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### Electron Transfer Reactions in Pulping Systems (III): A Study of Steric Effects in Lignin Model/Aq Reactions

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ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (III):  
A STUDY OF STERIC EFFECTS IN LIGNIN MODEL/AQ REACTIONS

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ABSTRACT

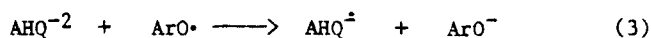
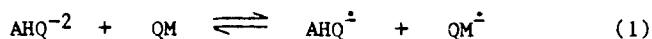
The reactions of five  $\beta$ -aryl ether lignin model dimers with three anthrahydroquinone (AHQ) analogs have been studied. Some of the models and AHQ analogs have bulky substituents strategically located in positions which would possibly inhibit adduct reactions but not single electron transfer (SET) reactions. The fact that the model fragmentation efficiencies were the same for both sterically hindered and unhindered AHQ analogs indicates that the reaction mechanism cannot involve a rate determining adduct formation step. The results can be best explained either by an SET mechanism or a mechanism which involves quinonemethide generation as a slow step, followed by adduct, SET, or other steps. Placing methyl groups on the  $\beta$ -carbon of the models favored model fragmentation reactions by NaOH. The  $\beta$ -methyl group may be promoting fragmentation reaction rates and/or retarding the rates of competing side reactions, such as vinyl ether generation.

INTRODUCTION

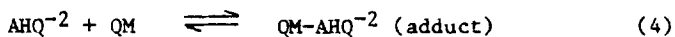
The high efficiencies of anthraquinone (AQ)-based pulping systems may be related to a unique chemistry, namely, that involving single electron transfer (SET) reactions between anthrahydroquinone (AHQ) species and lignin quinonemethides (QMs).<sup>1</sup> Previous electrochemical studies have shown that such chemistry exists between AHQ radical anions (AHQ<sup>-</sup>) and lignin-model QMs in **organic solvents** at room temperature;<sup>2</sup> of course, these conditions are quite different from pulping conditions. This report deals with an

attempt to find supporting evidence for the SET mechanism for model compound reactions under **pulping-like** conditions using steric effect arguments. A related study employing substituent electronic effect differences was inconclusive.<sup>3</sup>

The SET mechanism involves transfer of an electron from  $\text{AHQ}^{-2}$  to a quinonemethide, followed by fragmentation of the  $\text{QM}^{\dot{-}}$  intermediate to phenolic ions and radicals, and finally a second electron transfer step (Eq. 1-3). Although not shown, the transfer agent could also be  $\text{AHQ}^{\dot{-}}$  going to AQ in steps 1 and 3.



Our work is also related to establishing the validity of the "adduct" mechanism theory, the other major mechanism proposed for explaining  $\text{AHQ}$ -induced delignification reactions.<sup>1</sup> The adduct mechanism involves bond formation between  $\text{C}_{10}$  of  $\text{AHQ}^{-2}$  and  $\text{C}_{\alpha}$  of a QM, followed by rupture of the adduct to AQ and phenolic fragments (Eq. 4 and 5).



Model fragmentation (and delignification) via an adduct mechanism should be adversely affected by bulky substituents near the sites of bond formation, namely  $\text{C}_{\alpha}$  of the QM and  $\text{C}_{10}$  of the  $\text{AHQ}^{-2}$ . The approximately 1.6 Å bond distance<sup>4</sup> for the  $\text{C}_{\alpha}$ - $\text{C}_{10}$  bond of the adduct imposes a substantial steric strain between the substituents on the  $\text{C}_{\alpha}$ - $\text{C}_{\beta}$  bond. Although some crowded adducts are known,<sup>5</sup> the difficulties in preparing such adducts (especially in an all aqueous medium<sup>1</sup>) indicates that steric factors are important for obtaining high yields of adducts.

Single electron transfer reactions are known to proceed at astonishingly fast rates even across distances of 10 Å or greater.<sup>6</sup> The SET reaction for  $\text{AHQ}^{-2}$  and a lignin model (or



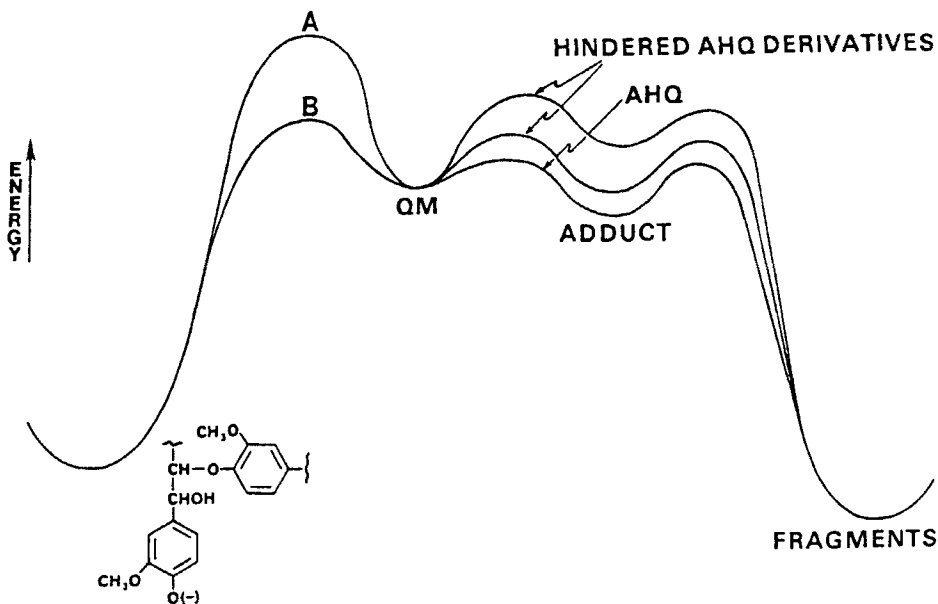


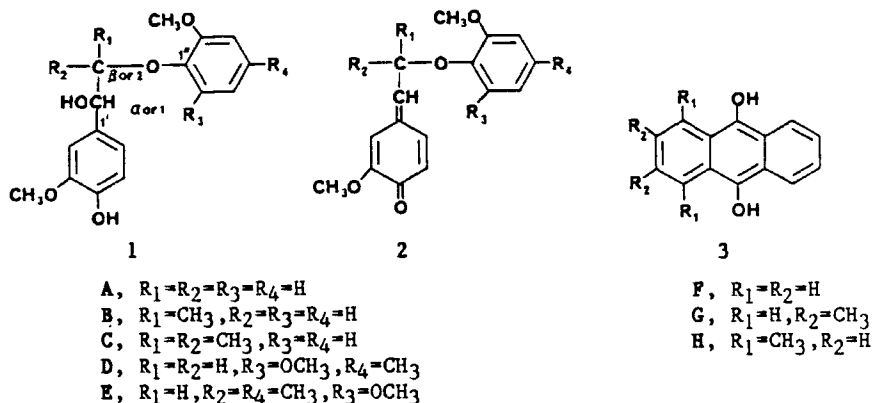
Figure 2. Hypothetical energy profiles for the reaction of AHQ analogs with a lignin quinonemethide via an adduct mechanism.

(case B). For SET reactions, steric effects should not exist, and thus reactions of a QM with different, but related, AHQ derivatives should occur at roughly the same rates.

There are two ways to study steric effects, and each has its shortcomings. One way is to place bulky groups on the AHQ<sup>-2</sup> reactant; however, the added substituents may not only affect size, but also SET ability and solubility of the molecule. The other way is to place bulky groups on the  $\beta$ -carbon of related lignin models; however, the rates of QM generation may change, thus interfering with the interpretation of steric effects. Both approaches have been studied.

The models we chose to study were free phenolic,  $\beta$ -aryl ethers 1A-1E. In alkali at high temperatures, these compounds will provide the corresponding QMs 2A-E. Three AHQ derivatives

were also studied; these were AHQ itself, 2,3-dimethyl and 1,4-dimethyl AHQ (3F-H). The latter will have a larger steric inhibition to reaction (via an adduct mechanism) than the other two, which should be similar. Both methylated AHQ analogs should be similar in electronic effects, solubility, and electron donating ability. Based on room temperature polarographic peak potentials,<sup>8</sup> the methylated AHQ<sup>-2</sup> compounds should be slightly better than AHQ<sup>-2</sup> in SET reactions.



If models 1A-E show the same fragmentation efficiency when reacted with catalysts 3F-H, steric effects are not important, meaning the mechanism of fragmentation is an SET-type or an adduct-type with a dominating QM formation step. If, however, the most hindered reactants lead to low levels of fragmentation, an adduct mechanism is indicated.

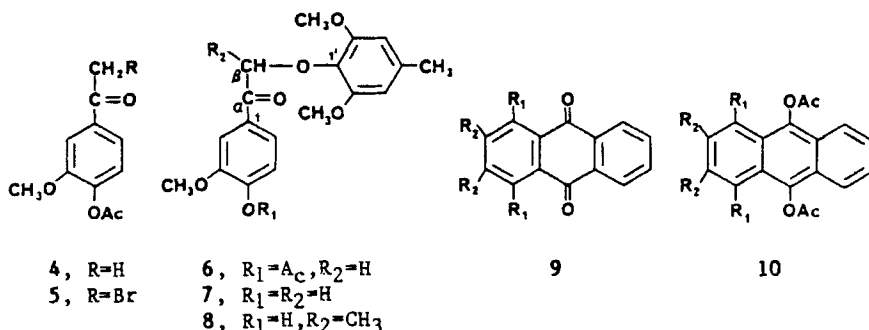
## RESULTS

### Synthesis, Reagent Generation and Analysis

The syntheses of models 1A-C have already been reported.<sup>9</sup> Model 1D was synthesized by the conversion of 4 to 5 to 6 to 7 and then NaBH<sub>4</sub> reduction of 7. Model 1E was synthesized by methylation of 7 to 8, followed by NaBH<sub>4</sub> reduction.

Our initial method for generating AHQ<sup>-2</sup> analogs in situ involved zinc reduction of AQs 9F-H in acetic acid to give diace-

tates 10F-H, which in turn could be hydrolyzed in alkali to give anthrahydroquinones 3F-H. The attractive feature of this procedure is that the hydrolysis of an AHQ diacetate should not generate any harmful by-products. Unfortunately, the procedure could not be used for the methylated anthraquinones 9G and H because (a) the zinc reductions to diacetates 10G and H gave low yields, (b) the stability of diacetate 10H was poor, and (c) both methylated diacetates 10G and H were difficult to hydrolyze in water because of their low solubility.



Two other methods, dithionite reduction and glucose reduction, were investigated as ways to generate AHQ<sup>-2</sup> analogs from AQ compounds. Separate experiments<sup>10</sup> showed that the glucose method was superior with the methylated AQ. For unsubstituted AHQ<sup>-2</sup>, all three methods of generation worked well, providing the reducing agents were used in excess and allowed to react before reaching a high temperature where both glucose and dithionite are unstable to alkali.

A problem associated with the reductive procedures was to select an appropriate condition for the "control" degradation. The control degradation would represent the yield of model fragmentation in the absence of the AHQ species. Reducing agents glucose and dithionite cause some model fragmentation when used in the absence of AQ. But how much of the reducing agent is available for reaction with the model if AQ is present?

Previous studies have demonstrated that adding glucose to a kraft degradation of a model had no effect.<sup>3</sup> Electrochemical stu-

dies indicate that AQ is easier to reduce than a lignin model QM.<sup>2</sup> Based on these two observations, we assume that in a reaction mixture of AQ, QM, and reducing agent, the latter will be principally consumed in reactions with AQ, generating  $AHQ^{-2}$  ions. In general, AQ and reducing agent were used in equivalent amounts and in a large excess relative to the model.

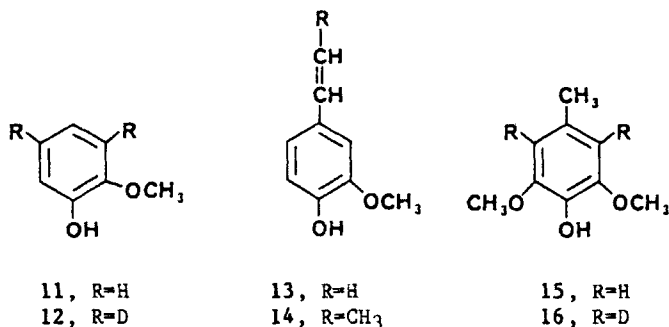
The key indicator of model fragmentation is formation of the *o*-phenol. Initially, we used a sensitive gas chromatography-mass spectroscopy (GC-MS) selective ion monitoring (SIM) technique which compared molecular ion signals of the liberated phenol, underivatized or methylated,<sup>3</sup> to a deuterated version of the phenol, added as an internal standard.<sup>11</sup> Later studies employed derivatization by methylation, *p*-isopropyl phenol as an internal standard (IS) after reaction, and GC analysis.<sup>3</sup>

#### **Peculiarities in Model Degradations**

Guaiacol (11) yields from degradations of the simplest, least hindered model 1A in the presence of alkali and AHQ at 150°C were dependent on whether guaiacol-3,5-d<sub>2</sub> IS (12) was added before or after the reaction and how much IS was present during the degradation. Guaiacol yields as high as 170% were observed on occasion. These yield variations appear to be related to secondary reactions of 4-vinylguaiacol (13), the other fragment produced in the degradations of 1A. The yields of 4-vinylguaiacol were always much less than those of guaiacol; in theory, the yields should be the same.

Stability checks showed that the combination of 4-vinylguaiacol and AHQ/AQ causes guaiacol to be lost under degradation conditions (150°C, aqueous alkali). Apparently, 4-vinylguaiacol underwent polymerization reactions (possibly radically induced by AHQ species) which incorporated some guaiacol. Model 1A degradations which were done in the presence of deuterated guaiacol IS probably consumed the IS in preference to liberated guaiacol because of the initial large difference in concentrations. This gave rise to the apparent (liberated) guaiacol yields in excess of 100% and a large scatter in the reproducibility.





If an IS was added during the work-up of degradation reactions of IA and great care was taken to handle all samples alike, the observed yields were generally below 100%. The reproducibility was still poor, as shown in Table 1; the underlined data, obtained from one experiment, show one trend at 20 min and a different trend at 40 min. Occasionally, the yields were less at the longer reaction times; behavior of this type has been observed in some similarly related models.<sup>3</sup> Because of these problems, model IA was not considered suitable for these studies.

TABLE 1  
Guaiacol Yields from the Degradation of Model IA<sup>a</sup>

Additive	Guaiacol Yield, % <sup>b,c</sup>	
	at 20 min	at 40 min
None	2.3	5.3, 3.6, 8.0
Glucose	35.8, 24.2, 29.8	37.7, 44.0, 41.7
Glucose + AQ	69.7, 65.6, <u>78.8</u>	82.0, 111.6, <u>71.1</u>
Glucose + 2,3-dimethyl AQ	78.5, 60.1, <u>84.2</u>	71.9, 85.6, <u>77.2</u>
Glucose + 1,4-dimethyl AQ	60.4, 61.4, <u>71.1</u>	67.3, 77.0, <u>78.4</u>

<sup>a</sup>All degradations were performed under oxygen-free conditions in sealed pressure vessels at 150°C in the presence of 25 equiv. of NaOH. Additive levels were 5 equiv. based on the model.

<sup>b</sup>Analysis by GC after methylation; isopropylphenol IS.

<sup>c</sup>Multiple numbers mean duplicates or triplicates done on different days, but using the same procedures and conditions.

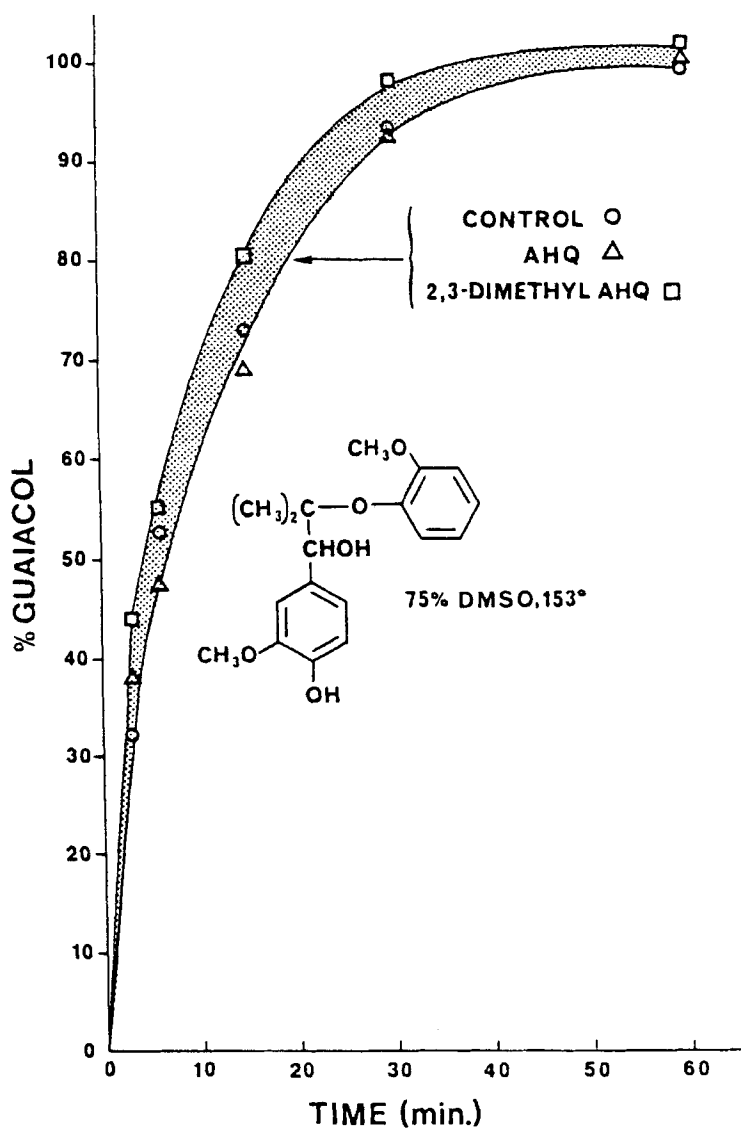


Figure 3. The variation in guaiacol yield with time for model 1C in 75% DMSO at 153° in the presence of hydroxide, O, and additives: AHQ,  $\Delta$ ; 2,3-dimethyl-AHQ,  $\square$ .

Fortunately, this yield problem appeared to be confined only to the one model. Stability checks established that guaiacol was not lost under degradation conditions in the presence of isoeugenol (14) and AHQ/AQ. Isoeugenol is the by-product fragment obtained in the degradation of the  $\beta$ -methyl models 1B and 1E in the presence of AHQ. The yield of isoeugenol is close to that of guaiacol, meaning the former does not readily polymerize under the conditions employed. Two of the models, 1D and 1E, give rise to 4-methylsyringol (15) as a primary fragmentation product; this phenol should be stable to the conditions because all of its reactive (ortho and para) sites are blocked by substituents.

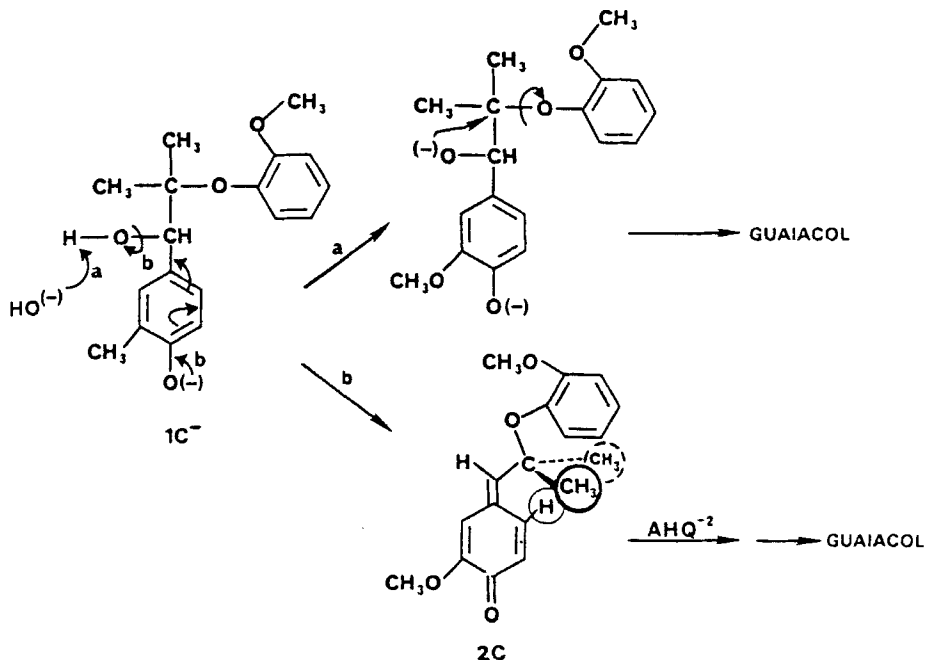
One other model, the  $\beta,\beta$ -dimethyl model 1C, had only limited utility. Unlike the other models, the fragmentation efficiency of 1C was not influenced by the presence of AHQ or AHQ analogs in either 50% aqueous dioxane or 75% DMSO (Fig. 3).

We interpret this behavior as an indication that the rate of the typical alkali induced fragmentation pathway (Scheme 1, path a) is favored due to relief of steric strain and/or that the rate of quinonemethide formation (Scheme 1, path b) is retarded due to severe internal strain. The quinonemethide (2C), which is a prerequisite for additive induced fragmentation reactions, is apparently not so strained that its formation is totally inhibited. Treatment of 1C in  $\text{CDCl}_3$  with  $\text{BrSiMe}_3/\text{Na}_2\text{CO}_3$  gave what appears (by  $^1\text{H-NMR}$ )<sup>12</sup> to be a mixture of syn and anti isomers of QM 2C.

The peculiarities associated with the degradations of the non-methyl and  $\beta,\beta$ -dimethyl models 1A and 1C in the presence of AHQ prevented a direct comparison of additive effects in the 1A-C homologous series. A comparison of the series was possible in the case of NaOH induced fragmentation reactions; this will be discussed later. [The loss of guaiacol due to competing side reactions of 4-vinylguaiacol appears to be a problem only when AHQ is present.]

#### Model Degradation in the Presence of Different Additives

The effect of changing the steric congestion in the AHQ re-



Scheme 1. Possible Fragmentation Reactions of Model 1C

actant was examined with several models and several solvent systems. Our most consistent results involved the reactions of the mono- $\beta$ -methyl guaiacyl model (1B); an example is shown in Table 2. In essence, there were no real differences in the efficiencies of the methylated AHQs and unsubstituted AHQ. The values for the 1,4-dimethyl reactant appeared slightly lower than the others; this may reflect a lower concentration of this reactant, since 1,4-dimethyl AHQ has the lowest solubility.<sup>10</sup>

As can be seen from the table, glucose by itself in aqueous alkali caused a significant amount of fragmentation. This "glucose effect" has been observed in other model degradations as well.<sup>3,13</sup> With the mono- $\beta$ -methyl syringyl model (1E) the glucose effect was quite large and approached that of the AHQ additives (Table 3).

TABLE 2

Guaiacol Yields from Degradations of Model 1B<sup>a</sup>

Additive	Guaiacol Yield, % <sup>b,c</sup>	
	at 20 min	at 40 min
None		6.8, 6.7
Glucose	36.6, 33.1	55.1, 52.1
Glucose + AQ	53.8, 51.4	81.2, 80.1
Glucose + 2,3-dimethyl AQ	53.2, 53.2	80.9, 76.9
Glucose + 1,4-dimethyl AQ	52.4, 50.9	78.1, 77.7

<sup>a,c</sup>See Table 1 footnotes.

<sup>b</sup>Analysis by SIM GC-MS of methylated samples containing guaiacol-d<sub>2</sub> internal standard and using standard response curves.

Degradation reactions of the simple  $\beta$ -syringyl model (1D) in water at 150°C, with analysis by methylation and GC, gave the results shown in Table 4. Over twenty direct comparisons of additive effects on the fragmentation of model 1D have been done. In these experiments the reaction time, the solvent composition, and the methods of analyses and AHQ generation were varied; an example comparing solvent composition effects is shown in Fig. 4.

TABLE 3

4-Methylsyringol Yields from Degradations of Model 1E<sup>a</sup>

Additive	4-Methylsyringol Yield, % <sup>b</sup>		
	10 min	at 20 min	at 40 min
None		25.2	30.6
Glucose	22.8	41.4	51.2
Glucose + AQ	26.5	45.6	53.0
Glucose + 2,3-dimethyl AQ	26.6	43.3	53.5
Glucose + 1,4-dimethyl AQ	25.8	42.6	52.2

<sup>a,b</sup>See Table 1 footnotes.

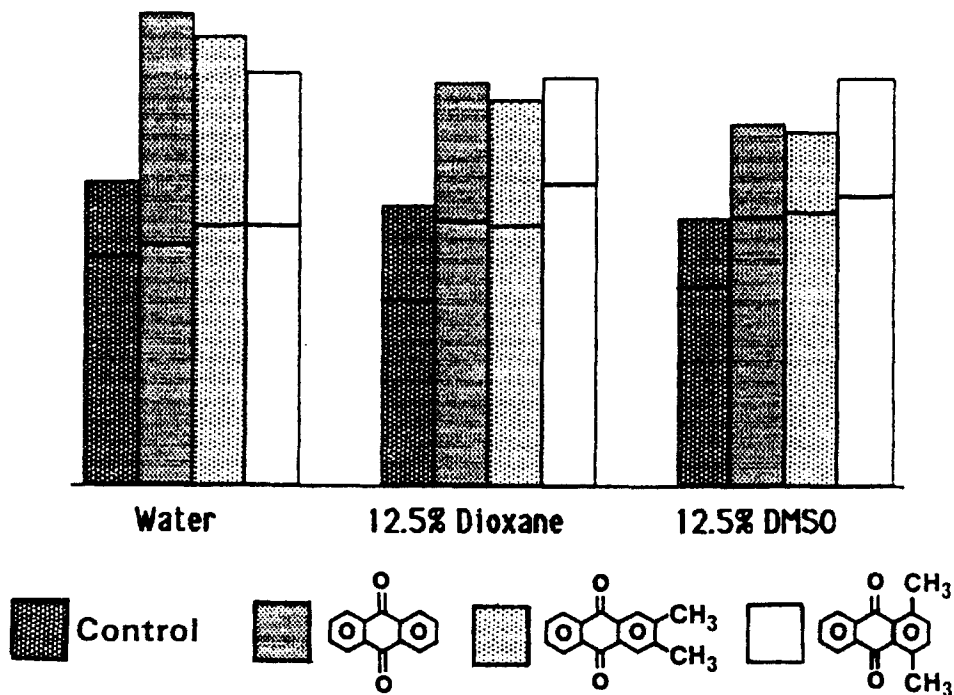


Figure 4. Relative comparison of 4-methylsyringol (15) yields from degradations of model 1E at 150°C for 30 min (mid-line) and 60 min (top) as a function of solvent composition. All runs have 5 equiv. of glucose and 25 equiv. of NaOH per equiv. of model and all but the control have 5 equiv. of the indicated additives. Analysis was performed by GC-MS SIM with 16 as an internal standard.

TABLE 4

4-Methylsyringol Yields from Degradations of Model 1D<sup>a</sup>

Additive	4-Methylsyringol Yield, % <sup>b,c</sup>	
	at 10 min	at 20 min
None		16.0, 18.7
Glucose	26.2, 26.1	45.5, 45.1
Glucose + AQ	56.0, 56.8	77.0, 77.5
Glucose + 2,3-dimethyl AQ	53.5, 58.7	78.5, —
Glucose + 1,4-dimethyl AQ	55.5, 55.2	71.9, 75.2

<sup>a,b,c</sup>See Table 1 footnotes.

TABLE 5

Guaiacol Yields from Degradations of Models 1A-C in Aqueous NaOH (67 Equiv.) at 150°C

Model	C <sub>β</sub> -Methyl	Guaiacol Yield, %	
		at 30 min	at 60 min
1A	None	14	21
1B	One	17	31
1C	Two	86	95

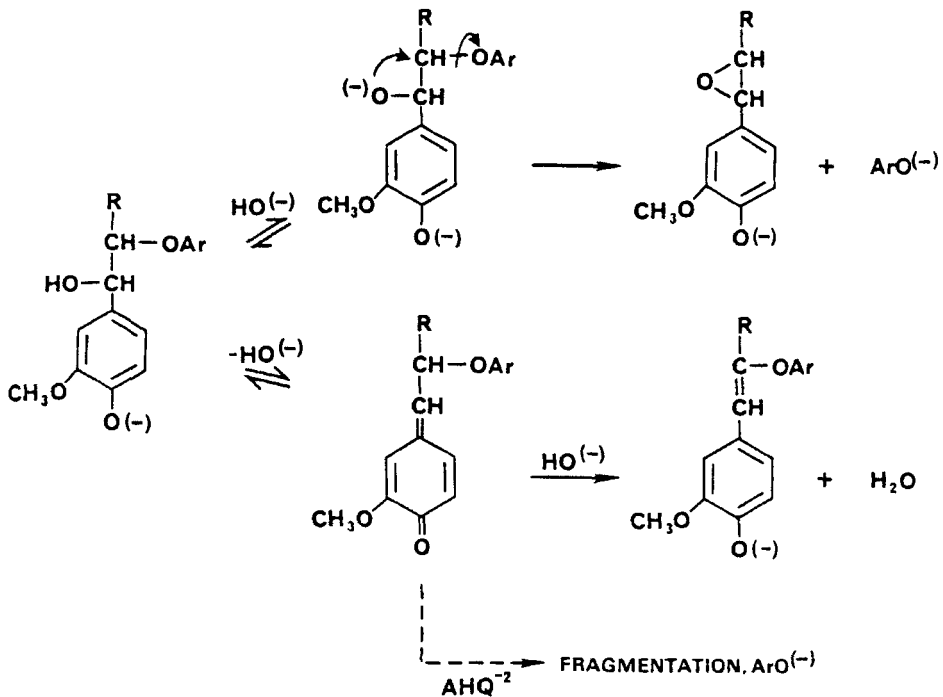
While the absolute values of the yields varied with these changes, the overwhelming conclusions were that: (a) both methylated AHQ analogs caused essentially the same degree of fragmentation as AHQ, (b) AHQ and its analogs are more effective than glucose, and (c) alkali alone is poor for fragmenting the model.

Multiple experiments were done with each of the models. The data in the tables represent only about a tenth of the experiments performed. For example, while the data in Table 3 may imply that 1,4-dimethyl AHQ (3E) is slightly inferior to the other AHQ analogs for fragmenting model 1E in water, the 1,4-dimethyl AHQ outperformed 2,3-dimethyl AHQ (3G) in 8/9 and simple AHQ in 7/9 comparative degradations which employed mixed solvent systems - 12.5 to 25% dioxane or DMSO.

Mixed solvent systems should help to minimize solubility differences. Some caution needs to be applied, however, when interpreting data from degradations done in mixed solvent systems since DMSO itself promotes model fragmentation,<sup>14,15</sup> and high levels of dioxane cause phase separation.<sup>16</sup>

#### Comparative Degradations of the Different Models

Previous studies have shown that the extent of fragmentation of a lignin model by NaOH is dependent on the structure of the β-



Scheme 2. Competing Reactions of the Lignin Model Compounds

phenoxy leaving group and the level of base used.<sup>3</sup> Another factor appears to be the nature of the side chain on the model - whether  $\text{C}_\beta$  is protonated or methylated. The more  $\text{C}_\beta$ -methyl groups that are present, the more prone the model is to fragmentation in  $\text{NaOH}$ . This is seen by comparing the "control" yields in Tables 2 and 3 and the data of Table 5.

Several explanations of the  $\text{C}_\beta$ -methyl effect appear plausible. First, added methyl groups increase the model's crowding and, thus, provide the impetus for fragmentation reactions which would relieve strain. Second, if  $\beta$ -aryl ether cleavages occur partially by an  $\text{S}_{\text{N}}1$  mechanism, methyl groups at  $\text{C}_\beta$  would help stabilize the resulting  $\text{C}_\beta$ -cation. Finally, methyl groups at  $\text{C}_\beta$  could alter the balance between fragmentation and competing vinyl ether product



formation (Scheme 2). Analysis of product mixtures showed a trend which has been observed before,<sup>17</sup> namely that vinyl ethers were produced in significant amounts in NaOH model degradations and only low levels in the NaOH/additive degradations.

Vinyl ether formation is blocked when there are two C<sub>β</sub>-methyl groups. With one β-methyl group, vinyl ether formation could be retarded by (1) decreasing the level of quinonemethides in the medium, (2) decreasing the level of C<sub>β</sub>-H abstraction due to a steric hindrance effect, and/or (3) decreasing the acidity of C<sub>β</sub>-H by an electron-feeding effect. Less vinyl ether formation means greater chances of model fragmentation.

A comparison of the **additive promoted** degradations of the two syringyl type models shows that the nonmethylated model 1D fragments to greater extent than the C<sub>β</sub>-methyl model 1E (see Tables 3 and 4). The most probable reason for this is that there is a higher concentration of quinonemethide with which to react with AHQ<sup>-2</sup> ions in the non-C<sub>β</sub>-methyl case; the quinonemethide will be less crowded here than in the C<sub>β</sub>-methyl case.

Another explanation for the differences in AHQ reactivities of models 1D and 1E is that the QM from nonmethylated 1D is less crowded and, therefore, better able to react by an adduct type mechanism. If this were the case, one would expect large differences in the reactivities of the methylated and nonmethylated AHQ additives; such differences were not apparent.

#### CONCLUSIONS

The fact that the efficiencies of fragmentation of lignin models are so similar for AHQ, 2,3-dimethyl-AHQ, and 1,4-dimethyl-AHQ argues against an adduct mechanism in which adduct formation is the slow step in the mechanism. The lack of steric inhibition to reaction for the different AHQ analogs is compatible with an SET mechanism.

In actual fact, however, the observed data leave the question of mechanism unanswered because quinonemethide formation could be the slow step for all the reactions studied. A dominance of reac-

tion rates due to QM formation has been observed in a related study.<sup>3</sup> If quinonemethide generation was substantially more energy consuming than the reactions which follow (Fig. 2, curve A), the rates of fragmentation of a given lignin model would be the same for different AHQ substrates. The sterically different AHQ additives may react at the same (SET mechanism) or different (adduct mechanism) rates with a QM, but this chemistry would be masked by the slow rate of QM generation.

Changing the bulkiness of groups at C<sub>β</sub> of the models not only puts steric constraints on the formation of adducts but also affects the extent to which QMs are generated and the relative rates of competing reactions. Attempting to sort out the relative impact that structural changes might have on pulping reactions is a difficult task. It is apparent, however, that placing methyl groups (and presumably other groups) at C<sub>β</sub> favors NaOH promoted model fragmentation reactions.

Finally, it should be pointed out that although AQ and the methylated AOs in alkaline glucose solutions cleave models with similar efficiencies, these additives display quite different reactivities in wood pulping experiments where solubility (or xylophilicity) differences appear to play a greater role.<sup>8</sup> Also, the models studied by us lack a  $\alpha$ -hydroxymethyl moiety, which is a common group in lignin. Such groups undergo retro-aldol reactions<sup>18</sup> which are in competition with additive reactions.

#### EXPERIMENTAL

The equipment,<sup>19</sup> guaiacol analysis by GC-MS SIMS with guaiacol-3,5-d<sub>2</sub> IS,<sup>11</sup> guaiacol analysis by methylation/GC with *p*-isopropylphenol IS,<sup>3</sup> and model degradation procedures<sup>3</sup> have been previously described. Analogous procedures<sup>3,11</sup> for the preparation 4-methylsyringol-3,5-d<sub>2</sub> IS and for the analysis of 4-methylsyringol were employed. The syntheses of compounds 1A-C have already been reported.<sup>9</sup> Melting points are corrected.

**4-Acetoxy-3-methoxy- $\alpha$ -(4'-methyl-2',6'-dimethoxyphenoxy) acetophenone (6).** The conditions for the coupling reaction were

patterned after a procedure described by Miksche for a similar reaction.<sup>20</sup> A sample of 4-methylsyringol (2,6-dimethoxy-4-methylphenol) (15) was prepared (70% yield) by an amalgamated zinc reduction<sup>21</sup> of syringaldehyde; the physical properties of 15 were: bp 92-109°C/0.5 mm; IR (mull)  $\text{cm}^{-1}$  3475 (OH) and 1610 (aryl); NMR (DMSO- $d_6$ )  $\delta$  2.21 (s, 3, ArCH<sub>3</sub>), 3.72 (s, 6, OCH<sub>3</sub>), 6.41 (s, 2, aryl), and 7.97 (s, 1, OH).

A mixture of 7.0 g (24.4 mmol) of 4-acetoxy-3-methoxy- $\alpha$ -bromoacetophenone (5),<sup>22</sup> 5.1 g (30 mmol) of 4-methylsyringol (15), 2.7 g KI, and 5.5 g K<sub>2</sub>CO<sub>3</sub> in 70 mL of freshly distilled (over KMnO<sub>4</sub>) acetone was refluxed for 165 min. The volume of the mixture was decreased to 25 mL by distillation, diluted with 50 mL H<sub>2</sub>O, and extracted with diethyl ether. The combined ether extracts were washed with 0.5M NaOH, water, and brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to give 10.5 g of a gold oil. The gold oil was redissolved in ethanol, whereupon standing, a heavy oil (9.5 g) settled out and hardened upon refrigeration. Proton NMR indicated that the hard oil was compound 6: <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  2.29 (s, 6, ArCH<sub>3</sub> and acetate CH<sub>3</sub>), 3.76 (s, 6, ArOCH<sub>3</sub>), 3.86 (s, 3, ArOCH<sub>3</sub>), 5.10 (s, 2, ArCOCH<sub>2</sub>), 6.37 (s, 2, syringyl aryl), 7.09 (d, J = 8 Hz, 1, C<sub>5</sub>-H), and 7.5-7.7 (m, 2, C<sub>2</sub> and C<sub>6</sub> protons).

**4-Hydroxy-3-methoxy- $\alpha$ -(4'-methyl-2',6'-dimethoxyphenoxy)acetophenone (7).** A mixture of 9.0 g of 6 dissolved in 100 mL methanol and 30 mL of 1M sodium methoxide in methanol was gently refluxed for 3 hr, cooled, diluted with 300 mL H<sub>2</sub>O, acidified to pH 2 with concentrated HCl, and extracted with diethyl ether. The ether extracts were washed with water, diluted with ethanol and evaporated to give 6.3 g of solid: m.p. 117.0-8.5°C (ethanol-water); IR (mull)  $\text{cm}^{-1}$  3410 (OH), 1670 (C=O), and 1595 (aryl); <sup>1</sup>H-NMR ( $d_6$ -DMSO)  $\delta$  2.26 (s, 3, Ar-CH<sub>3</sub>), 3.73 (s, 6, Ar'OCH<sub>3</sub>), 3.84 (s, 3, ArOCH<sub>3</sub>), 5.00 (s, 2, ArCOCH<sub>2</sub>), 6.50 (s, 2, aryl'), 6.88 (d, J = 8 Hz, 1, C<sub>5</sub>-H), 7.53 (s, 1, C<sub>2</sub>-H), 7.58 (d, 1, C<sub>6</sub>-H), and 10.04 (s, 1, ArOH); <sup>13</sup>C-NMR ( $d_6$ -DMSO)  $\delta$  21.3 (q, ArCH<sub>3</sub>), 55.5 and 55.7 (q, ArOCH<sub>3</sub>, Ar'OCH<sub>3</sub>), 74.4 (t, ArCOCH<sub>2</sub>), 106.1, 111.3, 114.9, and 123.0 (d, aryl), 126.5, 133.3, 133.6, 147.4, 151.9, and 152.3 (s,

aryl), and 192.7 (s, ArC=O), MS;  $m/e$  (%) 332 ( $M^+$ , 54), 167 (88), 151 (100), and 137 (38).

**4-Hydroxy-3-methoxy- $\alpha$ -(4'-methyl-2',6'-dimethoxyphenoxy)- $\alpha$ -methylacetophenone (8).** A 47% yield after a chromatography of **8** was obtained from **7** using our standard alkylation procedure.<sup>3</sup> The physical properties of **8** were: m.p. 116-118°C; IR (mull)  $cm^{-1}$  3425 (OH), 1670 (carbonyl) and 1590 (aryl);  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  1.55 (d,  $J = 7$  Hz, 3,  $\alpha$ -CH<sub>3</sub>), 2.30 (s, 3, Ar-CH<sub>3</sub>), 3.72 (s, 6, Ar'-OCH<sub>3</sub>), 3.94 (s, 3, Ar-OCH<sub>3</sub>), 5.26 (q,  $J = 7$  Hz, 1,  $\alpha$ -H), 6.03 (s, 1, Ar-OH), 6.36 (s, 2, C<sub>3',5'</sub>-H), 6.93 (d,  $J = 8$  Hz, 1, C<sub>5</sub>-H), and 7.80 (m, 2, C<sub>2,6</sub>-H)  $^{13}C$ -NMR ( $CDCl_3$ )  $\delta$  18.3 ( $\alpha$ -CH<sub>3</sub>), 21.8 (Ar'-CH<sub>3</sub>), 55.7 (q, Ar'-OCH<sub>3</sub>), 55.9 (q, Ar-OCH<sub>3</sub>), 80.5 (d, C<sub>α</sub>), 105.7 (d, C<sub>3',5'</sub>), 111.1, 113.4, and 124.3 (d, C<sub>2,5,6</sub>), 127.8, 133.4, 146.0, 149.8, and 152.5 (s, aryl), and 192.9 (s, ArC=O); MS,  $m/e$  (%) 346 ( $M^+$ , 53), 195 (47), 168 (37), 167 (93), 151 (100), 109 (34), 107 (33), and 91 (33).

**1-(4'-Hydroxy-3'-methoxyphenyl)-2-(4"-methyl-2",6"-dimethoxyphenoxy)ethanol (1D).** A 69% yield of **1D** was obtained from a  $NaBH_4$  reduction of **7** using our standard procedure.<sup>3</sup> The physical properties of **1D** were: m.p. 99-101°C (ethyl ether); IR (mull)  $cm^{-1}$  3300-3475 (OH) and 1590 (aryl);  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  1.61 (broad s, removed with D<sub>2</sub>O wash, 1, ROH), 2.34 (s, 3, Ar'-CH<sub>3</sub>), 3.64 (d of d,  $J = 9$  and 10 Hz, 1, -CH-CH<sub>A</sub>H<sub>B</sub>-OAr"), 3.86 (s, 6, Ar"-OCH<sub>3</sub>), 3.88 (s, 3, Ar'-OCH<sub>3</sub>), 4.34 (d of d,  $J = 3$  and 10 Hz, 1, -CH-CH<sub>A</sub>H<sub>B</sub>-OAr"), 4.87 (d of d,  $J = 3$  and 9 Hz, 1, -CH-CH<sub>A</sub>H<sub>B</sub>-OAr"), 5.58 (s, exchangable, 1, ArOH), 6.42 (s, 2, Ar"-H), and 6.8-7.0 (m, 3, Ar'-H);  $^{13}C$ -NMR ( $CDCl_3$ )  $\delta$  21.8 (q, Ar"-CH<sub>3</sub>), 55.7 (q, Ar'-OCH<sub>3</sub>), 55.8 (q, Ar"-OCH<sub>3</sub>), 72.0 (d, C<sub>1</sub>) 79.9 (t, C<sub>2</sub>), 105.5 (d, C<sub>3",5"</sub>), 108.5, 113.8, and 119.0 (d, C<sub>2',5',6'</sub>), 131.0, 133.7, 133.9, 144.8, 146.2, and 152.3 (s, aryl-C); MS,  $m/e$  (%) 334 ( $M^+$ , 4), 182 (4), 168 (100), 167 (6), 166 (7), 153 (20), 137 (4), 107 (5), and 93 (6).

**1-(4'-Hydroxy-3'-methoxyphenyl)-2-(4"-methyl-2",6"-dimethoxyphenoxy)-1-propanol (1E).** A quantitative yield of **1E** was obtained from **8** using our standard  $NaBH_4$  reduction procedure.<sup>3</sup> The physical properties of **1E**, which was a mixture of erythro and threo isomers

and was an oil that solidified after several months, were the following: m.p. 80-100°C; IR (mull)  $\text{cm}^{-1}$  3100-3600 (OH) and 1600 (aryl);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.17 and 1.22 (d,  $J = 6$  Hz, 3,  $\text{C}_2\text{-CH}_3$ ), 2.34 (s, 3,  $\text{Ar}''\text{-CH}_3$ ), 3.86 (s, 6,  $\text{Ar}''\text{-OCH}_3$ ), 3.87 (s, 3,  $\text{Ar}'\text{-OCH}_3$ ), 3.4-5.0 (m, 3,  $\text{-CH-CH-OH}$ ), 5.64 and 5.69 (s, 1,  $\text{Ar}'\text{-OH}$ ), 6.43 (s, 2,  $\text{C}_3''$ ,  $5''\text{-H}$ ) and 6.6-7.0 (m, 3,  $\text{Ar}'\text{-H}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  13.3 and 17.5 (q,  $\text{C}_3$ ), 21.6 and 21.7 (q,  $\text{Ar}''\text{-CH}_3$ ), 56.0, 56.1, and 56.2 ( $\text{ArOCH}_3$ ), 73.4 and 78.8 (d,  $\text{C}_1$ ), 82.6 and 86.4 (d,  $\text{C}_2$ ), 106.7 (d,  $\text{C}_3''$ ,  $5''$ ), 110.0 and 111.1 (d,  $\text{C}_2$ ), 114.8 and 114.9 (d,  $\text{C}_5'$ ), 119.0 and 120.6 (d,  $\text{C}_6'$ ), 132.7, 133.3, 133.5, 133.7, 134.0, 135.4, 145.8, 146.3, 147.5, 153.1, and 153.8 (s, nonprotonated aryl carbons); MS,  $\text{m/e}$  (%) 348 ( $\text{M}^+$ , 2), 318 (2), 195 (6), 168 (100), 167 (5), 153 (11), 151 (4), 107 (4), and 65 (3).

**Quinonemethide 2C.** Quinonemethide 2C was prepared according to the method of Ralph and Young,<sup>12</sup> starting with model 1C.<sup>9</sup> A NMR spectrum of 2C in  $\text{CDCl}_3$  (yellow solution) showed a small amount of residual 1C and signals indicating a mixture of syn (S) and anti (A) isomers<sup>12</sup> in an approximate ratio of 2:1; signals ( $\delta$  values) were at 1.43, 1.63, and 1.65 (s,  $\text{CH}_3$ ), 3.70, 3.78, 3.83, and 3.88 (s,  $\text{OCH}_3$ ), 5.61 and 5.64 (s,  $\text{C}_6\text{H}$ ), 6.36 and 6.45 (s, syringyl aryl protons), 6.20 (d,  $J = 2\text{H}_z$ ,  $\text{C}_2\text{AH}$ ), 6.5 (weak, ?), 6.7-7.1 (m, aryl), 7.44 (d,  $J = 2\text{H}_z$ ,  $\text{C}_2\text{SH}$ ), and 8.2 (dd,  $J = 2, 10 \text{H}_z$ ,  $\text{C}_6\text{AH}$ ).

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