Catalytic Conversions in Water. Part 21: Mechanistic Investigations on the Palladium-Catalysed Aerobic Oxidation of Alcohols in Water†

Gerd-Jan ten Brink, Isabel W. C. E. Arends, Roger A. Sheldon*

Laboratory for Biocatalysis and Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
Phone: (+31)-15-2782683, fax: (+31)-15-2781415, e-mail: secretariat-ock@tnw.tudelft.nl.

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Abstract: Water-soluble complexes of palladium(II) with phenanthroline-derivatives are stable, recyclable catalysts for the selective aerobic oxidation of a wide range of alcohols to aldehydes, ketones, and carboxylic acids in a biphasic liquid-liquid system. The active catalyst is a dihydroxy-bridged palladium dimer. Kinetics of the reaction, ligand and anion effects are discussed.

Keywords: alcohols; kinetics; oxidation; palladium; water as solvent

Introduction

The world production of compounds containing carbonyl functionalities is well above 10^7 tonnes per annum[1] and a fair percentage of these aldehydes, ketones, and carboxylic acids are produced via alcohol oxidation. Traditionally, oxidations of alcohols are performed with stoichiometric amounts of inorganic oxidants, notably chromium(VI) reagents.[2] These oxidants are not only relatively expensive, they also generate copious amounts of heavy-metal waste. Moreover, the reactions are often performed in environmentally undesirable solvents, typically chlorinated hydrocarbons. In a constant search for cleaner ('greener') technologies, there is a definite need for catalytic oxidations employing dioxygen or hydrogen peroxide as the stoichiometric oxidant.[3] These oxidants are atom efficient,[4] producing water as the only by-product. Although the advantages of using oxygen in alcohol oxidation are evident, reports on this particular subject were scarce until recently. Many reports involve the oxidation of activated allylic and benzylic alcohols,[5,6] or use the Mukaiyama co-oxidation method in which oxygen is used in combination with >1 equivalent of a reactive aldehyde and peracids are the actual oxidants.[7] Nowadays, more and more examples involving oxidations of non-activated alcohols with dioxygen are reported. Many examples of homogeneous systems make use of palladium,[8,9,10] copper,[11] cobalt,[12] or ruthenium compounds,[13] usually in aromatic or halogenated hydrocarbon solvents. However, most of these catalysts are not very active (TOF $<10\ h^{-1}$) and therefore require fairly large amounts of catalyst (5 mol %) and sometimes co-catalysts (10–20 mol %). Furthermore, most systems operate under anhydrous conditions, while by definition water is formed during the reaction and many times pure oxygen is bubbled through a flammable solvent such as toluene at elevated temperatures.

It is obvious that more active catalysts are desired, preferably those that are stable (and soluble) in water. Such catalyst systems would be considerably safer, cheaper, and more environmentally friendly than many of the processes in use today. Moreover, when a water-soluble catalyst is used in a biphasic system, most products can be separated by simple decantation, the catalyst solution can be recycled, and a tedious distillation step is avoided.[10]

Supported noble metals, e.g., Pd/C or Pt/C are already known to catalyse the aerobic oxidation of alcohols in an aqueous medium, but the method is generally limited to water-soluble substrates, e.g., carbohydrates.[14] Moreover, primary alcohols are oxidised to carboxylic acids and one equivalent of base is required.[15]

Previously,[16] we reported on aerobic oxidation of alcohols with a water-soluble palladium complex of bathophenanthroline disulfonate (PhenS*). This catalyst was more active (TOF $\sim 100\ h^{-1}$) than the systems in organic solvents mentioned earlier, and was also recyclable. In this paper, we expand on this subject by discussing kinetic effects of the reaction and show some interesting differences between reactions in water and in conventional organic media.

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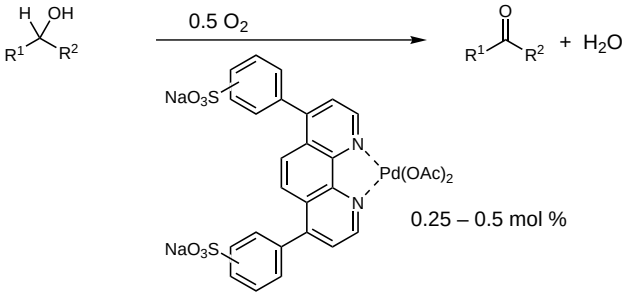


Figure 1. PhenS*Pd(OAc)$_2$-catalysed alcohol oxidation.

Results and Discussion

The catalytic system that we previously used under aqueous biphasic conditions is depicted in Figure 1.

The catalyst proved to be highly active in water and could be recycled several times without significant loss of activity or selectivity. Especially small (= more water-soluble), secondary aliphatic alcohols such as 2-pentanol or cyclopentanol were oxidised rapidly to their corresponding ketones and turn over frequencies (TOF) over 100 mmol mmol^{-1} h^{-1} were no exception. Another small alcohol, 2,2-dimethyl-3-butanol (Table 1, entry 1.1), reacted at >110 h^{-1}, seemingly unhindered by any steric effects. The reactivity of other aliphatic secondary alcohols seemed to follow their respective solubilities in water quite accurately (not shown).

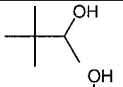
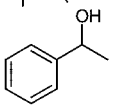
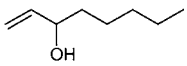
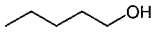
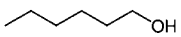
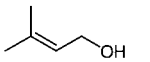
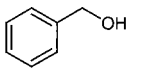
Surprisingly, the 'activated' benzylic alcohols reacted more slowly than expected, even when their low solubility in water was taken into account. For instance, while the alcohols should have similar solubilities in water, 1-phenylethanol (entry 1.2) reacted at a rate of ca. 20 h^{-1}, and the aliphatic 1-phenyl-2-propanol reacted at ca. 50 h^{-1}.

The 'activated' allylic alcohols also reacted relatively slowly, which might be due to competing coordination of the olefinic double bonds to palladium. Furthermore, when 1-octene-3-ol (entry 1.3) was oxidised some Michael addition of water to the double bond of the ketone and double bond isomerisation of the alkenol took place, decreasing the selectivity.

The primary allylic and benzylic alcohols afforded the corresponding aldehydes, as could be expected from previous results.[8] Surprisingly, primary aliphatic alcohols initially formed aldehydes, but under the reaction conditions these were oxidised further to the corresponding carboxylic acids. In the presence of a radical scavenger such as TEMPO, aliphatic aldehydes could also be obtained in high yields (entry 1.4). This is a significant difference from other (palladium-catalysed) aerobic oxidations in organic media where all primary aliphatic, allylic and benzylic aldehydes remained intact under the reaction conditions without any additives.[8] Further investigations are underway to explain the different reactivities of the various types of aldehydes in aqueous and organic solvents. Analogous to 3-penten-2-ol or 1-octen-3-ol the double bond in 3-methyl-2-buten-1-ol (entry 1.6, TOF $\sim$20 h^{-1}) or 1-penten-3-ol (TOF $\sim$20 h^{-1}, not shown) presumably coordinated to palladium as in Wacker-type reactions, but these only slowed the reaction down. Wacker-type products were not detected in these cases,[17] and no double bond isomerisation was observed.

Analogous to most other homogeneous catalysts for alcohol oxidation[8,13f] many functional groups in the substrate affect the catalyst performance, as they seem to coordinate more tightly to the metal centre than the hydroxy functionality. So far, only a single ether functionality – in butylproxitol – seems to be tolerated by the catalyst (Figure 2). When terminal olefinic double bonds are present in the molecule, at some distance from the alcohol moiety, as in 10-undecen-1-ol and 1-dodecen-11-ol (Figure 2), Wacker-type reaction is strongly preferred and in the initial stage of the reaction (even up to 50% conversion!) almost no alcohol oxidation is observed. Above 50% conversion the selectivity for the respective hydroxy ketones de-

Table 1. PhenS*Pd(OAc)$_2$-catalysed alcohol oxidation.[a]

entry	substrate	*t*/h	conv/%	sel/%[b]	yield/%[c]
1.1		5	100	100	90
1.2		10	90	100	85
1.3		12	97	80[d]	75
1.4		15	98	97[e,f]	90
1.5		12	95	90[g]	80
1.6		10	100	96[f]	88
1.7		10	100	99.8[f]	93

[a] Conditions: primary alcohol and 1-phenylethanol (10 mmol), secondary alcohol (20 mmol), PhenS*Pd(OAc)$_2$ (0.05 mmol), water (50 g), NaOAc (1 mmol), pH $\sim$6.5 – 11.5, 100 °C, 30 bar air.

[b] Based on the yield determined by GC using an external standard.

[c] Isolated yield.

[d] 3-Octanone ($\sim$15%) and 1-hydroxy-3-octanone (5%) were formed.

[e] TEMPO (4 equiv. to Pd) was added.

[f] Selectivity to aldehyde, acid was formed as the major by-product.

[g] Selectivity to acid, hexanal (7%) and hexyl hexanoate (2%) were also formed.

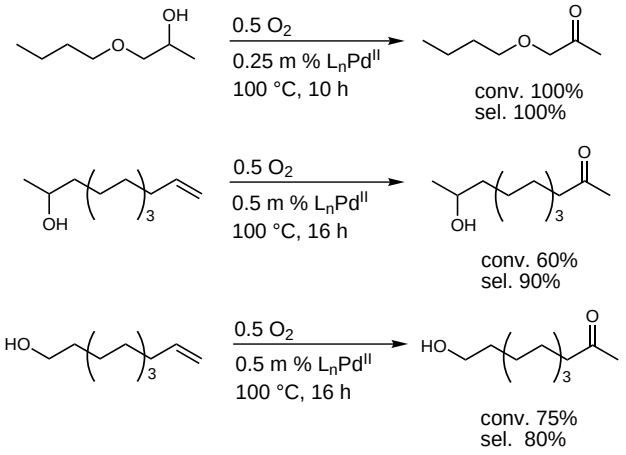


Figure 2. Reactive alcohols containing functional groups.

creased, but mainly due to further oxidation of the hydroxy ketone and not so much due to alcohol oxidation of the respective alkenols.

Interestingly, Nishimura et al. showed that, with a pyridine-palladium catalyst in toluene, selective alcohol oxidation takes place only under completely anhydrous conditions. With only traces of water present, olefin oxidation takes strong preference over alcohol oxidation.[8b, f]

Other functional groups such as sulfides, amines, or polyols, apparently coordinated strongly to palladium forming orange, red, or pale yellow complexes, respectively, and as a result no reaction was observed with alcohols containing these functionalities (Figure 3).

Ligand Effect (1): Preferred Ligand Type

Stoichiometric oxidation of alcohols by palladium salts is fairly straightforward,[18] as Berzelius already noted in 1828. Catalytic (aerobic) oxidation reactions are much more difficult, however. When the palladium salt is reduced it tends to form palladium black in an irreversible way ($\Delta H \approx -378$ kJ mol^{-1})[19] before reoxidation by dioxygen is effected. Therefore, to maintain a catalytic cycle, it is necessary to employ ligands[20] that either kinetically or thermodynamically facilitate reoxidation of Pd(0) to Pd(II). In solvents such as DMSO simple palladium salts [$Pd(OAc)_2$] were shown to be catalytically active in aerobic alcohol oxidation, probably because Pd(0)–DMSO complexes were formed that allowed (partial) reoxidation.[6,21] In water the use of a ligand is imperative because water cannot act as a strong ligand like DMSO. Such ligands must be oxidatively stable themselves and render palladium water-soluble. Table 2 shows a selection of water-soluble amines and phosphines that we have tested as ligands in the oxidation of 2-hexanol.

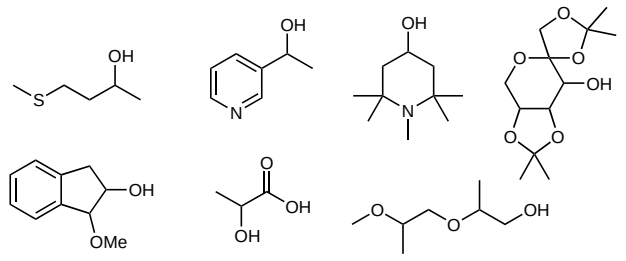
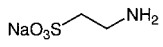
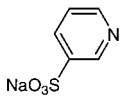
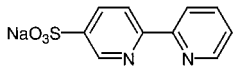
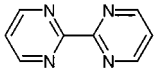
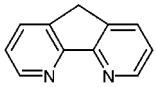
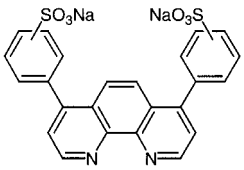
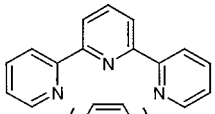
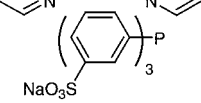


Figure 3. Unreactive alcohols containing functional groups.

Reduction of a palladium(II) salt by the alcohol leads to irreversible palladium black formation (entry 2.2), showing the necessity of a ligand for alcohol oxidations in water. Furthermore, the amine ligand has to be aromatic rather than aliphatic, enabling π-back-bonding from palladium to the ligand to ensure tighter coordination (entries 2.3 and 2.4).

Table 2. Ligands used in palladium catalysed oxidation of 2-hexanol.[a]

entry	ligand	conv/%	Pd_{black}[b]
2.1	Blank reaction	-	-
2.2	No ligand	0.5	++
2.3		9	++
2.4		19	+
2.5		35	+/-
2.6		>25[c]	+/-
2.7		<15[d]	+/-
2.8		60	-
2.9		0	-
2.10		25	++

[a] Conditions: 0.05 mmol (N^N)PhenS*Pd(OAc)$_2$, 20 mmol 2-hexanol, 50 mL water, 1 mmol NaOAc, pH ~6.5, 100 °C, 30 bar air, 5 h.
[b] Palladium black formation.
[c] Catalyst partly precipitated.
[d] Reaction at pH = 10, even poorer results obtained at neutral pH.

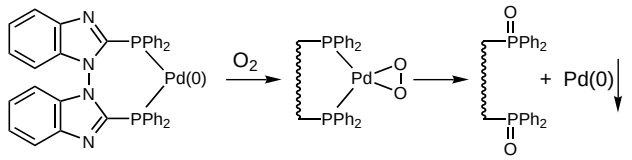


Figure 4. Palladium-catalysed phosphine oxidation.

Better coordination was achieved with bidentate ligands (entries 2.5 and 2.6), but even with sulfonated 2,2′-bipyridine some palladium black was formed. To enforce even stronger coordination from the ligand it should also have a rigid backbone such as the phenanthroline derivatives.[22] However, the ligand should also have the proper bite angle to give good overlap of the lone pairs of the amines with palladium.[23] This explains why the 4,5-diazafluorene ligand (entry 2.7) is a poor ligand for palladium in this reaction. The most suitable ligand for alcohol oxidation described here was the sulfonated bathophenanthroline (entry 2.8). These results contrast markedly with the pyridine-$Pd(OAc)_2$-catalysed aerobic alcohol oxidation in toluene. Nishimura et al. showed that in that case monodentate pyridine was a better ligand than 2,2-bipyridine, which in turn was much better than 1,10-phenanthroline.[8b]

The tridentate ligand terpy (entry 2.9) created a water-soluble palladium complex without the presence of sulfonate groups, but the resulting catalyst was completely inactive. This shows that palladium needs to have two labile coordination sites for a successful alcohol oxidation. The necessity of an oxidatively stable ligand is illustrated by tppts (entry 2.10). With this ligand an active "$(tppts)_2Pd(OAc)_2$" complex was obtained, but oxidation of the phosphine atom decreased its coordinating ability and after a few turnovers palladium black was formed in large amounts. Even with one of the most oxidatively stable phosphine ligands known (BIMIP, see Figure 4),[24] ligand oxidation could not be avoided, because palladium is also a catalyst for the oxidation of phosphines.[25]

Ligand Effect (2): Ratio of Ligand to Palladium

The ligand screening in Table 2 showed that bidentate ligands take preference over monodentate ligands, as the latter do not coordinate tightly to palladium. Bidentate ligands are also superior to tridentate ligands, probably because tridentate ligands do not provide the required free coordination site during catalysis. Varying the phenanthroline to palladium ratio exhibited a similar trend (see Figure 5).

The highest rate was observed with a ligand to palladium ratio of 1:1. When bathophenanthroline was used in more than stoichiometric amounts to palladium, the reaction rate decreased and the colour of the solution changed from yellow (ligand:palladium = 1:1)

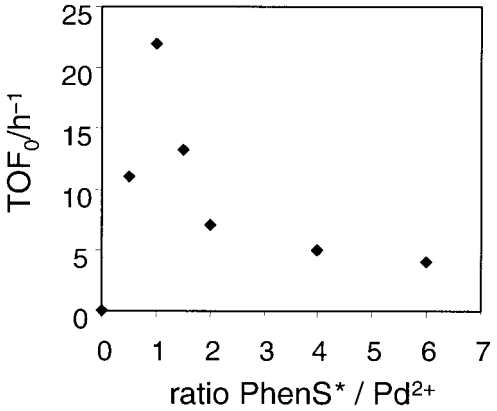


Figure 5. Optimum phenanthroline to palladium ratio for alcohol oxidation. Conditions: 0.05 mmol $Pd(OAc)_2$, 0 – 0.3 mmol PhenS*, 20 mmol 2-hexanol, 1 mmol NaOAc, 50 g water, 100 °C, 30 bar air, 5 h.

via orange (1.5:1) to red ($\geq$2:1). A similar red complex was observed by Bortolo[10] using phen/Pd^{2+} in a 2:1 ratio in alcohol oxidation, concomitant with deactivation of the complex. When, on the other hand, sub-stoichiometric amounts of ligands were used, the reaction rate also decreased. In this case it was due to formation of some palladium black.

Anion Effect

A certain amount of alkali salts of carboxylic acids has been used in many reactions that involve a catalytic cycle with the Pd(II)/Pd(0) redox couple. Wacker-type reactions,[26] Moiseev reaction,[27] oxidative cyclisation,[28] or Heck[29] reactions showed improved reoxidation of Pd(0) to Pd(II). These salts may hamper arrangement of ordered lattices in palladium clusters and thus facilitate penetration of substrates such as O_2. Alternatively, because palladium is a noble metal it is reoxidised reluctantly and acetate ions may compensate for this loss of electron density on the metal centre.

A number of counterions was tested to explore a possible anion effect in the phenS*-PdX_2-catalysed oxidation of 2-hexanol (see Table 3). Although acetate and acetylacetonate have some Brønsted basicity, this probably did not play a role because no pH effect was observed (see later).

The acetate and trifluoroacetate anions were beneficial to the reaction, giving the highest rates without palladium black formation. As could be expected, more tightly coordinating anions such as chloride and acetylacetonate retarded the reaction to a certain extent, while Pd(0) was still efficiently recycled to Pd^{2+}. However, when non-coordinating anions such as perchlorate, tetrafluoroborate, or triflate were used essentially all the palladium catalyst decomposed to palladium black and much less 2-hexanone was formed. It

Table 3. Anion effect in PhenS*PdX_2-catalysed alcohol oxidation.[a]

Entry	Anion	Conversion [%]	Pd_{black}[b]
3.1	CH_3CO_2	61	–
3.2	CF_3CO_2	61	–
3.3	NO_3[c]	39	–
3.4	Cl	14	–
3.5	acac[d]	12	–
3.6	ClO_4[c]	35	+
3.7	BF_4[c]	21	+
3.8	CF_3SO_3[c]	10	+

[a] Conditions: 0.05 mmol PhenS*PdX_2, 20 mmol 2-hexanol, 1 mmol NaX, 50 g water, 100 °C, 30 bar air, pH ~11, 5 h.
[b] Palladium black formation.
[c] Prepared from $phenPdCl_2 + 2$ AgX.
[d] No Na(acac) added.

seems that such anions cannot facilitate the reoxidation of zero-valent palladium.

The optimum catalyst system that we found so far consisted, therefore, of palladium acetate and one equivalent of sulfonated bathophenanthroline in neutral aqueous solution with one mmol of sodium acetate (20 equivalents to palladium) added for stability of the catalyst. With this system the kinetics of the reaction were investigated.

Reaction Order in Alcohol Concentration (Biphasic/Homogeneous)

When higher (partly water-soluble) alcohols were oxidised with oxygen catalysed by PhenS*$Pd(OAc)_2$ in an aqueous/organic biphasic system, a pseudo zero-order reaction in alcohol concentration was found because the concentration of alcohol *in the aqueous phase* did not change. Even though alcohol was converted, unreacted alcohol diffused from the organic phase and again saturated the aqueous phase. For example, when 10 mmol 2-hexanol was oxidised under the conditions mentioned in Figure 6 the concentration in the aqueous phase remained constant for 7 to 8 hours, until circa 7.5 mmol of 2-hexanol was converted. Only in the final stages of the reaction could the 'real' order in alcohol concentration be observed. Continuous monitoring of the oxygen uptake in time showed a pseudo-zero order in alcohol concentration at the beginning of the reaction and first order towards the end. This is analogous to the observed ketone formation in time as shown in Figure 6. The decrease in reaction rate was not caused by catalyst deactivation. When more alcohol was added at the beginning of the reaction the reaction rate remained constant for a longer period of time. It is also important to note that the reaction did not show a detectable induction period.[30]

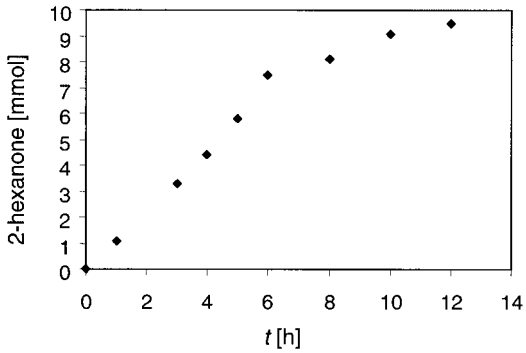


Figure 6. Conversion of 2-hexanol in time. Conditions: 0.05 mmol PhenS*$Pd(OAc)_2$, 10 mmol 2-hexanol, 1 mmol NaOAc, pH ~11, 50 g water, 30 bar air, 100 °C.

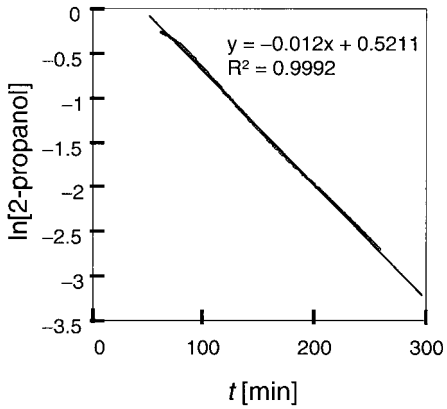


Figure 7. Order in (water-soluble) 2-propanol concentration, determined from O_2-consumption. Conditions: 0.05 mmol PhenS*$Pd(OAc)_2$, 40 mmol 2-propanol, 1 mmol NaOAc, pH ~11, 50 g water, 10 bar 8% O_2/N_2, 100 °C, flow rate 60 mL min^{-1} at 1 bar.

The real order in alcohol concentration could be determined more properly by using a completely water-soluble alcohol such as 2-propanol. In this case the logarithm of the alcohol concentration could be plotted against time and an order of one in alcohol concentration was now observed from t ~0 (Figure 7).

Reaction Order in Palladium Concentration

A large number of palladium(II) diamine[30,31] and diphosphine[32] complexes form dimeric species when dissolved in water. The solution becomes slightly acidic when complexes of the general structure $phenPd(X)_2$ are dissolved due to the formation of two equivalents of HX per palladium dimer (see Figure 8).[33]

In the case of the bathophenanthroline palladium complexes there was no exception. As was already observed for olefin oxidation using the same catalyst,[30] the precursor is a dihydroxy-bridged palladium dimer which is in equilibrium with (2 equivalents of) its monomer. The observed dependence of the reaction

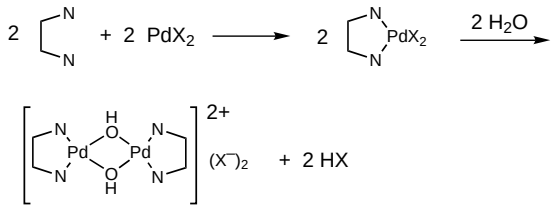


Figure 8. Formation of dimeric palladium species in water.

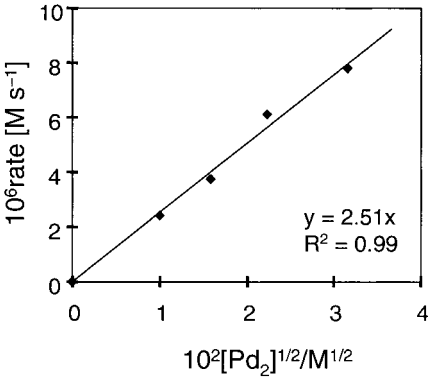


Figure 9. Order in palladium concentration. Experiments were carried out with 0 – 0.1 mmol PhenS*Pd$(OAc)_2$ in 50 g water, 20 mmol 2-hexanol, 1 mmol NaOAc, pH $\sim$11, 30 bar air, 100 °C, 2 – 24 h; [Pd_2] denotes the palladium dimer concentration.

rate on the square root of the palladium dimer concentration (see Figure 9) is consistent with this notion.

Consequently, we propose that the palladium dimer (shown schematically in Figure 8) is in equilibrium with 2 equivalents of the catalytically active palladium monomer. The substrate 2-hexanol was chosen deliberately because several palladium clusters[34] and palladium blacks[18a] are expected to be inactive in its oxidation, and can therefore be ruled out as active species. Furthermore, under sufficient oxygen pressure and mixing the catalyst solution did not show any change detectable by UV, which would be associated with the formation of giant palladium clusters.[21,35]

Oxidation of 2-hexanol under the experimental conditions is not diffusion-controlled. Neither the stirring speed nor the volume of the reaction had an influence on the reaction rate.

Base Effect

Many alcohol oxidations are carried out in the presence of a substantial amount of base, because the reaction often involves abstraction of a proton from an alcohol coordinated to the metal centre.[36] In initial reactions we also carried out the palladium-catalysed alcohol oxidation at pH $\sim$11 and with 1 mmol of NaOAc (20 equivalents to palladium). However, later experiments showed that a high pH was not necessary for a smooth reaction. Addition of some sodium acetate was beneficial to the reaction by preventing palladium black formation.[37] The salt was not required for its Brønsted basicity, and in HOAc/NaOAc buffers the concentration of buffer or pH did not show any clear relation with the reaction rate. Furthermore, even when the pH was varied between pH $\sim$6 and pH $\sim$11 through the addition of NaOH, no change in reaction rate was observed. Kozhevnikov[38] similarly showed that the reaction rate of alcohol oxidation by $Pd(H_2O)_4^{2+}$ salts does not necessarily depend on the pH. However, it is most likely that in that case giant palladium clusters were formed as the active species.[39] Only at pH $>$11.5 or higher, when a (PhenS*)$Pd(OH)_2$ species is formed[40] from the dimeric palladium species shown in Figure 8, is the catalyst system almost inactive.

The lack of base effect was rather surprising. It might be possible that splitting of the dimer assisted by the substrate is rate limiting. In that case base-catalysed deprotonation of the coordinated alcohol would not appear in the rate law. This is difficult to reconcile with the observation that the activation energy for 2-hexanol oxidation is estimated 70 kJ mol^{-1}, whereas the activation energy for 1-hexene oxidation[26] with the same complex is circa 90 kJ mol^{-1}. In competition experiments, however, olefins reacted more than 10 times faster than alcohols (Figure 2), suggesting preferential coordination to the palladium monomer or dimer. Furthermore, the palladium dimer reacted almost instantaneously with a number of substrates at room temperature, indicating that splitting of the dimer was facile.[31a,41] Several other explanations remain possible however.

Due to the nature of the diamine ligand some phenanthroline complexes of palladium are fairly strong acids,[40] e.g., (phen)$Pd(H_2O)_2^{2+}$ has pK_a $\sim$1, and coordinated alcohols are also expected to become more acidic upon coordination and, therefore, susceptible to deprotonation. However, should the alcohol coordinate and split the palladium dimer then a different situation arises with one hydroxy-ligand and one (perhaps less acidic) alcohol ligand. It is conceivable that palladium abstracts a hydride from the α-carbon atom directly, as was proposed by Kozhevnikov[38] and others (Figure 10, route A).[9b] Such a reaction is not totally unlikely, considering other existing C–H activation reactions by palladium.[42] Perhaps oxidative addition of the C–H bond to palladium creating five-coordinated palladium, or a direct attack as proposed in Figure 10 is feasible. This could create a Pd(I) α-hydroxyalkyl intermediate[43] that quickly reacts to the carbonyl compound, somewhat similar to the intermediate proposed in Wacker-type reactions.[44] This hydride abstraction mechanism would also imply that diisopropyl ether would be oxidised fairly easily to acetone and isopropanol.[45] However, no reaction of diisopropyl ether with PhenS*Pd^{2+} was observed, nor

was the tertiary 1-methylcyclohexanol affected.[46,47] Therefore, this mechanism can be ruled out for the PhenS*Pd^{2+}-catalysed reaction, but it may still be operative in Pd-cluster catalysis.

Alternatively, the coordinated hydroxide may abstract the proton from the alcohol, giving a palladium alkoxide[48] species and water as a leaving group. Most palladium-alkoxy complexes known are unstable species, yielding aldehydes or ketones and (an often unstable) palladium hydride. This mechanism (route C) would not be acid/base dependent and would create a vacant site at palladium for β-hydride elimination.[49] A somewhat similar active role for the hydroxide ligand has been proposed for Wacker-type reactions,[50] while the (terpy)Pd^{2+} complex lacking such a labile ligand was inert in alcohol oxidation (see Table 2). A similar elimination step has been proposed before in the reaction of alkene-palladium complexes with alcohols[51] and in the palladium-catalysed oxidation of hydroquinone.[52] The reverse mechanism – insertion of $R_2C=O$ into a metal-hydride – is operative in hydrogenation reactions.[53]

Other options that may not involve acid/base catalysis are that the alcohol

1) attacks the palladium dimer and exchanges for one or both hydroxide ligand(s) as shown in Figure 10, route B;
2) inserts into one or both palladium hydroxide bond(s) creating a six- or eight-membered[54] ring while keeping the dimer intact until the elimination step (not shown);
3) coordinates sideways to the hydroxide, keeping the dimer intact until the elimination step (not shown).[55]

In these cases either palladium centre of the dimer could in principle abstract the hydride from the alcohol. These routes seem less likely in view of the order 0.5 for palladium dimer concentration. Furthermore, such reactions would probably suffer from increased steric hindrance on the phenanthroline ligand[10] and alcohol. These effects were not observed, however. Therefore, based on these findings a pathway involving a palladium-alkoxy intermediate seems the most likely of the reactions mentioned above.

Primary Alcohol vs. Secondary Alcohol Competition

A comparison of the relative reactivities of primary and secondary alcohols also yields information about the path of the reaction. Secondary alcohols may often react faster than primary alcohols *in separate experiments*, due to the increased electron density on the secondary alcohol. This is the case with the PhenS*Pd^{2+}-catalysed oxidation of alcohols, as well. For instance, 2-propanol reacts faster than 1-propanol ($TOF_0 > 75\ h^{-1}$ vs. $\sim 20\ h^{-1}$). However, *in a competition experiment* the reverse may take place: primary alcohols reacting faster than secondary alcohols. This phenomenon hints at the presence of a metal-alkoxy species[48] as an intermediate in the catalytic cycle, rather than a complex that abstracts a hydride [$R_2C(OH)-H$] from the alcohol.[56] This preference is possibly due to a combination of decreased steric hindrance of the coordinated primary alkoxy group compared to the secondary alkoxy group and higher acidity of the primary alcohol. Due to the fact that oxidation of most alcohols in water proceeds under biphasic conditions comparison of different alcohols is nearly impossible. The respective alcohols have differ-

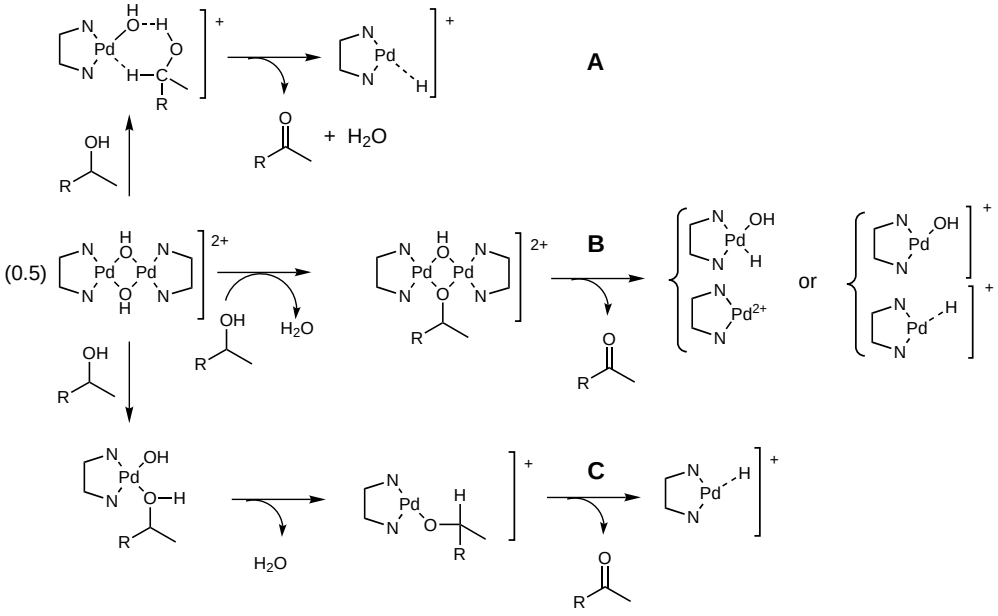


Figure 10. Possible routes for ketone formation.

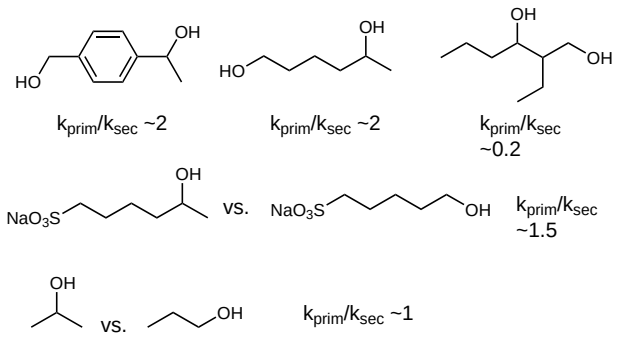


Figure 11. Competition of primary vs. secondary alcohols, standard conditions, pH 6.5, conversion $\sim$10%.

ent solubilities (concentrations) in the aqueous phase and react accordingly. When the reactivity of a primary alcohol is compared to that of a secondary alcohol it is imperative, therefore, that at the start of the reaction they are present in the same quantities. When operating in water there are two options (see Figure 11): 1) both alcohol functionalities are present in the same molecule (intramolecular competition), or 2) both alcohols are completely water-soluble (intermolecular competition).

Palladium-catalysed oxidation of α,ω-diols is often difficult due to chelation of the metal or prevalent ether formation.[57] Nonetheless, both benzylic 1-(4-hydroxymethylphenyl)ethanol and aliphatic 1,5-hexanediol could be oxidised and showed a preference for oxidation of the primary alcohol functionality at low conversions ($k_{prim}/k_{sec} \sim 2$ at 100 °C). The commercially available 2-ethyl-1,3-hexanediol, however, showed preference for oxidation of the secondary alcohol ($k_{prim}/k_{sec} \sim 0.2$ at 100 °C). An accurate measurement of the relative ratios was not possible due to the complicated product mixture arising from, e.g., retro-aldol reactions, but it seems that in this case the alcohol groups are too close and influence the relative rates.[58]

In the intermolecular competition experiments between the sulfonated alcohols there was again a preference for the primary alcohol ($k_{prim}/k_{sec} \sim 1.5$), albeit smaller than in intramolecular competition. Competition between the isomeric propanols did not show any clear preference ($k_{prim}/k_{sec} \sim 1$). Although the relative rates of primary and secondary alcohol oxidations were reversed in competition experiments, these observations do not constitute strong support for the presence of a palladium-alkoxy intermediate.[59] The values for k_{prim}/k_{sec} are low compared to $k_{prim}/k_{sec} \sim 10$ obtained for some ruthenium-catalysed reactions that are believed to proceed via a metal-alkoxy intermediate.[13] The values are very high, on the other hand, compared to that of $\sim$0.1 obtained in the oxidation of 1,6-heptanediol by the triphenylcarbenium ion, which is supposed to involve hydride abstraction.[56,60]

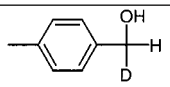
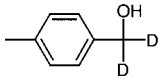
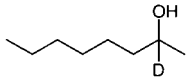
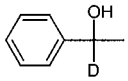
It is noteworthy that Kaneda[34,61] observed facile oxidation of primary allylic alcohols by palladium clusters, but very slow oxidation of secondary allylic alcohols and benzyl alcohol. This is another indication that clusters were not operative in the PhenS*Pd^{2+}-catalysed alcohol oxidation, as steric effects on the substrate can play a major role in cluster catalysis.[62]

Kinetic Isotope Effect

To obtain information about the rate determining step several deuterated alcohols were tested in the PhenS*$Pd(OAc)_2$-catalysed oxidation (see Table 4). Kinetic isotope effects were measured in intramolecular and intermolecular competition experiments.

In the case of monodeuterated *p*-methylbenzyl alcohol the concentration and conversion of the alcohol during reaction are not important to calculate the effect accurately. The product in this case is the *p*-tolualdehyde with either H or D incorporated. The value $k_H/k_D = 1.6 \pm 0.2$ at 100 °C is fairly close to that of 1.8 ± 0.1 at 96 °C found by Kozhevnikov et al. in *iso*-C_3D_7OD vs. *iso*-C_3H_7OH oxidation by palladium under acidic conditions.[38,63] In that case hydride abstraction from the alcohol by palladium leaving the hydroxy group intact was proposed to be the rate-limiting step. In acidic media this route is perhaps more likely than a mechanism involving a palladium-alkoxy intermediate.[64] Such a palladium-alkoxide intermediate was proposed by Henry, who found a value of 1.8 ± 0.1 at 25 °C in the oxidation of allyl alcohol[17b] and of 2–2.5 at 25 °C for benzyl alcohol.[65]

Table 4. Kinetic isotope effect in alcohol oxidation.[a]

entry	substrate	competition	*T*/K	k_H / k_D
4.1		intramolecular	383	1.6
4.2	"	"	373	1.6±0.2
4.3	"	"	363	1.9
4.4	"	"	353	1.6
4.5	"	"	343	2.1
4.6	"	"	333	2.0
4.7		intermolecular	373	1.4
4.8		"	373	1.2
4.9		"	373	1.4

[a] Conditions: 0.05 mmol PhenS*$Pd(OAc)_2$, 2–5 mmol alcohol, 1 mmol NaOAc, 30 bar air, temperature as indicated; conversion $\sim$10% for intermolecular reaction.

Both attack of palladium on the carbon hydride and the β-hydride elimination of the palladium alkoxy intermediate could proceed via an unsymmetrical transition-state of linear H-transfer. However, closer analysis of the k_H/k_D values at different temperatures could not corroborate this.[66]

The intermolecular competition experiments between *p*-methylbenzyl alcohol, 1-phenylethanol, and 2-octanol and their respective deuterated analogues show similar values of about $k_H/k_D \sim 1.4$ at 100 °C, although data from such intermolecular reactions should be treated with caution. The fact that a (small) KIE was observed, both with intramolecular and intermolecular competition experiments, indicates that the β-hydride elimination step is probably rate-limiting.

Reoxidation of PhenPd(0)

Two pathways (routes A and C) involving a palladium-alkoxide and direct attack of palladium on the carbon-hydride in Figure 10 yield a palladium hydride complex after reduction of the complex by alcohol. Several authors have proposed such a Pd-H species[67] to be the intermediate in alcohol oxidation by analogy with stable hydrides of Pt, Ru, and Ir.[53,68] Furthermore, palladium-(hydride) complexes are known to be active in transfer hydrogenation using alcohols as the hydride source.[69] But, contrary to the other metal hydrides mentioned above, palladium hydrides are often highly unstable and rarely isolated.[53,70] These hydrides can be stable in palladium clusters,[71] but a simple (phen)Pd-H]$^+$ species may not be long-lived enough to permit dioxygen insertion forming a palladium hydroperoxide.[72] Large amounts of strong acids are required (e.g., 1 equiv. camphorsulfonic acid) to protonate Pd(0) and allow dioxygen insertion. On the other hand, with $Pd(PPh_3)_4$, no acid is required to oxidise $Pd(PPh_3)_4$ to $(PPh_3)_2Pd(O_2)$ and start a catalytic cycle.[73] More interestingly, a very recent article by Stahl et al. described facile formation of (bathocuproine)$Pd(O_2)$ from a (bathocuproine)Pd(0) precursor (see Figure 12).[74]

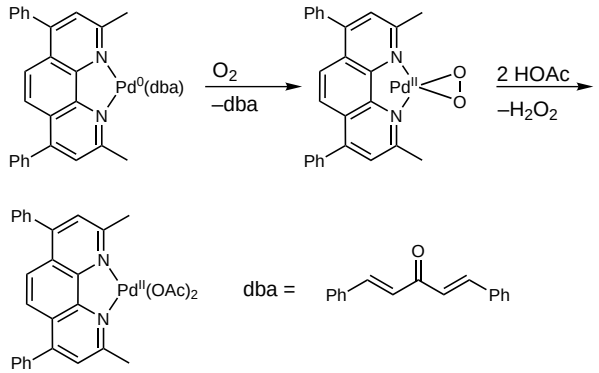


Figure 12. Reoxidation of (bathocuproine)Pd(0).

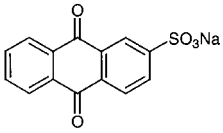
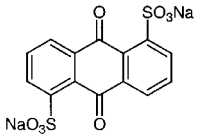
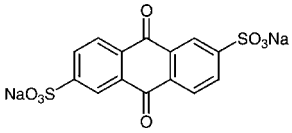
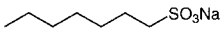
Therefore, if a transient palladium hydride complex [(phen)Pd-H]$^+$ is formed in the catalytic cycle (see later) it is expected to readily decompose to a proton and (phen)Pd(0). The latter reacts with dioxygen to form a palladium peroxide species analogous to triphenylphosphine palladium[73] or bathocuproine palladium[74] complexes. Alternatively, during catalysis the phenPd(0) species may find temporary stabilisation in a cluster small enough to allow (rapid) reoxidation. The palladium peroxide species are then protonated to form a palladium hydroperoxide.[75] Stahl[74] showed that only a weak acid such as acetic acid was required to protonate the basic peroxo moiety in (bathocuproine)$Pd(O_2)$ and induce the formation of hydrogen peroxide and the reoxidised Pd(II) complex. Even water would probably be a strong enough acid to do so, as Moiseev[76] observed the release of hydrogen peroxide from a small $Pd_{10}phen_4(OAc)_2(O_2)_3$ cluster formed from phenanthroline and $Pd(OAc)_2$ after partial reduction and a short exposure to air.

Nishimura used a similar palladium-pyridine system for aerobic alcohol oxidation in toluene and observed formation of hydrogen peroxide.[8] Interestingly, formation of hydrogen peroxide is only successful in a biphasic system when palladium is kept in an organic phase, separate from hydrogen peroxide.[10] With water-soluble palladium phenanthroline complexes *no* H_2O_2 was found due to the catalase effect of the complex, i.e., rapid decomposition into water and ½ equivalent of dioxygen.[10,16]

Stahl et al. also showed that starting from the Pd(0) complex the rate of reoxidation is first order in oxygen pressure. In contrast, in our case the oxygen pressure had little influence on the reaction rate. The PhenS*Pd^{2+}-catalysed reaction could be carried out with 8% O_2, 21% O_2, or 100% O_2 at 30 bar without affecting the reaction rate. Reoxidation of PhenS*Pd(0) with 8% O_2 at 10 bar was still efficient enough to prevent palladium cluster/black formation, but with pure dioxygen at atmospheric pressure the solution turned dark and little product was formed. In their analogous alcohol oxidation system Bortolo[10] et al. observed similar independence of the reaction rate on the oxygen pressure between 5 and 50 bar of oxygen. Kozhevnikov[77] noted that in palladium-HPA-catalysed oxidation of alcohols the reaction rate could become independent of the oxygen pressure already at ~ 1 bar O_2. These results indicate that reoxidation during catalysis occurs after the rate-limiting step. It should be noted, however, that it is necessary to apply oxygen pressure in our (aqueous) system, because the solubility of dioxygen in water is about an order of magnitude lower than in other commonly used organic solvents.[78]

The reoxidation step was not promoted by electron-mediators such as anthraquinones (Table 5) when 30 bar of air was applied. Addition of 2-AMS[79] (entry 5.2) had a positive effect on the reaction rate under the con-

Table 5. Promoting effect of electron mediators.[a]

entry	additive	TOF/h^{-1}	E_0 (neutral)[b]	E_0 (basic)[b]
5.1	-	45-50	-	-
5.2		105	0.187	-0.383
5.3		55	0.239	n.d.
5.4		50 (40)[c]	0.228	-0.325
5.5		85	-	-

[a] Conditions: 0.05 mmol PhenS*Pd(OAc)$_2$, 20 mmol 2-hexanol, 1 mmol NaOAc, 0.25 mmol RSO_3Na, 50 g water, 100 °C, 30 bar air, 2 – 5 h pH = 11.
[b] Vs. NHE.
[c] pH = 6.5.

ditions given below Table 5. This was probably due to an increased solubility of the alcohol in the aqueous phase and not due to its redox-properties. Symmetrical anthraquinones such as 1,5-ADS (entry 5.3) and 2,6-ADS (entry 5.4) did not increase the reaction rate. Although their redox-potentials are similar to that of 2-AMS these compounds have poor surfactant-like properties.[80] Furthermore, 1-heptanesulfonate does not have redox-properties, but gave a rate enhancement, presumably due to its surfactant-like behaviour.

The most plausible reaction cycle based on the results described above is depicted in Figure 13.

In this cycle the starting complex is the palladium dimer that dissociates upon coordination of alcohol. A palladium(II)-hydroxy-alcohol complex is formed that – without the aid of a base – eliminates water to give a palladium(II)alkoxy species with a vacant site on palladium. This undergoes β-hydride elimination to yield the carbonyl product, a proton, and the palladium(0) complex. The latter might find temporary stabilisation in a small cluster, but these clusters are not believed to play an active role in catalysis. Reoxidation of the Pd(0) complex with dioxygen yields a η-peroxide complex, which, on protonation, affords the starting palladium dimer and 'transient' hydrogen peroxide.

Conclusions

Based on the data collected in this paper a plausible catalytic cycle for palladium-phenanthroline-catalysed oxidation of alcohols in water is described. The order of ½ in palladium concentration and order of 1 in alcohol concentration indicate that the starting complex is a palladium dimer in equilibrium with two equivalents of palladium monomer. It is likely that this monomer reacts via alkoxide/β-hydride elimination rather than via hydride abstraction from the alcohol. Reoxidation of palladium is likely to proceed via direct formation of palladium peroxide, rather than insertion of O_2 in a palladium hydride. It is possible that some small clusters are formed during catalysis. However, these clusters are not believed to be active in alcohol oxidation.

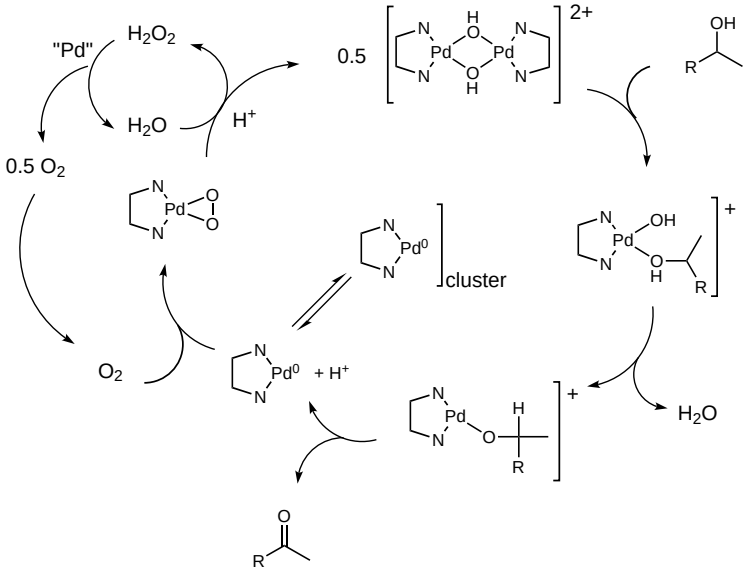


Figure 13. Total reaction cycle proposed for PhenS*Pd(OAc)$_2$-catalysed alcohol oxidation.

Experimental Section

Synthesis of 1-Dodecen-11-ol

A solution of 10-undecenal (60 mmol, 10 g, 12.3 mL) in anhydrous ether (20 mL) was added to a solution of MeMgI (66 mmol) in anhydrous ether (100 mL) under N_2 at 0 °C. The solution was then refluxed for 1 hour, cooled to 0 °C and poured on ice (250 g). The mixture was acidified with 1 M HCl until complete dissolution. The organic phase was separated and the aqueous phase extracted with ether (3 × 50 mL). The combined organic phases were washed with water (100 mL), 10% $NaHCO_3$ (100 mL), and dried over $MgSO_4$. The salt was filtered off, the filtrate was concentrated under vacuum, and the residue was purified via bulb-to-bulb distillation (bp 120 °C/0.4 mbar) to give a colourless oil; yield: 8.1 g (44 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 5.80 (1H, m, RC*H* =), 4.95 (2H, m, CH_2 =), 3.76 (1H, m, C*H*OH), 2.01 (2H, q, *J* 7.3 Hz, = CHC*H*$_2$), 1.93 (1H, s, OH), 1.5 – 1.2 (14H, m, -C_7H_{14}-), 1.17 (3H, t, *J* 6.2, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 139.2 (C-2), 114.1 (C-1), 68.1 (C-11), 39.4 (C-10), 33.8 (C-3), 29.7, 29.6, 29.5, 29.2, 29.0, 25.8 (C-9), 23.5 (C-12); MS: *m/z* = 184 (M^+, 2), 166 (5, M – H_2O), 138 (6), 124 (13), 109 (11), 96 (27), 95 (25), 82 (38), 81 (29), 69 (32), 68 (28), 67 (32), 55 (57), 45 (100).

Synthesis of 3-(1-Hydroxyethyl)pyridine[81]

A solution of 3-acetylpyridine (50 mmol, 6.25 g) in 50% aqueous MeOH (120 mL) was added dropwise to a suspension of $NaBH_4$ (250 mmol, 9.6 g) in 50% aqueous MeOH (120 mL) and the mixture was stirred overnight at room temperature. The solution was extracted with ether (3 × 100 mL) and the organic phase was dried over $MgSO_4$. The solid was filtered off, the filtrate was concentrated under vacuum, and the residue was purified via bulb-to-bulb distillation (bp 110 °C/0.6 mbar) to afford a colourless oil; yield: 5.5 g (45 mmol, 90%, lit. 98%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 8.41 (1H, s, H-2), 8.30 (1H, d, *J* = 4.3 Hz, H-6), 7.73 (1H, d, *J* = 7.9 Hz, H-4), 7.23 (1H, t, *J* = 4.9 Hz, H-5), 5.6 (1H, s broad, OH), 4.88 (1H, q, *J* = 6.4 Hz, C*H*OH), 1.46 (2H, d, *J* = 6.6 Hz, CH_3); 13C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 147.7 (C-6), 146.8 (C-2), 142.0 (C-3), 133.7 (C-4), 123.6 (C-5), 67.3 (CHOH), 25.2 (CH_3); MS: *m/z* = 123 (38), 108 (100), 80 (97), 51 (45).

Synthesis of 1-Methylthio-3-butanol

A solution of 3-methylthiopropanal (40 mmol, 4.28 g, 4.11 mL) in anhydrous ether (20 mL) was added under N_2 at 0 °C to a solution of methylmagnesium iodide (40 mmol) in anhydrous ether (100 ml). The reaction mixture was stirred overnight at room temperature and quenched with saturated NH_4Cl. The organic layer was separated, the aqueous solution was extracted with ether (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solid was filtered off, the filtrate was concentrated under vacuum, and the residue was purified via bulb-to-bulb distillation (bp 100 °C/0.6 mbar) to afford a colourless oil; yield: 2.5 g (21 mmol, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 3.95 (1H, m, C*H*OH), 2.62 (2H, t, *J* = 7.2 Hz, SCH_2), 2.38 (1H, s, OH), 2.12 (3H, s, SCH_3), 1.74 (2H, m, CH_2), 1.22 (3H, d, *J* = 6.3 Hz, CHOHC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 67.3 (C-3), 37.8 (C-2), 30.8 (C-1), 23.5 (C-4), 15.5 (SCH_3); MS: *m/z* = 120 (88), 105 (8), 102 (10), 87 (51), 72 (70), 61 (100), 57 (62), 45 (75).

Synthesis of Sodium 6-Hydroxyhexyl-1-sulfonate[82]

A mixture of 6-chloro-1-hexanol (40 mmol, 5.3 g) and Na_2SO_3 (45 mmol, 5.7 g) in water (30 mL) was refluxed for 12 h. The solution was cooled to room temperature, it was extracted with ether (2 × 20 mL) and the aqueous solution was evaporated under vacuum to dryness. Cold, concentrated HCl (32 mL, 35 – 37%) was added and after cooling to 0 °C a white solid was filtered off. The filtrate was reduced to about half its original volume, methanol (15 mL) was added and the solution was saturated with HCl at 0 °C. Again, a white solid was filtered off and the filtrate was dried under vacuum until no more acid could be smelled. The sulfonic acid was neutralised with a dilute NaOH-solution, the solution was again evaporated to dryness and dried further in an oven at 110 °C. Lastly, the solid was crystallised from methanol, furnishing a white crisp powder; yield: 6.5 g (80%). ^{1}H NMR (400 MHz, D_2O, *tert*-BuOH): δ = 3.56 (2H, t, *J* = 6.6 Hz, *C*H_2OH), 2.86 (2H, t, *J* = 7.9 Hz, CH_2SO_3Na), 1.69 (2H, p, *J* = 7.8 Hz, *C*$H_2$$CH_2SO_3Na$), 1.52 (2H, p, *J* = 7.0 Hz, CH_2), 1.4 – 1.3 (4H, m, 2 CH_2); ^{13}C NMR (100 MHz, D_2O, *tert*-BuOH): δ = 63.3 (C-6-OH), 52.6 (C-1-SO_3Na), 32.6 (C-5), 29.0 (C-3), 26.2 (C-2), 25.5 (C-4); LCMS: *m/z* = 227 (M^+ + Na, 70), 136 ($C_4H_8SO_3^+$, 50), 83 (56), 57 (50), 55 (100).

Synthesis of 6-Chlorohexanal

A mixture of PIPO[83] (0.5 g), 6-chloro-1-hexanol (66 mmol, 9.0 g), MTBE (200 mL) and NaOCl solution (0.35 M, 300 mL, pH adjusted to 9.1 with solid $KHCO_3$) was stirred for three hours. The organic phase was separated, the aqueous phase was extracted with ether (200 mL) and the combined organic phases were dried over $MgSO_4$. After filtration the filtrate was evaporated under vacuum and the resulting yellow-orange oil was purified via bulb-to-bulb distillation (bp 140 °C/2 mbar) to give a clear colourless liquid; yield: 5.5 g (41 mmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): d = 9.77 (1H, t, *J* = 6.6 Hz, CHO), 3.54 (2H, t, *J* = 6.6 Hz, CH_2Cl), 2.47 (2H, dt, *J* = 7.1 and 1.6 Hz, *C*H_2CHO), 1.80 (2H, p, *J* = 7.4 Hz, CH_2), 1.66 (2H, p, *J* = 7.6 Hz, CH_2), 1.48 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ = 202.3 (C = O), 44.7 (CH_2Cl), 43.7 (C-2), 32.3 (C-5), 26.4 (C-4), 21.3 (C-3); MS: *m/z* = 133 (M^+ – H, < 1), 116 (M^+ – H_2O, < 1), 106 (M^+ – CO, 6), 98 (M^+ – Cl, 5), 69 (10), 57 (20), 55 (28), 54 (22), 44 (100).

Synthesis of 1-Chloro-6-heptanol

A solution of 6-chlorohexanal (37.3 mmol, 5.0 g) in anhydrous ether (15 mL) was added to a solution of MeMgI (~41 mmol, 1.1 equiv.) in anhydrous ether (100 mL) under nitrogen at 0 °C. After addition the solution was refluxed for 2 hours, cooled to 0 °C and hydrolysed. The biphasic mixture was acidified with saturated NH_4Cl and further work-up was a usual. The crude alcohol was purified via bulb-to-bulb distillation (bp 105 °C/4 mbar) to afford a faint-yellow oil; yield: 4.5 g (30 mmol,

80%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 3.79 (1H, m, C*H*OH), 3.54 (2H, t, *J* = 6.8 Hz, CH_2Cl), 1.79 (2H, m, CH_2CHOH), 1.52 (1H, s, OH), 1.5 – 1.3 (6H, m, $ClCH_2CH_2CH_2CH_2$), 1.19 (3H, d, *J* = 6.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4 Si): δ = 68.0 (CHOH), 45.1 (CH_2Cl), 39.1 (C-5), 32.6 (C-2), 26.9 (C-3), 25.1 (C-4), 23.6 (C-7); MS: *m/z* = 149 (M^+ – H, 1), 135 (M^+ – Me, 4), 117 (M^+ – Me – H_2O, 1), 81 (10), 55 (19), 45 (100).

Synthesis of Sodium 6-Hydroxy-1-heptanesulfonate

The synthesis was similar to that of the 6-hydroxyhexyl-1-sulfonate, but the white solid that was obtained could not be crystallised from methanol or ethanol. It was therefore boiled in acetone and filtered hot. The sticky white residue was washed with cold acetone to give a voluminous 'dry' white powder; yield: 5.0 g (23 mmol, 76%). ^{1}H NMR (400 MHz, D_2O, *tert*-BuOH): δ = 3.78 (1H, sextet, *J* = 6.2 Hz, C*H*OH), 2.86 (2H, t, *J* = 7.9 Hz, CH_2SO_3Na), 1.70 (2H, pentet, *J* = 7.5 Hz, CH_2CHOH), 1.45 – 1.25 (6H, m, $CH_2CH_2CH_2CH_2SO_3Na$), 1.21 (3H, d, *J* = 6.3 Hz, CH_3); ^{13}C NMR (100 MHz, D_2O, *tert*-BuOH): δ = 69.4 (CHOH), 52.1 (CH_2SO_3Na), 39.2 (C-5), 29.2 (C-3), 26.0 (C-2), 25.5 (C-4), 23.4 (C-7); LCMS: *m/z* = 241 (M^+ + Na, 100), 155 (5), 139 (5), 59 (20).

Products

***n*-Butoxyacetone:** MS (CI): *m/z* = 131 (100), 115 (25), 95 (8), 85 (19), 74 (92).

1-Hydroxy-10-undecanone: MS: *m/z* = 186 (M^+, 6), 128 (5), 110 (26), 95 (10), 83 (16), 82 (25), 81 (20), 71 (53), 69 (49), 59 (60), 58 (100), 55 (57).

10-Undecenal: *m/z* = 168 (M^+, ~0), 150 (4), 121 (11), 98 (20), 83 (31), 82 (32), 81 (27), 69 (30), 68 (35), 67 (47), 55 (100), 54 (36).

10-Oxoundecanal: *m/z* = 184 (M^+, 1), 141 (10), 123 (10), 108 (27), 81 (22), 71 (45), 67 (21), 59 (42), 58 (100), 55 (37).

10-Oxoundecanoic acid: *m/z* = 200 (M^+, 2), 182 (7), 142 (7), 125 (36), 124 (28), 98 (19), 97 (26), 83 (20), 71 (31), 69 (23), 58 (100), 55 (49).

11-Hydroxy-2-dodecanone: *m/z* = 200 (M^+, 1), 185 (10), 182 (6), 156 (15), 124 (23), 96 (29), 82 (40), 71 (84), 69 (43), 58 (100), 55 (63), 45 (99).

1-Dodecen-11-one: *m/z* = 182 (M^+, 5), 167 (2), 164 (5), 124 (15), 97 (11), 96 (11), 82 (25), 71 (43), 58 (100), 55 (43).

2,11-Dodecanedione: *m/z* = 198 (M^+, 14), 183 (4), 141 (39), 123 (25), 97 (15), 83 (40), 71 (84), 58 (100), 55 (59).

Sodium 6-oxoheptyl-1-sulfonate: ^{1}H NMR (300 MHz, D_2O, *tert*-BuOH): δ = 2.86 (2H, t, *J* = 7.9 Hz, CH_2SO_3Na), 2.54 (2H, t, *J* = 7.3 Hz, CH_2CO), 2.16 (3H, s, CH_3), 1.69 (2H, p, *J* = 7.7 Hz, CH_2), 1.53 (2H, p, *J* = 7.4 Hz, CH_2), 1.38 (2H, p, *J* = 7.4 Hz, CH_2); ^{13}C NMR (75 MHz, D_2O, *tert*-BuOH): δ = 218.8 (CO), 52.4 (CH_2SO_3Na), 44.5 (C-5), 30.8 (C-7), 28.7 (C-3), 25.3 (C-2), 24.4 (C-4).

For analysis of products obtained in oxidation of 1-(4-hydroxymethylphenyl)ethanol and 1,5-hexanediol, see Dijksman et al.[13f]

Materials

$Pd(OAc)_2$ (98%), $PdCl_2$, $Pd(O_2CCF_3)_2$, bathophenanthroline-disulfonic acid disodium salt (98%), taurine (99%), 1-phenylethanol (98%), benzyl alcohol (99%), 2-ethyl-1,3-hexanediol (99%) and sodium heptanesulfonate (98%) were purchased from Acros; 2-pentanol (99%), 2-hexanol (99%), cyclopentanol (99 + %), 1-pentanol (99 + %) and 1-hexanol (99 + %) from Fluka; $Pd(acac)_2$, sodium pyridine-3-sulfonate (97%), terpy (98%), 3-penten-2-ol (96%), 3-methyl-2-buten-1-ol (99%), 10-undecen-1-ol (98%), 10-undecenal (95%) and 1,5-hexanediol (99%) from Aldrich; 2,2′-bipyrimidine (96%) from Lancaster; 1-propanol (99 + %) and 2-propanol (99 + %) from Baker; $NaOAc \cdot 3\ H_2O$ (> 99.5%) from Merck; 2-AMS, 1,5-ADS and 2,6-ADS from Janssen; 4,5-Diazafluorene was synthesised via oxidation of 1,10-phenanthroline,[84] subsequent treatment of the dione with sodium hydroxide[85] and reduction of 4,5-diazafluorenone with hydrazine hydrate.[86] Sodium 2,2′-bipyridine-5-sulfonate[87] was synthesised via sulfonation of 2,2′-bipyridine with oleum (30% SO_3) and $HgSO_4$. The diol 1-(4-hydroxymethylphenyl)ethanol was obtained via reduction of 4-acetylbenzoic acid with $LiAlH_4$.[13f] Deuterated alcohols were prepared according to literature procedures.[13f]

Catalytic Experiments

The catalyst solutions of PhenS*$Pd(OAc)_2$ were prepared by stirring $Pd(OAc)_2$ (0.112 g, 0.5 mmol) and PhenS* (0.274 g, 0.5 mmol) overnight in water (500 mL) to give a clear yellow-orange solution. Standard catalytic experiments were carried out in a closed Hastelloy C autoclave (175 mL). The autoclave was cooled to ca. 0 °C, charged with the catalyst solution (0.05 mmol catalyst in 50 mL water), alcohol (10 – 20 mmol), sodium acetate (1.0 mmol) and internal standard (*n*-heptane, *n*-octane or *n*-dodecane). The autoclave was pressurised with air or 8% O_2 in N_2 and heated to 100 °C (30 bar), while stirring (750 rpm). After reaction the autoclave was cooled to 0 °C and depressurised. Any volatile material was collected in a liquid nitrogen trap. The product mixture was extracted with Et_2O, the organic layer was dried over $MgSO_4$, a different external standard (*n*-dodecane or *n*-hexadecane) was added and the solutions were analysed by GC. Recoveries were always 100 ± 2% with this procedure. The oxidation of 2-propanol was followed by monitoring the oxygen uptake as a function of time, under a continuous stream (60 mL min^{-1} at 1 bar, pressure in autoclave: 10 bar) of 8% O_2 in N_2. Oxygen concentration of the outgoing flow was measured once per second.

Apparatus

^{1}H and ^{13}C NMR-spectra were recorded on a Bruker AC 300 or Varian VXR-400S spectrometer using TMS as an external reference. GC measurements were carried out with a Varian Star 3400 instrument equipped with a CP Sil 5-CB column (50 m × 0.53 mm) or carbowax column (50 m × 0.53 mm). Melting points were determined on a Buchi B540 Melting Point Apparatus with open capillary. Gas chromatography/mass spectrometry (GC/MS) analyses were performed on a VG 70-SE mass spectrometer equipped with a CP Sil 5-CB or carbowax column. LC/MS was carried out on a Micromass

Quattro LC. Oxygen concentration was measured with a Servomex 1800 Oxygen Analyzer.

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