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Heterogenized polymetallic catalysts: Part III[1]. Catalytic air oxidation of alcohols by Pd(II) complexed to a polyphenylene polymer containing β-di- and tri-ketone surface ligands

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Abstract

This paper describes further studies on mono- and bi-metallic catalysts attached to a polymer support by β-di- and tri-ketone surface ligands. The previous two papers described the oxidation of catechol by the heterogeneous catalysts using Cu(II), Fe(III) and Pd(II) as the metal species. The present study expands these studies to a series of mono- and polyfunctional alcohols using Pd(II) as the metal species. The final catalytic surfaces were prepared by treatment of the modified polymer with a very reactive form of Pd(II), $[Pd(CH_3CN)_4]^{2+}$. The simple alcohols gave increases in rates of up to 5-fold for the bimetallic systems. As might be expected glycols and α-D-glucose gave even higher increases in rate in going from the mono- to the bi-metallic catalyst. For ethylene glycol the factor was 30. Unsaturated alcohols gave the most dramatic results. With the monometallic catalyst, the products from allyl alcohol consisted of 25% acrolein resulting from direct alcohol oxidation and 75% 3-hydroxypropanal resulting from Wacker-type oxidation of the double bond. With the bimetallic catalyst the overall rate increased by a factor of 10 and the products consisted of 80% acrolein and 20% 3-hydroxypropanal. The actual rate increase for the direct alcohol oxidation is calculated to be a factor of 32. 4-Penten-2-ol and 4-penten-1-ol gave rates that were lower than the monofunctional alcohols. This is attributed to inhibition by olefin π-complex formation with the Pd(II).

Keywords: Polymetallic catalysts; Oxidation; Polyphenylene polymer; Palladium complexes; Surface catalysts; Alcohols; Allyl alcohol; Glycols

1. Introduction

1.1. Catalyst system

In the first two papers of this series the preparation and characterization of a new type of polymer supported heterogeneous catalytic system was described [1,2]. The polymer is a polyphenylene type

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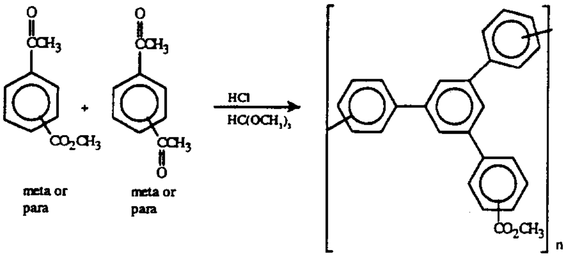
prepared by the cyclic trimerization of acetyl groups. In the latest version of the system the group used for the chemical modification is the methyl benzoate functionality. The monomers were methyl *m*- or *p*-acetylbenzoate polymerized with *m*- or *p*-diacetylbenzene



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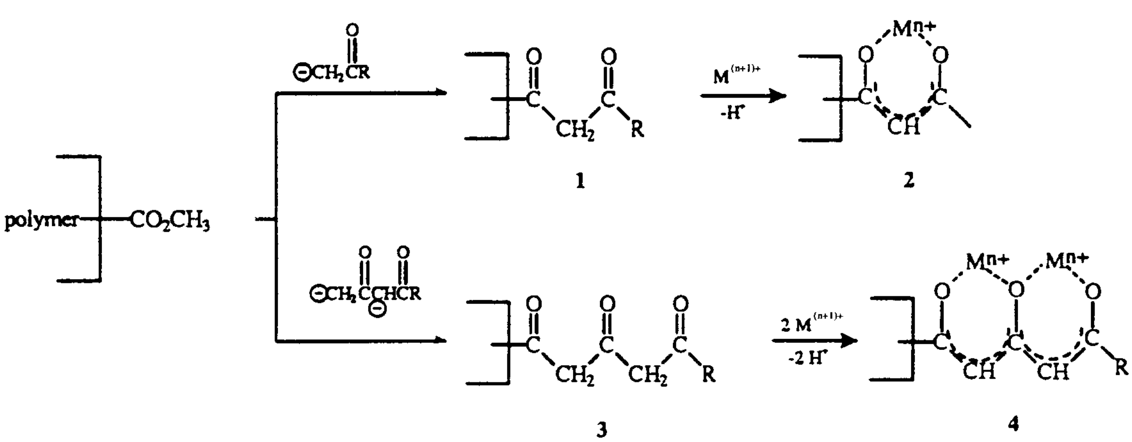
Since the methyl benzoate function is not involved in the polymerization, its concentration is quite high. The characterization of these polymers, as well as low molecular weight model systems, was carried out by mass spectra, ^{1}H NMR and FT-IR [2]. After polymerization to soluble low molecular prepolymer the signal due to the acetyl groups at 2.60 ppm had decreased and a new singlet at 7.35 ppm, resulting from the new trisubstituted aromatic ring appeared. The terminal ester group resonance at 3.93 and the FT-IR band of the ester group at 1721 cm^{-1} were unaffected by the polymerization.

As shown in Scheme 1, the chemical modifications involve the reaction of the methyl benzoate surface species with the anion of a methyl ketone to give **1** and with the dianion of a β-diketone to give the triketone, **3**. This reaction sequence places the two types of ligand groups on the polymer surface selectively. The first reaction only puts on the diketone species while the second reaction only puts on the triketone without any contamination from the diketone surface species. Thus, when treated with metal ions, pure **2** and **4** will be formed. The rigid polyphenylene-type polymer structure was chosen because the surface ligands, which are placed on the surface by the modifications described below, cannot diffuse together to form bis complexes. Since these surface complex species are coordinately unsaturated, these heterogeneous catalysts should be more reactive than their bis or tris complexed counterparts in homogeneous solution.

The feasibility of this approach was demonstrated with low molecular weight model systems which were characterized by the spectroscopic techniques described above. The formation of structures **1**, **2**, **3**, and **4** on the actual surfaces was confirmed by ^{1}H NMR studies on modified prepolymer and FT-IR

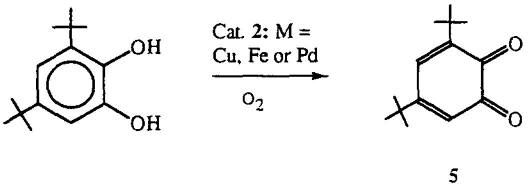


Scheme 1.

studies on polymer films [2]. After modification to give triketone the methyl ester group resonance disappeared and new signals at 2.05, 2.29, 5.30 and 5.50, consistent with triketone formation, appeared. In the FT-IR spectra new bands at 1707, 1696, and 1666 cm^{-1} appeared while the ester band at 1721 cm^{-1} disappeared. After treatment with $[Fe(CH_3CN)_6]^{2+}$, these bands shifted to 1567, 1536, and 1502 cm^{-1}. Similar results were obtained for the diketone modified surfaces. The presence of the catalytic species, **2** and **4**, on the surface was further evidenced by the oxidation studies described in Section 1.2.

1.2. Catechol oxidation studies

In the first two papers of this series the oxidation of 3,5-di-*tert*-butylcatechol (DTBC) by Cu(II), Fe(III) and Pd(II) catalytic surfaces were studied [1,2]. The results of these studies firmly established that bimetallic catalysts, **4**, based on the triketone surface ligand, **3**, have a very specific catalytic action for DTBC oxidation which the monometallic catalysts, **2**, based on the diketone surface ligand, **1**, does not possess. Thus, while **2**, M = Cu, Fe or Pd, catalyzes the air oxidation of DTBC to 3,5-di-*tert*-butyl-*o*-quinone, (DTBQ) **5** (Eq. (2)), the bimetallic catalyst, **4**, with all three metal species studied, causes ring cleavage. The most likely mechanism for this special reactivity is complexation of each oxygen in the intermediate DTBQ to one of the metal ions in the bimetallic catalyst followed by a simultaneous two electron transfer, with one electron being transferred to each of the two metal ions. This scheme is outlined in Eq. (3) where **7** is formed by further reaction of **6**. The monometallic catalyst



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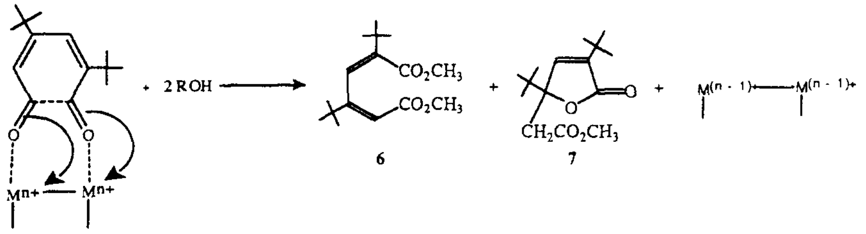

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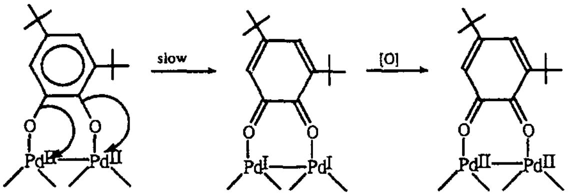
can only oxidize by a one electron transfer and thus give a free radical which would be a high energy species in this system. This result was particularly important because analogous monometallic homogeneous catalysts gave no reaction and bimetallic homogeneous catalysts gave only DTBQ. Thus the coordinately unsaturated heterogeneous catalysts are much more effective oxidants than their completely coordinated solution counterparts.

The Pd(II) bimetallic surfaces, in addition to giving the ring cleavage shown in Eq. (3), gave large rate increases over that observed for the monometallic catalysts for the initial oxidation to DTBQ shown in Eq. (2). Apparently, the reason is that the bimetallic catalysts can oxidize DTBC by the concerted route show in Eq. (4) to give a Pd(I)-dimer.



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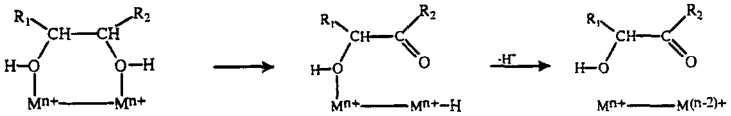
1.3. Aliphatic alcohol oxidation

The first two papers in this series showed that one electron oxidants, when incorporated into a bimetallic catalyst, can act in a cooperative fashion to convert what is normally a series of one electron oxidations into a concerted two electron process. It would be very informative to test other possible modes of rate enhancements for these bimetallic catalysts. One possibility is binding of polyfunctional molecules to the surfaces of the bimetallic catalysts at more than one metal site so the reaction can occur more readily. Thus in Eq. (4), the catechol is required to bind to two Pd(II)'s to give concerted electron transfer. However if a difunctional molecule such as a glycol replaced the catechol, the role of the second Pd(II) would be to hold the organic on the surface so the other Pd(II) can perform the oxidation (Eq. (5)).



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In order to test this mode of cooperative action by the bimetallic catalysts and distinguish from the type of cooperative action studied in the first two papers, it is necessary to use a substrate which is oxidized by a nonradical two electron step and, of course, a metal ion that is a two electron oxidant. A logical choice is the alcohol function since it is related to the catechols discussed in Section 1.2 but does not tend to undergo radical-type oxidations except with very strong oxidants. In regard to the metal oxidant, Pd(II), as with several other transition metal oxidants [3], can oxidize alcohols by a two electron hydride abstraction mechanism such as shown in Eq. (5) [4,5]. The effect of the addition of a second functional group, which can bind to the second Pd(II) of a bimetallic catalyst, on the rates of oxidation would be very informative in designing new catalytic systems. A particularly interesting case would be allylic alcohols since the olefin moiety can bind to the second Pd(II) by an olefin π-bond. Allyl alcohol oxidation by homogeneous Pd(II) species was studied previously by the author's research group [6]. In addition to the expected Wacker products, 3-hydroxypropanal and hydroxyacetone, appreciable amounts of acrolein, which must have been formed by hydride extraction, was found. Acrolein would not have been expected unless the presence of the double bond greatly increased the rate of hydride extraction. The present paper will attempt to expand the scope of potential bimetallic catalysis by Pd(II) treated surfaces by studying the oxidation of various monofunctional alcohols, glycols and unsaturated alcohols by these heterogeneous catalysts.

2. Experimental

2.1. Materials

Palladium sponge was obtained from Aesar. *p*-toluenesulfonic acid monohydrate (99%), 18-crown-6 (99.5%), triethylorthoformate (98%), *p*-acetylbenzoic acid (98%), *m*-acetylbenzonitrile, 18-crown-6 and NaH (60% dispersion in mineral oil) were obtained from Aldrich Chemical. *p*-Diacetylbenzene (99%) and $LiAlD_4$ were obtained from Fluka Chemika. The silica column packing (Sicilar Silica, 100–200 mesh, 60 Å) was obtained from Mallinckrodt. Celite (Chromosorb W [3]) was obtained from Altech Associates, Applied Science labs. The dioxygen (Airco Special Gases) was grade 5 and of commercial quality (99.5% v/v dioxygen). It was used without further purification. All other chemicals were of reagent grade.

2.2. Physical measurements

The ^1H NMR spectra were recorded on a Varian VXR-300 NMR spectrometer. The FT-IR spectra were recorded using an IBM FT-IR Model #98 spectrometer or an ATI Mattson Genesis Series FT-IR. Melting points were determined on a Laboratories Devices Mel-Temp apparatus using a calibrated thermometer. Benzaldehyde analysis was conducted on a GOW-MAC Series GLC instrument equipped with a 10 inch 80/100 C20 M column and a thermal conductivity detector. The column temperature was 150°C.

2.3. Preparative procedures

Catalysts were prepared as previously described [1,2].

2.3.1. Methyl m- and p-acetylbenzoates

Methyl *p*-acetylbenzoate (5.04 g; 3.07×10^{-2} mol) was prepared by refluxing the acid for 2.5 h in 200 ml methanol which was saturated with dry HCl gas. After workup by addition of brine and extraction with methylene chloride, the crude product was purified by column chromatography on a silica column using methylene chloride as eluant. The final yield was 3.56 g (65%). m.p.: 94–96°C. [4] *m*-Acetylbenzoic acid was prepared by the hydrolysis of the nitrile and esterified by the same procedure.

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[3] Chromosorb W is screened diatomaceous non-acid washed celite of white color; moisture content = 0.3%, BET surface area = 1.0–3.5 $m^2\ g^{-1}$, free fall density = 0.21–0.27 g cm^{-3}; true specific gravity = 2.30.

[4] This compound was characterized by standard ^1H and ^{13}C NMR spectroscopy. ^1H NMR: δ 2.63 (s, 3H); 3.93 (s, 3H); 7.99 (d, 2H, J = 8.25 Hz); 8.02 (d, 2H, J = 8.20 Hz). ^{13}C NMR: δ 26.88; 52.46; 128.19; 129.82; 133.88; 140.21; 165.73; 197.51.

2.3.2. Benzyl alcohol-1,1-d_2

This alcohol was prepared by a modification of a literature procedure [7]. To a freshly prepared solution of 1.18 g (28.1×10^{-3} mol) of lithium aluminum deuteride slurried in diethyl ether (distilled from sodium and benzophenone) in a 250 ml three neck round bottom flask was added 4.5 ml (ca. 32×10^{-3} mol) of methyl benzoate at 0°C over a period of 15 min. The mixture was allowed to warm to room temperature and then heated at reflux for 6 h. The reaction was cooled to room temperature and neutralized with 2.0 ml of 2.0 M KOH. The product was extracted with 2 × 50 ml of dichloromethane (CH_2Cl_2) and finally dried over anhydrous $MgSO_4$. It was purified using a 75 g silica gel column by eluting with 80% hexane/20% ethyl acetate. The product was characterized by ^1H and ^{13}C NMR.

2.3.3. 2,4-Dinitrophenylhydrazine reagent

To 3.0 g of 2,4-dinitrophenylhydrazine in a 400 ml beaker was added 15 ml of concentrated sulfuric acid. The solution was stirred until all the solids dissolved to give a light yellow solution. A 70 ml:20 ml mixture of 95% ethanol:de-ionized water was added over 10 min. The final color of the solution was orange-red.

2.4. Oxidation procedure

To provide good gas liquid mixing, the reactions were run in creased flasks at 25°C at a constant dioxygen pressure of one atmosphere. The progress of the oxidations were followed by dioxygen uptake measured by gas burets thermostated at the reaction temperature. The reaction flask was a 250 ml two necked coned shaped flask with the sides indented at four places to increase stirring efficiency. The apparatus is similar to that previously described [8]. In a typical run the flask containing 50 ml of reaction mixture was placed in a constant temperature bath and connected to the gas buret. The system was then evacuated for 10 min on the vacuum line with the stirrer running. The stirring was then stopped and the system pressured to 1.0 atmosphere with dioxygen. The mercury in the gas buret and the leveling bulb were then equalized and a reading taken. The stirrer was then turned on to start the run. Atmospheric pressure was maintained by continuously leveling the mercury in the gas buret. The volume of dioxygen consumed was measured at regular time intervals (t) to give a series of readings (V_t).

The reactions were analyzed in terms of a catalytic two electron oxidation of alcohol to aldehyde or ketone by the Pd(II)/Pd(0) couple. As the actual oxidant is O_2 and the reduction of dioxygen to water is a four electron process, the stoichiometry is 1 O_2/2 alcohol. Infinity readings, V_∞, were calculated using this stoichiometry. As the total dioxygen uptake always agreed with the calculated V_∞, the reduction of dioxygen must proceed to water rather than H_2O_2.

The amount of dioxygen taken up by the solvent is between 1.0–1.5 ml for the aqueous solutions under the conditions used. This value was subtracted from the V_t readings, and the corrected readings are called $V_{t(\mathrm{corr})}$. Thus $V_\infty - V_{t(\mathrm{corr})}$ corresponds to the amount of alcohol remaining. To change the volume to mmol of alcohol remaining, the value of $V_\infty - V_{t(\mathrm{corr})}$ was divided by 24.45 ml, the volume occupied by one mmol of gas at 25°C, and multiplied by two to give the correct stoichiometry.

Pseudo first order rate constants, k_{obs}, were obtained from the slope of a plot of the natural logarithm of ($V_\infty - V_{t(\mathrm{corr})}$) versus the corresponding time (t). Pseudo-bimolecular rate constants (in M^{-1} s^{-1}) were calculated assuming that the total amount of Pd(II) in the catalysts is homogeneously dissolved in the volume of the reaction mixture. Note that this pseudo second order rate constant is per Pd(II) atom, not per monomolecular or bimolecular site. If it were per site, the bimolecular constant would be twice as high.

Most oxidations were run in aqueous solution at pH = 8.0 using a phosphate buffer at a constant ionic strength of 0.20 adjusted with $LiClO_4$. The amount of polymer coated celite catalyst was always 0.5 g.

2.5. *Product identification and yields*

In most cases there was only the single product expected from oxidation of the alcohol substrate. Usually the aldehyde or ketone product was identified by preparing the 2,4-dinitrophenylhydrazone derivative and comparing the melting point with published values. In most cases the identification was confirmed by ^1H NMR. With some organic soluble products, the product was isolated by extraction with ether and identified by ^1H NMR. With the more complicated allyl alcohol reaction mixtures, the products were isolated as their 2,4-DNP derivative and the product distribution determined from the NMR's of the reaction mixtures. This procedure had been employed previously for allyl alcohol [6].

Products yields were determined for benzyl alcohol by GLC analysis for the oxidation by the bimetallic catalyst. Since the reaction mixture was too dilute for accurate analysis, it was concentrated by distillation. The reaction, which initially contained 2.9 mmol of benzyl alcohol in 25 mL, was run until 0.60 mmol of O_2, which corresponded to 1.2 mmol of alcohol oxidized, was taken up. The catalyst was removed by filtration and the filtrate concentrated to 0.5 mL using a fractionation column. GLC analysis of the residue, using a standard solution of benzaldehyde, indicated that 1.1 mmol of benzaldehyde was present for a yield of 92%. GLC analysis of the complete reaction mixture did not detect any other products.

3. Results

3.1. *Monofunctional alcohols*

Table 1 lists the second order rate constants for the oxidation of several alcohols. The largest difference between the mono- and bi-metallic catalysts is only five for this series of substrates and the

Table 1
Rate constants for the oxidation of several monofunctional alcohols [a]

No.	Substrate [b]	Catalyst type	k [c] (M^{-1} s^{-1})
1.	methanol	monometallic	0.0013
2.	methanol [d]	bimetallic	0.0018
3.	ethanol	monometallic	0.0048
4.	ethanol	bimetallic	0.025
5.	2-propanol	monometallic	0.0083
6.	2-propanol	bimetallic	0.035
7.	benzyl alcohol	monometallic	0.067
8.	benzyl alcohol	bimetallic	0.14
9.	benzyl alcohol-1,1-d_2	bimetallic	0.056

[a] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, $\mu = 0.10$ M) solutions at 25°C containing 0.5 g of polymer coated celite catalyst.

[b] Usually 2.5×10^{-2} M.

[c] Bimolecular rate constants were calculated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatment, by the [Pd(II)] calculated assuming all the Pd(II) were present in homogeneous solution.

[d] Methanol experiments were also run at 12.5×10^{-2} M and 25.0×10^{-2} M. The values of k were the same within experimental error.

Table 2
Rate constants for the oxidations of polyols [a]

No.	Substrate [b]	Catalyst type	k [c] (M^{-1} s^{-1})
10.	ethylene glycol	monometallic	0.00053
11.	ethylene glycol	bimetallic	0.016
12.	propane-1,2-diol	monometallic	0.0021
13.	propane-1,2-diol	bimetallic	0.020
14.	butane-2,3-diol	monometallic	0.0062
15.	butane-2,3-diol	bimetallic	0.041
16.	butane-1,3-diol	monometallic	0.0032
17.	butane-1,3-diol	bimetallic	0.0078
18.	α-D-glucose	monometallic	0.0072
19.	α-D-glucose	bimetallic	0.077

[a] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, $\mu = 0.20$ M) solutions at 25°C containing 0.5 g of polymer coated celite catalyst.

[b] 2.5×10^{-2} M.

[c] Bimolecular rate constants were calculated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatment, by the [Pd(II)] calculated assuming all the Pd(II) were present in homogeneous solution.

effect of structure on rate is not large compared with other alcohol oxidations. The rates of oxidation of methanol and benzyl alcohol differ by a factor of 50. Finally, the deuterium isotope effects are small; k_H/k_D is a little over 2.

Product yield was measured for the benzyl alcohol oxidation. The yields were calculated assuming 2 mol of product per mole of O_2. The yield of benzaldehyde was 92%. These are minimum yields since some product was lost in concentrating the reaction mixtures. No other products were detected by GLC.

The methanol oxidation was run at three different methanol concentrations. All gave the same 2nd order rate constant within experimental error.

3.2. Polyfunctional alcohols

3.2.1. Polyols

The data for oxidation of a series of diols and α-D-glucose by Pd(II) are given in Table 2. The rate differences between the mono- and bi-metallic catalysts is appreciable with most of these substrates. The difference for ethylene glycol is the highest; a factor of 30. This factor decreases to 10 for propane-1,2-diol and 7 for butane-2,3-diol. For butane-1,3-diol the difference is only a factor of 2.4. The bimetallic catalyst oxidizes α-D-glucose about 10 times faster than the monometallic catalyst.

3.2.2. Unsaturated alcohols

The rate data for a series of unsaturated alcohols is listed in Table 3. The 10-fold increase in rate in going from the monometallic to the bimetallic catalyst for allyl alcohol is expected since, as with the diols, it can coordinate to both metals. The very low reactivity of the homoallylic alcohol, 4-penten-2-ol, and 4-penten-1-ol, was surprising. The only measurable rate was the oxidation of 4-penten-2-ol with the bimetallic catalyst and this rate was 400 times slower than the corresponding oxidation of allyl alcohol.

Table 3
Rate constants for the oxidations of unsaturated alcohols [a]

No.	Substrate [b]	Catalyst type	k [c] (M^{-1} s^{-1})
20.	allyl alcohol	monometallic	0.15
21.	allyl alcohol	bimetallic	1.5
22.	4-penten-2-ol	monometallic [d]	$< 10^{-3}$
23.	4-penten-2-ol	bimetallic	0.0038
24.	4-penten-1-ol	monometallic [d]	$< 10^{-3}$
25.	4-penten-1-ol	bimetallic [d]	$< 10^{-3}$

[a] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, $\mu = 0.20$ M) solutions at 25°C containing 0.5 g of polymer coated celite catalyst.

[b] 2.5×10^{-2} M.

[c] Bimolecular rate constants were calculated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatment, by the [Pd(II)] calculated assuming all the Pd(II) were present in homogeneous solution.

[d] Almost no oxygen uptake in several days of reaction.

3.3. Product distributions

3.3.1. Saturated alcohols

The products from the oxidation of the saturated alcohols are listed in Table 4. The monofunctional alcohols gave only one oxidation product resulting from oxidation of the alcohol group to a carbonyl compound. In only two cases, propane-1,2-diol and butane-1,3-diol, were there two different possible positions for oxidation. The predominant oxidation site was the secondary carbon and only with butan-1,3-diol was any measurable amount of the other isomer, 3-hydroxybutanal, detected. As α-D-glucose has several possible sites for oxidation, and would thus be expected to give a complicated product mixture, no attempt was made to analyze the products of this reaction.

3.3.2. Unsaturated alcohols

The product distributions for these alcohols were more complicated than those for the saturated alcohols because there were two chemically different possible sites for oxidation, the alcohol function and the double bond. As the Wacker-type oxidation of olefins gives aldehydes and ketones, the products would be hydroxycarbonyl compounds [6]. Actually both acrolein and hydroxycarbonyl products were found in appreciable amounts but the distributions were different for the two types of catalysts. The monometallic catalyst gave 25% acrolein and 75% 3-hydroxypropanal, a distribution similar to that found for the homogeneous system [6]. However the bimetallic catalyst gave products

Table 4
Products from oxidation of saturated alcohols

Reactant	Product	m.p. of 2,4-DNP	^{1}H NMR($CDCl_3$)
methanol	methanal	164–166°C [9]	
ethanol	ethanal	163–165°C [9]	
2-propanol	2-propanone	124–126°C [9]	
benzyl alcohol	benzaldehyde		PhCHO: δ9.95 [10]
ethane-1,2-diol	2-hydroxyethanal	154–156°C [11]	
propane-1,2-diol	1-hydroxy-2-propanone		2,4-DNP: δ2.1 (s, 3H); 4.4 (s, 2H)
butane-2,3-diol	3-hydroxy-2-butanone		2,4-DNP: δ1.4 (d, $J_{a,b} = 6.8$ Hz, 3H); 4.5 (q, $J_{ab} = 6.8$ Hz, 1H); 2.1 (s, 3H) [12]
butane-1,3-diol	4-hydroxy-2-butanone		2,4-DNP: δ4.0 (t, $J_{a,b} = 5.4$ Hz, 2H); 2.7 (t, $J_{ab} = 5.4$ Hz, 2H); 2.1 (s, 3H) [11]

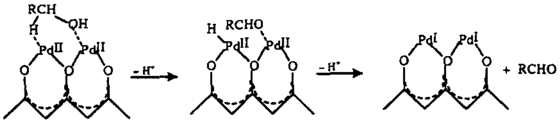
distributions much higher in acrolein; 80% acrolein and 20% 3-hydroxypropanal. The very low conversions and complicated reaction mixtures precluded the determination of product distributions for 4-penten-1-ol and 4-penten-2-ol.

4. Discussion

4.1. Monofunctional alcohols

Several observations can be made concerning the results in Table 1. First the difference between the mono- and bi-metallic catalysts is modest for this series of substrates. The reason is almost certainly the fact that Pd(II) is a two-electron oxidant and cooperative electron transfer, such as that shown in Eq. (3), is not required to give a two electron oxidation. Also the effect of structure on rate is small compared to some other alcohol oxidations. The rates of oxidation of methanol and benzyl alcohol by Ru(IV) differ by a factor of almost 10^4 [7] while in the Pd(II) oxidation the same ratio is only 50. The disparity lies in the different nature of the two oxidants. Pd(II) oxidizes by a concerted, nonpolar hydride transfer from carbon to metal ion to give a Pd(II)-hydride. On the other hand the Ru(IV) must go through a polar transition state that is either radical or hydridic. Also the hydride transfer is to oxygen rather than a transition metal. Finally, the deuterium isotope effect, k_H/k_D, for Pd(II) is only a little over 2. This is about the same as was found for other Pd(II) hydride transfers [6,13]. The most direct comparison is the oxidation of 2-propanol with $PdCl_4^{2-}$ in aqueous solution where an isotope effect of 1.8 was found [4]. The low value reflects the fact that bond making and bond breaking are taking place simultaneously. The analogous value for k_H/k_D for the Ru(IV) oxidation is 50. This high value for the deuterium isotope effect indicates bond breaking in the transition state is the important driving force of the reaction. Roecker and Meyer interpreted such a high deuterium isotope effect as consistent with a hydride transfer mechanism instead of a free radical mechanism [7]. Although cooperative electron transfer is not required with Pd(II) to give a two electron oxidation, there is evidence that some kind of synergistic action is taking place. Thus, for ethanol the value of k for the bimetallic catalyst is five times that for the monometallic catalyst. For 2-propanol this ratio is four while for methanol and benzyl alcohol this ratio is two or less. As shown in Eq. (6), one Pd(II) could be holding the substrate to the surface by weak oxygen–metal ion bonds while the second Pd(II) extracts the hydride.

In any case the most interesting case of bimetallic catalysis will be with one electron oxidants such as Cu(II) and Fe(III). If cooperative two electron transfer, such as that demonstrated previously for 3,5-di-*t*-butyl-*o*-quinone (Eq. (3)), can be shown for these oxidants with simple alcohols, it would be an exciting result.



(6)

The fact that the methanol oxidation by the bimetallic catalyst was strictly first order in methanol concentration is a significant result. The methanol oxidation must be the rate determining step rather than diffusion to the catalyst site or reoxidation of the Pd(0) to Pd(II). Also the fact that the second order rate constants remained constant indicates that the results are reproducible.

There is the possibility that the differences between the mono- and bi-metallic species might be related to their reaction with O_2. The rate of alcohol oxidation could be rate-determining for the bimetallic species but reoxidation of the Pd(0) to Pd(II) could be rate limiting for the monometallic species. This possibility is certainly unlikely for the simple alcohols because their rate constants for the mono- and bi-metallic catalysts are so similar. For a complete change in mechanism much larger differences in rate are expected. By analogy, the other alcohols would not be expected to display different rate limiting steps for the two catalytic species. In addition it has been observed that in fast reactions such as ethene oxidation, the monometallic catalyst deposits Pd metal while the bimetallic catalyst does not [14]. Thus, when reoxidation of Pd(0) to Pd(II) becomes rate limiting the monometallic Pd(0) species coagulate to form bulk palladium metal.

4.2. Polyols

In contrast to the simple monofunctional alcohols, the differences between mono- and bi-metallic catalysts should be larger for polyols which can coordinate to two sites on the bimetallic catalyst. The data for oxidation of a series of diols by Pd(II) in Table 2 shows the expected trends. The difference between the mono- and bi-metallic catalysts for ethylene glycol is a factor of 30. This factor goes down to 10 for propane-1,2-diol and 7 for butane-2,3-diol. The lower rates for the last two are most likely due to steric hindrance from the methyl groups which makes the chelation less favorable than for ethylene glycol. The factor for butane-1,3-diol is only 2.4. This result must reflect geometric factors in chelation of the glycol. Thus ALCHEMY II minimized estimates of the oxygen–oxygen distances in ethylene glycol gave 2.8 Å[5]. This is close to the value of 2.72 Å calculated for catechol, a substance which reacts very readily with these bimetallic Pd(II) catalysts [1,2]. Values of the oxygen–oxygen distances for the other two 1,2-diols were very similar. On the other hand, the corresponding distance for butane-1,3-diol is 4.4 Å, a distance which is, almost certainly, too large for effective chelation. The sugar, α-D-glucose, gives a rate increase of a factor of over 10 in going from the monometallic to the bimetallic catalyst. In addition it gives the highest rates for both types of catalyst. This sugar has three sets of hydroxyls that are at optimal distances for chelation, a fact that explains the appreciable rate increases with the bimetallic catalysts.

A comparison of the rates for the polyols to those for the simple alcohols reveals some subtle electronic effects. With the monometallic catalyst the rates of oxidation of ethanol and 2-propanol are 4–10 times higher than the rates of oxidation of the corresponding diols. This result must arise from the electron withdrawing ability of the hydroxyl group. On the other hand, the propane derivatives are faster than the ethane derivatives with the monometallic catalysts. This result can be explained by the electron releasing ability of the methyl group. These effects, combined with the steric effects of the methyl group discussed above, result in the rate constants for the bimetallic catalyst being very close for ethylene glycol and propane-1,2-diol.

4.3. Unsaturated alcohols

The most dramatic results occur with this particular type of substrate. The first result of note is that allyl alcohol gives the fastest rate of any of the substrates studied with the monometallic catalysts.

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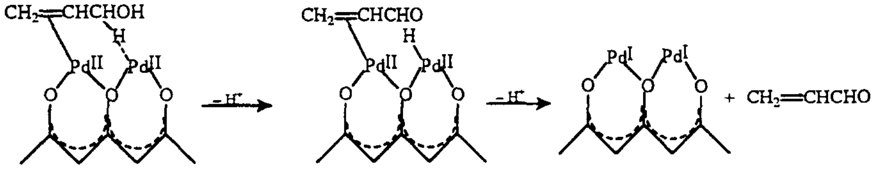
[5] ALCHEMY II is a registered tradename for a structure modeling program from TRIPOS Associates. The program performs a conjugate-gradient minimization to put the molecule in a minimal energy conformation.

However, in this system, the rate comparisons are complicated by the fact that only 25% of the oxidation is direct alcohol oxidation to give acrolein; the remaining oxidation is olefin oxidation to give 3-hydroxypropanal. Thus the actual rate of direct alcohol oxidation is $0.15\ M^{-1}\ s^{-1} \times 0.25 = 0.0375\ M^{-1}\ s^{-1}$, a value which is still exceeded only by the reactive benzyl alcohol. This same enhancement of rate was found in the homogeneous oxidation of allyl alcohol by $PdCl_4^{2-}$ in aqueous solution at 25°C where approximately the same product distribution was found. Since saturated alcohols required much more forcing conditions, the enhanced rate was attributed to π-complex formation between the olefin and Pd(II) [6]. This complex formation increases the concentration of the alcohol function in the region around the Pd(II) so hydride abstraction becomes a more favorable process. This increased activity was not observed with the diol oxidation because of the much weaker complexing of alcohol to Pd(II) as compared to olefin.

The enhancement of rate by π-complexing to the monometallic catalyst would be expected to overshadow any real bimetallic rate enhancement by bonding of the olefin to one Pd(II) followed by hydride extraction by the second Pd(II). Actually there is an increase of rate of 10 in going to the bimetallic catalyst. Furthermore the interpretation of data is complicated by the result that the product distribution changes from 25% acrolein for the monometallic catalyst to 80% acrolein for the bimetallic catalyst. Thus, the rate of direct alcohol oxidation is $1.5\ M^{-1}\ s^{-1} \times 0.80 = 1.2\ M^{-1}\ s^{-1}$ and the actual increase factor for the bimetallic catalyst over the monometallic catalyst is $1.2/0.0375 = 32$!



(7)

This factor is one of the largest observed and suggests that the geometry of the intermediate shown in Eq. (7) is ideal for hydride extraction by Pd(II). ALCHEMY II calculations indicate the distance between oxygen of the alcohol and the terminal carbon of the double bond is 2.83 Å, a distance close to that for the oxygen–oxygen distance in ethylene glycol.

A minor observation is that the rate of the olefin oxidation of allyl alcohol also increases in going from the monometallic to the bimetallic catalyst. The olefin oxidation rate of the monometallic catalyst is $0.15\ M^{-1}\ s^{-1} \times 0.75 = 0.11\ M^{-1}\ s^{-1}$, while that of the bimetallic catalyst is $1.5\ M^{-1}\ s^{-1} \times 0.20 = 0.3\ M^{-1}\ s^{-1}$. Thus the rate increases by the modest but significant factor; $0.3/0.11 = 2.7$.

The results with the homoallylic alcohol, 4-penten-2-ol, and the homoallylic alcohol, 4-penten-1-ol, are, at first glance, mystifying. Rather than giving enhanced rates, the fastest rate observed, $k = 0.0038\ M^{-1}\ s^{-1}$ (4-penten-2-ol with the bimetallic catalyst), was of the order of ethanol with the bimetallic catalyst. The remaining three systems (runs 22, 24 and 25) gave rates too slow to measure. The lower rates for alcohol oxidation can only be explained by *inhibition* from π-complex formation. For 4-penten-2-ol the ALCHEMY II calculations give oxygen to terminal carbon distances of 3.2 Å are just a little longer than those for allyl alcohol but, apparently, this difference is important. The corresponding distance for 4-penten-1-ol is 6.1 Å which is much higher than the optimum distance. Thus the direct oxidation without π-complex formation does not occur because olefin bonding is so much stronger than oxygen coordination and, once π-complex formation occurs, alcohol oxidation is discouraged. This effect is operative for both the mono- and bi-metallic catalysts.

It is more difficult to explain the lack of reactivity of these systems towards olefin oxidation. The distance between the oxygen function and the double bond should have little to do with the double bond reactivity. The hydrocarbon chain containing the alcohol function must somehow interfere with the attack of water on the double bond. One possibility is that the alcohol function is coordinating to the Pd(II), thus occupying the fourth coordination site required for *cis* hydroxypalladation leading to oxidation [15].

5. Conclusions

The present study describes quantitative rather than qualitative differences between the mono- and bi-metallic catalytic systems. Thus, there is no reaction, such as the cleavage of DTBQ, shown in Eq. (3), which occurs *only* with the bimetallic catalyst. However the rate increases are substantial and could be synthetically useful especially since these are catalytic air oxidations. The change in product distribution in going from the bimetallic catalyst is a significant result which could be of practical utility. The patterns can be complicated and subtle and, in some cases, can actually result in reduced reactivity for the bimetallic catalysts.

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