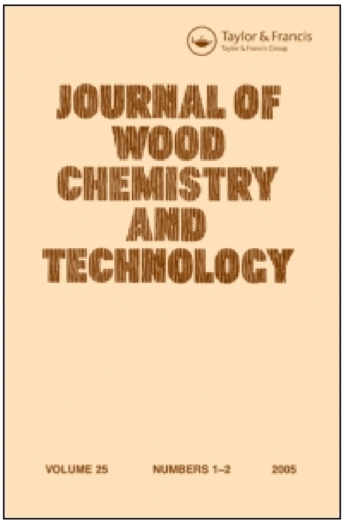

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PULPING REACTIONS OF VINYL ETHERS

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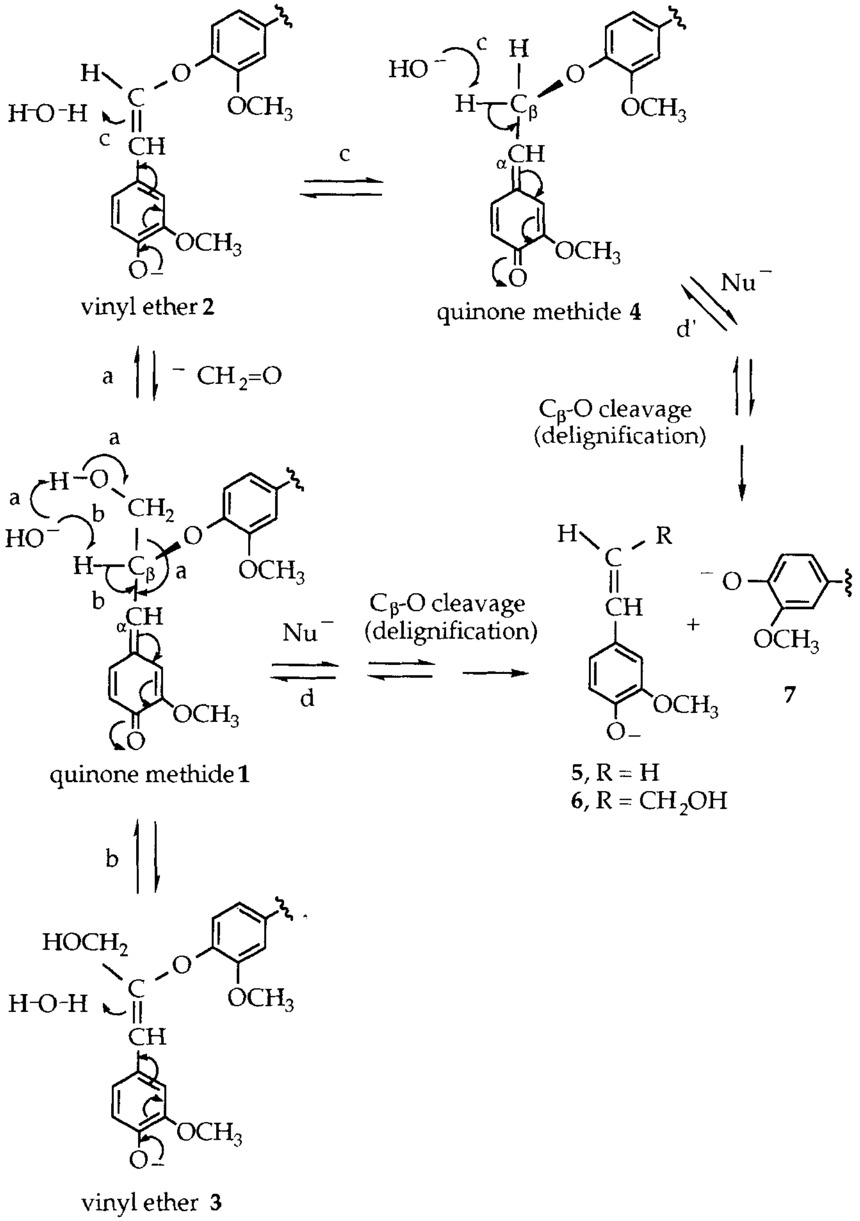
ABSTRACT

Model studies suggest that vinyl ethers are in equilibrium with quinone methides at 170°C in aqueous NaOH and that 25-30% of the vinyl ethers undergo fragmentation during kraft and AQ pulping.

INTRODUCTION

The delignification of wood chips during alkaline pulping consists of a complex set of reactions.[1,2] The goal of alkaline pulping is to fragment the lignin into water soluble pieces and separate the aqueous phase from the insoluble carbohydrate fibers. Many undesirable lignin reactions also occur in the process. One such reaction is vinyl ether formation from quinone methide intermediates (paths a and b, Scheme 1).[1]

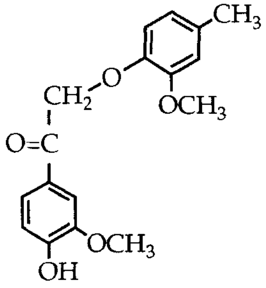
Vinyl ether structures, such as **2** and **3**, are considered to be relatively stable to alkali and, thus, interfer with desirable C_β-aryl ether fragmentation processes (path d, Scheme 1).[1,3] However, previous studies in our laboratory indicated that vinyl ethers are slowly fragmented in ~1M NaOH at 170°C.[4] The results suggested that vinyl ethers are in equilibrium with quinone methides, as indicated in steps b and c of Scheme 1. The following study verifies the reversibility of this step and defines more clearly the reactivity of vinyl ethers under pulping conditions.


vinyl ether 2
quinone methide 4
c
a
− CH₂=O
Nu⁻
d'
Cβ-O cleavage (delignification)
quinone methide 1
Nu⁻
d
5, R = H
6, R = CH₂OH
7
b
vinyl ether 3
OCH₃
HO⁻
H-O-H

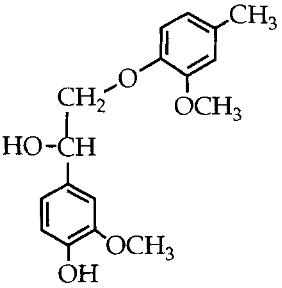
Scheme 1

RESULTS AND DISCUSSION

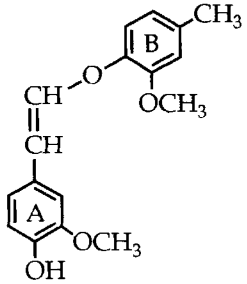
A lignin model vinyl ether was synthesized by coupling α-bromoacetoguaiacone with sodium creosolate to give ketone dimer **8**, reducing the ketone with sodium borohydride, and treating the resulting alcohol (**9**) with $NaOCH_3$ in methanol at 150°C for three hours. The procedure provides a relatively clean ~2:1 mixture of cis/trans isomers **10a/10b**. A key to the synthesis is that the quinone methide from **9** probably has only two reaction pathways available: (1) it can form a vinyl ether by C_β-proton abstraction by CH_3O^- (step c, Scheme 1) or (2) reversibly capture CH_3O^- to give **11**$^-$; the α-OCH_3 of **11**$^-$ cannot be ionized and, therefore, cannot participate in a neighboring group displacement which would break the adjacent C_β-aryl ether bond.[1] A creosol "B" ring was chosen to differentiate this ring from the guaiacol "A" ring, since both A and B ring phenols can be generated under pulping conditions.[2]



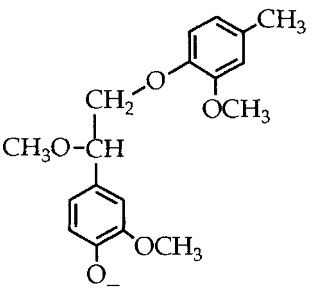
8



9



10a, cis
10b, trans



11$^-$

Table 1. Alkaline degradations of vinyl ether mixture **10a/10b** at 170°C.

	% Creosol[a]			
Additive	Set 1- 60 min	Set 1- 120 min	Set 2- 60 min	Set 2- 120 min[b]
none	11.6	12.5	15.9	14.0, 16.0
AQ	22.3	-----[c]	18.9	23.5, -----[c]
AQ/glucose	19.4	26.8	21.3	29.3, 29.6[d]
NaSH	-----[c]	24.6	18.8	25.3, 26.6

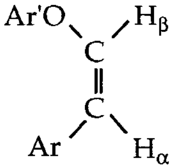
[a]different sets refer to different experiments; all employed 100 equiv. of NaOH and 5 equiv. of additive; [b]duplicate determinations; [c]vessel leaked; [d]glucose (5 equiv.) in NaOH gave 17.2% creosol after 120 min.

Treatment of the vinyl ether mixture **10a/10b** with different chemicals (NaOH, NaSH, AQ, glucose, and AQ/glucose) at 150°C for 15-120 minutes produced no creosol fragmentation product. This low reactivity is in contrast to compounds similar to **9**, which give $80^{+}\%$ yields of B ring phenols in 30 minutes at 150°C.[2] However, the vinyl ethers displayed some reactivity when the temperature was raised to 170°C (Table 1).

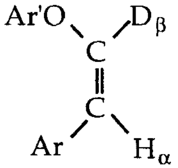
A relative comparison of the data sets in Table 1 shows fairly close agreement, meaning the temperature was reasonably constant for duplicate runs. The mixture of glucose and anthraquinone (AQ) generates anthrahydroquinone (AHQ).[2] Carbohydrates by themselves can promote lignin model fragmentation;[5] however, this was not the case for the vinyl ether (Table 1, footnote "d" and other unreported data). Glucose is rapidly degraded in NaOH at 170°C[6] and, thus, may not have been present to any appreciable extent during this slow developing reaction.

The data indicate that good pulping additives promote fragmentation of the model. They probably accomplish this by reacting with the quinone methide (QM), which is equilibrium with the vinyl ether, and promoting fragmentation by addition to C_α and then a neighboring group displacement mechanism[1] or by an electron transfer mechanism in the case of AHQ.[7] The better additives are about twice as effective as NaOH in promoting vinyl ether fragmentation.

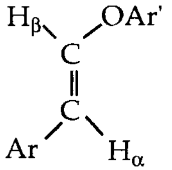
To further demonstrate the existence of a QM/vinyl ether equilibrium, we heated the **10a/10b** vinyl ether mixture at 170°C for 4 hr with 0.86M NaOD in D_2O and analyzed the resulting product by ^{1}H-NMR. The product mixture was composed mainly of vinyl ethers of the types shown below, with a ratio of **10a/10a-d**$_\beta$ and **10b/10b-d**$_\beta$ of about 60/40.



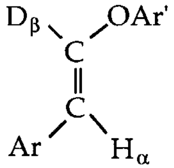
10a



10a-d$_\beta$



10b



10b-d$_\beta$

The partial exchange of the β-proton in **10a** and **10b** was indicated by a reduced signal area for H_β and the appearance of the H_α signal - a singlet, sandwiched between a doublet. The H_α doublet is due to coupling with a neighboring β-proton; the H_α singlet indicates the absence of a β-proton in the deuterium exchanged compound. The α- and β-cis and trans proton assignments were based on expected H_α-H_β coupling constants and chemical shifts values assigned to vinyl ethers.[8]

The incorporation of deuterium at the C_β-position is explained by the transfer of a deuterium from D_2O to C_β when the vinyl ether is converted to the quinone methide (step c, Scheme 1) and then removal of the H from the -C_βHD- unit of the quinone methide during its conversion back to a vinyl ether (reverse of step c, Scheme 1).

Additional support for the enhanced reactivity of vinyl ethers in the presence of AHQ comes from research results of Hise and co-workers.[9] The ratio of two lignin fragmentation products, vinylguaiacol (**5**) to coniferyl alcohol (**6**), changes with different cooking stages in the AQ pulping of pine; also, the absolute levels of vinylguaiacol are higher in AQ pulping than in kraft and soda pulping. These results have been interpreted to mean that formaldehyde is lost from C_γ-units of lignin quinone methides (**1**) to give vinyl ethers (**2**), which upon hydration and reaction with AHQ produce vinylguaiacol (path d', Scheme 1). Coniferyl alcohol is a fragmentation product of a β-aryl ether phenolic lignin end unit which has not lost formaldehyde (path d, Scheme 1).

In a brief report, Yaguchi and co-workers observed a low yield of β-aryl ether fragmention products after heating a vinyl ether lignin model at 160°C for 1 hour in the presence of THAQ, a reduced form of AQ.[10]

CONCLUSIONS

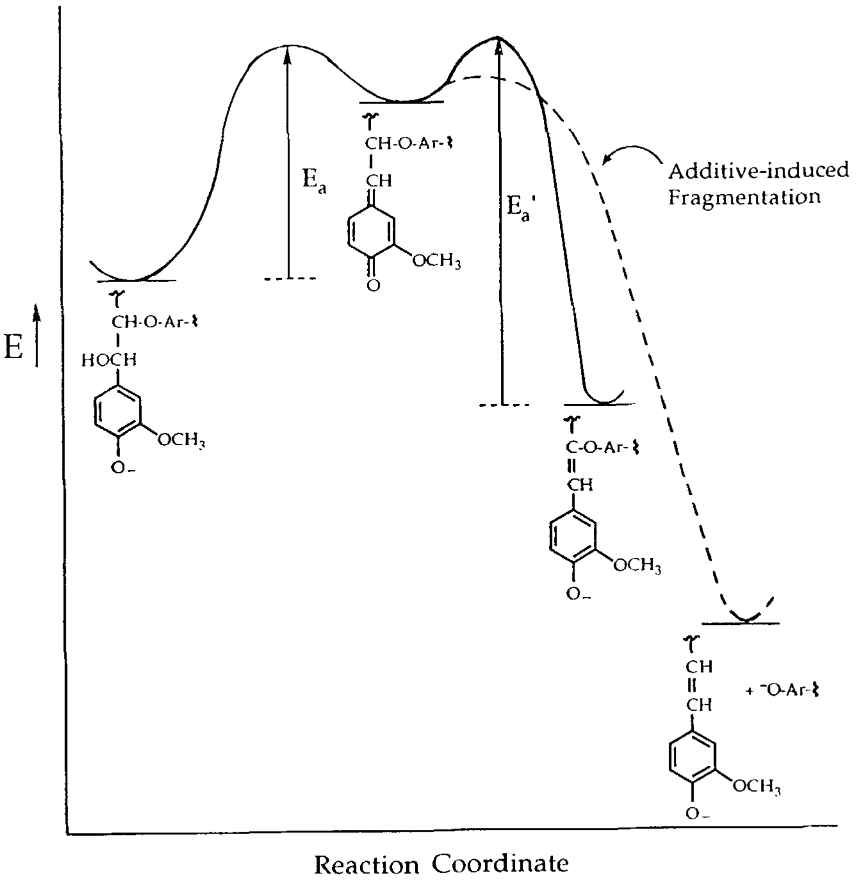
The greater amount of fragmentation with AHQ and NaSH (as compared to NaOH alone), together with the deuterium exchange results, indicate that vinyl ethers are in equilibrium with QMs at 170°C in aqueous NaOH. However, the equilibrium must favor the vinyl ether structure. If the equilibrium favored the QM, high yields of model fragmentation would be expected; however, only 15-30% yields were observed.

The results agree with our earlier suggested model for competing pulping reactions (partially shown in Scheme 2),[11] in which the energy needed to form a QM from a vinyl ether (E_a') is greater than that from an α-OH structure (E_a). Since QM formation is the slow step in additive-promoted β-aryl ether fragmentation,[11] delignification via a vinyl ether will be a slow reaction. However, based on the vinyl ether model results reported here, we predict that about 30% of the lignin vinyl ethers produced during kraft and AQ pulping will fragment.

EXPERIMENTAL

Materials. Oxygen-free water was prepared by boiling distilled water for 30 min, bubbling nitrogen into the water as it cooled, and sealing until needed. Oxygen-free NaOH solutions were prepared in a similar manner, using O_2-free water for dilution to the desired molarity.

β-(2'-Methoxy-4'-methylphenoxy)-4-hydroxy-3-methoxyacetophenone (8). The procedure for coupling 25.2g of α-bromo-4-hydroxy-3-methoxyacetophenone with eight equivalents of the sodium salt of 2-



Scheme 2

methoxy-4-methylphenol was identical to previously described couplings of this type in our laboratory.[12] The product was separated by chromatography[12] and crystallized from toluene to give 5.8 g of **8**; m.p. 109-111°C; IR (mull) cm^{-1} 3300 (OH), 1670 (C=0), and 1590 (aryl); ^1H-NMR ($CDCl_3$) δ 2.28 (s, 3, $ArCH_3$), 3.85 (s, 3, OCH_3), 3.91 (s, 3, OCH_3), 5.23 (s, 2, CH_2), 6.2 (br s 1, OH), 6.6-7.0 (m, 4, ArH) and 7.3-7.6 (m, 2, C_2 and C_6-ArH); ^{13}C-NMR (d_6-acetone) ppm 21.0 (q, $ArCH_3$), 56.1, 56.2 (q, OCH_3), 72.5 (t, CH_2), 111.5, 114.2, 115.2, 115.5, 121.3, 123.7 (d, Ar-H), 128.0, 131.9, 146.5, 148.0, 150.2, 152.3 (s, Ar-R and Ar-O) and 193.3 (s, C=0); MS *m/e* (%) 302 (M, 30), 151 (100), 137 (18), 91 (11), and 77 (10).

1-(4'-Hydroxy-3'-methoxyphenyl)-2-(2"-methoxy-4"-methylphenoxy)-1-ethanol (9). To a stirred slurry of 2.0g (6.6 mmoles) of β-(2'-methoxy-4'-methylphenoxy)-4-hydroxy-3-methoxyacetophenone **(8)** in 100 mL of ethanol was added dropwise 2.5g (66 mmoles) of sodium borohydride dissolved in 100 mL of water. After stirring for 2 hr, the reaction mixture was neutralized with 3M HCl and extracted three times with chloroform. The combined $CHCl_3$ extracts were dried (anh. Na_2SO_4) and evaporated. The residue was crystallized from toluene to give colorless crystals, mp 96-99° (one experiment), 86.5-88.5° (another experiment); both had identical spectra: IR (mull) cm^{-1} 3100-3600 (OH), 1600 (aryl); ^1H-NMR ($CDCl_3$) δ 2.30 (s, 3, $ArCH_3$), 3.65 (br s, 1, OH), 3.84 (s, 3, OCH_3), 3.86 (s, 3, OCH_3), 3.85 (d of d, J_{AX} = 9.3 and J_{AB} = 10.0Hz, 1, $ArCH_XC\underline{H}_AH_B$), 4.12 (d of d, J_{AB} = 10.0 and J_{BX} = 3.2Hz, 1, $ArCH_XCH_A\underline{H}_B$), 4.98 (d of d, J_{AX} = 9.3 and J_{BX} = 3.2Hz, 1, $ArC\underline{H}_XCH_AH_B$), 5.73 (s, 1, OH), 6.6-7.0 (m, 6, ArH); ^{13}H-NMR (d_6-acetone) ppm 20.9 (q, $ArCH_3$), 56.0 (q, OCH_3), 72.4 (d, $Ar\underline{C}H$), 76.3 (t, $Ar\underline{C}HCH_2$-), 110.5, 114.1, 115.0, 115.7, 119.5, 121.5 (d, Ar-H), 131.5, 133.5 (s, Ar-C), 146.3, 146.9, 147.6, and 150.2 (s, Ar-O); MS *m/e* (%) 304 (M,19), 153 (45), 152 (27), 138 (100), 137 (22), 123 (28), and 93 (25).

2-(2'-methoxy-4'-methylphenoxy)-1-(4'-hydroxy-3-methoxyphenyl)-ethene (10a/10b). To thirteen 4.5 mL bombs was added 40 mg of 1-(4'-hydroxy-3'-methoxyphenyl)-2-(2"-methoxy-4"-methylphenoxy)-1-ethanol **(9)**. In a nitrogen atmosphere, 3.5 mL of a 0.1 M $NaOCH_3$ solution in dry methanol was added to each bomb. The bombs were sealed and placed in a 150°C oil bath for 3 hours. After being pulled and cooled, all bombs were emptied and rinsed twice with water. The bomb contents and rinsings were combined, acidified to pH 5 with dilute HCl, and chloroform extracted (4 x 25 mL). The chloroform extracts were dried over Na_2SO_4 and evaporated to leave an oil (500 mg), which was a mixture of cis and trans vinyl ethers (**10a/10b**).

Column chromatography of the oil resulted in partial separation of the trans isomer; however, the yield was low. A ^1H-NMR of the separated cis isomer showed ($CDCl_3$) δ 2.32 (s, 3, Ar-CH_3), 3.85 (s, 3, OCH_3), 3.89 (s, 3, OCH_3), 5.48 (d, J = 7Hz, 1, ArCH=), 5.58 (s, 1, OH), 6.46 (d, J = 7Hz, 1, =CH-O), 6.6-7.1 (m, 5, Ar-H), and 7.57 (d, J = 2.7Hz, 1, Ar-H). The crude oil shows the same set of ^{1}H-NMR signals, and additional ones assigned to the trans vinyl ether: ($CDCl_3$) δ 3.86 (s, OCH_3), 6.22 (d, J = 12.4Hz, ArCH=). Proton coupled and decoupled ^{13}C-NMR spectra of this oil were complex; however, the following signals were apparent: ($CDCl_3$) ppm 21.1 (q, $ArCH_3$), 55.5, 55.7, and 55.8 (q, OCH_3), 140.7 and 143.4 (d, =CHO-), 108-150 (many signals, aryl and vinyl carbons). A mass spectrum of the oil (direct insertion probe) showed: *m/e* (% of base peak) 286 (M,100), 257 (14), 225 (36), 149 (14) 137 (18), 133 (16), and 77 (16). Integration of the ^{1}H-NMR spectrum of the crude oil indicated an ~ 2:1 mixture of cis/trans isomers.

Vinyl Ether Degradations. The reactions were conducted in a nitrogen atmosphere with oxygen-free water in 4 mL stainless steel pressure vessels (bombs). Typically, the bomb contained 30 mmoles of vinyl ether mixture **10a/10b** and 3.5 mL of 0.86M NaOH. The bombs were charged in a glove bag with 1.0 mL of 0.5M NaOH containing **10a/10b** and mixed with 1 mL of 1.0M NaOH containing glucose or Na_2S, depending on the experiment, and diluted with 1.0M NaOH to a volume of 3.5 mL. In the appropriate experiment, 31.2 mg of anthraquinone was added. The sealed bombs were rotated for selected time periods in a 170°C oil bath, cooled quickly, and opened. A small volume of 1.0M NaOH, containing a known amount of *p*-isopropylphenol (GC internal standard), was added; the contents of the bombs were then transferred to a flask.

The reaction mixture was treated with dimethyl sulfate, to convert the phenols to methyl ethers,[4] and then extracted with chloroform. The chloroform solution was washed with water, dried (anh. Na_2SO_4), and analyzed by gas chromatography (Hewlett-Packard HP 5890 GC, HP-17 packed column). The amount of *m*-creosol in the sample was determined by comparing the GC signal area of methylated creosol to that of methylated *p*-isopropylphenol. Initially, standard mixtures of *m*-creosol and *p*-isopropyl-phenol were methylated and analyzed by GC to develop a response factor.

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