

Polyoxometalate oxidation of non-phenolic lignin subunits in water: Effect of substrate structure on reaction kinetics

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Summary

The effect of lignin-biopolymer structure on the mechanism of its oxidative depolymerization by polyoxometalates (POMs) was investigated by reacting an equilibrated POM ensemble with a series of ring-substituted benzyl alcohols. Under anaerobic conditions in mixed water/methanol, observed pseudo-first order reaction rates (150°C) of 8.96×10^{-3} and $4.89 \times 10^{-3} \text{ sec}^{-1}$ were obtained for oxidations of 1-(3,4-dimethoxyphenyl)ethanol (**1**) and 1-(3,4,5-trimethoxyphenyl)ethanol (**2**), respectively. Organic products from the oxidation of **2** (95% recovery) indicate the reaction proceeds via successive oxidations of the benzylic carbon atom; aromatic-ring cleavage was not observed. A primary kinetic-isotope effect of 1.6 and 1.7 was observed for the reactions of **1** and **2** deuterated at the benzylic-carbon atoms. This combined with the relatively large activation energies, indicate that C-H bond breaking (either H-atom or proton-coupled electron transfer) occurs late along the reaction coordinate of the rate-determining step. Replacing the 4-CH₃O- group in **2** by CH₃CH₂O- to give 1-(4-ethoxy-3,5-dimethoxyphenyl)ethanol (**3**), had a substantial effect on the temperature dependence of the observed reaction rate, suggestive of a possible change in mechanism.

Keywords: etherified benzyl alcohols; kinetic isotope effect; oxidation; kinetics; polyoxometalate (POM).

Introduction

Polyoxometalates (POM) have recently been proposed as potential environmentally benign oxidants for the selec-

tive removal of lignin from wood (a composite of lignin and cellulose) to provide high-quality cellulose fibers for paper manufacturing (Weinstock et al. 1996, 1997, 1998a,b; Evtuguin and Neto 1997; Evtuguin et al. 1998, 2000a,b). POMs are a rapidly growing class of metal oxygen cluster anions, many of which behave as outer-sphere electron-transfer oxidants and catalysts (Pope and Muller 1991; Hill and Weinstock 1997; Muller et al. 1998; Weinstock 1998; Birchmeier et al. 2000; Grigoriev et al. 2000). They are single electron oxidants reported to efficiently and selectively remove lignin (via oxidation of phenolic lignin substructures) from wood pulps without severely damaging carbohydrates (Weinstock et al. 1997; Evtuguin et al. 1998, 2000a,b). Although there have been a considerable number of studies published on the reactions of POMs with wood pulp (Evtuguin and Neto 1997; Evtuguin et al. 1998; Balakshin et al. 2001) and phenolic lignin model compounds (Weinstock et al. 1996, 1997, 1998a; Evtuguin et al. 2000a), reactions with non-phenolic (non-hydroxylated aromatic) lignin structures have not been reported. Detailed information on the kinetics and mechanisms of oxidation of non-hydroxylated aromatic lignin moieties would significantly contribute to a more comprehensive understanding of the chemistry of POM-oxidation of lignin, and help improve process operation. In particular, information is lacking regarding both fundamental mechanisms of homogeneous oxidation as well as the effects of interactions between POMs and polymeric (insoluble) lignin in wood-cell walls. We herein use a prototypical industrially relevant POM system, abbreviated Na_{5(+1.9)}[SiV_{1(-0.1)}MoW_{10(+0.1)}] (dominant oxidatively active species present are Na₅[SiVW₁₁O₄₀] and Na₅[SiVMoW₁₀], (Weinstock et al. 2001) and a series of non-hydroxylated aromatic lignin-model compounds to provide data that address both issues.

Materials and methods

3,4-dimethoxy acetophenone, 3,4,5-trimethoxy acetophenone, 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone, sodium borohydride (NaBH₄), sodium borodeuteride (NaBD₄), sodium hydroxide (NaOH), iodoethane, 2,4,6-tribromophenol and all solvents were purchased from Aldrich Chemicals and used as received. All GC analyses were carried out with a HP 5890 (splitless injection) instrument equipped with a flame ionization detector, using He as the carrier gas. Injector and detector temperatures were 280°C . Separations were achieved on a J&W DB-1 fused silica capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 μm). Typical temperature programs were from 150°C to 170°C at a rate of $4^{\circ}\text{C min}^{-1}$ with an initial time delay of 5 min and a final time at temperature of 2 min. In quantitative studies 2,4,6-tribromophenol was used as an internal standard and the relative peak areas and corresponding response factors were used to calculate model compound concentrations. Compounds **1**, **2** and **3** (Fig. 1) were stable up to 180°C in the absence of POM. All GCMS analyses

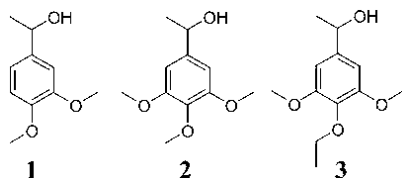


Figure 1 Lignin model compounds studied.

were conducted as per GC analysis on a HP 5985B GCMS, equipped with a DB-1 capillary column and using the same temperature program as per GC-analysis. In the EI mode, the electron energy used was 70 eV. $^1\text{H-NMR}$ spectra were determined using a GE 300 MHz instrument. Samples were dissolved in CDCl_3 . Chemical shifts are given in ppm downfield from TMS (tetramethylsilane). POM quantification was performed using UV/Vis spectroscopy. Specifically, at prescribed time intervals, an aliquot of the reaction solution was withdrawn and mixed with an excess of 7 mmol l^{-1} $\text{K}_2[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]$ dissolved in 0.1 mol l^{-1} sodium sulfate buffer solution at pH 2.0; $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ oxidizes the reduced form of the POM back to the oxidized form in turn being reduced to $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$. The amount of reduced POM, that is the reacted POM, is then calculated from the absorbance at 625 nm of the reduced $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ using the oxidized form, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ as the reference.

Compound synthesis

1-(3,4-Dimethoxyphenyl)-ethanol (1) 1-(3,4-Dimethoxyphenyl)-ethanol (1) was prepared by reacting 2 equivalents of NaBH_4 (0.42 g, 11.0 mmol) with 3,4-dimethoxy acetophenone (1.0 g, 5.5 mmol) in 3:1 EtOH:H₂O (50 ml) and heated under reflux for 3 h. The reaction mixture was then cooled, neutralized by bubbling CO_2 through the supernatant solution, and extracted with 1,2-dichloroethane ($3 \times 50\text{ ml}$). A quantitative conversion of the acetophenone was obtained. MS m/z (rel. int.) 182(M+,59), 167(87), 153(47), 139(100), 124(32), 108(21), 93(50), 77(21), 65(25), 51(11), 43(41). $^1\text{H-NMR}$ δ 1.48(d,3H), 3.90(d,6H), 4.83(q,1H), 6.84(q,1H), 6.86(q,1H), 6.93(d,1H).

1-(3,4,5-Trimethoxyphenyl)-ethanol (2) 1-(3,4,5-Trimethoxyphenyl)-ethanol (2) was prepared from 3,4,5-Trimethoxy acetophenone (7) (1.0 g, 4.8 mmol) using 2 equivalents of NaBH_4 (0.36 g, 9.5 mmol) as outline for 1. MS m/z (rel. int.) 254(M+42,67), 212(44), 195(100), 169(52), 154(9), 121(8), 91(12), 43(62). $^1\text{H-NMR}$ δ 1.48(d,3H), 3.80(d,9H), 4.73(q,1H), 6.24(m,2H).

1-(4-Ethoxy-3,5-dimethoxyphenyl)-ethanol (3) 1-(4-Ethoxy-3,5-dimethoxyphenyl)-ethanol (3) was quantitatively prepared by first reacting 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone (1.0 g, 5.1 mmol) with 2 equivalents of NaBH_4 (0.39 g, 10.2 mmol) in 1 mol l^{-1} NaOH at room temperature followed by Williamson ether synthesis using potassium carbonate and an excess of iodoethane (7.8 g, 50 mmol) in acetone at 50°C . MS m/z (rel. int.) 268(M+42,59), 226(15), 209(25), 197(19), 181(73), 155(54), 137(12), 123(10), 109(8), 91(15), 77(14), 43(100), 29(12). $^1\text{H-NMR}$ δ 1.30(t,3H), 1.48(d,3H), 3.80(s,6H), 3.98(q,2H), 4.73(q,1H), 6.24(m,2H).

1-(3,4,5-Trimethoxy-phenyl)-(1- ^2H)ethanol (4) 1-(3,4,5-Trimethoxyphenyl)-(1- ^2H)ethanol (4) was prepared as per 1-(3,4,5-Trimethoxyphenyl)-ethanol using 1.5 equivalents of NaBD_4 . $^1\text{H-NMR}$ δ 1.48(s,3H), 3.80(d,9H), 6.36(d,2H).

1-(3,4-Dimethoxy-phenyl)-(1- ^2H)ethanol (5) 1-(3,4-Dimethoxyphenyl)-(1- ^2H)ethanol (5) was prepared as per 1-(3,4-Dimethoxy-

phenyl)-ethanol using 1.5 equivalents of NaBD_4 . $^1\text{H-NMR}$ δ 1.48(s,3H), 3.83(d,6H), 6.56(q,1H), 6.59(q,1H), 6.63(d,1H).

$\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) was synthesized as described by Weinstock et al. (2001). The POM concentration was 0.405 mol l^{-1} .

POM reaction conditions

In a typical reaction, a lignin model compound (75 μmol) was dissolved in and transferred to a 25 ml volumetric flask containing 10 ml of the equilibrated POM solution and 10 ml of sodium acetate buffer solution (0.2 mol l^{-1} , pH 5.0) using an additional 0.1 ml of methanol and made up to 25 ml with deionized water. All air was displaced by purging repeatedly with argon. The final concentration of the lignin model compound and POM were 3.0 and 162 mmol l^{-1} , respectively (54 molar equivalents of POM). The reaction solution was then transferred to the Teflon cup of the pressure reactor (Parr Instrument Co., Moline, IL, USA), thoroughly purged with argon and quickly brought up to temperature while being mechanically stirred. Time 0 was defined as the time when the reaction temperature was reached.

Work-up procedure

Organic compound concentrations were determined by gas chromatography. Reaction products were analyzed by withdrawing 1 ml of the reaction solution through the sampling bulb of the reactor at prescribed time intervals. The reaction was quenched by adding 0.5 ml of 0.476 mol l^{-1} sodium sulfite solution to reduce all of the oxidized POM. (Note: As the density of the reduced form of the POM was different from that of the oxidized form, the density of the reaction solution gradually changed during reaction. Therefore, the amount of the solution withdrawn was not provided by its volume but rather by its weight, 1.388 g.) In the analysis of the neutral oxidation products, 0.3 ml of water was added to decrease the density of the solution, followed by the addition of 0.5 ml of the internal standard methanol solution (5 mmol l^{-1} of 2,4,6-tribromophenol). This mixture was extracted 4 times with 0.5 ml of chloroform, collected, dried over sodium sulfate, and concentrated under vacuum. The neutral materials were then acetylated with 0.25 ml of pyridine and 0.25 ml of acetic anhydride for 60 min at 80°C . This solution was then directly injected onto the GC.

The analysis of acidic reaction products was conducted as per the neutral degradation products with the exception that the reaction mixture was first acidified with 0.1 ml of concentrated hydrochloric acid prior to the chloroform extraction. In addition, the extracted products were derivatized with 0.1 ml of *N,O*-bis(trimethylsilyl) acetamide for 30 min at 50°C . The trimethylsilylated sample was then diluted with 0.5 ml of pyridine and injected onto the GC.

Reaction product characterization

3,4,5-Trimethoxyacetophenone (6) MS m/z (rel. int.): 210(M+,46), 195(100), 152(13), 139(14), 137(12), 124(10), 109(13), 77(8), 43(35). $^1\text{H NMR}$: δ 2.58 (s, 3H), 3.81 (s, 9H), 6.89 (d, 2H).

3,4,5-Trimethoxybenzaldehyde (7) MS m/z (rel. int.): 196(M+,100), 181(31), 125(8), 110(8), 95(5), 77(8). $^1\text{H NMR}$: δ 3.81 (s, 9H), 6.77 (d, 2H), 9.87 (s, 1H).

3,4,5-Trimethoxybenzoic acid (8) MS m/z (rel. int.): 284(M+72 (TMS),77), 269(72), 225(95), 195(100), 168(8), 151(12), 137(14), 134(17), 119(15), 73(56), 45(11). $^1\text{H NMR}$: δ 3.93(d,9-H), 7.544(d,1-H), 7.681(m,1-H).

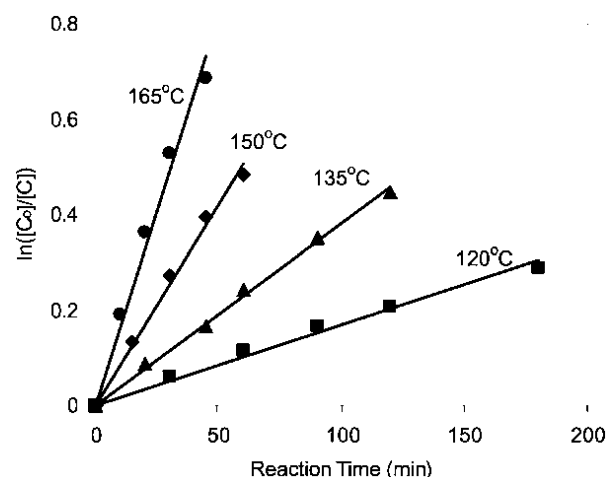


Figure 2 Observed pseudo-first order kinetic analysis of the reaction between $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) and 1-(3,4-Dimethoxy-phenyl)-ethanol (**1**): $[\mathbf{1}]_0 = 3 \text{ mM}$, $[\text{POM}]_0 = 162 \text{ mM}$.

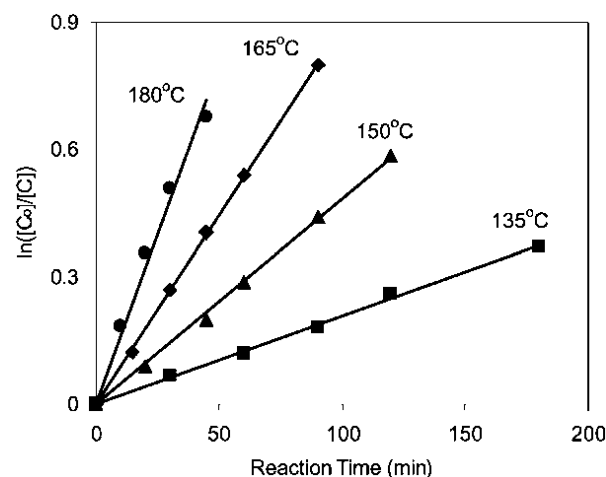


Figure 3 Observed pseudo-first order kinetic analysis of the reaction between $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) and 1-(3,4,5-Trimethoxy-phenyl)-ethanol (**2**): $[\mathbf{2}]_0 = 3 \text{ mM}$, $[\text{POM}]_0 = 162 \text{ mM}$.

Table 1 Observed pseudo-first order rate constants for the reaction between $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ and **1**, **2**, and **3**.

Compound	Rate constant $k_{\text{obs}} \times 10^{-3} (\text{sec}^{-1})$	Activation energy $E_a (\text{kJ mol}^{-1})$	Frequency factor $A (\text{s}^{-1})$
1	165°C 17.20 ± 1.4	70.9 ± 1.4	4.97×10^6
	150°C 8.96 ± 0.7		
	135°C 4.09 ± 0.4		
	120°C 1.88 ± 0.2		
2	180°C 16.80 ± 1.5	68.4 ± 0.8	1.28×10^6
	165°C 8.69 ± 0.8		
	150°C 4.89 ± 0.3		
	135°C 2.21 ± 0.3		
3	180°C 12.30 ± 1.2	58.7 ± 1.3	6.92×10^4
	165°C 6.95 ± 0.6		
	150°C 3.81 ± 0.3		
	135°C 2.22 ± 0.4		

Results and discussion

Kinetic analysis of POM oxidation of 1-(3,4-dimethoxyphenyl)-ethanol (**1**) and 1-(3,4,5-trimethoxyphenyl)-ethanol (**2**)

Rates of reactions of 1-(3,4-dimethoxy-phenyl)-ethanol (**1**) and 1-(3,4,5-trimethoxyphenyl)-ethanol (**2**) with an equilibrated polyoxometalate (POM) ensemble, $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$, were measured at various temperatures. While phenolic analogues of **1** and **2** (hydroxyl rather than methoxyl groups at the 4 position) are oxidized rapidly by the POM ensemble at room temperature (data not shown), **1** and **2** do not react at an appreciable rate under ambient conditions. To obtain kinetic data, reaction temperatures in excess of 120°C were required.

Results for oxidation of **1** and **2** are shown in Figures 2 and 3. Observed initial rate constants (k_{obs}) for both **1** and **2** at several temperatures are listed in Table 1. At each temperature, initial observed rate constants for oxidation of **1** were slightly larger than those for **2**, wherein both **1** and **2** appear to follow pseudo-first order kinetics. In both cases, activation energy (E_a) and Frequency or Pre-exponential Factor (A) values appear quite similar.

In electron-transfer reactions whose mechanisms involve direct rate-limiting oxidation of aromatic moieties to radical cations, electron-donating ring-substituents increase the rate of oxidation (Weinstock 1998). No such effect, however, was observed here. At the same time, the small but statistically significant decrease in reaction rate upon increased ring substitution may imply a reaction mechanism whose rate-determining step involves oxidation of a benzylic C-H bond to give a benzylic radical. In this case, the additional methoxyl substituent at the *meta* position (as in **2**) would be expected to increase the benzyl C-H bond-dissociation energy, thereby decreasing k_{obs} .

Mechanism of POM oxidation of 1-(3,4,5-trimethoxyphenyl)-ethanol (**2**)

Detailed analysis of the products obtained from the POM oxidation of **2** reveals a series of oxidation products with successively larger oxidation states of the benzylic carbon. Figure 4 shows the products identified and their quantified yields. Mass-balance calculation confirms that the total yield of oxidation products detected **6**, **7**, and **8** accounts for approximately 95% of reacted **2**.

Included in Figure 4 is the product distribution for the POM oxidation of 3,4,5-trimethoxyacetophenone (**6**). Products analogous to those seen in the oxidation of **2** (i.e., 3,4,5-trimethoxybenzaldehyde (**7**) and 3,4,5-trimethoxybenzoic acid (**8**)) were detected, with **7** accounting for more than 80% of the observed products. By contrast, **7** was unreactive towards the POM, being recovered quantitatively. The observed pseudo-first order reaction rate constant ($k_{\text{obs}} = 0.0085 \text{ s}^{-1}$) for the reaction of **6** with the POM at 165 °C is identical to that of **2** under the same reaction conditions (Table 1). These results suggest that the formation of **7** and **8** can arise from both **2** and **6**. The fact that **7** is stable towards POM oxidation, however, implies **8** does not arise from the step-wise ox-

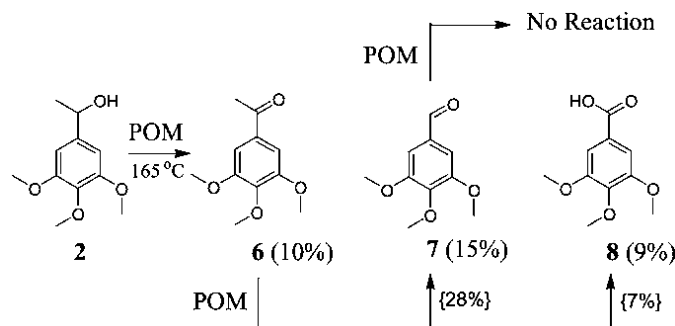


Figure 4 Detected oxidation products (% yield) in the reaction of $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) with **2** at 165°C after 60 min; 3,4,5-Trimethoxyacetophenone (**6**), 3,4,5-Trimethoxybenzaldehyde (**7**) and 3,4,5-Trimethoxybenzoic acid (**8**) Included are the yields of oxidation products for the POM oxidation of **6**.

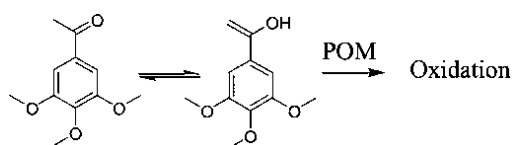
ation of the benzylic carbon (i.e., the sequential oxidation of **7** to **8** to **9**).

The conclusion that **7** is relatively stable to POM oxidation, while **6** reacts readily, is consistent with published reports that some POM oxidations of carbonyl-containing compounds are proceeded by keto-enol tautomerization (Scheme 1) (Gupta et al. 1988, 1990a,b). The larger implication is that the presence of hydrogen atoms on carbon atoms alpha to carbonyl groups in lignin-polymer substrates may, in certain cases, be critical to oxidative depolymerization of lignin by POM oxidants.

The mechanism of reaction of the POM with **1** and **2** was further probed by isotope-labeling studies (Wiberg 1954, 1955; Wiberg and Slaugh 1958; Zollinger 1964). Accordingly, models identical to **1** and **2** but deuterated at the benzylic-carbon atoms, 1-(3,4-Dimethoxy-phenyl)-(1-²H)ethanol (**4**) and 1-(3,4,5-Trimethoxy-phenyl)-(1-²H)ethanol (**5**), were reacted with the POM solution. Figure 5 shows plots of $\ln([1_0]/[1])$ and $\ln([4_0]/[4])$ versus time for reactions at 150°C and of $\ln([2_0]/[2])$ and $\ln([5_0]/[5])$ versus time for reactions at 135°C. A kinetic isotope effect was observed for both sets of compounds: $k_H/k_D = 1.6$ for **1** and **4**, and $k_H/k_D = 1.7$ for **2** and **5**, respectively. These results, combined with the activation parameters (Table 1) indicate that in the oxidations of both **1** and **2**, the benzylic C-H bond is broken in the rate-determining step ($k_H/k_{D1.5}$) and is likely nearly completely broken at the transition state (large E_a implying a late transition state). These results do not, however, differentiate between hydrogen-atom transfer or proton-coupled electron transfer mechanisms.

POM oxidation of 1-(4-ethoxy-3,5-dimethoxyphenyl) ethanol (**3**)

To begin to model the properties of larger, more hydrophobic (oligomeric or polymeric) lignin substructures (while keeping the electronic properties of the substrate



Scheme 1

as constant as possible), the size and hydrophobicity of **2** was increased by substitution of the 4-CH₃O- group by CH₃CH₂O- to give 1-(4-ethoxy-3,5-dimethoxyphenyl)ethanol (**3**). The oxidation of **3** followed pseudo-first order kinetics at all of the temperatures employed, and the Arrhenius plot produced a straight line (Figure 6). While the observed pseudo-first order rate constant (150°C) for oxidation of **3** ($3.81 \times 10^{-3} \text{ sec}^{-1}$) is close to those of **1** ($8.96 \times 10^{-3} \text{ sec}^{-1}$) and **2** ($4.89 \times 10^{-3} \text{ sec}^{-1}$), temperature-dependence data indicate that a different mechanism may be operative. Notably, a substantial decrease in temperature dependence of k_{obs} (i.e., a decrease in the slope of the plot of $\ln(k_{\text{obs}})$ vs. $1/T$) is observed. This indicates a possible change in mechanism, perhaps to one involving pre-association of the more hydrophobic substrate with the oxidatively active POM cluster prior to H (or H⁺-coupled-electron) transfer (Weinstock 1998a) If so, it bears noting that the activation parameters obtained from the temperature-dependence of the observed pseudo-first order rate constants for the oxidation of **3** cannot be directly compared with those associated with oxidations of **1** and **2**. Significantly, however, the possible change in mechanism appears to be brought about by a modest increase in the hydrophobic

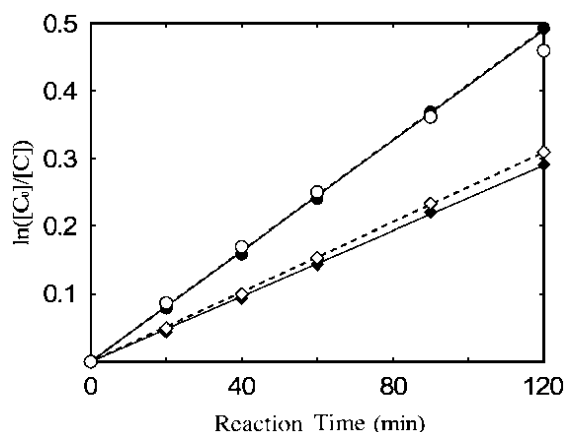


Figure 5 Kinetic isotope effect for the reaction of $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) and 1-(3,4-dimethoxy-phenyl)-ethanol (●) and 1-(3,4-dimethoxy-phenyl)-(1-²H)ethanol (◆) at 135°C; and 1-(3,4,5-Trimethoxy-phenyl)-ethanol (○---) and 1-(3,4,5-Trimethoxy-phenyl)-(1-²H)ethanol (◇---) at 150 °C. Pseudo-first order reaction conditions: $[\text{substrate}]_0 = 3 \text{ mM}$, $[\text{POM}]_0 = 162 \text{ mM}$.

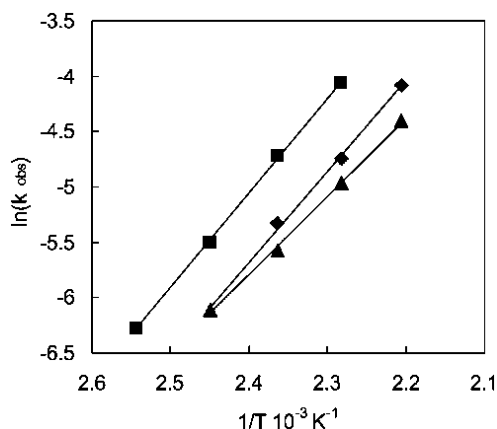


Figure 6 Arrhenius Plots of the kinetic data for the reaction between $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$ (POM) and 1-(3,4-Dimethoxy-phenyl)-ethanol (**1**) ■, 1-(3,4,5-Trimethoxy-phenyl)-ethanol (**2**) ◆, 1-(4-Ethoxy-3,5-dimethoxy-phenyl)-ethanol (**3**) ▲.

nature of the substrate: the addition of a single methylene ($-\text{CH}_2-$) group to one ring substituent. We are currently investigating this phenomenon.

Conclusions

Reactions between the equilibrated and self-buffering polyoxometalate (POM) ensemble $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}]$, and several benzyl alcohols were examined under anaerobic conditions in a mixed water/methanol solvent system. 1-(3,4-Dimethoxy-phenyl)-ethanol (**1**) and 1-(3,4,5-Trimethoxy-phenyl)-ethanol (**2**) were oxidized at similar rates, and appeared to follow pseudo-first order reaction kinetics over the conditions studied. Detailed analysis of the oxidation products from **2** (95% recovered) revealed successive oxidations at the benzylic carbon. Reactions of 1-(3,4-Dimethoxy-phenyl)-(1- ^2H)ethanol (**4**) and 1-(3,4,5-Trimethoxy-phenyl)-(1- ^2H)ethanol (**5**) (**1** and **2** deuterated at the benzylic-carbon atoms) revealed a primary kinetic-isotope effect, with $k_{\text{H}}/k_{\text{D}}$ values of 1.59 and 1.69, respectively. This, combined with the relatively large activation energies calculated from temperature-dependence data for both **1** and **2** ($E_{\text{a}} = 70.9$ and 68.4 kJ mol^{-1} , respectively) indicate that C-H bond breaking in the transition state (either H-atom or proton-coupled electron transfer) likely occurs late along the reaction coordinate. A modest increase in the hydrophobic nature of the substrate, achieved by replacing one of the methoxyl groups on the aromatic ring of **1** with an ethoxyl group (to give 1-(4-Ethoxy-3,5-dimethoxyphenyl)-ethanol (**3**)), resulted in a substantial decrease in the slope of the plot of $\ln(k_{\text{obs}})$ versus $1/T$. This may indicate a change in mechanism, possibly to one involving pre-association of the more hydrophobic substrate with the metal-oxygen (POM) cluster prior to H (or H^+ -coupled-electron) transfer. This result suggests that pre-association may play an important role in metal-oxygen cluster-anion (POM) oxidations of larger lignin fragments, and ultimately of polymeric lignin in wood fibers and other biopolymer composites.

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