Oxidation of Propylene to Acrylic Acid and its Esters Catalysed by Palladium Giant Clusters

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Propylene has been catalytically oxidized by dioxygen to acrylic acid and/or its esters in high yield (60–80%) in acidified aqueous and/or alcoholic solutions of palladium–561 giant clusters, whereas ethylene has been converted to acetic acid; this is the first example of acid–promoted palladium catalysis of alkene oxidation.

The presence of a base is commonly agreed to be a critical requirement in carrying out the oxidative acetoxylation of alkenes by dioxygen catalysed by both palladium(II) and low-valent Pd clusters.[1] Alkaline carboxylate additives to $PdCl_2$ or $Pd(OAc)_2$,[2] Pd black[3] and supported Pd/SiO_2 catalyst[4,5] were used to perform the oxidation of ethylene to vinyl acetate and propylene to allyl acetate. In this paper the first example of palladium-catalysed alkene oxidation promoted by acids is reported.

Palladium giant clusters of idealized formulation $Pd_{561}Phen_{60}(OAc)_{60}$ **1** and $Pd_{561}Phen_{60}O_{60}(PF_6)_{60}$ **2**† are known to be effective catalysts for selective oxidation of ethylene and propylene to vinyl and allyl acetates, respectively, in acetic acid solutions.[6] In other solvents, the use of giant clusters as catalysts for alkene oxidation has not, to our knowledge, been described. In this context, we attempted to study the catalytic properties of clusters **1** and **2** towards low alkene oxidation in aqueous and alcoholic solutions.

Our experiments suggested‡ that an ethylene–O_2 gas mixture (1:1 by volume) might on absorption be expected to convert into acetone. However, experiments with propylene–O_2 and an aqueous solution of clusters **1** and **2** slowly yielded, successively, acetaldehyde and acetic acid. The reaction was accelerated noticeably by addition of dilute $HClO_4$, H_2SO_4, CF_3COOH or AcOH. By analogy with the ethylene reaction, propylene as a (1:1) gas mixture resulted in only a minor amount of acetone (~5% of products sum), whereas the reaction products essentially involved allyl alcohol, acrolein and acrylic acid, with acrylic acid prevailing (Table 1). When 1–1.6 mol dm^{-3} of H_2SO_4 was added to the reaction solution, the rate of propylene oxidation increased proportionally with the acid concentration. Over all the interval of solvent acidity the sum of the products of allylic oxidation (allyl alcohol, acrolein and acrylic acid) remain nearly constant, around 80%.

The distribution of the allylic oxidation products is influenced by two factors: (*a*) acceleration of allyl alcohol formation from propylene with increasing H_2SO_4 concentration (see column 4 in Table 1); (*b*) retardation by acid of further oxidation of allyl alcohol and acrolein. For example, the oxidation rate of allyl alcohol in the solution containing 1.23×10^{-4} mol dm^{-3} of cluster **1** and 1.67 mol dm^{-3} H_2SO_4 was 4.5 times slower than that in the solution with no acid added. These facts, along with the shape of the product accumulation curves (see S-like curves for acrolein and acrylic acid, Fig. 1), imply that propylene to acrylic acid oxidation proceeds *via* intermediate allyl alcohol–acrolein formation.

In alcoholic solutions of Pd giant clusters acidified with H_2SO_4, allylic oxidation of propylene also occurs to give acrylic esters along with acrylic acid and acrolein (Table 2). In parallel to the main reaction, the oxidation of saturated alcohols into esters (MeOH into HCOOMe and EtOH to MeCOOEt) takes place under those conditions. In the absence of added acid, alcohol oxidation dominated, and propylene was virtually

Table 1 Propylene oxidation in aqueous solutions of cluster **1**.[a]

$[H_2SO_4]$ /mol dm^{-3}	Cluster **1** concentration /10^{-4} mol dm^{-3}	Initial rate of C_3H_6 consumption/ 10^{-3} mol dm^{-3} min^{-1}	Reaction products	Yield (% mol on propylene consumed[b])
0	2.34	0.32	CH_2=$CHCH_2OH$	14
			CH=CHCHO	2
			CH_2=CHCOOH	60
			MeCOMe	5
0.36	2.34	1.43		
0.67	2.34	2.30		
1.67	2.34	4.04	CH_2=$CHCH_2OH$	38
			CH_2=CHCHO	14
			CH_2=CHCOOH	20
			MeCOMe	4
			MeCH(OH)Me[c]	11
1.67	4.64	5.40 (303 K)		

[a] T = 323 K, 1 atm. of C_3H_6:O_2 = 1:1 gas mixture, time of reaction 1 h. [b] The difference between 100% and the sum of the products listed corresponds to non-identified and polymer substances. [c] Isopropyl alcohol was formed due to acid-catalysed propylene hydration, independently of the presence of Pd cluster; this was confirmed by blank experiments with no cluster added.

Table 2 Propylene oxidation in alcoholic solutions of cluster **1**.[a]

Alcohol	$[H_2SO_4]$ /mol dm^{-3}	Initial rate of propylene consumption /10^{-3} mol dm^{-3} min^{-1}	Reaction products	Yield (% mol on propylene consumed[b])
Methanol	1.61	5.25	CH_2=CHCHO	4
			CH_2=CHCOOH	40
			CH_2=CHCOOMe	40
			MeCOMe	4
			HCOOMe	2
Ethanol	1.67	1.30	CH_2=CHCHO	5
			CH_2=CHCOOH	6
			CH_2=CHCOOEt	7
			MeCOMe	12
			MeCHO	3
			MeCOOH	25
			MeCOOEt	25

[a] [**1**] = 1.13×10^{4} mol dm^{-3}, 1 atm. of C_3H_6:O_2 = 2:3 gas mixture, T = 323 K, time of reaction 1 h. [b] See footnote *b*, Table 1.

† In this case the base molecules, phen and O^{2-}, are constituents of the catalyst as ligands coordinated to Pd atoms of the cluster.

‡ In a typical experiment, 0.2–0.3 g of giant cluster in 10 ml of water was stirred in a thermostated glass reaction vessel with a magnetic stirrer under 1 atm of propylene–dioxygen (1:1) gas mixture at 50 °C for 1–2 h. Reaction products were followed periodically by GLC.

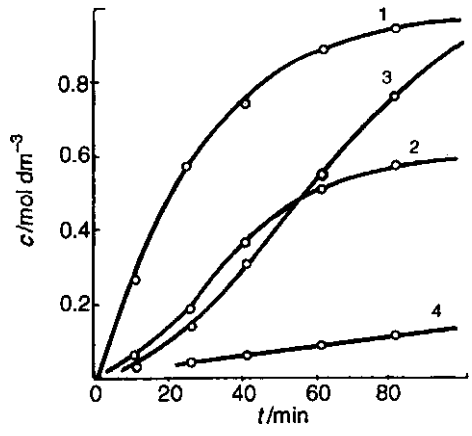
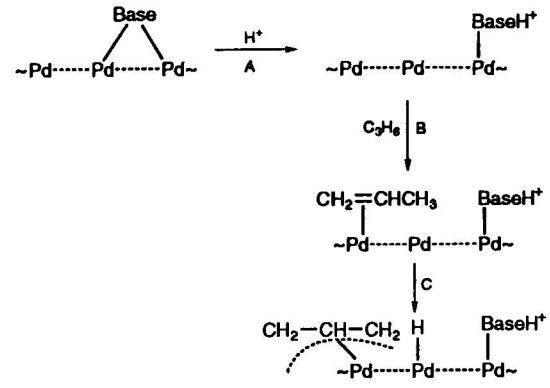


Fig. 1 Curves for product accumulation *vs.* reaction time for propylene oxidation by O_2 in an aqueous solution of cluster **1** containing H_2SO_4: $T = 323$ K, 1 atm. of propylene:O_2 = 1:1 gas mixture, [**1**] = 2.5×10^{-4} mol dm^{-3}, [H_2SO_4] = 1.62 mol dm^{-3}; curves: 1, allyl alcohol; 2, acrolein; 3, acrylic acid; 4, acetone.

unreacted. Methanol was found to be the best choice of solvent because its oxidation was markedly slower than that of other alcohols under the reaction conditions.

In contrast to propylene oxidation in aqueous solution, allyl alcohol or/and its ethers were not found, within ~0.1% experimental error of concentration, among the reaction products in methanol or ethanol solutions, suggesting the oxidation of allyl alcohol and its ethers to proceed faster in alcoholic media than in water.

Acceleration of propylene oxidation by acids, an effect found in this study, seems to be of uncommon occurrence for palladium-mediated alkene oxidations. This effect could be explained by taking into consideration the results of our earlier experiments with inhibitors where the surface of clusters **1** and **2** was shown to be screened substantially by bulky phen ligands, so that no more than 10–15% of Pd atoms at a cluster surface are accessible for alkene and O_2 molecules when reacted in acetic acid solution.[6–8] Protonation of bidentately-coordinated base molecules (phen, dipy or O^{2-} ligands) would make the surface of the Pd cluster more accessible for substrate molecules, as shown by Scheme 1, steps A and B.



Scheme 1

On the other hand, protonation of the phen or O ligand should change drastically the local surrounding of Pd atoms in the vicinity of the reaction centre. The higher charge on the Pd atom facilitates the transfer of $H^{\delta-}$ to the Pd atom from the π-coordinated propylene molecule, transforming it into a π-allyl group (see Scheme 1, step C), a process assumed to be the reaction 'bottleneck'.

We are grateful for financial support from the Russian Foundation for Fundamental Science under Contract No. 93–03–4415.

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Received: Moscow, 25th June 1993
Cambridge, 15th September 1993; Com. 3/03701K