Selective Transition-Metal Catalysis of Oxygen Delignification Using Water-Soluble Salts of Polyoxometalate (POM) Anions.

Part II. Reactions of α-[SiVW$_{11}$O$_{40}$]$^{5-}$ with Phenolic Lignin-Model Compounds

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Summary

When heated under anaerobic conditions, aqueous solutions of the polyoxometalate anion α-[SiVW$_{11}$O$_{40}$]$^{5-}$(POM$_{ox}$, 1). supplied as the salt K$_5$[SiVW$_{11}$O$_{40}$]· 12H$_2$O, selectively delignify unbleached mixed-pine kraft pulps. During delignification. 1 is reduced by residual lignin to α-[SiVW$_{11}$O$_{40}$]$^{6-}$ (POM$_{red}$, 2) : α-[SiVW$_{11}$O$_{40}$]$^{5-}$ + 1e- ⟶ α-[SiVW$_{11}$O$_{40}$]$^{6-}$. E^0= + 0.69 V vs. NHE, Model studies suggest that phenolic (hydroxylated phenyl) groups present in residual lignin are substrates for the reduction of **1.** Reactions of **1** with phenolic arylglycerol β-aryl ethers and other phenolic lignin models suggest that anaerobic POM degradation of residual lignin may occur via sequential single-electron oxidation reactions of phenolic substructures, first to cyclohexodienyl radicals and subsequently to cyclohexadienyl cations. Hydrolysis of these cationic intermediates results in alkyl-side-chain cleavage, a likely route to polymer degradation.

Introduction

Reusable POM salts could make it possible to use oxygen indirectly to selectively delignify wood or wood pulp to low kappa numbers. The chemical principles fundamental to the use of POMs in this context, and the process concepts essential to their application, are outlined in the preceding paper in this series (Part I). Data reviewed there show that the POM anion α-[SiVW$_{11}$O$_{40}$]$^{5-}$ (POM$_{ox}$, **1.** Fig. 1) is an effective and selective oxidant for the delignification of softwood kraft pulp. The present contribution (Part II) describes the reactions of **1** with several phenolic lignin-model compounds.

Polyoxometalate delignification

As described in Part I, reusable POM salts might be used in a two-step delignification process. In the first step, delignification, the POM is applied to wood or pulp under anaerobic conditions. Oxygen, excluded during delignification, is used in the second step to regenerate (reoxidize) the POM anion and to degrade dissolved lignin fragments to carbon dioxide and water (mill closure).

The reduction potential of aqueous solutions of **1** is 0.69 V vs, a normal hydrogen electrode (NHE) over a pH range of 2 to 8 (Weinstock *et al.* 1997). During anaerobic delignification, molecules of **1** are reduced by one electron each to give the stable, soluble anion α-[SiVW$_{11}$O$_{40}$]$^{6-}$

(POM$_{red}$, **2,** Fig. 2). Under anaerobic conditions, **1** is the only inorganic oxidant present throughout delignification; no oxygen or reduced oxygen species are present. In addition, unlike chlorine- or oxygen-based oxidants, neither **1** nor **2** are believed to combine with lignin. Thus, after reaction of a lignin substructure with 1 equivalent (equiv) of **1,** the only pathways available for further reaction are with an additional equivalent of **1,** with other
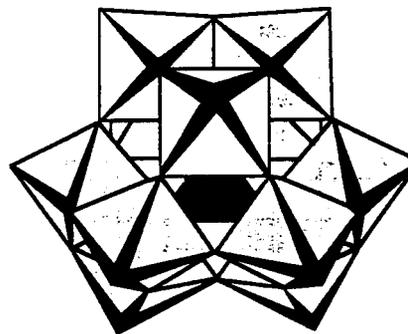
Fig. 1. The α-Keggin POM anion [SiVW$_{11}$O$_{40}$]$^{5-}$ in polyhedral notation. The silicon heteroatom resides in a tetrahedral hole at the center of the structure (the SiO$_4$ unit is shown in black). In polyhedral notation, *MO*$_x$ units are depicted; the WO$_6$ octahedra are shown in gray, while the VO$_6$ octahedron is shown in white. Oxygen atoms reside at the vertices of the dark lines that define the MO$_x$ polyhedra.
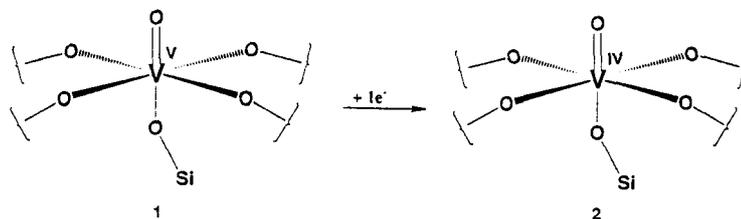
Fig. 2. The electron-accepting site of the V(V)-containing anion α-[SiVW$_{11}$O$_{40}$]$^{5-}$ (POM$_{ox}$, **1**) and its reduction by one electron to the V(IV) complex α-[SiVW$_{11}$O$_{40}$]$^{6-}$ (POM$_{red}$, **2**).

lignin or polysaccharide components or with water or buffer.

Reactions of **1** with solutions and dispersions of phenolic lignin-like (phenylalkane) model compounds are herein described. Phenols were chosen for this initial study for two reasons: (a) they are known substrates for oxidation by a vanadium-containing POM anion (Kholdeeva *et al.* 1992; Lissel *et al.* 1992), and (b) they are present at relatively high concentrations in residual kraft lignin (native softwood lignin typically contains ca. 12 phenolic hydroxyls per 100 phenylpropane units, while the value for residual softwood-kraft lignin is ca. 30) (Yang and Goring 1980; Gellerstedt and Lindfors 1984a, 1984b; Lai *et al.* 1990; Francis *et al.* 1991; Lai and Guo 1991; Li and Lundquist 1994; Lachenal *et al.* 1995; Lai *et al.* 1995; Sun and Argyropoulos 1995). Non-phenolic lignin substructures are also believed to react with **1** during delignification; reactions of non-phenolic lignin-model compounds are currently under investigation.

Experimental

General methods

Model studies were carried out using the potassium vanadoundecatungstosilicate salt α-K$_5$[SiVW$_{11}$O$_{40}$] · 12H$_2$O (1). The preparation, charcterization and use of this salt in bleaching were carried out as described elsewhere (Weinstock *et al.* 1995; Weinstock *et al.* 1996; Weinstock *et al.* 1997).

Delignification

Delignification was carried out in a stirred, glass-lined, high-pressure Parr reaction vessel. The pulp was slurried at 3% consistency (csc) in a bright yellow 0.5 M solution of **1** (sodium salt form) in 0.35 M pH 5.2 acetate buffer. After purging with nitrogen, the reactor was heated to 125°C (ramp time of 40 min) and held at temperature for 30 min. The reactor pressure was sustained with nitrogen at about 340 kPa. During heating, 30% of the vanadotungstosilicate was reduced to α-[SiVW$_{11}$O$_{40}$]$^{6-}$ (2), and the pH dropped to 4.7. The pulp was collected in a Büchner funnel, washed three times with water and extracted with 2.5% NaOH (oven-dried weight of pulp) at 10% csc for 1 hr at 50°C under air.

preparation and reactions of lignin-model compounds

The guaiacyl and syringyl β-O-4 dimers 1 -(3-methoxy-4-hydroxyphenyl)-2-(phenoxy)propane-1,3-diol (**3,** Fig. 4) and 1-(3,5-dimethoxy-4-hydroxyphenyl)-2-(phenoxy)propane- 1.3-diol (7, Fig. 4) were prepared according to literature methods (Landucci *et al.* 1981). The diphenylmethane model 1-(3,4,5-trimethoxyphenyl)-1-(3,5-dimethoxy-4-hydroxyphenyl)methane **(14,** Fig. 4) was obtained by methylation (methyl iodide and potassium carbonate in dimethylformamide (DMF)) of bis(3,5-dimethoxy-4-hydroxyphenyl)methane. The latter was prepared by alkaline condensation of 2,6-dimethoxyphenol and formaldehyde (Steelink 1966).

Unless specified, all reactions were carried out at room temperature in 200 mM potassium acetate buffer. An example of the reaction procedure and work-up protocol is provided in detail as follows for the oxidation of 1-(3,5-dimethoxy-4-hydroxyphenyl)-2-(phenoxy)propane-1,3-diol **(7)**. Compound **1** (60mg, 18.9 x 10^{-3}mmol) was dissolved in 1 mL of 200mM pH 5 potassium acetate buffer and flushed with N$_2$ in a septum-sealed vial. Compound **7** (2.0mg, 6.3 x 10^{-3}mmol) was dissolved in 20mL of DMF and added via syringe to the stirred solution of **1**. After 1 hr at room temperature, the reaction was acidified with 2N HCl and extracted three times with a 2 : 1 mixture of chloroform and acetone. The remaining aqueous phase was then stripped of residual volatile organics by flushing it with N$_2$ and diluted with H$_2$O to a standard volume for spectrophotometric determination (496 nm) of the concentration of reduced **1**. The organic layer was washed with brine and dried over Na$_2$SO$_4$, and a portion was removed for GC-MS analysis. The remainder was concentrated to dryness, redissolved in 100 mL of DMF and analyzed by HPLC on a Hamilton PRP-1 reverse-phase column. The column was eluted with 15% acetonitrile/H$_2$O/0.1% H$_3$PO$_4$ for 15 min at 1.0mL min^{-1}, followed by a 35 min linear gradient to 65% acetonitrile/H$_2$O/0.1% H$_3$PO$_4$ at the same flow rate. The absorbance of the eluate was monitored at 260 nm.

In some experiments involving the oxidation of **3** and **7,** the reaction mixture was reduced with NaBH$_4$ before HPLC analysis, This procedure was adopted because no authentic standard was available for product **5** (see Fig. 5) whereas a standard of compound **6** (see Scheme 1) was readily synthesized from phenol and bromomalonate diethyl ester as previously described (Tuor *et al.* 1992). The reactions were stirred with NaBH$_4$ overnight, after which unreacted reductant was quenched with saturated NH$_4$Cl and the mixture was extracted three times with chloroform. The extract was washed with brine, dried with Na$_2$SO$_4$, concentrated to dryness and analyzed by HPLC as described.

Oxidation of acetosyringone: Isolation and characterization of 7-acetyl-3,5-dimethoxy-1,2-rnaplthaquinone

Acetosyringone **(10,** 100 mg, 0.51 mM) in 0.1 mL DMF under N$_2$ was added to a stirred, degassed solution of **1** (16.0g, 5.1 mM) in 100 mL of 0.2M pH 5 potassium acetate buffer; the mixture was stirred overnight at room temperature. The reaction mixture was worked-up as described above. Concentration of the resultant dark red solution (chloroform/acetone) gave 37 mg of black crystalline material. Due to extensive band overlap and the small sample size, only a small portion of pure compound (1.8 mg, **11**) was isolated from a mixture of products by preparative thin-layer chromatography. This compound, the major reaction product (HPLC), was identified by GC-MS (C$_{14}$H$_{12}$O$_5$, 260.25 a.m.u.) and by 1D and 2D NMR.

NMR characterization of **11** was accomplished with a 360 MHz ARX spectrometer (90 MHz ^{13}C). Deuterated methylene chloride was used as solvent. Standard Brüker pulse programs were used for both 1D and 2D experiments. The proposed structure was consistent with all spectral data. ^{1}H (CD$_2$Cl$_2$, TMS); 2.61 (s), acetyl CH$_3$; 3.87(s), 3-OCH$_3$; 4.00(s), 5-OCH$_3$; 6.97(s), H4; 7.71 (s) H6;

8.09(s) H8. ^{13}C (CD$_2$Cl$_2$, TMS); 26.9, acetyl CH$_3$; 56.4, 3-OCH$_3$; 56.8, 5-OCH3; 108.1, C4; 116.4, C6; 122.6, C8; 129.0, C7; 129.7, C8a; 137.6, C4a; 152.7, C3; 156.2, C5; 176.4, C2; 178.7, Cl; 196.5, acetyl C=O.

Results and Discussion

Delignification by α-[SiVW$_{11}$O$_{40}$]$^{5-}$

Under anaerobic conditions, aqueous solutions of **1** selectively delignify unbleached softwood kraft pulps (see Part I in this series). For example, treatment of softwood kraft pulp (kappa number 24.1, viscosity 27.8 mPa·s) with **1** in phosphate buffer at pH 7, followed by extraction with alkali, provides a pulp with kappa number and viscosity of 4.7 and 23.1 mPa·s.

However, as discussed in Part I, **1** reacts with phosphate at near-neutral pH values. Thus, for the present study, a pH 5 acetic acid/acetate buffer system was chosen. Softwood kraft pulp (kappa number 30.6, viscosity 26.1mPa·s) was reacted at 3% csc with a 0.50M solution of **1** in 0.35M acetate buffer at an initial pH of 5.2 for 0.5hr at 125°C under a nitrogen atmosphere. The pulp obtained had a kappa number of 12.0 and viscosity of 26.8 mPa·s. After extraction with alkali (2.5% NaOH on pulp, 1 hr at 50°C), the pulp had a microkappa number of 10.4 and viscosity of 25.7 mPa·s (Fig. 3).

Thus, in acetate buffer **1** is an effective and selective oxidant for the delignification of kraft pulp. This buffer is used exclusively in the work discussed below.

Reactions with phenolic lignin models

The work of Lissel *et al.* (1992) and Kholdeeva *et al.* (1992) pointed to phenolic hydroxyl groups as likely candidates for oxidation by **1** (see full discussion in Part I). In addition, due to the cleavage of aryl ether linkages during kraft pulping, residual kraft lignin becomes enriched in phenolic substructures. Thus, the oxidation of several phenolic lignin model compounds (Fig. 4) by **1** were examined in detail. Although these models merely approximate the many
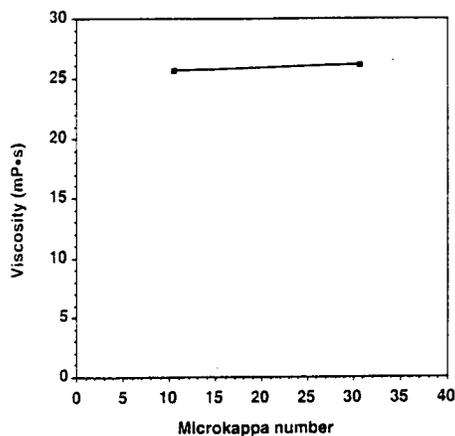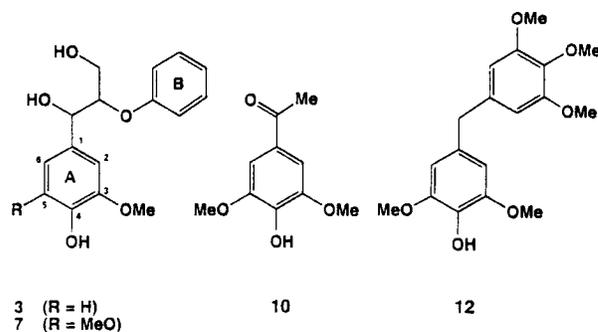
Fig. 4. Phenolic lignin-model compounds used to investigate the reactivity of α-[SiVW$_{11}$O$_{40}$]$^{5-}$ (**1**) with phenolic substructures in lignin: a guaiacyl β-O-4 dimer, **3**; a syringyl β-O-4 dimer, **7**; acetosyringone, **10**; and a diphenylmethane model. **12.** The phenyl rings of the β-O-4 dimers are designated A and B.

phenolic structures present in residual kraft lignin, study of the reactivity of these models toward **1** is a first step toward understanding the mechanism of delignification.

A rapid reaction was observed at room temperature when 0.5 equiv of the phenolic guaiacyl dimer 1-(3-methoxy-4-hydroxyphenyl)-2-(phenoxy)propane-1,3-diol (**3,** Fig. 4), dissolved in a minimum of methanol, was added quickly to an acetate buffered solution of **1** under nitrogen. After 1 min, an organic-soluble precipitate, probably consisting of a large number of oligomeric products, was observed. Phenoxyl radicals derived from unsubstituted phenols are known to couple at near diffusion limited rates in homogeneous solution. If the guaiacyl dimer (**3**) were oxidized by **1** to intermediate phenoxyl radicals, these could couple rapidly at the 5 position of the A ring (see numbering in Fig. 4).

This result illustrates a limitation in the use of homogeneous solutions or dispersions of simple organic compounds to model reactions of structures present within pulp fibers. Much of the residual kraft lignin present in the unbleached pulp fibers is immobile. This immobility is due to the residual lignin's low solubility, to the presence of covalent lignin-carbohydrate linkages and to steric constraints imposed by cell wall polysaccharides. Thus, opportunities for oxidation intermediates to react with one another are more limited in the cell wall than they are in homogeneous solution. Finely divided dispersions of slightly soluble organic models, such as **3,** also fail to represent the spatial and diffusional characteristics of lignocellulosic matrices.

Nonetheless, the oligomerization of **3** suggests that its oxidation by **1** involves the initial formation of phenoxyl radicals. Under the conditions used here, **1** is a single-electron oxidant. Hence, it would not be surprising if single-electron oxidation products (i.e., phenoxy radicals) were generated (eq. (1)).

In homogeneous solution, unsubstituted phenoxyl radicals couple rapidly. In the guaiacyl model, **3,** in which the *para* position is blocked by an alkyl side chain, coupling probably occurs at the 5 position. Intermediate phenoxyl radicals are also likely to form during delignification by **1.** However, if radical coupling were the only pathway

Fig.3. Microkappa vs. viscosity for delignification of unbleached mixed-pine kraft pulp (3.0% csc) by α-[SiVW$_{11}$O$_{40}$]$^{5-}$ (1, 0.50M in 0.35M, pH 5 acetate buffer solution for 0.5hr at 125°C, followed by extraction with 2.5% alkali).

(1)
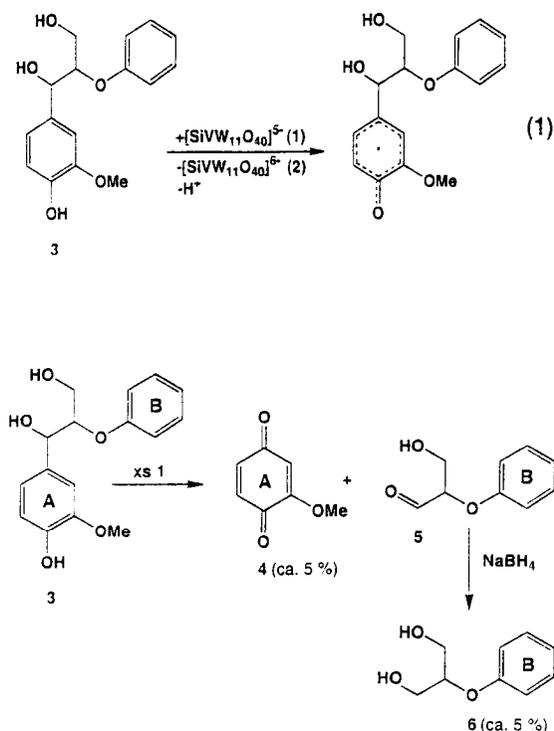
Scheme 1

available for further reaction, it is unlikely that delignification would occur. Apparently, constraints imposed by the polysaccharide matrix limit the rates of radical coupling relative to those of pathways that lead to lignin degradation.

Cleavage of phenolic lignin models

The rate expression for radical coupling is of the form $rate_c = k_c[\text{phenoxy radical}]^2$. If an alternative pathway exists that is first order in phenoxy radical (i. e.. $rate_{alt} = k_{alt}[\text{phenoxy radical}]$) then the relative rate of coupling, to that of the alternative pathway, should be directly proportional to

the concentration of phenoxy radicals: $rate_c/rate_{alt} = (k_c/k_{alt})[\text{phenoxy radical}]$. Thus, one way to decrease the rate of radical coupling, relative to that of alternative pathways, might be to decrease the concentration of radical intermediates. This can be accomplished by very slow addition of the phenolic substrate to the oxidant solution. A similar approach was used to observe *in vitro* lignin depoly - merization by lignin peroxidase (Hammel *et al.* 1993).

After slow addition (over 16 hrs) of **3** into it solution containing a large excess of **1,** a small (less than 5%) amount of 2-methoxy-*p*-benzoquinone (**4**) was observed by HPLC and confirmed by GC-MS (TMS derivative). As expected, oligomerization products had still formed (ca. 95%). Observation of **4** required that reaction and work-up be cm-tied out in the dark. The expected B-ring fragment, **5,** was observed by HPLC after reduction to the dihydroxyl derivative (**6**) with NaBH$_4$(Scheme 1). Observation of **4** and **5** suggests that oxidation of phenolic lignin substructures by **1** can lead to side-chain cleavage (depolymerization) of guaiacyl lignin.

In order to study the cleavage reaction in more detail, a phenolic syringyl model, l-(3.5-dimethoxy-4-hydroxy-phenyl)-2-(phenoxy)propane- 1,3-diol (**7,** Fig. 4), was used. Here, radical coupling is blocked by the methoxy group at the 5 position of the A ring. At room temperature. **1** reacted very rapidly with **7,** giving an approximately 1:1 mixture of a ketone, **8,** and 2.6-dimethoxy-*p*-benzoquinone, **9** (Fig. 5). Significantly, no organic precipitate was observed. The B-ring fragment, **5,** was observed as the diol, **6,** after borohydride reduction.

The stoichiometry of the reaction with respect to **1** was established by locating the break point in the plot of percent reduction of **1** as a function of equivalents added (Fig. 6), It can be seen by inspection that all of the POM is consumed by reaction with **7** when less than or equal to ca. 2.9 equivs of **1** are added. After this point, unreacted POM$_{ox}$ remains, reducing the percent reduction of the POM solution to below 100.

The amounts of the products **8** and **9,** along with the amount of unreacted **7,** were also quantified as a function of
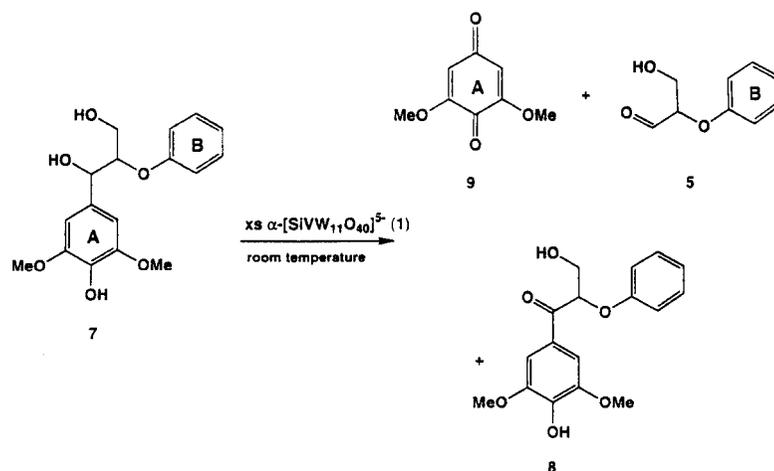
Fig. 5. Products of the reaction of on excess of α-[SiVW$_{11}$O$_{40}$]$^{5-}$ (**1**) with **7** at room temperature.
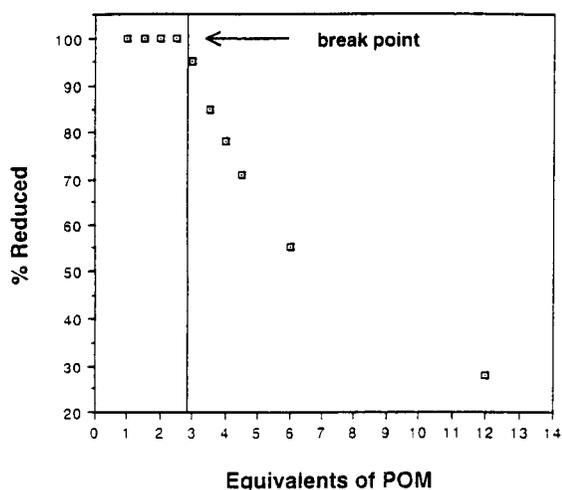
Fig. 6, Percent reduction of α-$[SiVW_{11}O_{40}]^{5-}$ (**1**) observed after completion of the anaerobic reaction of **7** with 1 to 12 equivs of **1** in pH 5 acetate buffer at room temperature. Approximately 2.9 equivs of **1** are consumed for each equivalent of **7** reacted.

equivalents of **1** added. These data, along with the total amount of material recovered, are presented on a molar basis in Figure 7. The scatter in the plot is due to error introduced during reaction set-up and sampling: data were obtained by HPLC analysis of aliquots taken from successive reactions.

These data (Figs. 6 and 7) show that **8** and **9** (and by inference **5**) are the dominant products of the reaction at room temperature, that no significant quantities of other stable intermediates are formed when substoichiometric amounts (< 3 equivs) of **1** are used and that conversion of **7** to **8** and **9** (1:1 mixture) consumes ca. 3 equivs of **1**. The ketone, **8**, results from dehydrogenation of the benzylic hydroxyl group of **7**. while compounds **5** and **9** are products of cleavage at C-1 of the phenyl ring. Oxidation of **7** to **8** is a two-electron process. while conversion to **5** and **9** requires the removal of four electrons. Thus, oxidation to a 1:1 mixture of **8** and **9** should require the reduction of 3 equivs of **1** per mol of **7** consumed, as observed (Fig. 6).

A possible reaction pathway for cleavage of **7** at C-1, taking into account all available data, is shown in Figure 8. Formation of a cyclohexadienyl cation intermediate, though not observed, may be inferred by product analysis. Initially formed phenoxy radicals might be further oxidized to cyclohexadienyl cations by a second equivalent of **1**, as shown. (Alternatively, two phenoxy radicals might disproportionate to a cyclohexadienyl cation and phenolate anion.) Hydrolytic cleavage at C-1 of cyclohexadienyl cations, such as that proposed in Figure 8, has been observed (Steelink and Britton 1974), and oxidation of hydroquinones to quinones is well established. Dehydrogenation of **7** to give the ketone (**8**, Fig. 5) might occur via a number of pathways, between which the data fail to differentiate.

An analogous mixture of oxidation products was obtained upon oxidation of a phenolic arylglycerol β-arylether dimer by manganese peroxidase (MnP). This enzyme, a heme peroxidase excreted by a number of lignin-degrading fungi, catalyzes the peroxide oxidation of Mn(II) to Mn(III)

(Kofujita *et al.* 1991; Tuor *et al.* 1992). It was proposed that 2 equivs of Mn(III) oxidized the phenolic moiety to a cyclohexadienyl cation that either (a) lost a proton to give an α-ketone or (b) was hydrolytically cleaved to give a hydroquinone. The hydroquinone could then be oxidized to a *p*-benzoquinone by 2 additional equivalents of Mn(III). Laccases also react with closely related phenolic arylglycerol β-arylether (β-O-4) and β-aryl (β-1) lignin models, giving analogous products (Kawai *et al.* 1987; Kawai and Ohashi 1993). Homolytic α–β cleavage of cyclohexadienyl radical intermediates is also possible, and this has been observed to a limited extent in reactions of lignin peroxidase, MnP and of lacasses (Kawai *et al.* 1988; Yokota *et al.* 1991; Tuor *et al.* 1992). We have not observed products indicative of this fragmentation pathway.

Reaction of the phenolic ketone, **8**, with **1** is very slow at room temperature. In reactions of phenolic lignin models with MnP and laccases, analogous ketones were isolated from room temperature reactions (Kawai *et al.* 1987; Tuor *et al.* 1992). In general, electron-withdrawing substituents, such as α-carbonyl groups, stabilize phenols toward oxidation (Saijonmaa 1974; Chupka *et al.* 1981). However, upon heating an aqueous dispersion of **8** to 125°C for 3 hrs in the presence of an excess of **1**, most of the ketone was consumed, and a mixture of products was obtained. The cleavage product, **9**, was observed in low yield.

Alternative hydrolysis pathways

The side-chain cleavage observed in the oxidation of **7** likely results from the nucleophilic attack of water at C-1 of the proposed intermediate cyclohexadienyl cation intermediates. However, water might also attack at the 3 or 5 positions of the ring, leading to the formation of *o*-benzoquinones (Britton and Steelink 1974; Holthuis *et al.* 1985). Acetosyringone, **10** (Scheme 2),was reacted with **1** in an attempt to find evidence for *o*-benzoquinone formation.

Indirect evidence for *o*-benzoquinone formation was observed in the reaction of **10** with **1** at room temperature. The reaction is rapid, and a small amount of 2.6-dimethoxy-*p*-
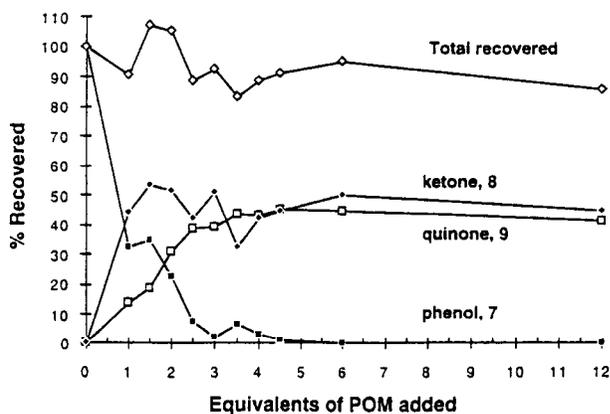
Fig. 7. Relative molar concentrations of unreacted **7,** the products (**8** and **9**) of its reaction with α-$[SiVW_{11}O_{40}]^{5-}$ (**1**) and the total amount of material recovered, as a function of the number of equivs of **1** added.
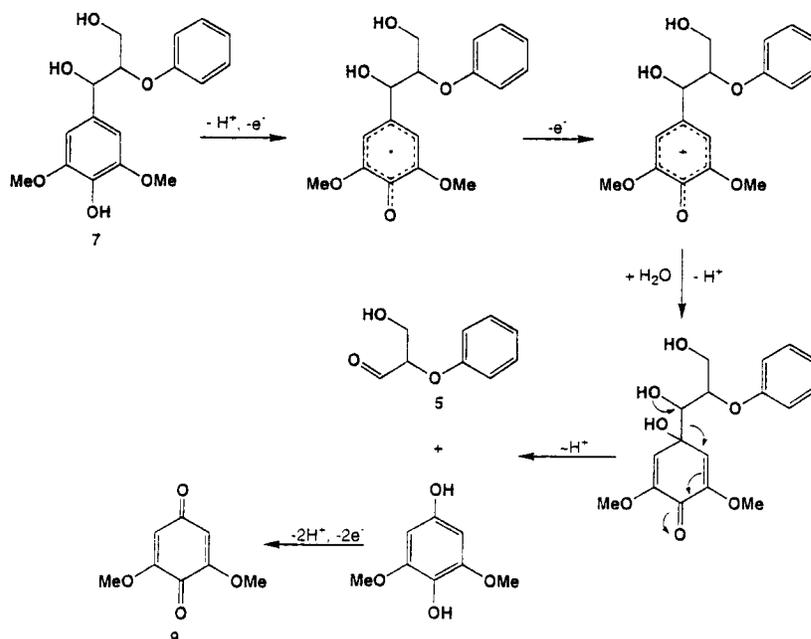
Fig. 8. Proposed pathway for formation and hydrolytic cleavage of the cyclohexadienyl cation likely generated upon oxidation of **7** by 2 equivs of α-[SiVW$_{11}$O$_{40}$]$^{5-}$ (**1**).

benzoquinone, **9** (yellow), was observed. However, the major product was the bright red *o*-naphthaquinone, **11** (Scheme 2).

One plausible route to formation of this compound is via Diels-Alder condensation of two intermediate *o*-benzoquinones, followed by additional oxidation by **1** and
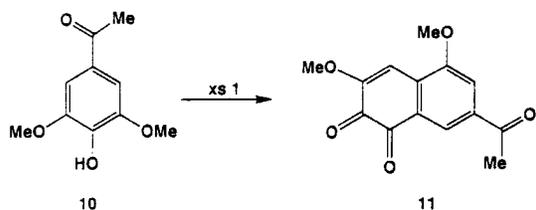
Scheme 2
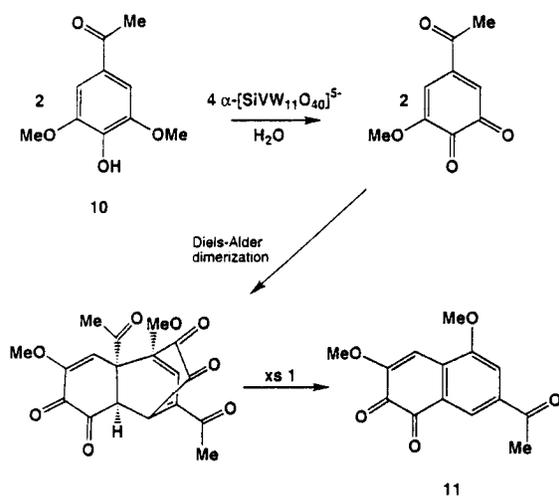
Scheme 3

re-aromatization (Scheme 3). This pathway, including isolation of an initially formed Diels-Alder adduct (Scheme 3), was observed in the stepwise periodate oxidation and hydrolysis of methoxy-substituted phenols (Adler *et al.* 1960a, 1960b).

Initially, when unbleached kraft pulp is treated with **1,** the brightness of the pulp drops, and it becomes slightly reddish in color. This is a characteristic of POM delignification and bleaching (Weinstock *et al.* 1993). The reddish color, which is discharged upon further POM treatment, might be attributed to the initial formation of quinonoid compounds from phenolic lignin substructures.

Degradation of diphenylmethane

Under alkaline pulping conditions, condensation reactions are believed to generate a variety of phenolic diphenylmethanes (Fig. 9) (Chiang and Funaoka 1988; Lai *et al.* 1994). The extent to which these are formed and survive kraft pulping remains uncertain (Chan *et al.* 1995).

Nonetheless, phenolic diphenylmethanes are readily degraded by oxygen in alkali (Xu *et al.* 1995) and are clearly substrates for **1.** For example, compound **12** was rapidly consumed when reacted with **1** at room temperature. Observed products are shown in Scheme 4. The alcohol **13** (ca. 5-10%) was observed by HPLC and GC-MS (TMS derivative) along with a mixture of products, including small amounts of the *p*-benzoquinone, **9** (5%), and 3,4,5-trimethoxybenzaldehyde, **14** (3.2%). When the reaction is carried out at elevated temperature, the alcohol (**13**), a likely intermediate, is not observed.

The data presented here suggest that phenol oxidation reactions play an important role in the delignification of kraft pulp by **1.** The ability of **1** to oxidize phenolic
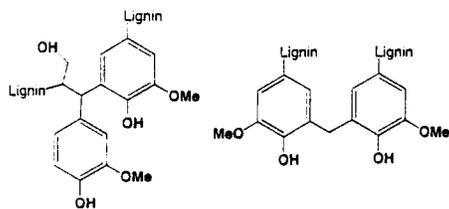
Fig. 9.   Phenolic diarylmethane compounds believed to form during alkaline pulping.

substructures is analogous to that of MnP and laccases. At the same time, the full extent of the reactivity of **1** with residual lignin substructures, particularly with non-phenolic ones, is not yet known. Based on the work of Neumann and Levin (1991), non-phenolic structures possessing α-hydroxyl groups are likely candidates for dehydrogenation by **1**. Perhaps more significantly, outer-sphere oxidation of these and other non-phenolic structures to radical cations is also possible (Eberson 1983; Kersten *et al.* 1990; Weinstock 1998). Reactivity of this nature is typical of the lignin peroxidases, which oxidize a variety of non-phenolic lignin substructures to cationic radicals (Kirk *et al.* 1986; Miki *et al.* 1986). Study of the reaction of **1** with non-phenolic lignin-model compounds is in progress.

Conclusions

The polyoxometalate (POM) anion α-$[SiVW_{11}O_{40}]^{5-}$ (**1**) is a single-electron oxidant capable of selectively removing residual lignin under anaerobic conditions. Studies using lignin-model compounds suggest that phenolic hydroxyl groups present in residual lignin are important substrates for **1**. Based on reactions with a limited set of phenolic lignin models, delignification appears to result, in part, from sequential single-electron oxidations of phenolic
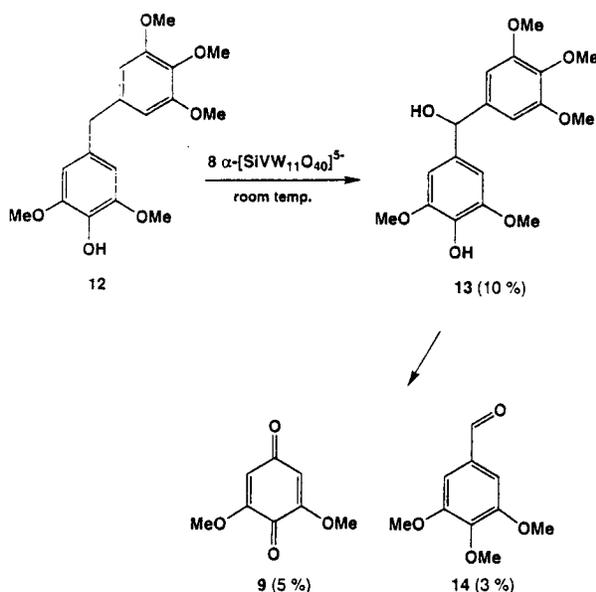
lignin substructures, followed by the hydrolysis of cationic intermediates. Before more general conclusions regarding the mechanism of delignification by POM anions, such as **1**. can be made, the oxidations of non-phenolic lignin structures must also be investigated.

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8 α-$[SiVW_{11}O_{40}]^{5-}$

room temp.

12

13 (10 %)

9 (5 %)

14 (3 %)

Scheme 4

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