

Kinetic Analysis of Polyoxometalate (POM) Oxidation of Non-Phenolic Lignin Model Compound

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ABSTRACT

Kinetic and reaction mechanism of non-phenolic lignin model compounds under anaerobic polyoxometalate (POM), $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}\text{O}_{40}]$, bleaching conditions were examined. Analyses using a syringyl type model, 1-(3,4,5-trimethoxyphenyl)ethanol (**1**), a guaiacyl type, 1-(3,4-dimethoxyphenyl)ethanol (**2**), and 1-(4-ethoxy-3,5-dimethoxyphenyl)ethanol (**3**) suggest the significance of steric factor in POM oxidation of these compounds. A kinetic isotope effect was observed in isotope labeling experiments. It is suggested that the rate-determining step of POM oxidation of non-phenolic lignin model compound is the abstraction of benzylic hydrogen. An α -carbonyl type model compound, 1-(3,4,5-trimethoxyphenyl)ethanone (**6**), was degraded by the same rate with **1** while 3,4,5-trimethoxybenzaldehyde (**7**) was fairly stable. The existence of carbon-hydrogen bond at the β -position could be necessary for POM oxidation of α -carbonyl compound. A carbohydrate model compound, methyl β -D-glucopyranoside (**9**), was very stable even when phenolic and non-phenolic lignin models were present together in the reaction system. This indicates that carbohydrates are stable and reactions of POM with lignin do not produce any active oxygen species under anaerobic POM bleaching conditions.

INTRODUCTION

The pulp and paper industry has searched for environmentally benign bleaching agents to introduce efficient ECF and TCF methods into bleaching processes. Polyoxometalates (POMs) have been recognized as one of candidates to efficiently remove lignin from wood pulp without severe damage on carbohydrates (1-4). POMs are metal oxygen cluster anions and rapidly growing class of synthetic inorganic compounds (5). It has been reported that a sufficient delignification is attained without the loss of pulp viscosity when an unbleached softwood kraft pulp is subjected to POM bleaching under

anaerobic conditions at 125°C (1, 2). Similar results have also been obtained under aerobic conditions (3, 4).

Although there are considerable amounts of studies published on the reaction of POM with wood pulp and phenolic lignin model compounds (1-4, 6), kinetic and reaction mechanism of non-phenolic lignin model compounds have not been reported. Kinetic and mechanistic information of the reaction between POM and non-phenolic models significantly contribute to an understanding of the chemistry in POM bleaching and an improvement of the process operation.

In this paper, non-phenolic lignin model compounds were subjected to the reaction with an equilibrated solution of POM, $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}\text{O}_{40}]$, under anaerobic conditions. Kinetic and reaction mechanism of non-phenolic lignin model compound under anaerobic POM bleaching conditions are discussed.

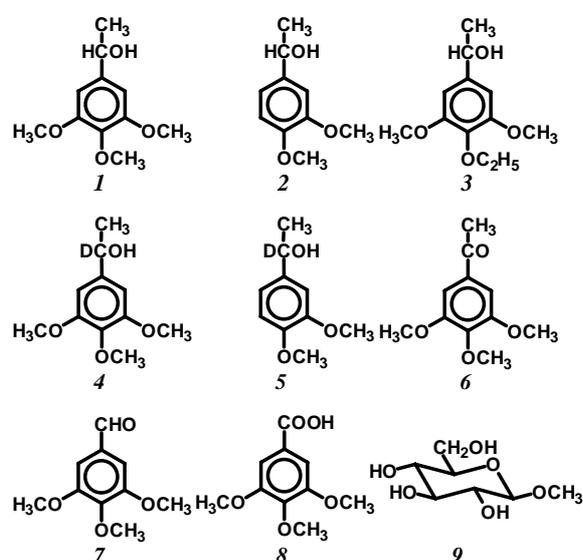


Fig. 1. Structure of model compounds used in this study.

MATERIALS AND METHODS

Materials

Compounds **1-2** and α -deuterium analogues **4-5** were synthesized by the reduction of the corresponding α -carbonyl compounds using NaBH_4 and NaBD_4 , respectively. The reduction of acetosyringone using NaBH_4 followed by the reaction with iodoethane produced **3**. Compounds **6-9** were commercially available. Structure of **1-9** is shown in Fig. 1.

POM used, $\text{Na}_{5(+1.9)}[\text{SiV}_{1(-0.1)}\text{MoW}_{10(+0.1)}\text{O}_{40}]$, was an equilibrated solution, which was synthesized as described in the literature (5). The subscripted numbers in the parentheses refer to deviations of the equilibrated POM solution from the stoichiometry of a particular,

target POM compound. Concentration of the POM solution was 0.405 mol/L.

POM reaction under anaerobic conditions

In a typical reaction, reaction solution was 25 mL and contained 75 μmol of model compound, 10 mL of the POM solution, 10 mL of sodium acetate buffer solution (0.2 mol/L, pH 5.0), and an aliquot of methanol to dissolve model compound. Final concentration of model compound and POM was 3 and 162 mmol/L, respectively. All the reactions were conducted in the Parr reactor using the Teflon cup with electrically heating and stirring. The reaction solution was thoroughly bubbled with argon before running. Time 0 was defined as the time when temperature was reached at a target degree. In experiments using **9**, 75 μmol of **1** and 7.5 μmol of apocynol, a phenolic model, were added together.

Work-up procedure

At prescribed times, 1 mL of the reaction solution was withdrawn and the residual oxidized form of POM was quenched by the addition of sodium sulfite. The mixture was extracted with chloroform by 4 times together with an internal standard, 2,4,6-tribromophenol. The organic layers were collected and evaporated followed by acetylation or silylation for GC analysis. When acid degradation products were analyzed, an aliquot of concentrated hydrochloric acid was added before the chloroform extraction.

RESULTS AND DISCUSSION

Kinetic analysis of non-phenolic models

All the compounds shown in Fig. 1 were stable in their blank runs at 165°C so that their degradation observed in this study was caused by the existence of POM.

In the preliminary experiments, phenolic lignin model compounds were degraded too fast to follow the kinetic even at room temperature under the identical conditions (data not shown). On the other hand, non-phenolic lignin model compounds were resistant toward POM oxidation. An elevated temperature was required to examine the kinetic of non-phenolic model compounds.

Kinetic property of the degradation of **1** and **2** is realized from Figs. 2 and 3, respectively. All the lines are clearly straight, which shows that the degradation of both compounds follows pseudo-first-order rate law. This is reasonable because an excess amount of POM was present in the reaction mixture. The degradation of **3** also follows pseudo-first-order rate law. Fig. 4 is the Arrhenius plots for **1-3**, all of which are good straight lines. It is suggested that the degradation mechanism of each compound is independent on temperature in the whole range employed in this study. Table 1 lists kinetic parameters observed.

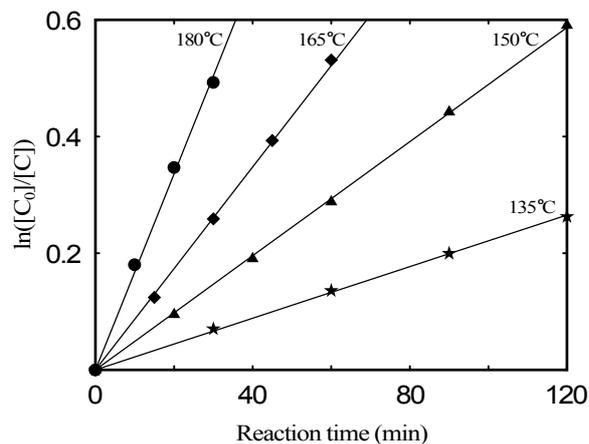


Fig. 2. Pseudo-first-order kinetic analysis for **1**.

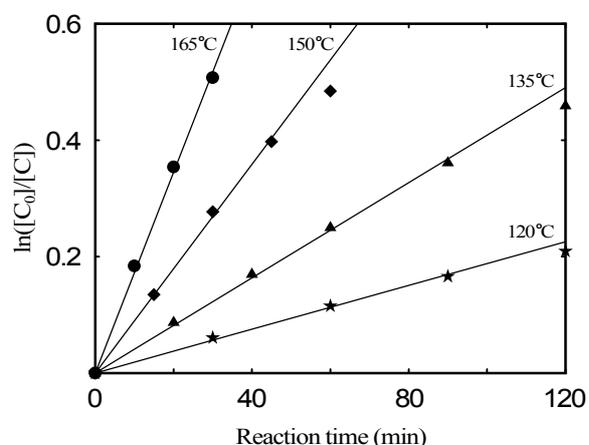


Fig. 3. Pseudo-first-order kinetic analysis for **2**.

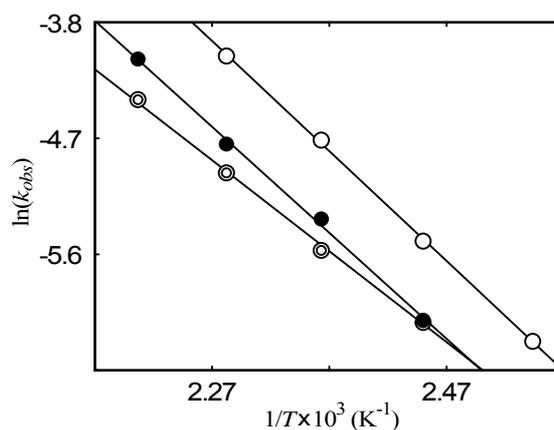


Fig. 4. Arrhenius plots for **1**, **2**, and **3**.
●: **1**, ○: **2**, ⊙: **3**

A syringyl type model **1** was degraded slower than a guaiacyl type model **2** in the whole range of temperature employed. This result is significant because syringyl type compounds are generally more labile toward oxidation than guaiacyl counterparts. However, there is little difference in ΔG^\ddagger between **1** and **2**. According to the transition-state theory, reaction rate constant (k_r) is shown by the equation: $k_r = \nu^\ddagger e^{(-\Delta G^\ddagger/RT)}$. Qualitatively, the term $e^{(-\Delta G^\ddagger/RT)}$ means a proportion of a number of molecules, which have a sufficient energy to go over the potential energy maximum, and ν^\ddagger represents a frequency of actually going over the potential energy maximum among such high-energy molecules. Taking these into consideration, a molecule of **1** cannot go over the potential energy maximum easily even when the molecule has a sufficient energy to go over the energy maximum. This suggests that POM oxidation is mainly controlled by steric factor of model compound. Only when POM comes into collision with **1** from a strictly proper direction, the reaction between POM and **1** would progress. A similar tendency is also recognized from the Arrhenius constants. Namely, **1** has almost the same Arrhenius activation energy and a much smaller Arrhenius frequency factor than **2**. The significance of steric factor was confirmed by comparing the results of an ethoxylated model **3** with **1**. There is also little difference in ΔG^\ddagger between **1** and **3** although the rate constant of **1** is larger than **3** in the most cases.

Mechanism of POM oxidation of non-phenolic models

To examine the mechanism of POM oxidation, α -deuterium compounds, **4** and **5**, were subjected to the reaction with POM under the identical conditions, and the results obtained were compared with those of **1** and **2**. It is recognized from Fig. 5 that a kinetic isotope effect is observed. The degradation of **4** and **5** was clearly slower than **1** and **2**, respectively. The ratio of the rate constant (k_H/k_D) for **1** & **4** and **2** & **5** was 1.69 and 1.59, respectively, which suggests that the isotope effect observed is primary and that the rate-determining step of the reaction between these model compounds and POM is the abstraction of the benzylic hydrogen.

Fig. 6 illustrates the degradation of **6**, **7**, and **9**. An α -carbonyl compound **6** was degraded almost the same rate with the corresponding α -carbinol compound **1**. On the other hand, a benzaldehyde type derivative **7** was fairly stable toward POM oxidation. These phenomena suggest that the presence of carbon-hydrogen bond at the β -position is necessary for POM oxidation of α -carbonyl compounds. However, it cannot be concluded what step is the rate-determining in POM oxidation of **6**. There are two candidates as the rate-determining step, which are the abstraction of hydrogen from the β -position and the one electron oxidation of the enol form of **6**.

The identification of degradation products of **1**, **6**, and **7** is shown in Table 2. Although **6** was quantitatively converted to **7** and **8**, fairly amounts of **1** was degraded to unidentified products. This fact suggests that **6** is not the only first compound produced from **1** although the rate-determining step of the reaction between POM and **1** is the abstraction of benzylic hydrogen. Because **7** is stable under the conditions, **8** is not produced from **7** but directly from **6**.

A carbohydrate model compound **9** was very stable at 165°C when **1** and a phenolic lignin model compound, apocynol, were subjected together to POM oxidation under otherwise the identical conditions. This result indicates that carbohydrates are not degraded under anaerobic POM bleaching conditions and reactions of lignin with POM do not produce any active oxygen species harmful to carbohydrates.

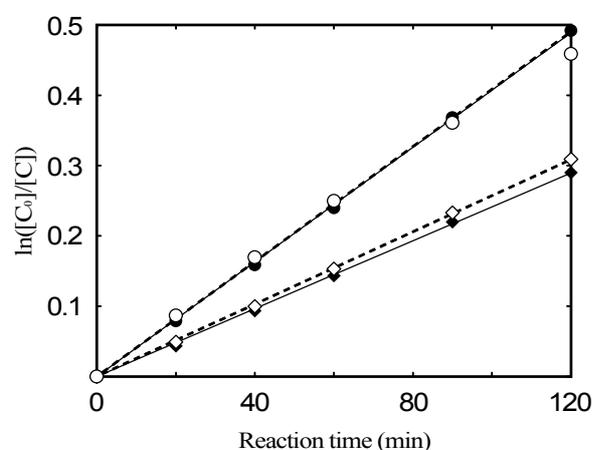


Fig. 5. Kinetic isotope effect analysis for **1** and **2**.
 ●—: **1** at 150°C, ○---: **2** at 135°C
 ◆—: **4** at 150°C, ◇---: **5** at 135°C

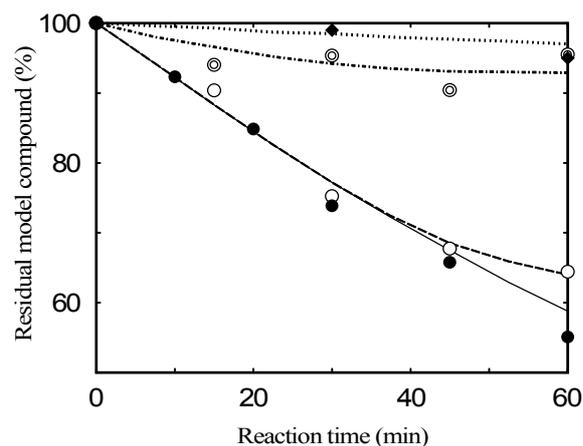


Fig. 6. Degradation of **1**, **6**, **7**, and **9** at 165°C.
 ●: **1**, ○: **6**, ⊙: **7**, ◆: **9**

CONCLUSIONS

Kinetic and reaction mechanism of the degradation of non-phenolic lignin model compounds were examined under anaerobic POM bleaching conditions.

The degradation of **1** and **2** followed pseudo-first-order rate law and the Arrhenius plots for **1** and **2** produced good straight lines. The degradation of **1** was slower than **2** although free energy of activation of **1** is almost the same value with **2**. This suggests the significance of steric factor of model compound in the reaction with POM. The experiments using **3** strongly support the importance of steric factor.

A kinetic isotope effect was observed when the isotope labeling experiments of **1** and **2** were conducted. The ratio of the rate constant (k_H/k_D) for **1** & **4** and **2** & **5** was 1.69 and 1.59, respectively, which suggests that the isotope effect observed is primary and that the rate-determining step of the reaction between these model compounds and POM is the abstraction of the benzylic hydrogen.

The degradation of **6** was almost the same rate with **1**, while **7** was fairly stable. The presence of carbon-hydrogen bond is necessary for the reaction between POM and α -carbonyl compounds.

A carbohydrate model **9** was very stable at 165°C. This indicates that carbohydrates are not degraded and reactions of lignin with POM do not produce any active oxygen species harmful to carbohydrates.

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Table 1. Kinetic constants observed.

Compound	Temp. °C	Rate constant k_{obs} (sec ⁻¹)	ΔG^\ddagger kJ·mol ⁻¹	ΔH^\ddagger kJ·mol ⁻¹	ΔS^\ddagger J·K ⁻¹ ·mol ⁻¹	E_a kJ·mol ⁻¹	A sec ⁻¹
1	135	0.00221	121.8	65.0	-139.1	68.4	1.28×10^6
	150	0.00489	123.6	64.9	-138.8		
	165	0.00869	126.0	64.7	-139.8		
	180	0.0168	128.0	64.6	-139.8		
2	120	0.00188	117.7	67.7	-127.3	70.9	4.97×10^6
	135	0.00409	119.7	67.5	-127.8		
	150	0.00896	121.5	67.4	-127.7		
	165	0.0172	123.5	67.3	-128.3		
3	135	0.00222	121.8	55.3	-162.9	58.7	6.92×10^4
	150	0.00381	124.5	55.1	-163.8		
	165	0.00695	126.8	55.0	-163.9		
	180	0.0123	129.1	54.9	-163.8		

Table 2. Yield of degradation products when **1**, **6**, or **7** was subjected to 60 min POM oxidation at 165°C

Compound	1	6	7	8
1	residual 64.3%	5.0%	1.1%	6.7%
6	—	residual 64.4%	30.8%	7.0%
7	—	—	residual 95.5%	0.5%

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