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Oxidation of Lignin Model Compounds Using Single-Electron-Transfer Catalysts

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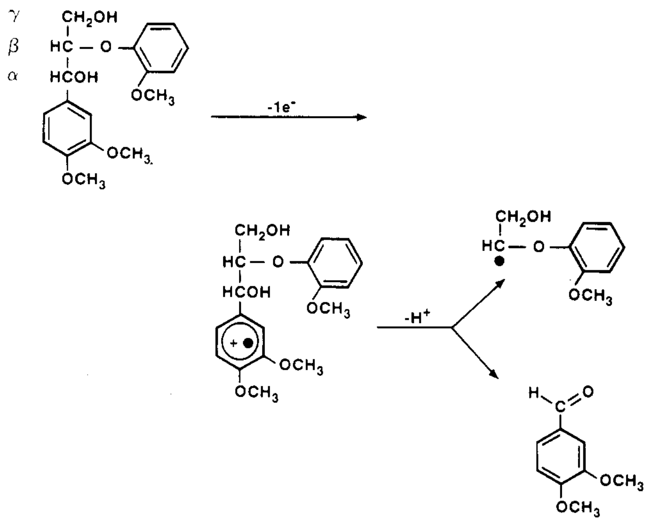
The single-electron-transfer oxidation of model compounds representative of the arylglycerol β-aryl ether and 1,2-diarylpropane linkages of lignin has been examined by using Co(II), Mn(II), or Co(II)/Mn(II) as catalysts. Catalytic oxidation of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (DMMP) in 80% acetic acid with 500 psi of 4% oxygen in nitrogen and at 170 °C resulted predominantly in products of C_α–C_β bond cleavage when using Co(II)/Mn(II) as catalyst. C_α–C_β bond cleavage of DMMP results from an initial single-electron oxidation to produce an intermediate aromatic radical cation; in the absence of oxygen and catalyst, acid-catalyzed β-aryl ether cleavage was the predominant reaction pathway. Dihydroanisoin (DHA) and 1,2-bis(4-methoxyphenyl)propane-1,3-diol (BMPD) were oxidized by stoichiometric quantities of Co(III) to give solely products of C_α–C_β bond cleavage but produced only acid-catalyzed dehydration products under reaction conditions necessary for catalytic oxidation. The application of this oxidation reaction as a replacement for chlorine bleaching of paper pulp is discussed.

Introduction

Chemical bleaching of paper pulp is currently employed for the manufacture of white paper products, but disposal of effluents from bleaching plants represents a serious environmental problem for the pulp and paper industry. Bleaching of paper pulp whitens the pulp by removal of lignin or by destroying the chromophores of lignin. Lignin is, after cellulose, the principal constituent of the woody structure of higher plants and is a highly branched, structurally intricate polymer comprised of phenylpropanoid units.[1] Because of its selectivity toward lignin and its cheapness in comparison to other chemicals, chlorine has proved to be a useful reagent for complementing the delignification taking place during pulping, although chlorine use for bleaching is declining slightly as chlorine dioxide is substituted. The chemical bleaching of kraft pulp results in the formation of between 45 and 90 kg of organic waste material/ton of pulp, which contains 4–5 kg of organically bound chlorine/ton.[2] The toxicity of these kraft bleaching effluents to fish and other aquatic fauna has been known for some time,[3] and regulations that will limit concentrations of polychlorinated aromatics in waste streams will make alternative to the chemical bleaching of paper pulp with chlorine or chlorine dioxide increasingly desirable.

Scheme I



Recently, the enzyme "ligninase" was isolated from the white-rot fungi *Phanerochaete chrysosporium* and was shown to be able to degrade the lignin component of wood.[4] The extracellularly excreted enzyme utilizes hydrogen peroxide to generate an oxy–heme complex capable of oxidizing the aryl groups of lignin or lignin model compounds by a single-electron transfer.[5] The relatively stable aromatic radical cations that result decompose via C_α–C_β bond cleavage (Scheme I).[6] This same C_α–C_β bond cleavage of lignin model compounds has been demonstrated by using tetraphenylporphyrinatoiron(III) chloride in the presence of *tert*-butyl hydroperoxide or iodosylbenzene as an active oxygen source[7] and with hemin (a natural porphyrin of the prosthetic group of heme enzymes such as ligninase) in the presence of hydrogen peroxide.[8] Oxidants other than oxy-metalloporphyrins have also been employed for the degradation of lignin model compounds by one-electron oxidation; stoichiometric oxidation with $Fe(phen)_3{}^{3+}$ or ceric ammonium nitrate,[9] and by copper peroxydisulfate,[10] has been described, which indicates that non-heme, non oxy-ferryl type catalysts may also function in this capacity. The alkali-oxygen degradation of lignin

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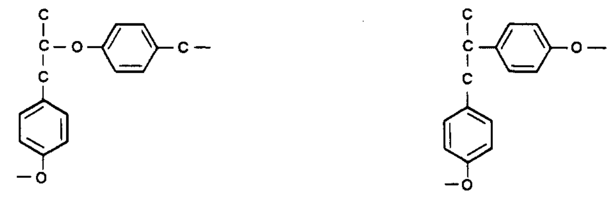
Scheme II



arylglycerol β-aryl ether 1,2-diarylpropane

catalyzed by cobalt(III) hydroxide has been reported to result in small increases in phenolic products such as vanillin, vanillic acid, and acetoguaiacone.[11]

Oxidation of a series of 1,2-diarylethanes and 1,2-diarylethanols,[12] and arylalkanols,[13] by Cu(II) $S_2O_8^{2-}$ has been demonstrated to proceed via formation of an aryl radical cation, which subsequently undergoes C_α–C_β bond cleavage. The photosensitized electron-transfer oxidation of these same organic compounds proceeds by a similar mechanism.[14] The autoxidation of alkylbenzenes to aldehydes and carboxylic acids, catalyzed by a number of different transition metals, also proceeds by an initial electron transfer, resulting in a one-electron reduction of the metal catalyst and concomitant formation of a substrate radical cation (eq 1 and 2).[15] The ease of elec-

$$M^{n+} + ArCH_3 \rightarrow M^{(n-1)+} + [ArCH_3]^{\cdot+} \qquad (1)$$

$$[ArCH_3]^{\cdot+} \rightarrow ArCH_2^{\cdot} + H^+ \qquad (2)$$

tron-transfer oxidation of aromatic hydrocarbons to produce radical cations is directly related to the ionization potential of these compounds, with electron-donating substituents such as methoxyl (almost every aryl group of lignin has one or two methoxyl substituents) lowering the oxidation potential. Examination of the ionization potentials for variously substituted aromatic molecules[16] indicates that oxidants such as Mn^{3+} and Co^{3+} should be quite efficient in catalyzing the autoxidation of lignin and lignin model compounds via a "biomimetic" mechanism that parallels the oxidation of lignin by ligninase, and we now report the results of a study of the autoxidation of lignin model compounds by these catalyst systems.

The lignin model compounds whose oxidations have now been examined by using autoxidation catalysts have all previously been employed as lignin models in degradative reactions using *Phaenerochaete chrysosporium*, which produces the enzyme ligninase, or in reactions that examined the effect of kraft pulping or other chemical or microbial oxidations on lignin model compounds.[17-20] These model compounds represent the arylglycerol β-aryl ether and 1,2-diarylpropane linkages of lignin, which make up 30%–50% and ca. 7%, respectively, of the major types of bonds connecting the phenylpropanoid units of lignin (Scheme II).[1,21] Scheme III depicts the four lignin model compounds used in this study and the expected products of the C_α–C_β bond cleavage of these compounds by their single-electron-transfer oxidation. Oxidation of dihydroanisoin (DHA) produces 2 equiv of anisaldehyde. 1,2-Bis(4-methoxyphenyl)propane-1,3-diol (BMPD) was oxidized to yield anisaldehyde and 1-(4-methoxyphenyl)-1,2-ethanediol, the latter capable of undergoing further oxidation to produce additional anisaldehyde. C_α–C_β bond cleavage of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (HMMP) was expected to produce guaiacol, vanillin, and hydroxyacetaldehyde, as has been reported for the oxidation of HMMP by *Pseudomonas cepacia 122*;[22] however, a likely competing reaction is dimerization of HMMP to produce *o,o′*-dihydroxyphenols (vide infra). 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (DMMP) oxidation yields 3,4-dimethoxybenzaldehyde (DMB), guaiacol, and hydroxyacetaldehyde.

Results and Discussion

The stoichiometric and catalytic oxidation of two basic types of lignin structures, 1,2-diarylpropanes and arylglycerol β-aryl ethers, has been examined. The stoichiometric oxidation of the lignin model compounds DHA, BMPD, HMMP, and DMMP was first performed to determine the ability of single-electron-transfer oxidants such as Co(III) to produce C_α–C_β bond cleavage of the substrates (see paragraph at the end of paper about supplementary material). The diarylpropane model DHA was completely oxidized to yield 2 equiv of anisaldehyde. The diarylpropane BMPD produced at least 1 equiv of anisaldehyde; further oxidation of the C_β fragment (1-(4-methoxyphenyl)-1,2-ethanediol) produced additional anisaldehyde. The arylglycerol β-aryl ether model compounds HMMP and DMMP were also oxidized by stoichiometric amounts of Co(III), but C_α–C_β bond cleavage was only observed for DMMP, which produced DBA and guaiacol. Oxidation of HMMP by Co(III) in 80% acetic acid produces no products of C_α–C_β bond cleavage, and no other low-molecular-weight (monomeric) products are observed; it is likely that once oxidized to a resonance-stabilized phenoxyl radical, dimerization to biphenyl is the primary reaction pathway. The oxidation of 2-methoxy-4-alkylphenols is known to result in ortho carbon coupling of two monomers to produce *o,o′*-dihydroxybiphenyls, which are in turn subject to further oxidation.[23] This same ortho coupling reaction of para-substituted phenols is responsible for the formation of biphenyl linkages in lignin (accounting for ca. 11% of total linkages between phenylpropane units), via the enzyme-catalyzed one-electron oxidation of coniferyl and sinapyl alcohol.[1]

After having used stoichiometric amounts of electron-transfer oxidants for the oxidation of DHA, BMPD, and DMMP to C_α–C_β bond-cleavage products, the generation of catalytic amounts of electron-transfer oxidants was first demonstrated by using peracetic acid to oxidize Co(II) to Co(III) in situ.[24] Five equivalents of BMPD were oxidized

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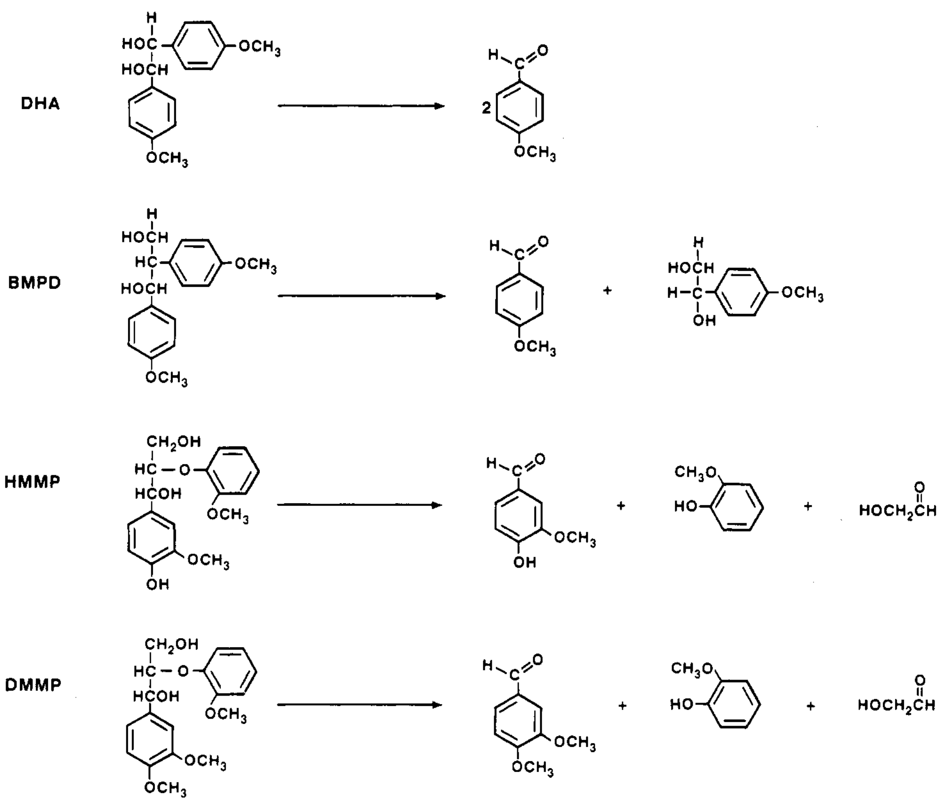
Scheme III



with 1 equiv of Co(III) in glacial acetic acid at 25 °C by using 8 equiv of peracetic acid to regenerate Co(III). Anisaldehyde was produced with 100% selectivity at 100% conversion of BMPD. The reaction of 1 equiv of BMPD with 1 equiv of peracetic acid in the absence of added catalyst gave only 30% selectivity to anisaldehyde at 87% conversion. The catalytic oxidation of DMMP using peracetic acid as the cooxidant was also demonstrated: 4 equiv of DMMP was oxidized in the presence of 1 equiv of cobalt(II) acetate by using 4 equiv of peracetic acid as the cooxidant. A 48% selectivity to DMB at 90% conversion was obtained, and three turnovers of Co(II) were achieved. DMMP is very stable in the presence of peracetic acid under the same conditions: a 92% recovery was obtained at 25 °C after 5 h. Because of the expense of using stoichiometric quantities of peracetic acid for lignin degradation, and the large quantities of the peracid that would be required for the application of this type of catalytic oxidation to a process such as paper pulp bleaching, an alternative method of catalyst oxidation is desirable. The most economical way to generate the desired electron-transfer oxidants in situ would use oxygen as the ultimate oxidant, and alkylperoxy or peroxyacid intermediates formed during the reaction of oxygen with the C_α–C_β bond-cleavage products of lignin (in this case, lignin model compounds) could reoxidize the catalyst.

In addition to C_α–C_β bond cleavage, both the diarylethane- and diarylpropanediols and the arylglycerol β-aryl ethers are subject to acid-catalyzed dehydration reactions. DHA and BMPD could be oxidized with stoichiometric amounts of Co(III) to give good to excellent selectivity to C_α–C_β bond-cleavage products under reactions conditions that would otherwise produce only the acid-catalyzed dehydration products desoxyanisoin and *trans*-4,4′-dimethoxystilbene, respectively, but these same model compounds were not stable at the higher reaction temperatures and pressures (>150 °C, 500 psi 4% O_2 in nitrogen) required to obtain catalytic reaction with oxygen and the Co(II), Mn(II), or Mn(II)/Co(II) catalysts. HMMP was unsuitable as a model compound since it did not undergo C_α–C_β bond cleavage when oxidized by Co(III). In contrast, the arylglycerol β-aryl ether DMMP could be catalytically oxidized to give predominantly C_α–C_β bond-cleavage products under the required high-temperature, high-pressure reaction conditions, where in the absence of catalyst and oxygen, acid-catalyzed dehydration and β-aryl ether cleavage were also observed.[25]

The stability of the lignin model compound DMMP under the reaction conditions and in the solvents to be used for catalytic oxidations was first determined in the absence of added catalyst. After heating for 3 h at 170 °C and under 4% oxygen in nitrogen in glacial acetic acid, no DMMP remained, and the products were the diacetate 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol diacetate (DMPD, 66% yield), the monoacetate 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propyl acetate (DHMA, 2.2% yield) (where acetylation of the primary hydroxyl group of DMMP has taken place), 3,4-dimethoxybenzaldehyde (DMB, 7.6%), 3,4-dimethoxybenzoic acid (DBA, 9.9%), and guaiacol (7.3%). A minor product also formed is the monoacetate at the secondary hydroxyl group. In 80% aqueous acetic acid, 5% DMMP remained, and DMPD (5.8%), DHMA (12%), DMB (20%), dimethoxybenzaldehyde (DBA, 16%), and guaiacol (35%) were produced; similar yields were observed in 50% acetic acid, except for guaiacol (56%).

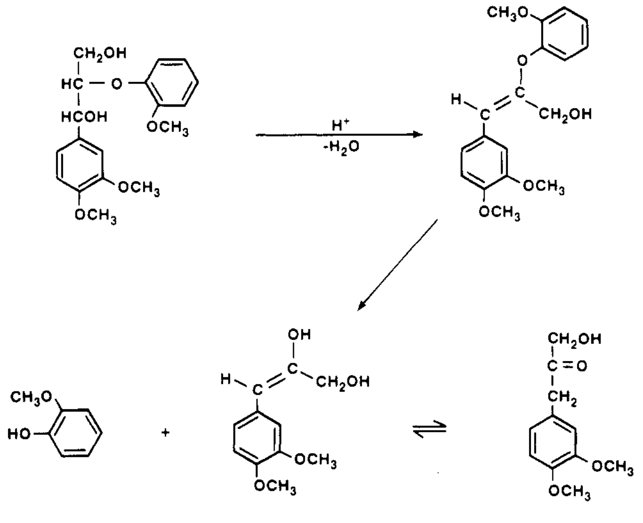
The production of DHMA and DMPD as byproducts was observed in most reactions of DMMP with Co(II) or Mn(II)/Co(II) (1:9), oxygen, and acetaldehyde (added as a cooxidant for the generation of Mn(III)/Co(III), vide infra) in glacial acetic acid. In aqueous acetic acid, DHMA is the major acetylated DMMP derivative and is catalytically oxidized to produce DMB and guaiacol, the expected products of C_α–C_β bond cleavage, as well as DBA, the oxidation product of DMB. DHMA was reacted with Co(II) in the presence of acetaldehyde in 50% acetic acid

Table I. Catalytic Oxidation of DMMP[a]

catalyst	reactant gas	convers (%)	selectivity (%) DMB	DBA	guaiacol
	N_2	92	4	6	77
	4% O_2 in N_2	77	26	21	49
Co(II)	4% O_2 in N_2	49	34	28	54
Mn(II)	4% O_2 in N_2	89	41	33	0
Mn(II)/Co(II)	4% O_2 in N_2	79	29	42	9
Mn(II)/Co(II)	N_2	53	6	5	64

[a] Reactions were run for 3 h in 80% acetic acid at 170 °C and 500 psi pressure of nitrogen or oxygen/nitrogen, using 10 mM DMMP and 100 mM catalyst; Mn(II)/Co(II) ratio was 1:9. DMB = 3,4-dimethoxybenzaldehyde, DBA = 3,4-dimethoxybenzoic acid.

Scheme IV



under 500 psi of 4% O_2 in nitrogen at 170 °C for 3 h to give 68% selectivity to DMB and 24% selectivity to DBA at 96% conversion. In 80% acetic acid, the monoacetate gave 54% selectivity to DMB and 18% selectivity to DBA at 73% conversion. Repeating this reaction in glacial acetic acid, most of the DHMA is converted to DMPD and selectivities to DMB, DBA, and guaiacol of 33%, 26%, and 28%, respectively, were obtained at 31% conversion. DMPD appears not to be as reactive as DHMA, and for this reason conversions of DMMP were lower in glacial acid than in aqueous acetic acid for any given reaction conditions. DMPD and DHMA were considered to be unreacted starting material when determining conversions of DMMP and selectivity to products.

The effect of the addition of oxygen and Co, Mn, and Mn/Co (1:9) oxidation catalysts on the reaction of DMMP in 80% acetic acid at 170 °C is illustrated by the examples listed in Table I. Heating a 10 mM solution of DMMP in 80% acetic acid in the absence of catalyst or oxygen results in acid-catalyzed β-aryl ether cleavage to produce guaiacol and 3-(3,4-dimethoxyphenyl)-2-oxo-1-hydroxypropane (Scheme IV),[25] with very little C_α–C_β bond cleavage. Adding oxygen but no catalyst leads to an increase in C_α–C_β bond cleavage and decrease in β-aryl ether cleavage, while adding both oxygen and catalyst produces the highest selectivities (60–70% combined selectivities for DMB and DBA) to C_α–C_β bond cleavage. Running the reaction with catalyst but no oxygen leads to acid-catalyzed β-aryl ether cleavage as the predominant reaction pathway, but conversions (related to the rate of reactions) are much lower than in the absence of catalyst, indicating a possible stabilization of DMMP to acid-catalyzed reactions by chelation to the catalyst.

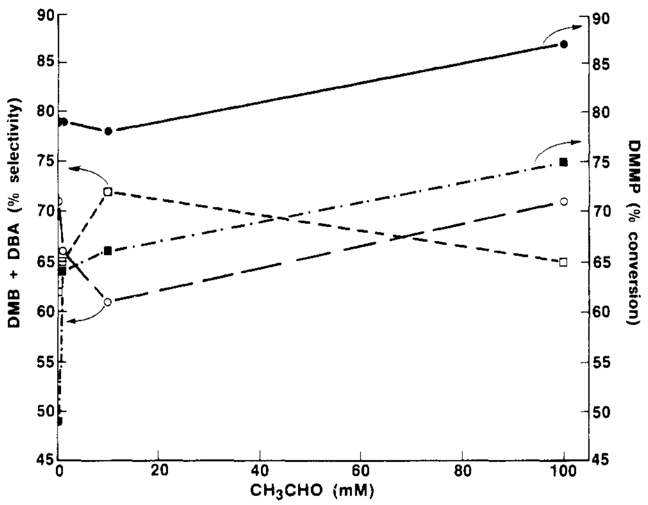


Figure 1. Selectivity to DMB and DBA and conversion of DMMP, as a function of acetaldehyde concentration. Reactions were performed by using 500 psi of 4% O_2 in nitrogen and either Mn(II)/Co(II) (1:9, 0.10 M; ●, conversion of DMMP; ○, selectivity, to DMB and DBA) or Co(II) (0.10 M; ■, conversion; □, selectivity), in 80% acetic acid with DMMP (0.010 M) at 170 °C for 3 h.

Acetaldehyde was added to the reaction mixtures as a cooxidant for catalyst regeneration; acetaldehyde is oxidized under these reaction conditions to peracetic acid, which is capable of reoxidizing Co(II) to Co(III) and Mn(II) to Mn(III).[26] Increasing the concentration of acetaldehyde from 1.0 mM to 100 mM in reaction mixtures containing DMMP (10 mM) and Mn/Co (100 mM) resulted in only a small increase in the conversion of DMMP and the selectivity to DMB and DBA (Figure 1), and a similar effect on conversion and selectivity was obtained when using Mn(II) as catalyst. When using Co(II) as catalyst, a marked increase in conversion was observed between reactions run with no added acetaldehyde and those containing 1–100 mM acetaldehyde.

Of the different catalysts used (Co(II), Mn(II), and Mn(II)/Co(II) (1:9)), the mixed catalyst Mn/Co (1:9) gave the best selectivities and conversions in the presence of added acetaldehyde; a similar synergistic effect when using Co(II) and Mn(II) for the autoxidation of p-xylene has been previously reported.[27] Mn(II) alone gave higher selectivity to C_α–C_β bond-cleavage products than Co(II), but the combination of Mn(II)/Co(II) (1:9) generally resulted in the highest conversion and selectivities to the desired products. The catalytic oxidation of 10 mM DMMP using various concentrations of Mn/Co (1:9) (0–500 mM) in 80% acetic acid with 100 mM acetaldehyde at 170 °C and 500 psi 4% oxygen in nitrogen was examined (Figure 2). Selectivity to products of C_α–C_β bond cleavage increased from 39% with no added catalyst to 71% with 100 mM Mn/Co (1:9); further increases in catalyst concentration only produced moderate increases in selectivity at this partial pressure of oxygen. Conversions of DMMP remained fairly constant up to Mn/Co concentrations of 100 mM, but were slightly lower at higher concentrations.

Increasing the concentration of DMMP while maintaining the concentration of catalyst, acetaldehyde, and

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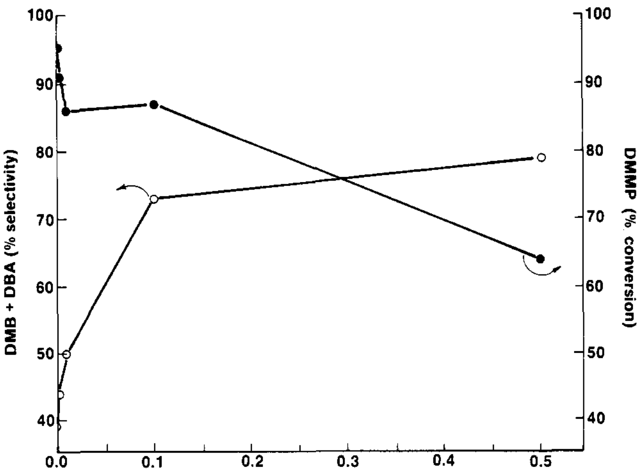

Figure 2. Selectivity to products of C_α–C_β bond cleavage (○) and conversion of DMMP (●) as a function of catalyst concentration. Reactions were performed by using 500 psi of 4% oxygen in nitrogen in 80% acetic acid with DMMP (0.010 M) and acetaldehyde (0.10 M) at 170 °C for 3 h; Mn(II)/Co(II) = 1:9.

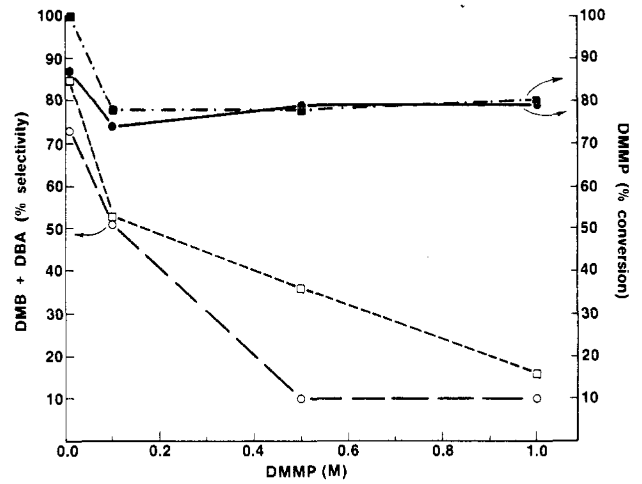

Figure 3. Selectivity to products of C_α–C_β bond cleavage as a function of DMMP concentration. Reactions were performed by using 500 psi of 4% O_2 in nitrogen (●, conversion of DMMP; ○, selectivity to DMB and DBA) and 8% O_2 in nitrogen (■, conversion; □, selectivity), in 80% acetic acid with Mn(II)/Co(II) (1:9, 0.10 M) and acetaldehyde (0.10 M) at 170 °C for 3 h.

oxygen constant resulted in a decrease in selectivity to the C_α–C_β bond-cleavage products DBA and DMB (Figure 3). A concomitant increase in the production of guaiacol was observed with increasing concentration of DMMP, indicating that the acid-catalyzed decomposition of DMMP becomes the predominant reaction pathway as the concentration of oxygen becomes limiting: increasing the partial pressure of oxygen in the reaction produces an increase in the selectivity to DBA and DMB at any given concentration of DMMP. The optimum ratio of reactants favoring C_α–C_β cleavage was 10 Mn/Co (1:9):10 acetaldehyde:1 DMMP using 10 mM DMMP and 8% oxygen in nitrogen. When the concentrations of all reactants except oxygen were increased at this same ratio, higher concentrations again gave lower selectivities to DMB and DBA. The rate of conversion of DMMP decreased slightly with increasing concentration of DMMP, all other reaction parameters being held constant.

The transition-metal-catalyzed electron-transfer oxidation of DMMP requires oxygen for catalyst reoxidation. A blank check performed by heating a solution of 10:10:1 Mn/Co(1:9):acetaldehyde:DMMP (10 mM) in 80% acetic acid and at 500 psi of nitrogen and 170 °C for 3 h produced selectivities of 4% DMB and 11% DBA at 47% conversion, with a 64% selectivity to guaiacol; with no oxygen present, the predominant reaction of DMMP was acid-catalyzed dehydration and β-aryl ether cleavage. In contrast, the same reaction with 8% O_2 in nitrogen gave 63% selectivity to DMB and 21% selectivity to DBA at 100% conversion, and no guaiacol was observed. Similar results were obtained when using either Co(II) or Mn(II) alone as catalysts. The conversions of DMMP and yields of DMB, DBA, and guaiacol were approximately the same when solutions of DMMP were heated to 170 °C in either the presence or absence of added catalyst and/or acetaldehyde in the absence of oxygen. Attempts to use air to generate peracidic intermediates capable of reoxidizing Co(II) to Co(III) in the presence of acetaldehyde were not successful when the reaction was performed by heating the reaction mixture to reflux at atmospheric pressure and bubbling air through the reaction mixture; a 96% recovery of DMMP was obtained.

Using a ratio of Mn(II)/Co(II):acetaldehyde:DMMP of 10:10:1 and 100 mM Mn/Co(1:9), running the reaction at 170 °C and 500 psi of 4% oxygen in nitrogen gave high selectivities to DMB and DBA at almost complete conversion of DMMP in glacial, 80%, and 50% aqueous acetic acid. In glacial acetic acid, the selectivity to DMB and DBA was 82% and 16%, respectively, at 97% conversion. In 80% acetic acid, the selectivity to DMB and DBA was 58% and 29%, respectively, at 99% conversion. In 50% acetic acid, the selectivity to DMB and DBA was 58% and 24%, respectively, at 100% conversion. These same reactions were examined at temperatures of 100 °C, 130 °C, and 150 °C. Low conversions (10–20%) were obtained when running reactions at 100 °C or 130 °C for 3–5 h; at 150 °C, DMMP conversions increased to 50–60% at selectivities similar to those obtained at 170 °C.

The ability to reuse the catalyst was demonstrated by carrying out the catalytic oxidation of DMMP at a 10:10:1 ratio of Mn/Co:acetaldehyde:DMMP in 80% acetic acid at 170 °C for 3 h and then adding the same amount of DMMP and acetaldehyde and repeating the reaction; a total of 57% selectivity to DMB and 26% selectivity to DBA at 100% conversion was obtained. This procedure was repeated a second time, and three separate additions of DMMP and acetaldehyde were added to the original reaction mixture, each followed by heating to 170 °C for 3 h under 500 psi of 4% O_2 in nitrogen; a total of 35% selectivity to DMB and 38% selectivity to DBA at 93% conversion of DMMP was obtained, compared to a 21% selectivity to DMB and 20% selectivity to DBA at 54% conversion for the oxidation of a 10:10:4 mixture of the same reactants. The thermal decomposition of DMMP to unwanted byproducts can be reduced by keeping the concentration of DMMP low.

Conclusions

Under appropriate reaction conditions, i.e. high catalyst and oxygen concentration and low DMMP concentration, the catalytic oxidation of the lignin model compound DMMP proceeds almost completely by C_α–C_β bond cleavage of the arylglycerol β-aryl ether. Although DMMP undergoes autoxidation to produce some products of C_α–C_β bond cleavage in the presence of oxygen alone, significant increases in C_α–C_β bond cleavage are produced by the addition of catalysts capable of one electron-transfer oxidation of C_α-aryl group. The mechanism of this catalytic oxidation mimics the oxidation of this same lignin model compound by the enzyme ligninase. The development of a "biomimetic" catalyst for the oxidative degradation of lignin, which does not depend on hydrogen peroxide for catalyst reoxidation (as is found for ligninase and heme proteins), would provide a distinct advantage for the use of such systems over ligninase or other peroxide-dependent microbial or enzymatic systems. It is possible that hydroperoxy–lignin intermediates are produced during the aerobic microbial degradation of lignin, but because the heme is enzyme-bound, it is not physically accessible to reoxidation by the hydroperoxy intermediates; metal acetates such as cobalt(II) or manganese(II) acetate should easily react with these same hydroperoxy intermediates and be reoxidized. Also, the microbial and enzyme systems are currently limited to temperatures below 40 °C and are used in aqueous systems at an optimum pH of 4.5–5.0, while the catalyst systems that have already been developed for the selective oxidation of alkylaromatics (such as *p*-xylene to terephthalic acid), and which may be adapted to the oxidative degradation of lignin, can be run in organic or acidic or basic aqueous solvents at temperatures up to 200 °C.

One disadvantage of this "biomimetic" catalyst system for lignin degradation is that only the nonphenolic arylglycerol β-aryl ether DMMP was oxidized via C_α–C_β bond cleavage. Under the conditions for catalytic oxidation employed, models of 1,2-diarylpropane structures of lignin (DHA and BMPD) gave primarily acid-catalyzed dehydration products, while the phenolic arylglycerol β-aryl ether HMMP was oxidized but did not produce products of C_α–C_β bond cleavage. The enzyme ligninase can oxidize these same diarylpropane structures via C_α–C_β bond cleavage and as a substitute for the chlorine bleaching of paper pulp for residual lignin removal, the enzymatic reaction may produce greater amounts of delignification than catalytic oxidation. However, both the studies of ligninase and biomimetic models of ligninase have focused primarily on reactions of arylglycerol β-aryl ethers, which are representative of the major type of structures found in lignin, but the structure of residual lignins remaining in paper pulps after cooking is not well-known.[28] Kraft cooking of pulp is believed to degrade β-aryl ether structures to styryl aryl ethers, diaryl ethers, and biphenyls, which are not easily degraded and are removed in a subsequent chemical bleaching step.[29] Rather than breaking carbon–carbon bonds for dissolution of residual lignin, oxidation by a biomimetic catalyst, or by ligninase itself, may result in further polymerization of the β-aryl ether degradation products. The treatment of kraft pulp with *P. chrysosporium* has been reported, and although treatment did not result in any bleaching, the remaining pulp was easier to bleach by conventional chlorine treatment due to degradation of some of the residual lignin.[30] An examination of the catalytic oxidation of residual lignin in paper pulp which utilizes oxygen and Mn/Co acetates in aqueous acetic acid needs to be performed before the efficacy of such a method can be judged in comparison to chlorine bleaching.

Experimental Section

General Remarks. *Extreme caution should be taken when working with peroxides or peracids directly or when employing reaction conditions where peroxides or peracids will be generated in situ.*[31] No metal-ware (e.g. syringe needles) should be employed. Only all-glass reaction vessels, gas-tight syringes with Teflon luer-lock hubs, and Teflon syringe needles and cannulas were used. Dihydroanisoin (1,2-bis(4-methoxyphenyl)ethane-1,2-diol, DHA)[17] and 1,2-bis(4-methoxyphenyl)propane-1,3-diol (BMPD)[18] were prepared as previously described, whereas 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (HMMP) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol (DMMP) were prepared according to slight variations of published procedures[32] as described below. Cobalt(II) acetate, manganese(II) acetate, manganese(III) acetate, acetaldehyde, and 35% peracetic acid were obtained from commercial sources and used as received. Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate according to a published procedure.[33] Reactions using oxygen/nitrogen mixtures at greater than atmospheric pressure were performed in Parr Model 4740 Hastelloy C high pressure reaction vessels equipped with glass liners and Teflon-coated stirring bars. Dry column chromatography was performed by using adsorbent silica gel DCC (Universal). Product selectivities were calculated on the basis of product yields and the amount of substrate reacted (conversion). Yields of products and recovered starting materials were determined quantitatively by HPLC on a Waters Model 680 automated gradient controller in conjunction with two Waters Model 510 solvent pumps and a Waters Model 441 UV absorbance detector. Analyses were performed at 280 nm. A radial-compression Waters Nova-Pak C_{18} column (5 mm × 10 cm) was used. The mobile phase was a gradient mixture of (A) methanol/acetonitrile (1:1) and (B) 0.087% phosphoric acid. The column was equilibrated with a 30:70 A–B mixture and then a curvilinear gradient to 60:40 A–B over the first 8 min of the analysis was run using curve no. 8 on the Waters gradient controller; total analysis time was 20 min. Proton magnetic resonance spectra were run in deuteriochloroform and are reported in ppm (δ units) downfield of internal tetramethylsilane (Me_4Si).

Preparation of 1-(4-Hydroxy-3-methoxphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (HMMP). β-Hydroxy-α-(2-methoxyphenoxy)-4-hydroxy-3-methoxypropiophenone[32a] (10 g, 31 mmol) was dissolved in 800 mL of 0.1 N sodium hydroxide solution under argon. Sodium borohydride (1.5 g, 40 mmol) was added and the solution was stirred at room temperature overnight. Dilute HCl was then added to adjust the pH to 3 and the solution was extracted with ethyl acetate (600 mL × 3). The organic layer was washed with 600 mL of brine, dried over $MgSO_4$, and filtered. The solvent was removed by evaporation under reduced pressure to give a viscous oil, which was chromatographed on dry column silica gel using ethyl acetate/hexane (1:1) as solvent. The resulting viscous oil was heated to 35 °C under vacuum (0.05 Torr) for 72 h to remove residual solvent, yielding a colorless, waxy solid (7.5 g, 75% yield, mixture of erythro and threo isomers, hygroscopic). ^1H NMR ($CDCl_3$): [a mixture of threo and erythro isomers] δ 2.8 (m, 1 H, CH_2OH), 3.4–3.8 (m, 2 H, CH_2O), 3.7 (d, 1 H, $CHOH$), 3.89 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 3.95–4.25 (m, 1 H, OCH), 4.95–5.1 (m, 1 H, $CHOH$), 5.65 and 5.69 (2 s, Ar OH), 6.8–7.2 (m, 7 H, Ar). ^{13}C NMR: [threo isomer] δ 56.2 (OCH_3), 61.3 (CH_2OH), 74.3 (ArCH), 89.9 (HCOAr): [erythro isomer] δ 56.1 (OCH_3), 61.0 (CH_2OH), 73.0 (ArCH), 87.8 (HCOAr). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.75; H, 6.38.

Preparation of 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (DMMP). To a round-bottom flask equipped with a reflux condenser was added a solution of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (HMMP, 3.5 g, 11 mmol) in 20 mL of dry acetone (dried over K_2CO_3 and distilled). Powdered anhydrous K_2CO_3 (1.6 g, 12

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mmol) and methyl iodide (1.0 mL, 2.3 g, 15 mmol) were added. The mixture was heated to reflux for 4 h and the reaction was monitored by HPLC. Additional methyl iodide was added until no starting material remained. Water was added and the solution was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. After the solvent was removed under reduced pressure, the residue was chromatographed on a dry column of silica gel using methylene chloride/methanol (97/3) as solvent. The resulting viscous oil was heated to 35 °C under vacuum (0.05 Torr) for 72 h to remove residual solvent, yielding a viscous oil (3.3 g, 90% yield, mixture of erythro and threo isomers, very hygroscopic). ^1H NMR ($CDCl_3$): [a mixture of threo and erythro isomers] δ 2.75 (m, 1 H, CH_2OH), 3.4–3.7 (m, 2 H, CH_2), 3.7 (d, 1 H, CHO*H*), 3.85–3.95 (m, 9 H, OCH_3), 4.0–4.2 (m, 1 H, OCH), 5.0 (m, 1 H, *C*HOH), 6.8–7.2 (m, 7 H, Ar). ^{13}C NMR: [threo isomer] δ 55.7 (OCH_3), 60.9 (CH_2OH), 73.6 (ArCH), 88.7 (HCOAr); [erythro isomer] δ 55.7 (OCH_3), 60.7 (CH_2OH), 72.5 (ArCH), 86.7 (HCOAr). Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 65.19; H, 6.90.

Stoichiometric Oxidation of Lignin Model Compounds with Cobalt(III) Acetate. In a typical procedure, a solution of DMMP (6.8 mg, 0.018 mmol) and cobalt(III) acetate (84.3%, 10.5 mg, 0.037 mmol) in 18 mL of glacial acetic acid was heated to reflux in 20 min with stirring. One hour later, the color turned from greenish black to pink. The solution was cooled to room temperature and veratrole (10.2 mg, 0.074 mmol) was added as an internal standard for HPLC analysis. A 67% selectivity to DMB at 99% conversion of DMMP was obtained. For reactions where cobalt(III) acetate still remained, an aqueous solution of ferrous sulfate was added dropwise until the color of the solution turned from green to pink; then veratrole was added as internal standard.

Regeneration of Co(III) for the Oxidation of DMMP by the Addition of Peracetic Acid. To a solution of DMMP (23.9 mg, 0.072 mmol) and cobalt(II) acetate (3.4 mg 0.019 mmol) in 60 mL of glacial acetic acid with stirring was added peracetic acid (35%, 4.2 μL, 0.25 mmol). This solution turned from pink to greenish black. After 2 h, the color turned back to pink and another aliquot of peracetic acid (4.2 μL) was added. Two more aliquots of peracetic acid were added each time the greenish black color disappeared. Finally the color stayed yellow. Veratrole (42.5 mg, 0.31 mmol) was added as an HPLC internal standard. The mixture was analyzed by HPLC to give 48% selectivity to DMB and 15% to DBA at 90% conversion.

Catalytic Oxidation of Lignin Model Compounds. In a typical procedure, a Pyrex glass liner containing a Teflon-coated magnetic stirring bar, DMMP (8.4 mg, 0.025 mmol), manganese(II) acetate (4.3 mg, 0.025 mmol), cobalt(II) acetate (39.8 mg, 0.23 mmol), and acetaldehyde (14 μL, 0.25 mmol) in 2.5 mL of 80% acetic acid was placed in a 71-mL Parr Hastalloy C high pressure reaction vessel (Model 4740). The reactor was sealed, purged three times by pressurizing to 320 psi of N_2 and then venting to atmospheric pressure, and then charged with 336 psi of 4% O_2 in N_2). The reactor was put in a heating block preheated at 170 °C and the reaction mixture stirred for 3 h; at 170 °C, the reactor pressure increased to 500 psi. The reactor was then rapidly cooled to room temperature by placing it in an ice/water bath and the vessel subsequently vented to atmospheric pressure. Veratrole (11.2 mg, 0.081 mmol) was added to the reaction mixture as an HPLC internal standard and the mixture was analyzed to yield DMB (37%), DBA (25%), and guaiacol (2.4%) at 87% conversion.

Registry No. BMPD, 85272-48-6; DHA, 4464-76-0; DMPD, 35863-57-1; DHMA, 113303-19-8; HMMP, 7382-59-4; DMMP, 10535-17-8; DMB, 120-14-9; DBA, 93-07-2; Co(III) acetate, 917-69-1; Mn(II) acetate, 638-38-0; 4-$H_3COC_6H_4CH(OH)CH_2OH$, 13603-63-9; 4-$H_3COC_6H_4CHO$, 123-11-5; 2-$H_3COC_6H_4OH$, 90-05-1; β-hydroxy-α-(2-methoxyphenoxy)-4-hydroxy-3-methoxypropiophenone, 22317-34-6; lignin, 9005-53-2.

Supplementary Material Available: Table containing the results of the stoichiometric oxidation of lignin model compounds by cobalt(III) acetate (2 pages). Ordering information is given on any current masthead page.

Direct Osmylation of Benzenoid Hydrocarbons. Charge-Transfer Photochemistry of Osmium Tetraoxide

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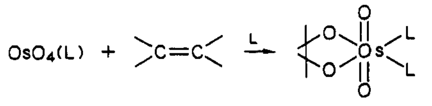
Benzene and related arenes are well-known to be inert to osmium tetraoxide and are often employed as solvents for alkene osmylations. However, when these mixtures are deliberately exposed even to roomlight, a facile addition of OsO_4 occurs to arenes such as benzene, mesitylene, and hexamethylbenzene to afford 2:1 adducts. This photoactivated osmylation is shown to derive from the charge-transfer (CT) excitation of the electron-donor–acceptor (EDA) complex of OsO_4 with the aromatic donor (ArH). The spectral properties of the EDA complexes vary with the ionization potentials of the arenes in accord with the expectations of Mulliken theory. Indeed the limited magnitudes of the association constants of $K < 1$ M^{-1} for the formation of [ArH, OsO_4], as measured by the Benesi–Hildebrand procedure, classify these as contact charge transfer in which the photochemical excitation of the CT band leads to the ion pair [$ArH^{\bullet+}$ $OsO_4^{\bullet-}$]. The collapse of the ion pair to the 1:1 osmylated cycloadduct is discussed, together with the eventual formation of the ternary adduct that is routinely isolated as the pyridine complex with the stoichiometry $(ArH)(OsO_4)_2(py)_4$. The common role of EDA complexes as intermediates in both the CT osmylation of arenes as well as the ubiquitous thermal osmylation of alkenes is considered in the context of a unifying activation process.

Introduction

Osmium(VIII) tetraoxide is an effective reagent for the cis hydroxylation of alkenes under stoichiometric conditions[1] as well as in a variety of catalytic systems.[2,3] In both, the critical step depends on the formation of an osmium(VI) cycloadduct[4] which is promoted by bases L, typically pyridine, i.e.[1,5]

$$OsO_4 + L \rightleftharpoons OsO_4(L) \qquad (1)$$



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