

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

**IPC TECHNICAL PAPER SERIES
NUMBER 165**

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

DONALD R. DIMMEL AND LOIS F. PERRY

OCTOBER, 1985

**Property of
GEORGIA-PACIFIC CORPORATION
Technical Information Center
Atlanta, Georgia**

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

Donald R. Dimmel and Lois F. Perry
The Institute of Paper Chemistry
P.O. Box 1039, Appleton, Wisconsin 54912

ABSTRACT

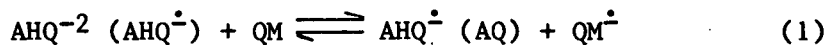
The reactions of five β -aryl ether lignin model dimers with anthrahydroquinone (AHQ) analogs have been studied in anticipation of verifying or denying the existence of single electron transfer (SET) and adduct mechanisms. The models and AHQ analogs have bulky substituents strategically located in positions which would inhibit possible adduct reactions but not 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. Placing methyl groups on the β -carbon of the models favored model fragmentation reactions by NaOH. The β -methyl group may be promoting fragmentation reaction rates and/or retarding the rates of competing side reactions, such as vinyl ether generation.

INTRODUCTION

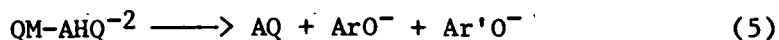
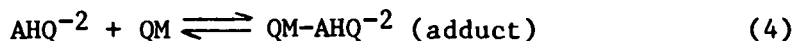
The high efficiencies of AQ-based pulping systems may be related to a unique chemistry, namely, single electron transfer (SET) reactions between anthrahydroquinone (AHQ) species and lignin quinonemethides (QMs).¹ Previous electrochemical studies have shown that such chemistry exists between AHQ radical anions (AHQ⁻) and lignin-model QMs in organic solvents at room temperature.² This report deals with an attempt to verify or reject

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.³

The SET mechanism involves transfer of an electron from AHQ⁻² (or AHQ^{•-}) to a quinonemethide, followed by fragmentation of the QM^{•-} intermediate to phenolic ions and radicals, and finally a second electron transfer step (Eq. 1-3).



Our work is also related to establishing the validity of the "adduct" mechanism theory, the other major mechanism proposed for explaining AHQ-induced delignification reactions.¹ The adduct mechanism involves bond formation between C₉ of AHQ⁻² and C_α 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 C_α of the QM and C₉ of the AHQ⁻². The approximately 1.5 Å bond distance for the C_α-C₉ bond of the adduct imposes a substantial steric strain between the quaternary substituted C₉-carbon and the C_β-substituents.¹ On the other hand, SET reactions are known to proceed at astonishingly fast rates even across distances of 10 Å or greater.⁴ The SET reaction for AHQ⁻² and a lignin model (or lignin itself) probably will not require a specific orientation, as in the adduct case; transfer of an electron from the side ring of the AHQ⁻² to the ring proton of the QM is possible (Fig. 1).

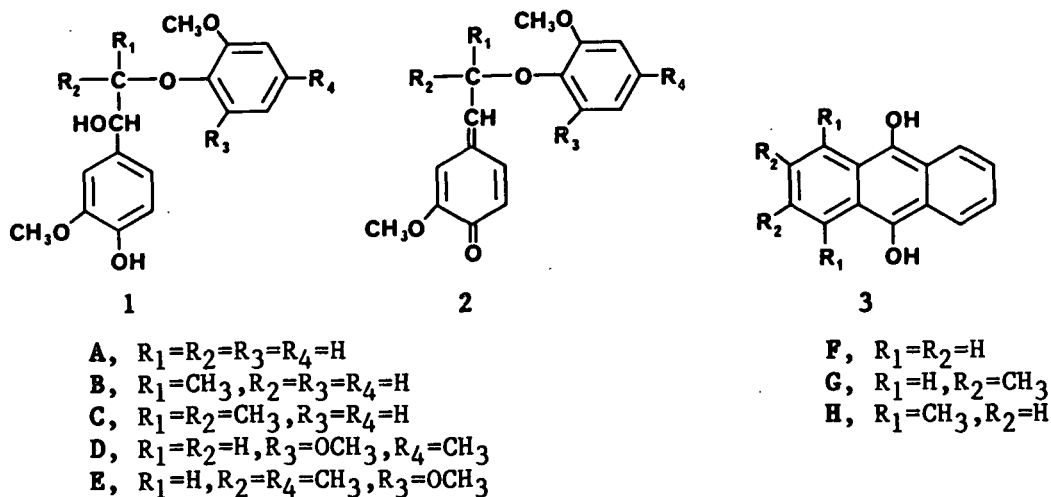
Consequently, the steric requirements for interaction of AHQ⁻² with QM are substantially different for the adduct and SET mechanisms. These differences may or may not be apparent when comparing rates of reactions between models and AHQ derivatives having varying degrees of "bulkiness" because the QM/AHQ interactive step may or may not be the rate determining step. For most simple systems, production of QMs appears to be the rate determining step in lignin model fragmentation reactions.^{3,5}

The relative energies for the QM/AHQ reactions and QM formation reactions are not known; however, Fig. 2 presents two possibilities for adduct reactions. The energy required to produce a QM may be significantly larger than the energy needed for subsequent steps (case A), and thus steric effect differences would not be observed from reaction rates of different AHQ derivatives with the same model. With moderate relative energy requirements for QM production, steric effects could possibly be observed (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⁻² 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 β -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, β -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 polarographic peak potentials,⁶ the methylated AHQ⁻² compounds should be slightly better than AHQ⁻² 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.

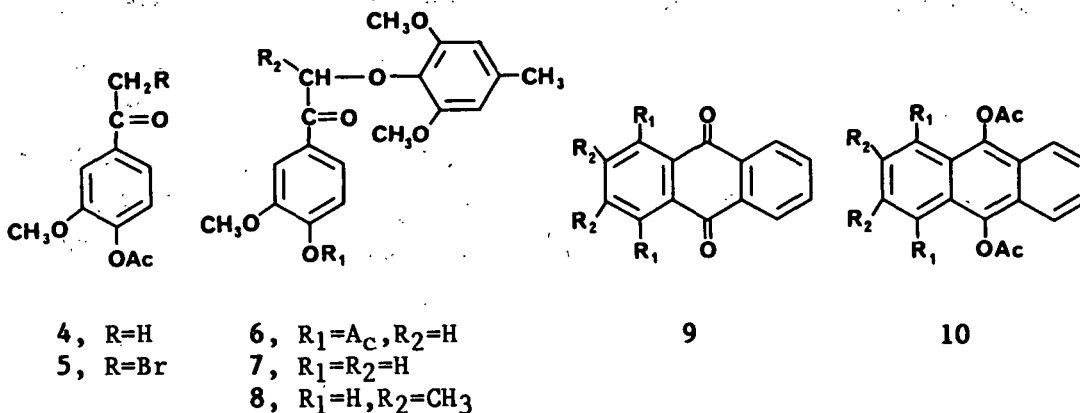
RESULTS

Synthesis and Reagent Generation

The syntheses of models 1A-C have already been reported.⁷ Model 1D was synthesized by the conversion of 4 to 5 to 6 to 7 and then NaBH₄ reduction of 7. Model 1E was synthesized by methylation of 7 to 8, followed by NaBH₄ reduction.

Since AHQ is unstable in air, several methods were examined to generate AHQ⁻² in situ in the reaction mixtures. One method involved zinc reduction of Aqs 9F-H in acetic acid to give diacetates 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 used to generate the AHQ⁻² compounds involved warming a solution of the lignin model compound, NaOH, AQ, and a reducing agent, either sodium dithionite or glucose, at 60°C for 30 min prior to reaction at 150°C. During the prewarming, most of the AQ should be converted to AHQ and the reducing agent should be consumed. If not consumed, the reducing agent may cause model fragmentation at the 150° reaction conditions. Separate experiments⁸ showed that glucose is more effective than dithionite for reduction of AQ to AHQ and that the dimethyl anthraquinones (**9G** and **H**) were not reduced as completely as AQ.

Table 1 presents some degradation results of model **1B** using different methods of AHQ⁻² generation. In general, the best fragmentation yields were with AQ/glucose using > 1 equiv. of reagent per model. With only 1 equiv. of AQ and glucose the yield was somewhat low, probably because the alkaline conditions led to destruction of some of the glucose before it had a chance to reduce the AQ. The data of Table 1 indicate that AQ/dithionite and AHQ-diAc/NaOH procedures are reasonable for model **1B** and that in many cases the AHQ is completely consumed (or not regenerated

by the reducing agent), since the typical red color of AHQ^{-2} is absent.

TABLE 1

Degradation of Model IB Using Different Methods of AHQ Generation^a

NaOH (equivalents)	AHQ Precursor (equivalents)	Reducing Agent (equivalents)	Guaiacol Yield, (%)
30	AHQ d1Ac (1)	--	48.7, 56.0
30	AHQ d1Ac (3)	--	54.0 ^b
30	AQ (1)	Na ₂ S ₂ O ₄ (1)	46.8, 51.9
30	--	Na ₂ S ₂ O ₄ (1)	19.3
30	AQ (1)	Glucose (1)	45.4, 39.7
30	--	Glucose (1)	7.2
50	AQ (1)	Glucose (3)	68.0
50	AQ (3)	Glucose (3)	57.8
50	AQ (3)	Glucose (5)	60.2 ^b
50	--	Glucose (2)	13.2

^a150°C for 20 min with a 30 min prewarm at 60°C.

^bRed color present when the bomb was opened.

A problem associated with using AQ/glucose or AQ/dithionite 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.³ Electrochemical studies indicate that AQ is easier to reduce than a lignin model QM.² 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; the dominant partners in reactions with the QMs will then involve AHQ ions and

not reducing agents. In general, AQ and reducing agent were used in equivalent amounts and in a large excess relative to the model.

Analyses

During the course of this study several different methods of phenol analysis were tried. 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 to a deuterated version of the phenol, added as an internal standard.⁹ While the method works well, it requires calibration of a set of standards with each analysis, and the GC-MS was not always available for our use. The method employed underivatized, as well as methylated³ phenols, and addition of the internal standard either before or after the reaction. Later studies employed derivatization by methylation, *p*-isopropyl phenol as an internal standard (IS) after reaction, and GC analysis.³

Peculiarities in Model Degradations

Degradations of our simplest, least hindered model 1A in the presence of alkali and AHQ at 150°C gave fragmentation yields of guaiacol (11) which depended on whether guaiacol-3,5-d₂ 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 (presumably polymerization reactions) of 4-vinylguaiacol (13), the other fragment produced in the degradations of 1A. The yields of 4-vinylguaiacol were always much less than that of guaiacol; in theory, the yields should be the same.

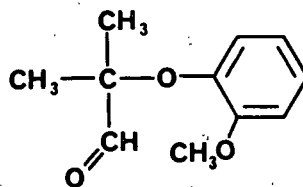
Stability checks showed that the combination of 4-vinylguaiacol and AHQ/AQ causes guaiacol to be lost under degradation conditions (150°C, aqueous alkali). Apparently, the polymerization of 4-vinylguaiacol (possibly radically induced by AHQ species) incorporates some guaiacol. Model 1A degradations done in the presence of deuterated guaiacol IS probably consume the IS in preference to liberated guaiacol because of the initial large

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 β -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-methylsyringyl (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 β,β -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 typical alkali induced fragmentation pathway (Scheme 1, path a) is favored due to relief of steric strain and/or that quinonemethide formation (Scheme 1, path b) is retarded due to severe internal strain. The quinonemethide (2C) is a prerequisite for additive induced fragmentation reactions.

Another indication of the strain which exists in model 1C is its behavior during GC analysis. The GC-MS of a pure sample of 1C shows three signals, which correspond to 1C, guaiacol, and a component of mass 194 (and an intense m/e 165 MS signal) which appears to be the aldehyde 17. Guaiacol and 17 could arise by a rupture of the C_1-C_α bond. A degradation of model 1C in $D_2O/NaOH$ at $100^\circ C$ (a temperature where ArH/D exchange is slow¹⁰) gave nondeuterated guaiacol; this indicates that the guaiacol liberated during reaction came from the β -aryl ring and not the other ring.



17

The peculiarities associated with the degradations of the non-methyl and β, β -dimethyl models 1A and 1C in the presence of AHQ prevented a direct comparison of additive effects on 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 reactant was examined with several models and several solvent systems. Our most consistent results involved the reactions of the mono- β -methyl guaiacyl model (1B); an example is shown in Table 3. 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.⁸

TABLE 3

Guaiacol Yields from Degradations of Model 1B^a

Additive	Guaiacol Yield, % ^{b,c}	
	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

^{a,c}See Table 2 footnotes.

^bAnalysis by SIM GC-MS of methylated samples containing guaiacol-d₂ internal standard and using standard response curves.

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.^{3,11} With the mono- β -methyl syringyl model (1E) the glucose effect was quite large and approached that of the AHQ additives (Table 4).

TABLE 4

4-Methylsyringyl Yields from Degradations of Model 1E^a

Additive	4-Methylsyringyl Yield, % ^b		
	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

^{a,b}See Table 2 footnotes.

Degradation reactions of the simple β -4-methylsyringyl model (1D) in water at 150°C, with analysis by methylation and GC, gave the results shown in Table 5. 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 5

4-Methylsyringyl Yields from Degradations of Model 1D^a

Additive	4-Methylsyringyl Yield, % ^{b,c}	
	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

^{a,b,c}See Table 2 footnotes.

While the absolute values of the yields varied with these changes, the overwhelming conclusion was that both methylated AHQ analogs caused approximately the same degree of fragmentation as AHQ, that AHQ and its analogs are more effective than glucose, and that alkali alone is poor for fragmenting the model.

Multiple experiments were done with all the models. The data in the tables represent only about a tenth of the experiments performed. For example, while the data in Table 4 may imply that 1,4-dimethyl AHQ is slightly inferior to the other AHQ analogs for fragmenting model 1E in water, the 1,4-dimethyl outperformed the 2,3-dimethyl 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 equalize 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,¹² and high levels of dioxane cause phase separation.¹³

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 -phenoxy leaving group and the level of base used.³ Another factor appears to be the nature of the side chain on the model - whether C_{β} is protonated or methylated. The more C_{β} -methyl groups present, the more prone the model is to fragmentation in NaOH. This is seen by comparing the "control" yields in Tables 3 and 4 and the data of Table 6.

Several explanations of the C_{β} -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 β -aryl ether cleavages occur partially by an S_N1 mechanism, methyl groups at C_{β} would help stabilize the resulting C_{β} -cation. Finally, methyl groups at C_{β} could alter the balance between fragmentation and competing vinyl ether product

formation (Scheme 2). Analysis of product mixtures showed that vinyl ethers were produced in significant amounts in NaOH model degradations and only low levels in the NaOH/additive degradations.

TABLE 6

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

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

Vinyl ether formation is blocked when there are two C β -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 β -H abstraction due to a steric hindrance effect, and/or (3) decreasing the acidity of C β -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 β -methyl model 1E (see Tables 4 and 5). The most probable reason for this is that there is a higher concentration of quinonemethide with which to react with AHQ⁻² ions in the non-C β -methyl case; the quinonemethide will be less crowded here than in the C β -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 reaction rates due to QM formation has been observed in a related study.³ 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_β 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_β 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.⁶

EXPERIMENTAL

The equipment,¹⁴ guaiacol analysis by GC-MS SIMS with

guaiacol-3,5-d₂ IS,⁹ guaiacol analysis by methylation/GC with *p*-isopropylphenol IS,³ and model degradation procedures³ have been previously described. Analogous procedures^{3,9} for the preparation of 4-methylsyringyl-3,5-d₂ IS and for the analysis of 4-methylsyringyl were employed. The syntheses of compounds 1A-C have already been reported.⁷ Melting points are corrected.

4-Acetoxy-3-methoxy- α -(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.¹⁵ A sample of 4-methylsyringyl (2,6-dimethoxy-4-methylphenol) (15) was prepared (70% yield) by an amalgamated zinc reduction¹⁶ of syringaldehyde; the physical properties of 15 were: bp 92-109°C/0.5 mm; IR (mull) cm⁻¹ 3475 (OH) and 1610 (aryl); NMR (DMSO-d₆) δ 2.21 (s, 3, ArCH₃), 3.72 (s, 6, OCH₃), 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- α -bromoacetophenone (5),¹⁷ 5.1 g (30 mmol) of 4-methylsyringyl (15), 2.7 g KI, and 5.5 g K₂CO₃ in 70 mL of freshly distilled (over KMnO₄) acetone was refluxed for 165 min. The mixture was decreased to 25 mL by distillation, diluted with 50 mL H₂O, and extracted with diethyl ether. The combined ether extracts were washed with 0.5N NaOH, water, and brine, dried (Na₂SO₄) 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: ¹H-NMR (CDCl₃) δ 2.29 (s, 6, ArCH₃ and acetate CH₃), 3.76 (s, 6, ArOCH₃), 3.86 (s, 3, ArOCH₃), 5.10 (s, 2, ArCOCH₂), 6.37 (s, 2, syringyl aryl), 7.09 (d, J = 8 Hz, 1, C₅-H), and 7.5-7.7 (m, 2, C₂ and C₆ protons).

4-Hydroxy-3-methoxy- α -(4'-methyl-2',6'-dimethoxyphenoxy) acetophenone (7). A mixture of 9.0 g of 6 dissolved in 100 mL methanol and 30 mL of 1N sodium methoxide in methanol was gently refluxed for 3 hr, cooled, diluted with 300 mL H₂O, acidified to pH 2 with concentrated HCl, and extracted with diethyl ether. The ether

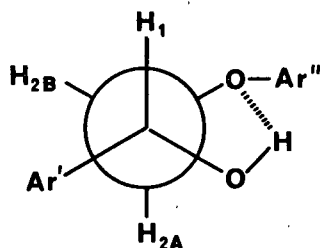
extracts were washed with water, diluted with ethanol and evaporated to give 6.3 g of solid: m.p. 117.0-8.5°C (ethanol-water); IR (mull) cm^{-1} 3410 (OH), 1670 (C=O), and 1595 (aryl); $^1\text{H-NMR}$ (d_6 -DMSO) δ 2.26 (s, 3, Ar- CH_3), 3.73 (s, 6, Ar'OCH $_3$), 3.84 (s, 3, ArOCH $_3$), 5.00 (s, 2, ArCOCH $_2$), 6.50 (s, 2, aryl'), 6.88 (d, J = 8 Hz, 1, C $_5$ -H), 7.53 (s, 1, C $_2$ -H), 7.58 (d, 1, C $_6$ -H), and 10.04 (s, 1, ArOH); $^{13}\text{C-NMR}$ (d_6 -DMSO) PPM 21.3 (q, ArCH $_3$), 55.5 and 55.7 (q, ArOCH $_3$, Ar'OCH $_3$), 74.4 (t, ArCOCH $_2$), 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- α -(4'-methyl-2',6'-dimethoxyphenoxy)- α -methylacetophenone (8). A 47% yield after a chromatography of 8 was obtained from 7 using our standard alkylation procedure.³ The physical properties of 8 were: m.p. 116-118°C; IR (mull) cm^{-1} 3425 (OH), 1670 (carbonyl) and 1590 (aryl); $^1\text{H-NMR}$ (CDCl_3) δ 1.55 (d, 3, α -CH $_3$), 2.30 (s, 3, Ar-CH $_3$), 3.72 (s, 6, Ar'-OCH $_3$), 3.94 (s, 3, Ar-OCH $_3$), 5.26 (q, 1, α -H), 6.03 (s, 1, Ar-OH), 6.36 (s, 2, C $_3'$, $_5'$ -H), 6.93 (d, J = 8 Hz, 1, C $_5$ -H), and 7.80 (m, 2, C $_2$, $_6$ -H) $^{13}\text{C-NMR}$ (CDCl_3) PPM 18.3 and 21.8 (α -CH $_3$, Ar'-CH $_3$), 55.7 (q, Ar'-OCH $_3$), 55.9 (q, Ar-OCH $_3$), 80.5 (d, C $_{\alpha}$), 105.7 (d, C $_3'$, $_5'$), 111.1, 113.4, and 124.3 (d, C $_2$, $_5$, $_6$), 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)-1-ethanol (1D). A 69% yield of 1D was obtained from a NaBH_4 reduction of 7 using our standard procedure.³ The physical properties of 1D were: m.p. 99-101°C (ethyl ether); IR (mull) cm^{-1} 3300-3475 (OH) and 1590 (aryl); $^1\text{H-NMR}$ (CDCl_3) δ 1.61 (broad s, removed with D_2O wash, 1, ROH), 2.34 (s, 3, Ar'-CH $_3$), 3.64 (d of d, J = 10 and 10 Hz, 1, -CH-CH $_A$ H $_B$ -OAr''), 3.86 (s, 6, Ar''-OCH $_3$), 3.88 (s, 3, Ar'-OCH $_3$), 4.34 (d of d, J = 3 and 10 Hz, 1, -CH-CH $_A$ H $_B$ -OAr''), 4.87 (d of d, J = 3 and 10 Hz, 1, -CH-CH $_A$ H $_B$ -OAr''), 5.58 (s, exchangeable, 1, ArOH), 6.42 (s, 2, Ar''-H), and 6.8-7.0 (m, 3,

Ar'-H); ^{13}C -NMR (CDCl_3) PPM 21.8 (q, Ar''-CH₃), 55.7 (q, Ar'-OCH₃), 55.8 (q, Ar''-OCH₃), 72.0 (d, C₁) 79.9 (t, C₂), 105.5 (d, C_{3''}, 5''), 108.5, 113.8, and 119.0 (d, C_{2'}, 5', 6'), 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).

The ^1H -NMR data suggest that the molecule has a fairly rigid structure about C₁ and C₂; a Newman projection of C₁-C₂ bond, which fits the NMR data, is shown below:



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.³ The physical properties of 1E, which is 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) cm^{-1} 3100-3600 (OH) and 1600 (aryl); ^1H -NMR (CDCl_3) δ 1.17 and 1.22 (d, J = 6 Hz, 3, C₂-CH₃), 2.34 (s, 3, Ar''-CH₃), 3.86 (s, 6, Ar''-OCH₃), 3.87 (s, 3, Ar'-OCH₃), 3.4-5.0 (m, 3, -CH-CH-OH), 5.64 and 5.69 (s, 1, Ar'-OH), 6.43 (s, 2, C_{3''}, 5''-H) and 6.6-7.0 (m, 3, Ar'-H); ^{13}C -NMR (CDCl_3) PPM 13.3 and 17.5 (q, C₃), 21.6 and 21.7 (q, Ar''-CH₃), 56.0, 56.1, and 56.2 (ArOCH₃), 73.4 and 78.8 (d, C₁), 82.6 and 86.4 (d, C₂), 106.7 (d, C_{3''}, 5''), 110.0 and 111.1 (d, C_{2'}), 114.8 and 114.9 (d, C_{5'}), 119.0 and 120.6 (d, 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, m/e (%) 348 (M, 2), 318 (2), 195 (6), 168 (100), 167 (5), 153 (11), 151 (4), 107 (4), and 65 (3).

ACKNOWLEDGMENTS

We are grateful to Patrick Apfeld for providing us with a sample of model 1D, to Donaline Shepard for some of the preliminary degradation work, and to Earl Malcolm for helpful discussions and moral support.

REFERENCES

1. D. R. Dimmel, J. Wood Chem. Technol., 5, 1 (1985).
2. D. R. Dimmel and L. F. Perry, J. Wood Chem. Technol., 5, 15 (1985).
3. D. R. Dimmel and L. F. Perry, submitted for publication.
4. J. R. Miller, L. T. Calcaterra, and G. L. Closs, J. Amer. Chem. Soc., 106, 3047 (1984) and Chem. Eng. News, April 16, 1984, p. 6.
5. G. E. Miksche, Acta Chem. Scand., 26, 4137 (1972).
6. R. C. Eckert and L. W. Amos, J. Wood Chem. Technol., 2, 57 (1982) and Canadian Wood Chemistry Symp., Niagara Falls, Ontario, September 13-15, 1982, The Extended Abstracts, p. 7.
7. D. R. Dimmel and D. Shepard, J. Wood Chem. Technol., 2, 297 (1982).
8. C. Storgard-Envall and D. R. Dimmel, to be published.
9. D. R. Dimmel, D. Shepard, and L. F. Perry, J. Wood Chem. Technol., 5, 229 (1985).
10. D. A. Smith and D. R. Dimmel, J. Wood Chem. Technol., 4, 75 (1984).
11. (a) L. J. Wright and T. J. Fullerton, J. Wood Chem. Technol., 4, 61 (1984); (b) T. J. Fullerton and L. J. Wright, Tappi, 67(3), 78 (1984); (c) T. J. Fullerton and A. L. Wilkins, J. Wood Chem. Technol., 5, 189 (1985).
12. D. R. Dimmel, D. Shepard, L. F. Perry, T. Joachimides, T. J. McDonough, and E. W. Malcolm, J. Wood Chem. Technol., 5, 229 (1985).
13. J. R. Obst, Holzforschung, 37, 23 (1983).
14. D. R. Dimmel, D. Shepard, and T. A. Brown, J. Wood Chem. Technol., 1, 123 (1981).
15. G. E. Miksche, Acta Chem. Scand., 27, 1355 (1973).
16. R. Schwartz and H. Hering, Org. Syn., IV, 203 (1963).
17. H. Erdtman and B. Leopold, Acta Chem. Scand., 3, 1358 (1949).

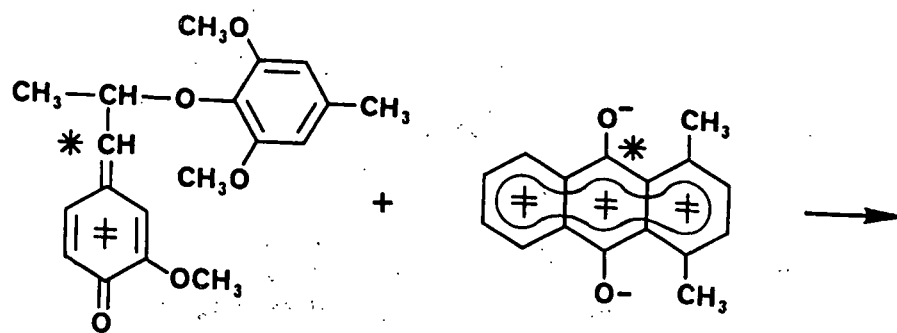


Figure 1. Sites of reaction between a hindered lignin model QM and 1,4-dimethylantrahydroquinone dianion: *, adduct mechanism; ‡, SET mechanism.

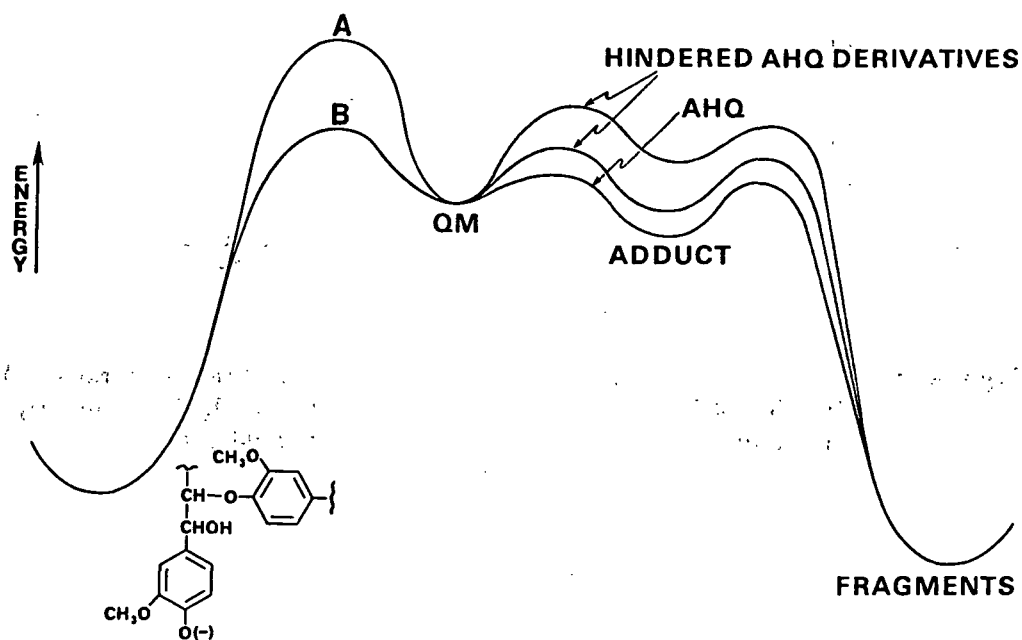


Figure 2. Hypothetical energy profiles for the reaction of AHQ analogs with a lignin quinonemethide via an adduct mechanism.

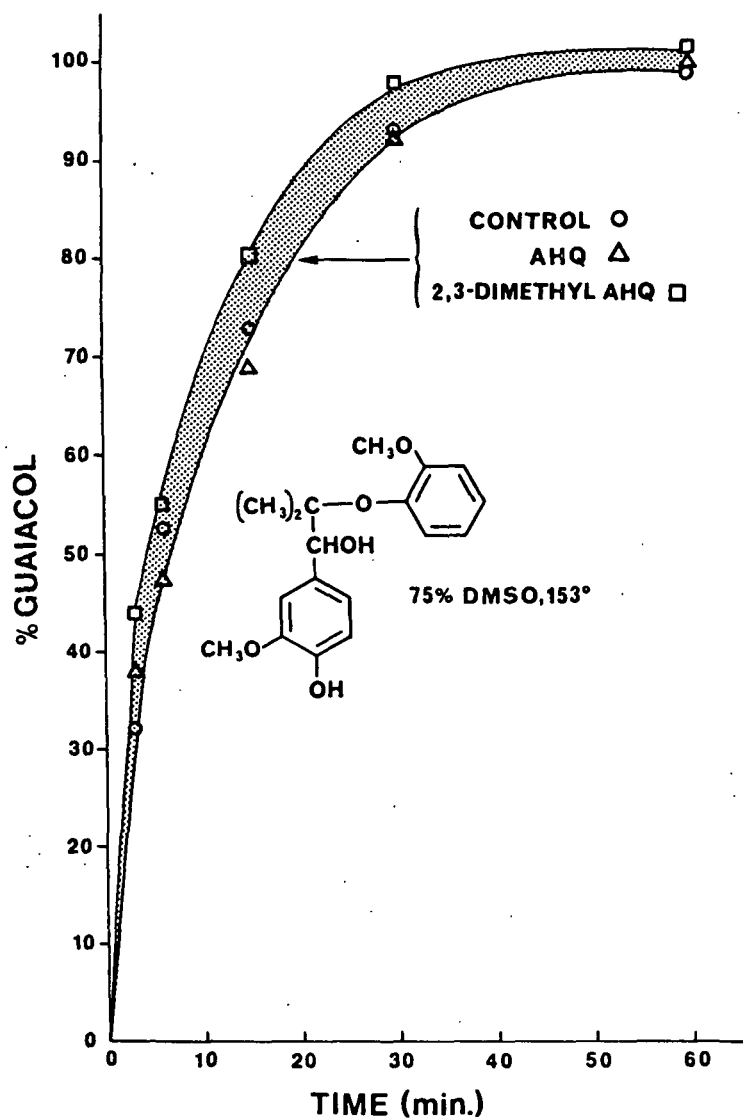


Figure 3. The variation in guaiacol yield with time for model 1C in 75% DMSO at 153° in the presence of hydroxide, O, and additives: AHQ, △; 2,3-dimethyl-AHQ, □.

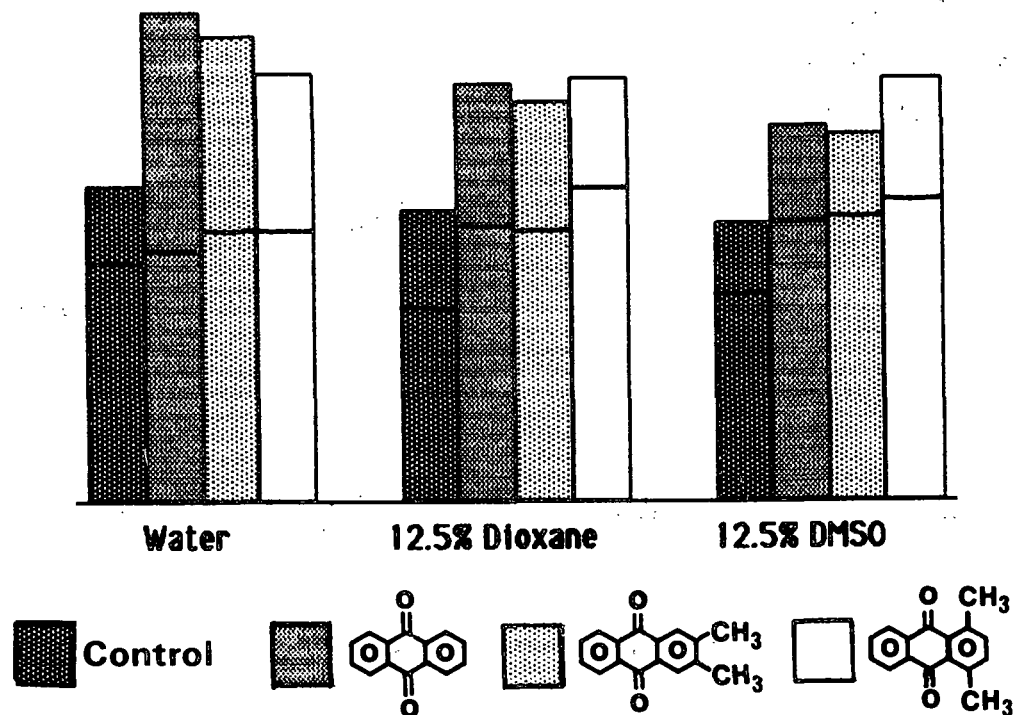
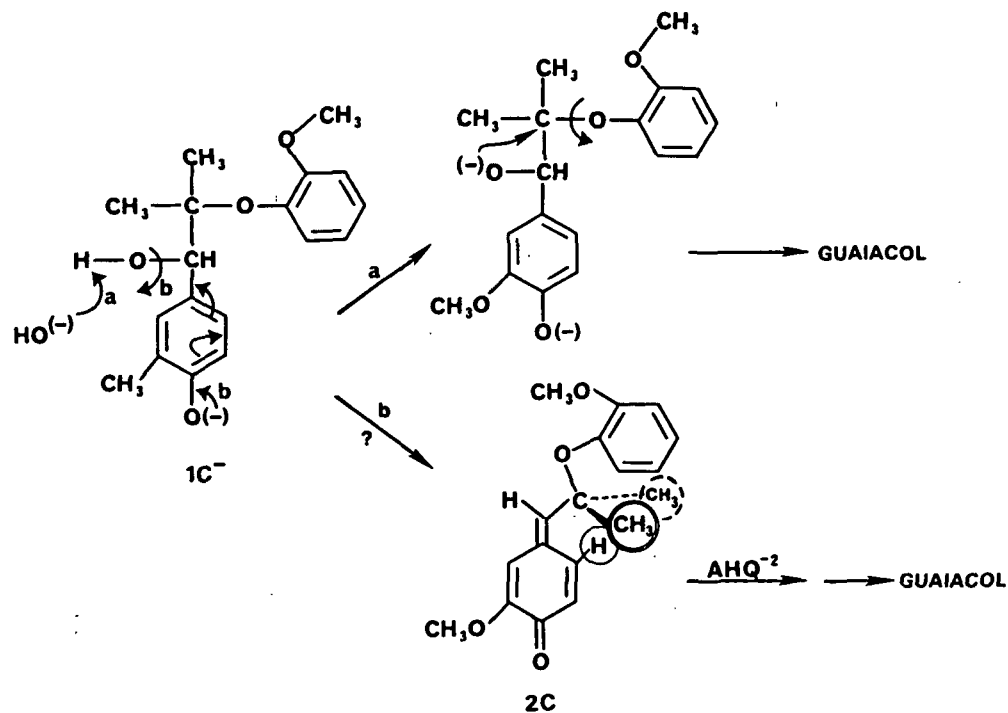
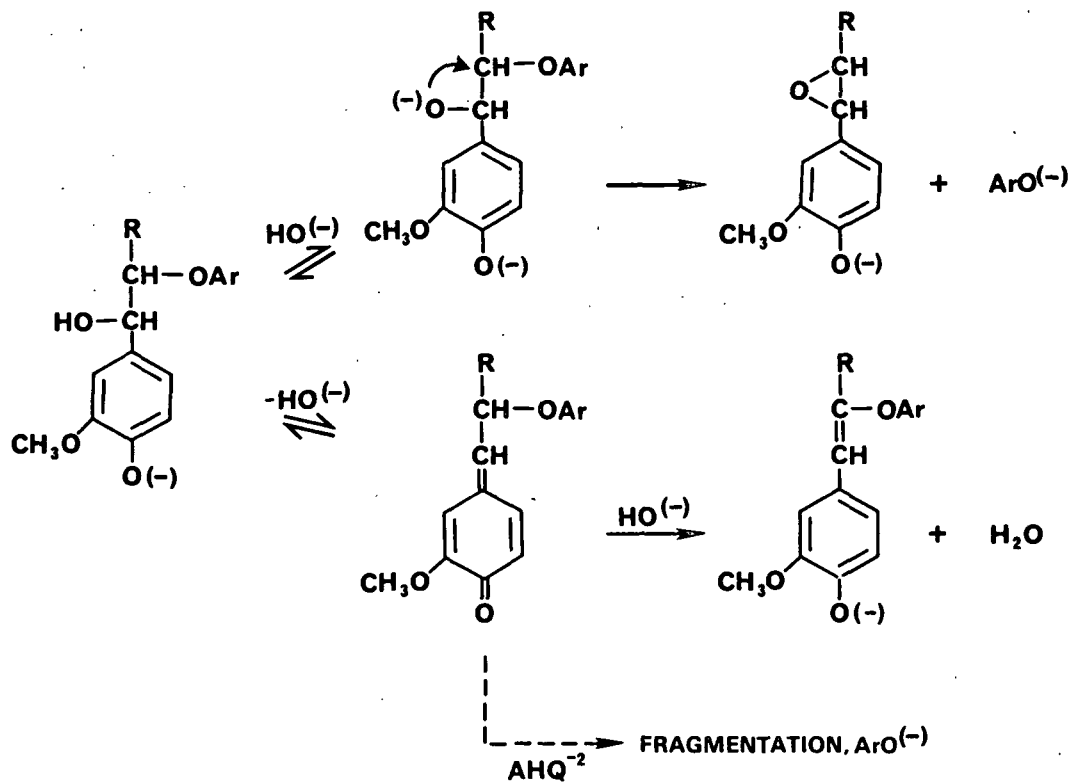


Figure 4. Relative comparison of 4-methylsyringyl (15) yields from degradations of model 1E at 150°C for 30 min (mid-line) and 60 min (top) as a function of solvent composition. All runs have 5 equiv. of glucose and 25 equiv. of NaOH per model and all but the control have 5 equiv. of the indicated additives.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



Scheme 1. Possible Fragmentation Reactions of Model 1C



Scheme 2. Competing Reactions of the Lignin Model Compounds

IPC TECH. Paper Series #165

Electron Transfer Reactions in
Pulping Systems (111): A Study
of Steric Effects in Lignin
Model/AQ Reactions.

IPC TECH. Paper Series #165

Electron Transfer Reactions in Pulping
Systems (111): A Study of Steric
Effects in Lignin Model/AQ Reactions.

**GEORGIA-PACIFIC
CORPORATION
ATLANTA, GEORGIA**