrOH oxidation started giving rise to acetone and water, while the concentration of benzaldehyde in the reaction solution became constant since the moment of cluster **1** introduction (see Figure 3).

All these facts suggested parallel rather than consecutive routes of 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 deoxygenated benzyl alcohol was stored under Ar during 120 min at 60 °C, ~8% of benzyl alcohol was converted into benzaldehyde and toluene. As shown in Figure 4, both the reaction products were formed in equal amounts.

Hence, even under anaerobic conditions, when oxidation to benzaldehyde does not occur, benzyl

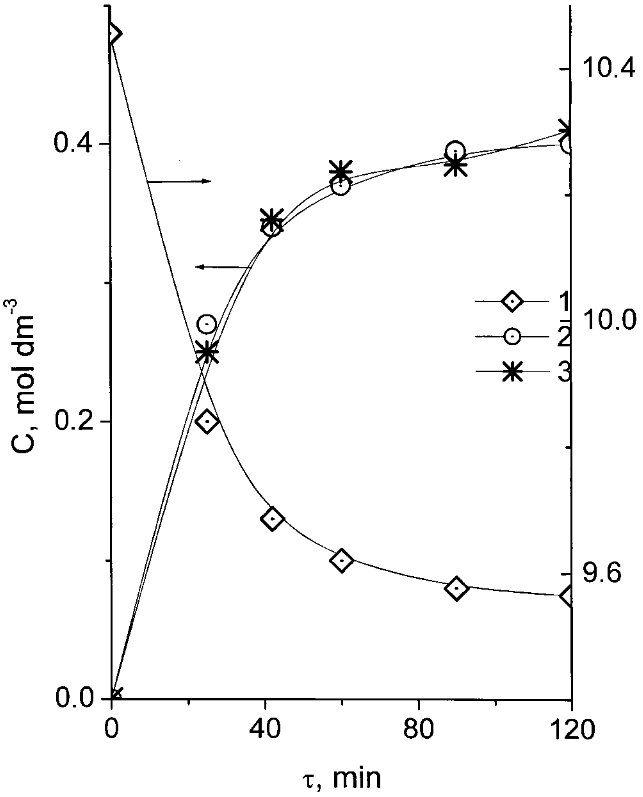


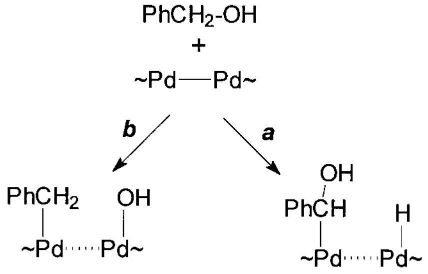
Figure 4. Curves for benzyl alcohol consumption and the products accumulation in the presence of cluster **1** (4.6 × 10^{-5} mol dm^{-3}) under Ar (1 atm) in neat benzyl alcohol at 60 °C: 1: benzyl alcohol, 2: benzaldehyde, 3: toluene.

alcohol undergoes redox disproportion catalysed by cluster **1**, giving rise to benzaldehyde and toluene (Eq. 2) and at least some fraction of benzaldehyde and toluene that formed under O_2 can be due to the redox conversion of benzyl alcohol.

$$2\,PhCH_2OH \rightarrow PhCHO + PhCH_3 + H_2O \qquad (2)$$

Based on these findings, we can suggest that cluster **1** not only effects the catalytic polar oxidation and redox disproportionation of benzaldehyde but also retards free-radical oxidation. It seems that the metal core of the cluster terminates the free-radical oxidation chains similarly to many other metal complex inhibitors.[17]

The found synchronism in the accumulation of benzaldehyde and toluene during a contact of benzyl alcohol with cluster **1** under Ar implies two parallel reaction pathways, which originate from two different modes of $PhCH_2OH$ coordination by the Pd atoms of the cluster **1** metal core. The first coordination mode is the oxidative addition of the $PhCH_2OH$ molecule *via* the C–H bond dissociation (route ***a*** in Scheme 1), and the second mode occurs *via* the C–OH bond cleavage (Scheme 1, route ***b***).



Scheme 1.

As a result, at least four different coordinated (adsorbed) species occur at the surface layer of the cluster **1** metal core: [$PhCH_2$], [PhCHOH], [H] and [OH]. The formation of benzaldehyde and toluene can be ascribed to the following recombinations of the adsorbed species (Eqs. 3 and 4).

$$[PhCHOH]_{ads} + [OH]_{ads} = PhCHO + H_2O \qquad (3)$$

$$[PhCH_2]_{ads} + [H]_{ads} = PhCH_3 \qquad (4)$$

This mechanistic scheme allows one to explain the equal yields of benzaldehyde and toluene in the anaerobic reaction (Eq. 1, see Figure 3): both reactions (3) and (4) involve the adsorbed species originating from different coordination modes 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 (Eq. 5) whereas the adsorbed hydride species [H], which are necessary for reaction (Eq. 3) are removed (Eq. 6), thus decreasing the PhCHO:$PhCH_3$ ratio in the reaction products (see Table 1 and Figure 1).

$$[PhCH_2]_{ads} + [O]_{ads} \longrightarrow PhCHO + [H]_{ads} \qquad (5)$$

$$2\,[H]_{ads} + [O]_{ads} \longrightarrow H_2O \qquad (6)$$

Free Radical Oxidation

In order to check the above-mentioned suggestion that cluster **1** inhibits the free-radical oxidation of benzyl alcohol and benzaldehyde, we compared the effect of cluster **1** on the initiated and non-initiated oxidation of organic substrates (*viz*., benzyl alcohol, *sec*-butyl alcohol and styrene) by O_2 at 50–80 °C.

An earlier kinetic study[16] of benzyl alcohol autooxidation showed that this reaction proceeds *via* the chain radical mechanism in which the peroxyl ROO$^\cdot$ and alkyl R$^\cdot$ radicals are the chain carriers. Our experiments showed that the addition of cluster **1** to benzyl alcohol and the other above-mentioned organic substrates exerted the catalytic termination of the oxidation chains, which effect was manifested as a sharp slowing down of substrate oxidation without formation of the oxidation products (induction period). In the oxidation of benzyl alcohol and styrene at 50 °C initiated by azobisisobutyronitrile (AIBN), the apparent termination coefficient $f = \tau\, w_i/[\mathbf{1}]$ was found to be > 30, where τ is the induction period and $w_i = (1.5-3.0)\ 10^{-8}$ mol (dm^3 s)$^{-1}$ is the rate of the AIBN-produced initiation of the oxidation chains. A similar but somewhat weaker termination effect was exhibited by Pd-black consisting of dispersed metal particles (≤ 300 Å in size), whereas both free ligands (phen, OAc$^-$) and Pd(II) acetate added in the concentrations of 10^{-4}–10^{-6} mol dm^{-3} did not retard the autooxidation of the above organic substrates.

Our kinetic experiments (Figures 5 and 6) showed that the initial rate (w_0) of the AIBN-initiated oxidation of neat benzyl alcohol with the additives of glacial acetic acid (0.06 mol dm^{-3}) and cluster **1** [(0.2–1.8) 10^{-6} mol dm^{-3}] measured volumetrically by O_2 consumption at partial O_2 pressures of 0.02 - 0.1 MPa does not depend on the O_2 pressure and the rate of stirring (within 10–50 min^{-1}), obeying the kinetic equation (Eq. 7).

$$w_0 = \text{const}\ [O_2]_0\ w_i\ /\ [\mathbf{1}] \qquad (7)$$

These findings can be interpreted through the formal kinetic analysis for the radical chain autooxidation propagated with the R$^\cdot$ and RCOO$^\cdot$ chain carriers.[17–19a] Let us denote the initial rate for the oxidation in the presence of an inhibitor as w_0 and that for the reaction in the absence of an inhibitor as w. Then the plot [$w_0/w-w/w_0$] *vs.* the inhibitor concentration should be linear when the rate for chain termination *via* the self-reaction of two alkylperoxy radicals is comparable with that for the reaction of the alkylperoxy radical with the inhibitor,[17b] as seen in Figure 5.

According to the formal kinetic analysis, the R$^\cdot$ and RCOO$^\cdot$ steady-state concentrations are connected by the following relationship (Eq. 8) where k′ and k″ are the rate constants for the RCOO$^\cdot$ + RH and R$^\cdot$ + O_2 chain propagation stages, respectively, and P_{O_2} is the O_2 partial pressure. If the oxidation chains were terminated in the reaction between radicals R$^\cdot$ and cluster **1**, the oxidation rate should increase in parallel to P_{O_2}. The found zero order with respect to the O_2 partial pressure implies that the chain termination stages involve RCOO$^\cdot$ rather than R$^\cdot$ free radical species.

$$[R\cdot]\ /\ [RCOO\cdot] = k'\ [RH]\ /\ k''\ [O_2] = \text{const}\ /\ P_{O_2} \qquad (8)$$

The rate of benzyl alcohol oxidation approaches asymptotically to the minimal value $w_\infty = 2.2 \times 10^{-7}$ mol (dm^3 s)$^{-1}$ when the concentration of cluster **1** is increased to 3×10^{-6} mol dm^{-3} (see Figure 5). The chain length ($\nu = w_\infty/w_i$) is 12, and hence the reaction proceeds in the chain regime.

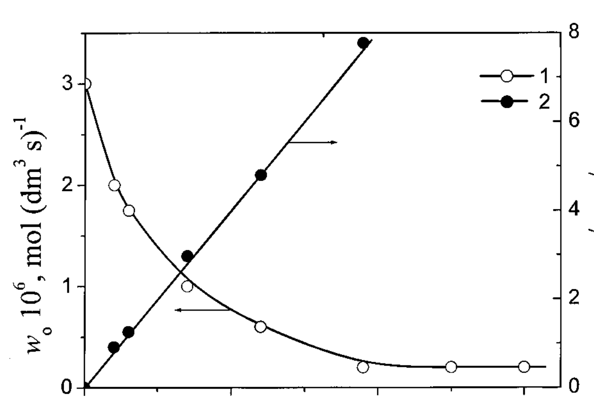


Figure 5. Oxidation rate [w_0/mol (dm^3 s)$^{-1}$] (curve 1) and the parameter $w_0/w - w/w_0$ (curve 2) plotted as a function of concentration of cluster **1** at 50 °C and initiation rate $w_i = 3.0 \times 10^{-8}$ mol (dm^3 s)$^{-1}$].

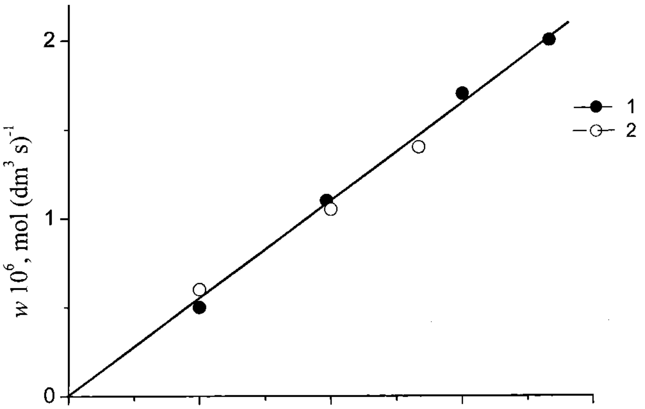
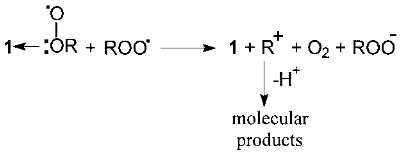


Figure 6. Plot of the rate of benzyl alcohol oxidation [w/mol (dm^3 s)$^{-1}$] as a function of the rate of initiation [w_i/mol (dm^3 s)$^{-1}$] at 50 °C, [**1**] = 1.8×10^{-6} mol dm^{-3} and O_2 partial pressure of 0.02 (points 1) and 0.1 MPa (points 2).

The asymptotically minimal reaction rate w_∞ obeys the same kinetics (Eq. 7). Such a kinetic regularity can imply the termination stage to be preceded by the coordination of the ROO$^\bullet$ radical to the metal core of cluster **1** (Eq. 9).[20]

$$1 + ROO^\bullet \rightleftharpoons 1 \leftarrow :\overset{{}^\bullet O\,|}{O}R \quad (9)$$

This reaction enhances the electrophilicity of the chain carrier (ROO$^\bullet$ radical) and facilitates the next stage, the reduction of another peroxyl radical (Eq. 10).



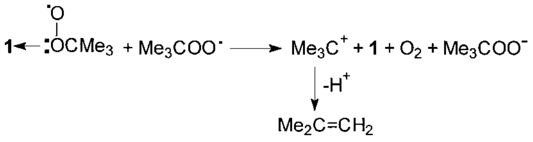
$$1 \leftarrow :\overset{{}^\bullet O\,|}{O}R + ROO^\bullet \longrightarrow 1 + \underset{\text{molecular products}}{\underset{\downarrow -H^+}{R^+}} + O_2 + ROO^- \quad (10)$$

Experiments with a 4 × 10^{-4} mol dm^{-3} solution of hydroperoxide t-BuOOH in benzyl alcohol showed that t-BuOOH disappeared in 1 – 2 min after the addition of cluster **1** (2 × 10^{-6} mol dm^{-3}), suggesting a fast decomposition of peroxides by the Pd cluster.

The alternation of stages (Eq. 9) and (Eq. 10) forms the catalytic cycle of termination of the oxidation chains with the stoichiometric termination coefficient f ≥ 100, and cluster **1** functions as a multi-action antioxidant. Since the asymptotical oxidation rate w_∞ is linearly proportional to the initiation rate w_i (see Fig. 6), we can conclude that the radical coordination (Eq. 9) is the rate-determining stage of the inhibited oxidation. If the chain termination were determined by stage (Eq. 10), the asymptotical rate w_∞ should be proportional to $w_i^{1/2}$.[17]

The mechanism of chain termination *via* reactions (Eq. 9) and (Eq. 10) suggests that the coordination of the peroxyl radical with cluster **1** is accompanied with only a partial electron density transfer from ROO$^\bullet$ to the Pd atoms of the Pd cluster and the coordinated ROO$^\bullet$ group is still capable of participating in the propagation of the oxidation chains ($w_\infty \gg w_i$, see Figure 5). Note that the partial or even complete electron transfer from the O-centred radicals upon their coordination with transition metal atoms is a known effect, which has been quantitatively investigated in several cases.[21]

The intermediate formation of carbenium cation in stage (Eq. 9) was confirmed by the finding by GLC of isobutene formation in the water-free system cluster **1**-Me$_3$COO$^\bullet$-C$_6$H$_6$ according to the reaction scheme (Eq. 11).



$$1 \leftarrow :\overset{{}^\bullet O\,|}{O}CMe_3 + Me_3COO^\bullet \longrightarrow \underset{Me_2C=CH_2}{\underset{\downarrow -H^+}{Me_3C^+}} + 1 + O_2 + Me_3COO^- \quad (11)$$

When water (~0.01 mol dm^{-3}) was added to the reaction system, *tert*-butyl alcohol was formed besides isobutene (GLC analysis) according to Eq. 12.

$$Me_3C^+ + H_2O = Me_3COH + H^+ \quad (12)$$

In these experiments the *tert*-butyl radicals were generated by photodecomposition of azobis(*tert*-butyl) in O$_2$ atmosphere at 30 °C. When cluster **1** was absent, the molecular reaction products were *tert*-butyl peroxide (found by IR spectrum) and traces of *tert*-butyl alcohol (GLC analysis) as shown in Eq. 13.

$$2\,Me_3COO^\bullet \longrightarrow \overbrace{[Me_3CO^\bullet \cdots O\text{-}O \cdots {}^\bullet OCMe_3]}^{\textbf{Solvent cage}} \longrightarrow Me_3COOCMe_3 + O_2 \quad (13)$$

The apparent rate constants of the chain termination for the cluster **1**-inhibited oxidation [k_{app}=(2.6 ± 0.3) × 10^6 (50 °C), (2.5 ± 0.5) × 10^5 (70 °C) and (3.2 ± 0.4) × 10^5 dm^3 (mol s)$^{-1}$ (50 °C)] for benzyl alcohol, *sec*-butyl alcohol and styrene, respectively, were estimated from the dependence of the parameter $w_0/w - w/w_0$ at [**1**] = 0. Note that for benzyl alcohol oxidation inhibited by the commercial stabilisator 2,6-di-*tert*-butyl-4-methylphenol ("Agidol", Russia) under similar conditions k_{app} was found to be (1.3 ± 0.2) × 10^4 dm^3 (mol s)$^{-1}$ at 50 °C.[22]

Conclusions

This study showed benzyl alcohol to be efficiently converted into benzaldehyde by oxidation with O$_2$ in the presence of the Pd-561 giant cluster. Surprisingly, benzaldehyde turned out to be rather stable toward further oxidation when the Pd cluster was present in the solution. Under anaerobic conditions, the redox disproportionation of benzyl alcohol to benzaldehyde and toluene catalysed by the Pd-561 cluster was found. The Pd-561 cluster was found to function as an efficient inhibitor of free-radical oxidations as well.

Hence, the high-nuclear Pd cluster is capable of performing three functions: (i) polar oxidation catalyst, (ii) redox disproportionation catalyst, and (iii) inhibitor of free-radical reactions.

Experimental Section

Solvents, Reagents and Catalyst

Solvents [acetonitrile, isopropyl alcohol, glacial acetic acid and benzene, all Reakhim (Russia), reagent grade] were purified by standard procedures.[23]

Benzyl alcohol (reagent grade, from Reakhim, Russia) was purified from inhibiting admixtures by vacuum distillation (Ar flow), collecting the fraction whose oxidisability parameter $k_p/k_t^{1/2}$ was $(2.75 \pm 0.5) \times 10^{-3}$ dm^3 (mol s)$^{-1/2}$ (*cf.* 2.7×10^{-3} in Ref.[16]) at 65 °C, where k_p and k_t are the constants of chain propagation and termination, respectively.[19] Azobisisobutyronitrile (AIBN, Aldrich) was recrystallised from ethanol. *sec*-Butyl alcohol (Aldrich, reagent grade) and styrene (Reakhim, reagent grade) were distilled under vacuum before use. 1,10-Phenanthroline and 2,2′-azoisobutane (Aldrich, reagent grade) were used as received. High-purity dioxygen and argon from cylinders were used without additional purification.

Palladium(II) acetate $Pd_3(OAc)_6$ was prepared by the oxidation of Pd black (from $PdCl_2$ and $NaBH_4$) with concentrated HNO_3 in glacial AcOH by a published method.[24] The raw reaction product was purified from the traces of Pd(II) nitrato and nitrito complexes by refluxing in glacial AcOH with a fresh portion of Pd black until NO_2 evolution ceased and recrystallised from hot AcOH. Palladium giant cluster $Pd_{561}phen_{60}(OAc)_{180}$ **1** was synthesised from $Pd_3(OAc)_6$ and 1,10-phenanthroline in glacial AcOH according to the procedure described elsewhere.[5]

Experimental Procedures

Analysis Methods

GLC analyses of the reaction solutions were performed on chromatographs Varian 3600 (USA) and 3700 (Russia) with 50 m capillary columns, stationary phases OV-1, SE-30 and XE-60. The gaseous reaction products were analysed by GC on a Chrom 5 (Czechia) gas chromatograph (glass column 150 × 3 cm, Polysorb-1, He, 20 – 60 °C). GC/MS analyses of the reaction products were performed on an Automass 150 instrument (Delsi Nermag, EI, capillary column with OV-1). Hydroperoxides were analysed by iodometry [17,25] and IR spectroscopy.[26]

Polar Oxidation

Experiments were carried out according to previously published procedures.[5,8–11] A 20-cm^3 water-jacketed glass reactor connected with a 50 cm^3 gas volumeter (accuracy 0.1 cm^3) was charged with the working solution (5.0 cm^3) and cluster **1** (0.020 g). The thermostatted reaction solution was vigorously shaken with a frequency of 100 – 450 min^{-1} under O_2 at 60 °C, and the reaction solution was periodically sampled (0.1 cm^3) for GLC and GC/MS analyses. The reaction was monitored by O_2 absorption and GLC of the liquid reaction products.

Free Radical Oxidation

Experiments for non-initiated and AIBN-initiated oxidation were conducted on a similar volumetric glass installation. The compositions of the liquid and gas phases were monitored by GLC and GC, correspondingly. The AIBN initiation rate constants (k_i, s^{-1}) were calculated by the equation $\log k_i = 14.5 - 33800/4.57T$.[21]

Acknowlegements

Authors thank the Russian Foundation for Basic Research (Project Nos. 99-03-32291, 00-15-97429 and 02-03-32853) for financial support.

References

[1] R. A. Sheldon, J. K. Kochi, *Metal Catalysed Oxidations of Organic Compounds*, Academic Press, New York, **1981**.

[2] J. J. Berzelius, *Pogg. Annal.* **1828**, *13*, 435 – 441.

[3] A. V. Nikiforova, I. I. Moiseev, Ya. K. Syrkin, *Zhurnal Organicheskoy Khimii* **1963**, *33*, 3239 – 3243 (Russ. Journal of Organic Chemistry).

[4] I. I. Moiseev, π-*Complexes in liquid-phase olefin oxidation*, Nauka, Moscow, **1970**, pp.62 – 63 (in Russ.).

[5] M. N. Vargaftik, V. P. Zagorodnikov, I. P. Stolarov, I. I. Moiseev, D. I. Kochubey, V. A. Likholobov, A. L. Chuvilin, K. I. Zamaraev, *J. Mol. Catal.* **1989**, *53*, 315 – 348.

[6] A. Dijksman, I. W. C. E. Arends, R. A. Sheldon, *Platinum Metal Rev.* **2001**, *45*, 15 – 19.

[7] G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636 – 1639.

[8] M. N. Vargaftik, I. I. Moiseev, in *Catalysis by Di- and Polynuclear Metal Complexes*, (Eds.: A. Cotton, R. Adams), Wiley, New York, **1998**, pp. 395 – 442.

[9] M. K. Starchevsky, S. L. Hladiy, Yu. A. Pazdersky, M. N. Vargaftik, I. I. Moiseev, *J. Mol. Catal.* **1999**, *146*, 229 – 236.

[10] M .K. Starchevsky, S. L. Hladyi, Ya. V. Lastovyak, Yu. A. Pazdersky, M. N. Vargaftik, I. I. Moiseev, *Dokl. Akad. Nauk* **1995**, *342*, 772 – 775 (in Russ.).

[11] M. K. Starchevsky, S. L. Hladyi, Ya. V. Lastovyak, P. I. Pasichnyk, Yu. A. Pazdersky, M. N. Vargaftik, I. I. Moiseev, *Kinet. Katal.* **1996**, *37*, 408 – 415 (in Russ.).

[12] G. A. Kovtun, T. M. Kameneva, M. N. Vargaftik, I. I. Moiseev, *Doklady NAN Ukrainy* **2001**, 133 – 137 (in Russ.).

[13] S. L. Hladyi, M. K. Starchevsky, Yu. A. Pazdersky, M. N. Vargaftik, I. I. Moiseev, *Mendeleev Commun.* **2002**, 45 – 46.

[14] N. T. Tran, D. R. Powell, L. F. Dahl, *Angew. Chem., Int. Ed.* **2000**, *39*, 4121 – 4124.

[15] P.Chini, *J. Organometal. Chem.* **1980**, *200*, 37 – 59.

[16] A. N. Shendrik, I. A. Opeida, *Ukranskii Khimicheskii Zhurnal* **1978**, *44*, 855 – 858 (Ukrainian Journal of Chemistry, in Russ.).

[17] C. Walling, *Free Radicals in Solution*, New York, Wiley, **1957**, pp. 399 – 466.

[18] N. M. Emanuel, E. T. Denisov, Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, New York, Plenum Press, **1967**, pp. 132 – 136.

[19] (a)G. A. Kovtun, I. I. Moiseev, *Metallokompleksnye ingibitory okisleniya* [*Metal Complex Oxidation Inhibitors*], Kiev, Naukova Dumka, **1993**, pp. 75 – 95; b) *ibid*., pp. 194 – 195 (in Russ.).

[20] G. A. Kovtun, A. S. Berenblum, I. I. Moiseev, *Izvestiya Akad. Nauk SSSR. Ser. Khim*. **1981**, 1495 – 1501 (in Russ).

[21] V. D. Pokhodenko, A. A. Beloded, V. G. Koshechko, *Redox Reactions of Free Radicals*, Kiev, Naukova Dumka, **1977**, pp. 106 – 176 (in Russ.).

[22] G. A. Kovtun, V. A. Pluzhnikov, *Chemistry of Inhibitors for the Oxidation of Organic Compounds*, Kiev, Naukova Dumka, **1995**, p. 296 (in Russ.).

[23] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd edn., Oxford, Pergamon, **1988**.

[24] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, G. Wilkinson, *J. Chem. Soc*. **1965**, 3632 – 3641.

[25] G. A. Kovtun, V. A. Pluzhnikov, *Lewis Acids as Stabilizer of Organic Compounds*, Kiev, Institute of Bioorganic Chemistry and Inorganic Chemistry, Ukraine, **1994**, pp. 109 – 132.

[26] V. A. Antonovsky, M. I. Buzlanova, *Analytical Chemistry of Organic Peroxides*, Moskow, Nauka, **1965**, pp. 96 – 102.