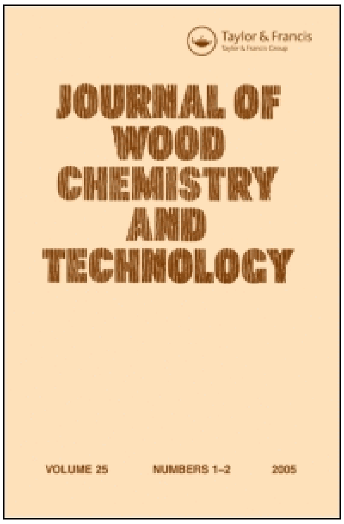

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HETEROPOLYACID CATALYZED OXIDATION OF LIGNIN AND LIGNIN MODELS TO BENZOQUINONES

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ABSTRACT

Several metal catalysts were examined for their effectiveness in activating hydrogen peroxide and oxygen as oxidants for conversion of lignin models to benzoquinones. Good yields of quinones were observed when certain heteropolymetallates were used as catalysts in the presence of hydrogen peroxide. Oxygen was generally less effective. Oxidation of lignin samples gave 2-3 wt% yields of 2,6-dimethoxybenzoquinone.

INTRODUCTION

The pulp and paper industry has embraced the concept of catalysis for the improvement of pulping processes. Predominant among the many different technologies investigated is the use of anthraquinone (AQ, **1**), a material proven

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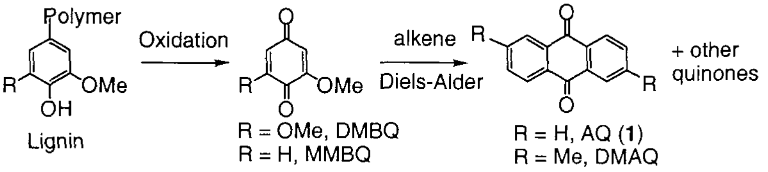
highly effective in catalyzing kraft pulping.[2] For several years, we have been investigating the production of AQ-like catalyst mixtures from lignin using the process shown in equation 1.[3]



[1]

This process oxidizes the electron rich aromatic rings in lignin to a mixture of monomethoxybenzoquinone (MMBQ) and dimethoxybenzoquinone (DMBQ). The MMBQ/DMBQ mixture is converted to a pulping catalyst by Diels-Alder reaction with isoprene to give dimethylanthraquinone (DMAQ) as the primary active component in the final mixture. DMAQ has been shown to have a twofold greater activity than AQ as a pulping catalyst.[4] Other quinone products are also formed in this process, but the catalytic behavior of this mixture has been shown to equal or surpass that of AQ.[5] Overall, this process is a good example of technology to convert renewable feedstocks into useful chemicals. It is also an excellent example of the concept of "indirect substitution", because the exact AQ structure is not duplicated. Rather, the *properties* and *performance* of AQ are duplicated.[6]

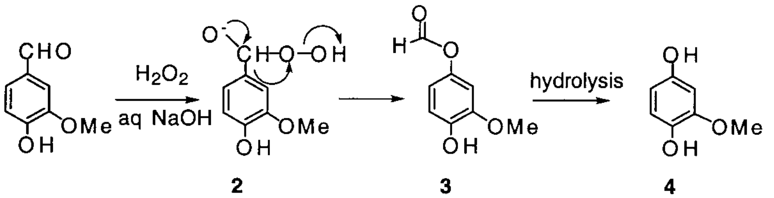
The most difficult step in this process is the oxidation of the starting lignin to MMBQ/DMBQ. Success in the first step requires that the polymeric lignin starting material, which is a heterogeneous mixture of dozens of different substructural units, be converted efficiently into a *single* material using a *single* reagent. The oxidation process must also be economically viable. Accordingly, we investigated the inexpensive oxidizing agents H_2O_2 and O_2 to carry out these transformations. These materials are well known in the paper industry for the oxidation of residual lignin during pulp bleaching. However, their activity under these conditions is nonselective, and leads to complex mixtures of lignin fragmentation products. In contrast, transition metal catalysts are well known to mediate that reactivity of these oxidants, allowing more selective reactions. For example, we reported a new synthesis of benzoquinones from lignin models using O_2 in the presence of Co(salen) catalysts.[7] In addition, we reported the use of catalytic amounts of NO_2 in the presence of oxygen for the formation of benzoquinones from lignin models.[8]

Heteropolyacids (HPAs) are reported to mediate the high reactivity of H_2O_2 and O_2 as oxidants. Moreover, they exhibit features that would make them attractive as catalysts for the process described in equation 1. The metal centers of these complexes exhibit high oxidation states, so that oxidative decomposition of the complex is not a problem. They also exhibit catalytic activity at very low levels, 1% or less. In addition, methods are known for adding different metals or ligands to the complex, allowing "tuning" of the reactivity of a given complex simply by choice of ligand.[9] The literature reveals many different uses of these materials as catalysts for different types of oxidations, all of which proceed by the formation of metal peroxo complexes.[10] These features led us to investigate, as reported here, the utility of HPAs for the conversion of lignin to benzoquinones. While our work was in progress, Weinstock reported elegant related applications of HPAs as catalysts for the nonselective oxidation of residual lignin in bleaching processes.[11]

RESULTS

Oxidations with H_2O_2

Initial results showed that H_2O_2 oxidized lignin models in 80%-90% yield in the absence of catalysts. However, a large excess of oxidant was needed for good yields and the conditions of the reaction gave hydroquinones **4** instead of benzoquinones (equation 2) via hydrolysis of formate ester 3 (formed by the Dakin reaction, **2** → **3**). In general, hydroquinones are readily oxidized to the corresponding benzoquinones, but such an oxidation would require an additional process step. In addition, hydroquinone **4** was found in related studies to be sensitive to the oxidation conditions. Moreover, when isolated lignins were treated under these conditions, the yields of oxidation products were discouragingly low.[12]



[2]

We turned to the use of H_2O_2 in the presence of HPAs as catalysts under phase transfer conditions, initially using vanillin as a model. Two general approaches for performing the oxidations were used. The first approach treated vanillin with excess H_2O_2 in the presence of either phosphomolybdic acid (PMA, $H_4PMo_{12}O_{40}$) or silicomolybdic acid (SMA, $H_4SiMo_{12}O_{40}$) and $(n\text{-heptyl})_4N^+Br^-$ as a phase transfer catalyst present in a three-fold excess with respect to the HPA.[13] The second approach used two types of preformed HPA catalysts (**5** - **7**, Figure 1) based on PMA and phosphotungstic acid (PTA, $H_4PW_{12}O_{40}$).[14] An additional catalyst (**8**) was studied for oxidation of vanillin. Compound **8** is an example of a lacunar HPA. Simple HPAs are well known to lose individual metal atoms in their structure to create a void. The void can subsequently be filled with a different metal. This procedure has allowed the synthesis of a wide range of heterometal substituted HPAs. A number of synthetic techniques have been reported for these materials.[15] Heterometal

$[(n\text{-hept})_4N]_3PW_{12}O_{40}$ (**5**) $[C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$ (**6**)
$[C_5H_5N(CH_2)_{15}CH_3]_3PMo_{12}O_{40}$ (**7**) $K_6SiCo(H_2O)Mo_{11}O_{39}$ (**8**)

Figure 1 - HPA Catalysts Used for Activation of H_2O_2

substituted complexes are of interest because they are models of metal surfaces used in heterogeneous catalysis with the heterometal acting as a defect and serving as a catalytically active site on the complex. These complexes have been used in conjunction with the phase transfer techniques by a number of workers[16] for the oxidation of olefins,[17] alkanes,[18] and phenols.[19]

A number of observations were similar to all HPA catalyzed oxidations, regardless of the conditions employed, especially when vanillin is used as the lignin model. Molybdenum based complexes were the most active. Those based on tungsten were frequently unreactive. Each oxidation normally afforded a mixture of three primary products, characterized by the appearance of three different methoxy peaks in the NMR spectrum. These peaks correspond to MMBQ (δ 3.85), vanillin (δ 3.95), and a third oxidation product (δ 3.88) which was identified by NMR and GC/MS as the formate ester **3**. Formation of compound **3** was favored under non-optimum conditions, and was isolated as the major product when the overall material balance of the reaction was low. The ratio of these compounds can vary significantly, depending on the conditions of the oxidation. Optimum conditions for the production of quinone from these reactions include low (ambient or lower) temperatures, solvents of moderate polarity ($CHCl_3$ and 20% MeCN/PhMe), and relatively short reaction times (6-8 h). Qualitatively, the reaction is rapid at the start, as indicated by the formation of quinone within the first 10 minutes after peroxide addition (observed by thin layer chromatography). However, the rate appears to level off as the reaction proceeds. Under optimum conditions, quinone yields of 50 - 70% (by NMR integration) are observed.

Table 1

Phase Transfer Oxidation of Vanillin with Simple HPA Catalysts

Entry	Catalyst Amount	Peroxide Amount	Solvent Amount	MMBQ Yield[b]
1	PMA, 2%	3.5 eq	$CHCl_3$, 5 mL	51%
2	PMA, 2%	7.5 eq	$CHCl_3$, 5 mL	47%
3	PMA, 2%	2.5 eq[a]	$CHCl_3$, 5 mL	40%
4	SMA, 2%	3.5 eq	$CHCl_3$, 5 mL	71%
5	SMA, 1%	5.0 eq	$CHCl_3$, 5 mL	62%
6	SMA, 0.2%	3.5 eq	$CHCl_3$, 5 mL	21%
7	SMA, 2%	7.0 eq[a]	$CHCl_3$, 5 mL	60%
8	SMA, 2%	5.0 eq	$CHCl_3$, 1 mL	47%
9	SMA, 1%	3.0 eq	$CHCl_3$, 1 mL	58%
10	SMA, 2%	3.5 eq	PhMe, 5 mL	31%

[a]peroxide added in small portions over several hours; [b]yields calculated from NMR integration

Table 1 summarizes the results of a series of oxidations carried out using the first approach of forming the catalytically active species *in situ* by mixing the starting HPA with a quat salt and H_2O_2 under phase transfer conditions.

Table 1 shows that SMA is a markedly superior catalyst to PMA for the production of MMBQ from vanillin. The yields are noticeably higher than those obtained with PMA under similar conditions (entries 4, 5, 7). The yield drops somewhat at a 1% level of catalyst (entry 5), and significantly at a 0.2% level (entry 6). However, the amount of quat salt remained constant for each of these reactions. The lower yield could be the result of a larger excess (with respect to the amount of catalyst) of quat salt. A subsequent set of experiments indicate that excess quat salt completely transfers the HPA to the organic layer, impeding the partition between the organic and aqueous phases necessary for reaction. An appropriate control reaction shows that no oxidation occurs in the absence of

Table 2

Phase Transfer Oxidation of Vanillin with Preformed Catalysts 5 - 7

Entry	Catalyst	Peroxide Amount	Solvent Amount	MMBQ Yield[d]
1	**7**	3 eq, 70%	$CHCl_3$, 5 mL	21%
2	**7**	6 eq, 70%	$CHCl_3$, 5 mL	4%
3	**7**	3 eq, 50%	$CHCl_3$, 5 mL	33%
4	**7**	3 eq, 35%	$CHCl_3$, 5 mL	12%
5	**7**	3 eq, 70%	$CHCl_3$, 1 mL	<5%
6	**7**	3 eq, 70%	$CHCl_3$, 25 mL	61%
7	**7**	3 eq, 70%	$CHCl_3$, 15 mL	34%
8	**7**	3 eq, 70%	PhMe, 5 mL	17%
9	**7**	2 eq, 70%	PhMe, 5 mL	19%
10	**7**	1.5 eq, 70%	PhMe, 5 mL	24%
11[a]	**7**	3 eq, 70%	PhMe, 5 mL	17%
12	**7**	3 eq, 50%	PhMe, 5 mL	25%
13	**7**	3 eq, 70%	PhMe, 25 mL	28%
14	**7**	3 eq, 70%	EtOAc, 5 mL	11%
15[b]	**7**	3 eq, 70%	EtOAc, 25 mL	14%
16[b]	**7**	3 eq, 70%	MeCN, 25 mL	25%
17	**5**	3 eq, 70%	$CHCl_3$, 5 mL	12%
18	**5**	3 eq, 70%	PhMe, 5 mL	8%
19[b]	**5**	3 eq, 70%	PhMe, 5 mL	trace
20	**5**	3 eq, 70%[c]	PhMe, 5 mL	trace
21	**6**	3 eq, 70%	PhMe, 5 mL	9%
22	**6**	3 eq, 70%	MeCN, 5 mL	trace

[a]reaction performed between 5-10°C; [b]reaction performed at 50°C; [c]peroxide added in small portions over several hours; [d]yields calculated from NMR integration

catalyst. A control reaction performed in the absence of quat salt shows that the oxidation still proceeds, but the presence of quat appears to give an overall cleaner reaction. The oxidation can be carried out in toluene (entry 10), but the yield and material balance are adversely affected. Reaction concentration had minimal effect on the reaction yield (entries 7, 8, 9).

Table 2 summarizes the results of using catalysts **5** - **7** as preformed materials. Each reaction used vanillin as the substrate in the presence of 1% of catalyst. These catalyst systems proved to be less efficient than those described in Table 1, as evidenced by the generally lower overall yields of MMBQ. The material balances were also considerably lower, with a few exceptions, than previous reactions, indicating nonselective consumption of the starting material.

Many of these reactions produced significant amounts of formate ester **3**. In a few cases, **3** was present as the major product (entries 2, 8, 9, 11, 12). Performing the oxidation in toluene promoted lower material balances. Ethyl acetate and acetonitrile were not effective solvents for quinone production (entries 14, 15, 16). The yield of quinone is favorably affected by both the concentration of peroxide and the reaction medium (entries 3, 6, 7). These observations could be the result of a combination of effects, including greater solubility of the quinone product and relatively less oxidizing power of the peroxide. When 35% peroxide was employed, little oxidation was observed and starting vanillin was the primary product (entry 4). A series of reactions was performed using the tungsten-based catalysts **5** and **6** at a 1% level (entries 17-23). Clearly, tungsten-based catalysts are much less effective for the production of quinone from vanillin.

The results for the use of lacunar catalyst **8** are summarized in Table 3. The conditions were similar to those described in equation 5, however, the reactions were normally performed in toluene solution instead of chloroform. Addition of a few drops of water at the beginning of the reaction was necessary to dissolve the HPA catalyst. Catalyst **8** is also much less effective than catalysts described in Table 1 above. The yields are low, and the material balances of the reactions are poor. Reactions performed in PhMe using catalyst **8** proceeded more rapidly, but with poorer material balance than those performed in $CHCl_3$ (Table 1 above). The low yields in these reactions persisted over a wide range of solvents (entries 8-10). As in other phase transfer reactions, the amount of quat salt added has a significant effect on the yield of MMBQ.

Table 3

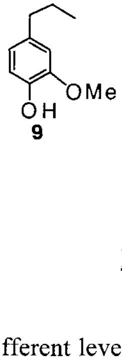
Phase Transfer Oxidation of Vanillin with Heterometal Catalyst 8

Entry	Quat Amount	Peroxide Amount	Solvent Amount	MMBQ Yield
1	6%	3 eq	PhMe, 5 mL	low
2	4%	3 eq	PhMe, 5 mL	low
3	2%	3 eq	PhMe, 5 mL	29%
4	1%	3 eq	PhMe, 5 mL	27%
5	2%	5 eq	PhMe, 5 mL	26%
6	2%	5 eq	PhMe, 15 mL	43%
7[a]	2%	3 eq	PhMe, 5 mL	low
8	2%	3 eq	MeCN, 5 mL	0%
9	2%	3 eq	t-BuOH, 5 mL	0%
10	2%	3 eq	EtOAc, 5 mL	0%
11[b]	1%	5 eq	PhMe, 15 mL	28%
12	1%	5 eq	PhMe/MeCN, 80/20, 15 mL	39%

[a] reaction performed at 40° C; [b] reaction performed using 0.5% catalyst

Complete transfer of the catalyst to the organic layer gives a low quinone yield (entry 1). The yield increases when the catalyst is partitioned between the two phases (entries 3 and 4). The oxidation gave higher yields of MMBQ upon changing concentration (entries 6 and 12). The relative solubility of the substrate and the products could be a factor. In addition, increased solvent polarity gave a complete consumption of vanillin (entry 12). Although the material balance of this reaction was only moderate, the spectral data revealed that a very clean reaction had occurred, with MMBQ being the major product.

Other substrates (**9** - **11**) were also studied with catalysts **5** - **8** but were unreactive. Reaction of **9** with H_2O_2 in the presence of preformed catalyst **6** under phase transfer conditions in $CHCl_3$ at room temperature was unsuccessful, giving a recovery of starting material in high yield.[20] When the reaction was performed at higher temperature, starting material was consumed but the reaction was not selective; several products were observed. The failure of this reaction was apparently not a function of the presence of the *para*-propyl group. Reaction of guaiacol (**10**) under the same conditions gave only recovery of starting material. Surprisingly, reaction of 2,6-di-t-butyl-4-methylphenol (**11**), a widely used, easily oxidizable phenol, under the same conditions also resulted in the recovery of starting material. Despite a considerable variation in conditions, (time, temperature, phase transfer conditions and phase transfer catalysts, solvent), catalyst **8** was also ineffective. These reactions usually returned starting material when the oxidation was carried out with H_2O_2 in $CHCl_3$ under phase transfer conditions. Changing the solvent to toluene completely shifted the reactivity of the process. Under these conditions, substrate **9** was completely, but nonselectively consumed.



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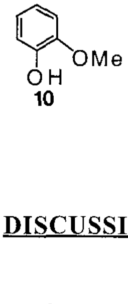

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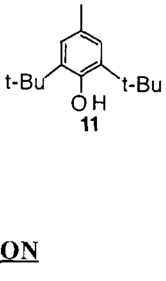

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DISCUSSION

Despite the different levels of structural complexity observed for starting HPA catalysts, the literature reveals that their interaction with H_2O_2 frequently results in a convergence upon a few similar structural types. Each of these structures can exhibit catalytic activity. A summary of the observed reactivity between different metal complexes and H_2O_2 is shown in Figure 2.

A number of different Mo or W based complexes are observed to undergo reaction with H_2O_2 to form three different structures, a reactive and fairly

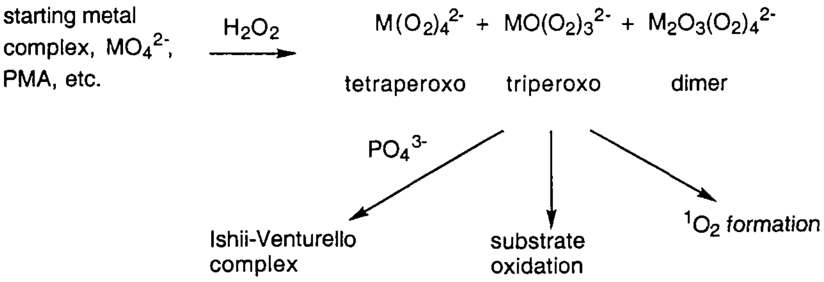
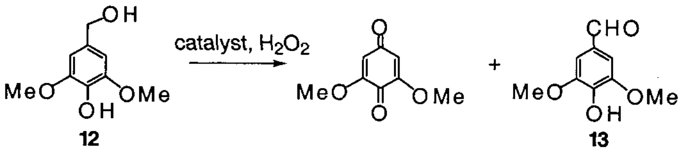


Figure 2 - Interaction of Mo and W Based Oxidation Catalysts with H_2O_2

unstable tetraperoxo complex, a triperoxo metal oxide, and a dimeric peroxo complex. The proportion of each of these materials depends on the pH of the reaction medium.[21] Depending on the substrate and the reaction conditions employed, each of these materials can exhibit catalytic activity for oxidation of different substrates. In the absence of substrate, singlet oxygen formation is observed with Mo based catalysts. Finally, treatment of many of these materials with H_2O_2 and PO_4^{3-} results in the assembly of these species into a four-metal complex (the Ishii-Venturello complex[22]), a material proven useful in the oxidation of several different substrates.[23] Not all HPAs undergo this transformation. For example, $H_4SiW_{12}O_{40}$ and $H_5BW_{12}O_{40}$ are found to maintain their structural integrity upon treatment with H_2O_2.[24] However, their catalytic activity (using epoxidation of olefins as the model) is almost zero. It appears that, for some oxidations, the formation of the species shown in Figure 2 is a necessary prerequisite for catalytic activity.

The initial structure of the catalyst does not affect this transformation. More complex peroxo species are broken down into these simpler complexes upon dissolution in water and treatment with H_2O_2, while simpler species are assembled to the higher structures of Figure 2. Phosphomolybdic acid undergoes this reaction with H_2O_2.[25] However, simple species, such as Na_2MoO_4 are also converted to these intermediate complexes. Tungsten-based species behave similarly with only minor variations. Accordingly, catalyst **8** may not break down upon treatment with H_2O_2, and is therefore catalytically inactive as indicated by the results of Table 3. Structurally similar complexes do not break down in the presence of H_2O_2.[20]

Oxidation of syringyl alcohol (**12**) qualitatively supported these hypotheses. Several oxidations were carried out with this substrate using $NaMoO_4$, $NaWO_4$, and $H_4PMo_{12}O_{40}$ as catalysts. In each case, the results of the reaction were the same. Compound **12** was converted into a mixture of DMBQ as the major product (50 - 60%) with syringaldehyde (**13**) as a minor side product (equation 3).



[3]

In several cases, highly nonselective reactions were observed. The poor material balance observed in many of these reactions indicates that electron-rich aromatics, as are found in lignin, have many oxidation paths available to them. Singlet oxygen may also be involved as an oxidant in these systems because its formation is a viable reaction path for HPAs and H_2O_2. If this material is the active oxidant, it would be as uncontrolled as H_2O_2 or O_2. Work suggests that some of the complexes (for example, the $Mo(O_2)_4^{2-}$ dimer) shown in Figure 2 may react through a $^1O_2$ based mechanism.[26]

There are also indications that MMBQ is sensitive to the reaction conditions. Reactions run for extended periods of time, or at elevated temperatures (40-50° C) show an initial formation of MMBQ, followed by a gradual consumption, as indicated by thin layer chromatography and a low material balance at the end of the reaction.

Decomposition of H_2O_2 by the metal catalyst is also possible, removing the oxidant and slowing the reaction. However, the nature of the oxidation products could determine whether this is a nonproductive decomposition. HPAs have been shown to react with H_2O_2 in the absence of substrate.[27] A peroxy metal complex is suggested as one of the possible products. Such peroxy complexes are catalytically active species in the oxidation of a number of substrates and, therefore, this reaction, while technically a peroxide decomposition, is productive with respect to the substrate. In the absence of substrate, H_2O_2 is most likely oxidized to give O_2. The relative rate of oxygen production to substrate oxidation from the HPA peroxy complex would determine the catalyst's effectiveness.

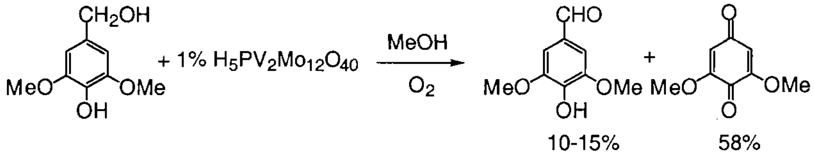
Oxidations with O_2

We have also investigated the use of oxygen as an oxidizing agent for these models. Several workers have reported that HPAs based on vanadium successfully activate oxygen.[28] We have studied oxidation of phenolics with oxygen activated by $H_5PV_2Mo_{10}O_{40}$ (**14**).[29] Phenols have been reported to undergo selective oxidation to materials closely related to quinones using oxygen and molybdovanadate complexes as catalysts.[30] Quinones can also be prepared from phenols using these reagents.[31] These complexes have also been used to activate oxygen in the oxidation of MeOH[32] and higher alcohols[28] amines,[33] and alkyl aromatics.[34] In contrast to the Mo and W complexes described above, these catalysts are not broken down to simpler species under the reaction conditions. Rather, redox chemistry occurs at the vanadium center according to equations 4 and 5:[28] Several molybdovanadate complexes were prepared according to literature method[29] and tested as oxygen activation catalysts.

$$SH_2 + H_5PV^{V}{}_2Mo_{10}O_{40} \longrightarrow S + H_7PV^{IV}{}_2Mo_{10}O_{40} \qquad [4]$$

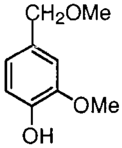
$$H_7PV^{IV}{}_2Mo_{10}O_{40} + 1/2O_2 \longrightarrow H_5PV^{V}{}_2Mo_{10}O_{40} + H_2O \qquad [5]$$

The vanadate catalyst promotes the oxidation of syringyl alcohol to give syringaldehyde and DMBQ at catalyst levels much lower than similar reactions using cobalt catalysts (equation 6).



[6]

Previous results obtained from the oxidation of syringyl alcohol using oxygen and a cobalt catalyst suggest that syringaldehyde is not an intermediate in DMBQ production but a competitive path for oxidation of the starting material.[7] The reaction has been performed at double the catalyst level to give a 59% yield of DMBQ. When the substrate is changed to vanillyl alcohol, the reactivity changes. Cobalt catalyzed oxidations performed with vanillyl alcohol and oxygen revealed that these substrates are more resistant to oxidation than their syringyl counterparts. Use of the vanadate catalyst in MeOH solvent give compound **15** as the major product.



15

Compound **15** is the result of Lewis acid catalyzed etherification of the starting material with complex **14** acting as the catalyst. Small amounts of other materials are observed in the reaction mixture.

Successful oxidation appears to be limited to syringyl alcohol. Other lignin models treated with oxygen and the vanadate catalyst showed little reactivity. Even substrates reported to undergo ready oxidation with this catalyst displayed low reactivity. 2,6-Dimethylphenol was consumed very slowly, in contrast to the literature report,[28] despite modification in temperature, oxygen pressure, and solvent. Attempts were made to promote the reaction through the addition of Cu(II) salts, but the conversion of starting material to product remained low.

Some consumption of starting material was observed when the reaction solvent was changed to 95/5 AcOH/H_2O, while using an oxygen pressure of about 340 kPa (~50 psi). 2,6-Dimethylphenol under these conditions was converted to 2,6-dimethylquinone in about 50% yield (by NMR), confirming the literature report.[28] However, **9** was consumed nonselectively to give no identifiable products other than trace amounts of vanillin. Vanillyl alcohol was treated under these conditions, but instead of oxidation, the benzyl alcohol was esterified to give the corresponding benzyl acetate. Syringyl alcohol was oxidized to syringaldehyde under these conditions. Application of these conditions to other substrates resulted in similar nonselective reactions.

The reaction was also carried out in MeCN as the primary solvent, with a small amount of added HOAc. Vanillyl alcohol was completely consumed and converted to a mixture of the benzyl acetate and vanillin. However, these products were less than 10% of the mixture. The bulk was an insoluble material. A similar result was observed with syringyl alcohol.

Lignin Oxidations

Samples of low molecular weight (LMW) kraft lignin (softwoods) were oxidized with H_2O_2 using HPAs as catalysts. Analysis by GC/MS and ^1H NMR verified formation of MMBQ in addition to other compounds. However, it was not possible to isolate the MMBQ from the remainder of the reaction mixture. Hardwood lignins undergo oxidation to give both MMBQ and DMBQ. The DMBQ can be isolated from the oxidation mixtures by washing the crude oxidation mixture with diethyl ether. Using a LMW aspen lignin, we observed 2-3 wt% yields of pure DMBQ upon reaction with PMA and H_2O_2 in acetic acid, followed by ether purification.

These low yields may be due to competitive pathways that result in the formation of muconic, maleic, and oxalic acids. Ample literature precedence exists for this.[35] Figure 3 shows a proposed partial mechanism for the formation of the acids and quinone at pH 7; analogous mechanisms have been proposed at other pH values. It should be noted that the mixture of H_2O_2 in acetic acid results in the formation of peracetic acid ($MeCO_3H$). Depending on the substituents at the benzylic carbon, lignins display significant differences in reactivity to give a variety of products. For example, no benzoquinone is formed from a substrate lacking an oxygen function at the alpha position (R = H) of the side chain. This is a result of attack by H_2O_2 on the aromatic ring in the first step, which eventually leads to the formation of acids. In Path B, oxidation, oxygen insertion and hydrolysis leads to intermediate **16**. Intermediate **16** can then produce *p*-quinones, which are stable to peracetic acid, or peracetic acid can attack at the

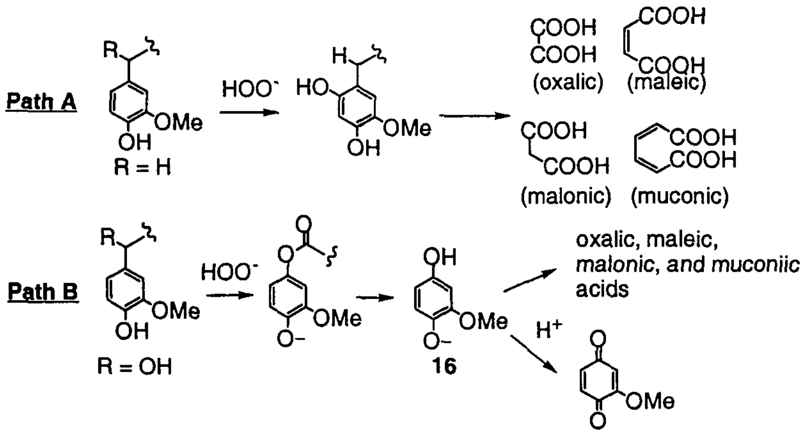


Figure 3 - Mechanism of Quinone Formation from Peracetic Acid

aromatic ring producing *o*-quinones which are readily oxidized to acids. It appears that 70% H_2O_2 in acetic acid (forming peracetic acid) is an unacceptable solvent for large scale formation of DMBQ and MMBQ.

An additional problem is the absence of oxygen functionality at the benzylic side chains. The presence of oxygen appears to be a requirement for formation of quinones in acceptable yields. Precedence for this is found in the literature from studies with model compounds.[7] As shown in Figure 4, the yields of quinone are greatly reduced in the absence of oxygen functionality.[5]

In order to establish the concentration of lignin subunits bearing a benzylic oxygen, we performed ^{13}C NMR spectroscopy on an aspen organosolv lignin (Figure 5). The range of the two partial spectra is from 70-88 ppm, which is the area that benzylic alcohol resonances appear.[36] The spectrum on the left is a milled wood lignin (MWL) of spruce, which has an abundant amount of benzylic oxygens.[37] The spectrum on the right is the aspen lignin used in the oxidation

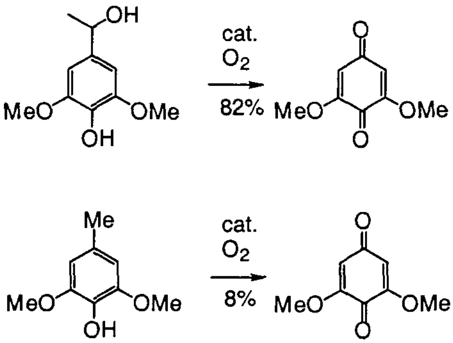


Figure 4 - Oxidation of Substrates with and without Benzylic Oxygen

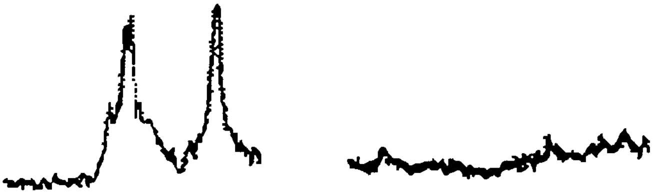


Figure 5 - ^{13}C NMR of MWL[37] and Aspen Organosolv Lignin (this work)

studies. Compared to the MWL, the amount of benzylic oxygen in our aspen sample is much lower. It appears that one of the contributing factors to the quinone yield is the oxidation state of the lignin side chains.

CONCLUSIONS

HPAs can catalyze H_2O_2 oxidation of certain lignin models to benzoquinones in good yield. The catalytic activity appears to be related to conversion of a given HPA to various intermediate complexes. However, oxidation of actual lignin samples occurs at too low a yield to be synthetically useful. Use of oxygen in the presence of vanadium based catalyst is generally ineffective for conversion of lignin models to benzoquinones.

EXPERIMENTAL

Methods and Materials

Proton and carbon nuclear magnetic resonance spectra were measured in $CDCl_3$ solution using a Varian Unity 300 instrument at 300 and 75.2 MHz, respectively. Chemical shifts were measured relative to tetramethylsilane or against the solvent signal. Solvents were reagent grade and used without further purification. Thin layer chromatography (TLC) was carried out on BakerFlex IB2-F silica gel plates visualized by UV or cerium molybdate staining.

Vanillin, guaiacol (**10**), 2,6-di-t-butyl-4-methylphenol (**11**), all quaternary ammonium salts, sodium molybdate, sodium tungstate, phosphomolybdic acid, and phosphotungstic acid were purchased from Aldrich and used as received. 4-Propylguaiacol (**9**) was purchased from Frinton and used as received. Complexes **5**,[38] **6**,[39] **7**,[14] **8**,[15] and **12**[15] were prepared according to literature procedures.

General procedure for phase transfer oxidation using complexes 5-8: The catalyst (1 - 5 mol%), quaternary ammonium salt (1 - 6 equiv based on catalyst) and solvent (5 mL/mmol substrate) were mixed and stirred at room temperature for 15 minutes. The substrate (1 mmol) was added and the solution was cooled to 0°C. The H_2O_2 (generally 3 - 5 equivalents, based on substrate) was added dropwise via syringe. The reaction was stirred until TLC indicated that no starting material remained. The reaction was poured into a separatory funnel, mixed with CH_2Cl_2 (40 mL), and washed three times with H_2O (5 mL/wash). The organic layer was dried over $MgSO_4$, filtered, and the solvent removed on the rotary evaporator.

The crude material was completely dissolved in $CDCl_3$ and analyzed by NMR. The NMR spectrum typically exhibited three methoxy peaks in the region 3.8 - 4.0 ppm, corresponding to MMBQ (δ 3.85), vanillin (δ 3.95), and formate ester **3** (δ 3.88). Yields of each material were calculated based on the integration of these three peaks.

General procedure for lignin oxidation using complexes 5-8: Oxidation of lignin samples was carried out similarly to oxidation of the model compounds. At the completion of the reaction, any undissolved lignin material was filtered. The soluble fraction was worked up as described above, and the products analyzed by NMR.

General procedure for vanadium catalyzed oxidation of lignin models: The lignin model (1 mmol) and catalyst (1 mol%) were mixed in MeOH (20 ml) in a Fisher-Porter bottle. The bottle was sealed with a pressure head and pressurized to about 340 kPA (~50 psi) with oxygen. The bottle was stirred at room temperature overnight. When syringyl alcohol was used as a substrate, DMBQ precipitated from solution and was isolated by filtration. In experiments using other substrates, the solvent was removed on the rotary evaporator, and the products analyzed by NMR.

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REFERENCES

1. Current address: Victoria University of Wellington, School of Chemical and Physical Sciences, PO Box 600, Wellington, New Zealand.
2. H. H. Holton, Pulp Paper Can., 78, T218 (1977).
3. D. R. Dimmel, K. Kuroda, X. Pan, and J. J. Bozell, J. Wood Chem. Technol., 17, 235 (1997); D. R. Dimmel, X. Pan, and J. J. Bozell, J. Wood Chem. Technol., 16, 205 (1996); D. R. Dimmel, X. Pan, K. Kuroda, and J. J. Bozell, J. Wood Chem. Technol., 16, 191 (1996); D. R . Dimmel, M. R. Karim, M. C. Savidakis, and J. J. Bozell, J. Wood Chem. Technol., 16, 169 (1996); D. R. Dimmel and J. J. Bozell, Tappi J., 239 (5) (1991).
4. J. C. Wozniak, D. R. Dimmel, and E. W. Malcolm, J. Wood Chem. Technol., 9, 535 (1989).
5. D. R. Dimmel, E. Althen, M. Savidakis, C. Courchene, and J. J. Bozell, Tappi J. (2000), in press.
6. J. J. Bozell, J. O. Hoberg, D. Claffey, B. R. Hames, and D. R. Dimmel, in Green Chemistry: Frontiers in Benign Chemical Synthesis and Processing, Chapter 2, P. T. Anastas and T. C. Williamson, eds. Oxford University Press, New York, 1998.
7. J. J. Bozell, B. R. Hames, and D. R. Dimmel, J. Org. Chem., 60, 2398 (1995).
8. J. J. Bozell, J. O. Hoberg, and D. R. Dimmel, Tetrahedron Letters, 39, 2261 (1998).
9. M. T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, New York, 1983; M. Misono, Catal. Rev. Sci. Eng., 29, 269 (1987); M. Misono, Mat. Chem. Phys., 17, 103 (1987).
10. L. S. Csanyi and K. Jaky, J. Mol. Catal., 61, 75 (1990).
11. For an overview of this work, see I. A. Weinstock, R. H. Atalla, R. S. Reiner, C. J. Houtman, and C. L. Hill, Holzforschung, 52, 304 (1998); I. A. Weinstock, K. E. Hammel, M. A. Moen, L. L. Landucci, S. Ralph, C. E. Sullivan, and R. S. Reiner, Holzforschung, 52, 311 (1998).
12. J. C. Wozniak, D. R. Dimmel and E. W. Malcolm, J. Wood Chem. Technol., 9, 491 (1989).
13. A variety of approaches using this technique are reported: M. Schwegler, M. Floor, and H. van Bekkum, Tetrahedron Letters, 29, 823 (1988); C. Venturello, E. Alner, and M. Ricci, J. Org. Chem., 48, 3831 (1983); O. Bortolini, F. DiFuria, G. Modena, and R. Seraglia, J. Org. Chem., 50, 2688 (1985); O. Bortolini, L. Bragante, F. DiFuria, and G. Modena, Can. J. Chem., 64, 1189 (1986); O. Bortolini, V. Conte, F. DiFuria, and G.

Modena, J. Org. Chem., 51, 2661 (1986); F. P. Ballistreri, S. Failla, and G. A. Tomaselli, J. Org. Chem., 53, 830 (1988).

14. Y. Matoba, H. Inoue, J.-i., Akagi, T. Okabayashi, Y. Ishii, and M. Ogawa, Synth. Comm., 14, 865 (1984).

15. The literature for the preparation of these complexes is scattered. The following give some representative syntheses: T. J. R. Weakley and S. A. Malik, J. Inorg. Nucl. Chem., 29, 2935 (1967); C. M. Tourné and G. F. Tourné, J. Inorg. Nucl. Chem., 32, 3875 (1970); F. Zonnevijlle, C. M. Tourné, G. F. Tourné, Inorg. Chem., 21, 2742 (1982).

16. F. Corigliano and S. Di Pasquale, Inorg. Chim. Acta, 12, 99 (1975); F. Zonnevijille, C. M. Tourné and G. F. Tourné, Inorg. Chem., 22, 1198 (1983).

17. C. L. Hill and R. B. Brown, Jr., J. Am. Chem. Soc., 108, 536 (1986).

18. M. Faraj, C.-H. Lin, and C. L. Hill, New J. Chem., 12, 745 (1988); M. Faraj and C. L. Hill, J. Chem. Soc., Chem. Commun., 1487 (1987).

19. D. M. Katsoulis and M. T. Pope, J. Chem. Soc., Dalton Trans., 1483 (1989).

20. C. Venturello and M. Ricci, J. Org. Chem., 51, 1599 (1986); S. Sakaue, Y. Sakata, Y. Nishiyame, and Y. Ishii, Chem. Lett., 289 (1992).

21. N. J. Campbell, A. C. Dengel, C. J. Edwards, and W. P. Griffith, J. Chem. Soc., Dalton Trans., 1203 (1989); V. Nardello, J. Marko, G. Verneersch, and J. M. Aubry, Inorg. Chem., 34, 4950 (1995).

22. C. Venturello, R. D'Allisio, J. C. J. Bart, and M. Ricci, J. Mol. Catal., 32, 107 (1985).

23. A. C. Dengel, W. P. Griffith, and B. C. Parkin, J. Chem Soc. Dalton Trans., 2683 (1993); A. J. Bailey, W. P. Griffith, and B. C. Parkin, J. Chem. Soc. Dalton Trans., 1833 (1995); H. Furukawa, T. Nakamura, H. Inagaki, E. Nishikawa, C. Imai, and M. Misono, Chem. Lett., 877 (1988).

24. C. Aubry, G. Chottard, N. Platzer, J.-M. Bregeault, R. Thouvenot, F. Chauveau, C. Huet, and H. Ledon, Inorg. Chem., 30, 4409 (1991).

25. J. M. Bregeault, C. Aubry, G. Chottard, N. Platzer, F. Chauveau, C. Huet, and H. Ledon, Stud. Surf. Sci. Catal., 66, 521 (1991); L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. D. Morin, G. Chottart, H. Ledon, Y. Jeannin, and J. M. Bregeault, Inorg. Chem., 33, 871 (1994).

26. J. M. Aubry, J. Amer. Chem. Soc., 107, 5844 (1985).

27. J. E. Toth, J. D. Melton, D. Cabelli, B. H. J. Bielski, and F. C. Anson, Inorg. Chem., 29, 1952 (1990).

28. M. Lissel and H. J. in de Wal, Tetrahedron Letters, 33, 1795 (1992); R. Neumann and M. Levin, J. Org. Chem., 56, 5707 (1991); R. Neumann and M. Lissel, J. Org. Chem., 54, 4607 (1989).

29. G. A. Tsigdinos and C. J. Hallada, Inorg. Chem., 7, 437 (1968).

30. R. Neumann and M. Levin, J. Amer. Chem. Soc., 114, 7278 (1992).

31. O. A. Kholdeeva, A. V. Golovin, R. I. Maksimovskaya, and I. V. Kozhevnikov, J. Mol. Catal., 75, 235 (1992).

32. K. Bruckman, J.-M. Tatibouet, M. Che, E. Serwicka, and J. Haber, J. Catal., 139, 455 (1993).

33. K. Nakayama, M. Hamamoto, Y. Nishiyama, and Y. Ishii, Chem. Lett., 1699 (1993).

34. R. Neumann and M. De la Vega, J. Mol. Catal., 84, 93 (1993).

35. G. Strumila and H. Rapson, Pulp and Paper Mag. Can., 76, T276 (1975); T. J. McDonough and W. H. Rapson, Transactions, 1, 12 (1975); W. Lawrence, R. D. McKelvey, and D. C. Johnson, Svensk Papperstidning, 1, 11 (1980); Y.-Z. Lai and K. V. Sarkanen, Tappi J., 51, 448 (1968); H. H. Nimz and H. Schwind, Cell. Chem. Technol., 13, 353 (1979).

36. Methods in Lignin Chemistry, p. 264, S. Y. Lin and C. W. Dence, eds., Springer-Verlag, New York, 1992.

37. Spectrum taken from K. P. Kringstad and R. Morck, Holzforschung, 37, 237 (1983).

38. Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, and M. Ogawa, J. Org. Chem., 53, 3587 (1988).

39. T. Okabayashi, K. Yamawaki, H. Nishihara, H. Yamada, T. Ura, Y. Ishii, and M. Ogawa, Sekiyu Gakkaishi, 30, 439 (1987).