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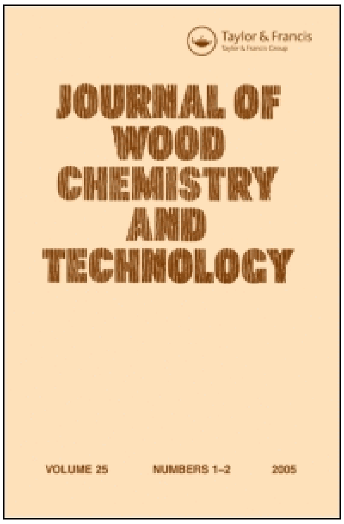

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# Structural/Reactivity Studies (II): Reactions of Lignin Model Compounds with Pulping Additives

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 6(4), 565-590 (1986)

# STRUCTURAL/REACTIVITY STUDIES (II): REACTIONS OF LIGNIN MODEL COMPOUNDS WITH PULPING ADDITIVES

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## ABSTRACT

Lignin model compounds, capable of forming quinonemethides and having different substituents on the quinonemethide (A) rings and β-aryl ether (B) rings, have been degraded under a variety of conditions in the presence of NaOH (soda), NaOH/$Na_2S$ (kraft), NaOH/glucose, and NaOH/AHQ (soda/AQ). Substituent changes on ring B had no effect on the extent of model fragmentation in the presence of excess AHQ and NaSH. Substituent changes on ring A had large effects on fragmentation under soda/AQ and kraft conditions. These substituent-reactivity relationships indicate that the slow step in the mechanism for model fragmentation under soda/AQ and kraft conditions is quinonemethide formation. Conditions aimed at demonstrating the existence of electron-transfer fragmentation of the model compounds gave results which were inconclusive, but demonstrated that equilibrium reactions between quinonemethide intermediates exist.

## INTRODUCTION

Single electron transfer (SET) reactions appear to offer a way to remove lignin from wood.[1] We are studying ways to demonstrate the importance of these reactions in anthraquinone (AQ) pulping systems and to utilize this chemistry to achieve favorable pulping results. Scheme I presents a mechanism by which SET reactions between anthrahydroquinone (AHQ) species and lignin quinonemethide (QM) species can lead to lignin bond ruptures (and thus delignification).

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The reactions outlined in Scheme I have been verified by room temperature electrochemical studies of lignin model QMs in organic solvents.[2]

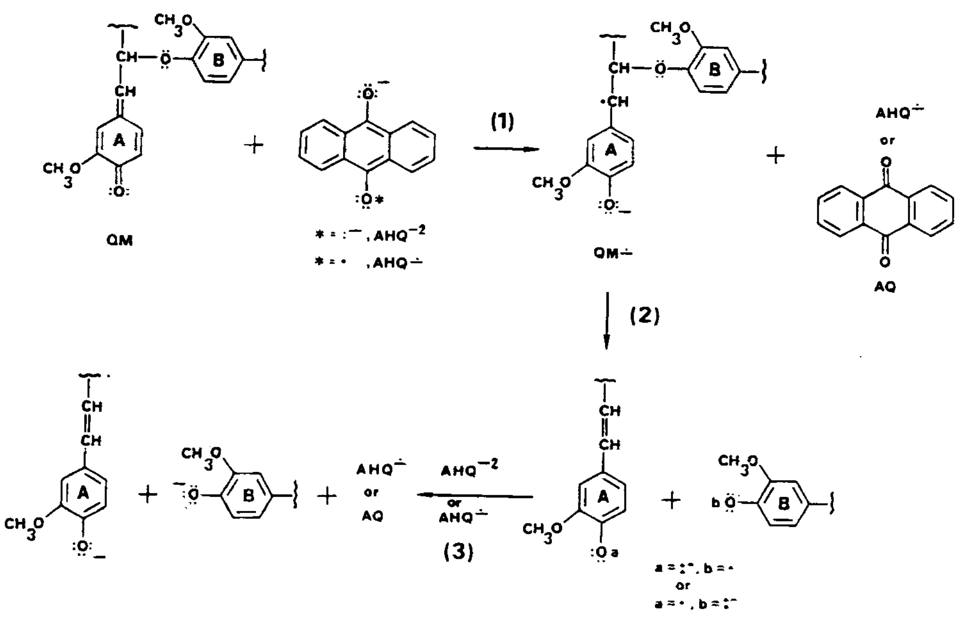
The SET mechanism predicts that a phenolate radical and ion will be produced from the fragmentation of the $QM^{\dot{-}}$ intermediate (step 2). The specific $QM^{\dot{-}}$ structure shown in Scheme I probably represents the most stable of several possible resonance forms for the $QM^{\dot{-}}$ intermediate. A homolytic, concerted cleavage of the β-aryl ether bond of the $QM^{\dot{-}}$ intermediate would produce a B ring radical and an A ring ion; heterolytic cleavage would produce a B ring anion and a $C_\beta$-cation, which upon electron shifts, would give an A ring radical. This latter mode of cleavage could also be concerted.

In contrast to this "radical" view of AHQ induced delignification chemistry, Scheme II offers a generally accepted "ionic" mechanism. Here $AHQ^{-2}$ adds to the α-carbon of a lignin QM to give an "adduct"; in a subsequent step, the adduct fragments to AQ and two phenolate ions.[3-6] This chemistry is analogous to some of the ionic mechanisms proposed for soda and kraft pulping systems.[7]

## MECHANISM DIFFERENTIATION

A key difference between the adduct and SET mechanisms of delignification is that the former produces only phenolate ion fragments, while the latter gives some phenolate radical fragments. If rupture of the β-aryl ether bonds is the slow step in delignification, the SET and adduct mechanisms predict that substitutent types on the aromatic fragments could have large effects on degradation rates. Phenolate ions, as produced in the adduct mechanism, are electron-rich species and thus are stabilized by electron-withdrawing ring substituents.[8] Phenolate radicals (SET mechanism) are electron-poor species and are therefore stabilized by electron-releasing ring substituents.[8]

Simple fragmentations of lignin model compounds are, however, multistep reactions, of which the fragmentation steps may not be

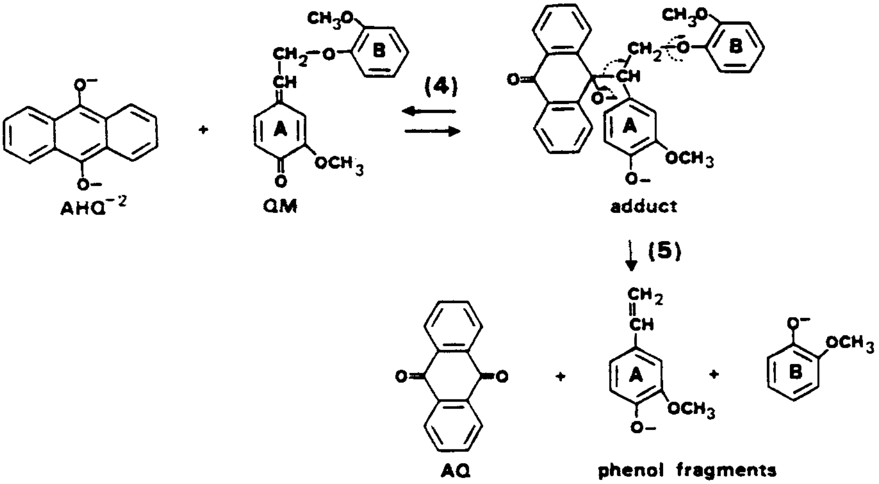


SCHEME I

Delignification via AHQ-Induced SET Reactions

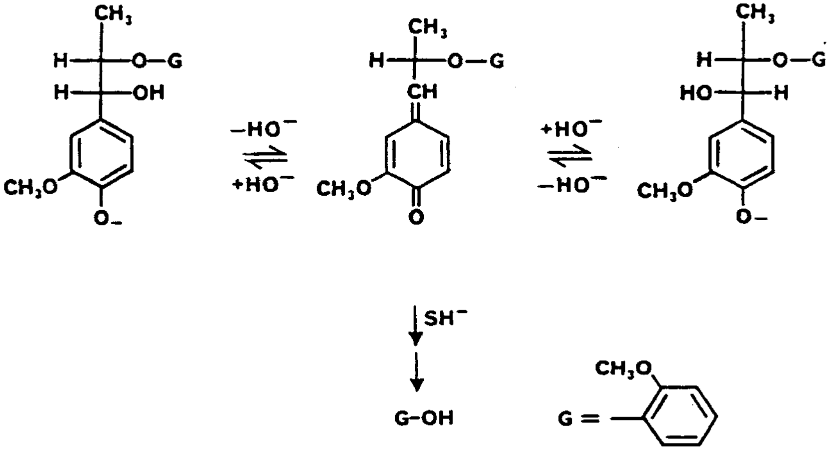
the slow steps in the mechanisms. In fact, quinonemethide generation is probably the slow step in NaSH-induced lignin model fragmentation reactions.[9] Miksche has shown that the rate of isomerization of model diastereomers is practically the same as the rate of guaiacol (G-OH) produced when either diastereomer is subjected to kraft pulping conditions (Scheme III). These data suggest that the difficult step in the isomerization, namely generation of the QM, is also the most difficult step in the multistep reactions leading to fragmentation of substrates.

Miksche's very interesting data leave some unanswered questions. For example, why was the rate of production of guaiacol from the erythro isomer only about 1/2 that of the



SCHEME II

Delignification via AHQ Adduct Reactions



SCHEME III

Model Isomerization and Fragmentation by Miksche[9] threo isomer? Also, why was the rate of guaiacol production roughly 40% greater than isomerization from the erythro isomer, but 20% less from the threo isomer? Miksche's study did not try to define the relative rates of the various steps. Quinonemethide formation may be significantly slower or roughly comparable to subsequent steps.

Using kinetic and competitive experiments with lignin model compounds, Gierer and Ljunggren have defined some relative rates of reactions involving quinonemethides.[10] In addition, there is evidence that $AHQ^{-2}$ reacts faster with QMs than does NaSH.[11] Although not a QM reaction, fragmentation of β-aryl ether bonds by α-$O^-$ assistance appears to be a slow reaction relative to the various QM reactions. [Further verification of this statement is part of this present study.] Figure 1 attempts to tie all of this information together in a hypothetical energy diagram.

The diagram, which relates only to α-hydroxy-β-aryl ether lignin units, indicates that the reaction options for a soda pulping system are poor, consisting of a high energy fragmentation pathway and numerous undesirable by-product pathways (two vinyl ether generation reactions and condensation reactions). A good pulping additive, such as $SH^-$ or $AHQ^{-2}$, provides a low energy route to fragmentation (delignification) which supercedes many of the undesirable reactions.

If the picture presented above is correct, studying the chemistry of additive induced delignification is a very complicated endeavor. Specifically, how do we define the chemisty of QM-$AHQ^{-2}$ interactions under pulping conditions if the reactions of importance come after the rate-determining step, namely QM generation? Substituent effects, in combination with competitive model degradation in the presence of limited amounts of additives, could possibly provide the answer; the theory behind this approach will be presented in a later section.

In this study, lignin model compounds with different ring A and ring B substituents were reacted in the presence of various pulping additives. Our goal was to detect reactivity differences

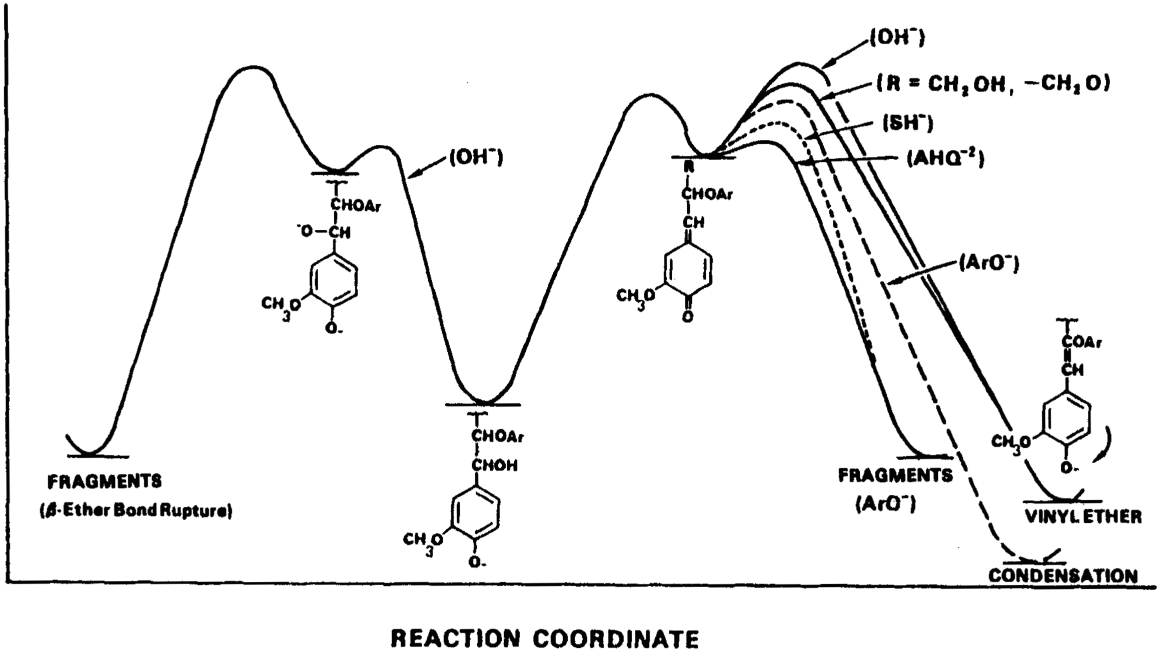


Figure 1. Hypothetical energy diagram for the reactions of phenolic lignin end units.

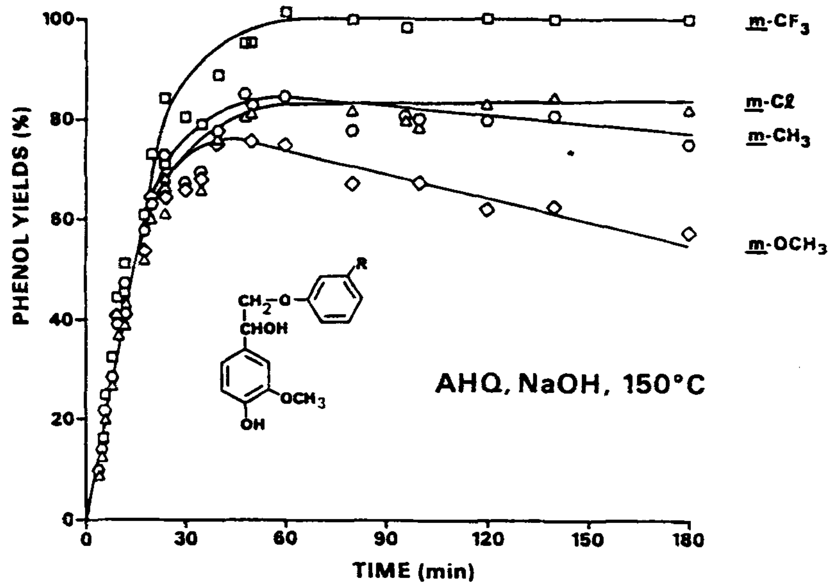


Figure 2. Phenol yields as a function of time for degradations of models 1A-D (1 equiv. each, in the same reactor) at 150°C in the presence of 180 equiv. of NaOH and 20 equiv. of AHQ diacetate. At the start of the reaction there should be 100 equiv. of NaOH (25/model) and 20 equiv. (5/model) of $AHQ^{-2}$ available.

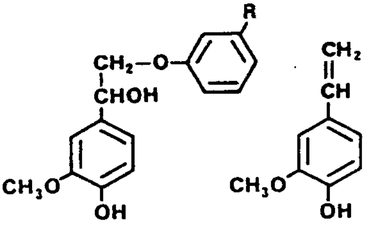
which would provide information defining specific reaction mechanisms with regard to QM-additive reactions. The previous report described the model synthesis, selection, and general degradation procedure, along with the product analysis.[12] That report demonstrated that the slow step in the mechanism for model fragmentation under soda conditions is cleavage of the β-aryl ether bond.

## RESULTS

### Degradation of Ring B Analog Models 1A-D

A mixture of models 1A-D was heated at 150°C in aq. alkali with 5 equiv. of $AHQ^{-2}$ per model for various time intervals, and the yields of phenols 3A-D determined. The data, as seen in Fig. 2, indicate no significant differences in phenol yield (i.e., fragmentation tendencies) for the four models at short reaction times. Thus, the electron-donating or releasing powers of the B ring substituents play no role in the rate determining step of the fragmentation mechanism.

The fact that there was a yield difference at long reaction times is probably due to secondary reactions. A gas chromatography-mass spectroscopy (GC-MS) analysis of the product mixtures showed starting materials, vinyl ethers (dehydration products of the starting materials), phenols 3A-D, and small amounts of vinylguaiacol (2) and guaiacol (from ring A cleavage). The low levels of 2 are a result of its tendency to polymerize in the presence of AHQ; sometimes this polymerization incorporates other phenol products,[13] leading to an apparent lower yield of simple phenols. Heating just the simple phenols in aq. NaOH at 150°C led to no phenol losses.



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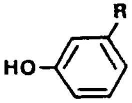


3

| # | R |
|---|---|
| A | $CH_3$ |
| B | $Cl$ |
| C | $OCH_3$ |
| D | $CF_3$ |

Many data points were collected to ensure the validity of the observed trends. The absolute yields may not be accurately known, but we are comfortable in comparing degradations done under identical conditions.

Each model was degraded in the presence of several different additives. These degradations were done at 135°C where (a) soda reactions play less of a role and (b) reactivity differences - as compared to 150° - will be more pronounced. We also began employing glucose as a reagent for reducing AQ to $AHQ^{-2}$; the glucose method appears to be more reliable than the AHQ-diacetate hydrolysis method for producing known levels of AHQ.[14] The glucose method involves prewarming a mixture of model, AQ, and glucose in aq. alkali at 60° for 30 minutes. These conditions promote the formation of $AHQ^{-2}$ and the partial destruction of glucose[15] at a temperature where QM formation should not occur. Workup of the prewarmed solutions showed no model fragmentation.

The numerous model degradations indicated that the order of fragmentation efficiency in the presence of an excess additive is soda/AHQ > soda/$SH^-$ > soda/glucose > soda (an example is given in Fig. 3).

The high efficiency of the soda/AHQ is not because of the presence of glucose or glucose by-products in this system. This point was established by performing several control runs, including prewarming a soda/$SH^-$ system in the presence of glucose and observing no increased phenol yields as compared to just a soda/$SH^-$ system. Apparently, glucose is a relatively poor reactant in the presence of the much better AHQ and SH ions. Interestingly, the effectiveness of glucose alone in alkali, as a promoter of fragmentation, is only slightly reduced (ca. 10%) by the 30 minute, 60°C prewarming procedure.

A statistical analysis program[16] was applied to the 135°C model-additive reactions to help determine whether fragmentation yields were different or identical. The upper right side of Table 1 compares confidence levels of yield differences for AHQ degradations of the various models. The statistical analysis indicates a low degree of confidence that the AHQ runs have different rates of fragmentation; the fact that the m-$CF_3$ model (1D) confidence is somewhat high in two cases is probably due more to yield differences at long reaction times rather than short reaction times (i.e., such as in Fig. 2).

The statistical analysis (lower left side of Table 1) also indicates a low degree of confidence that the $SH^-$ runs have different rates of fragmentation. There is, however, a high

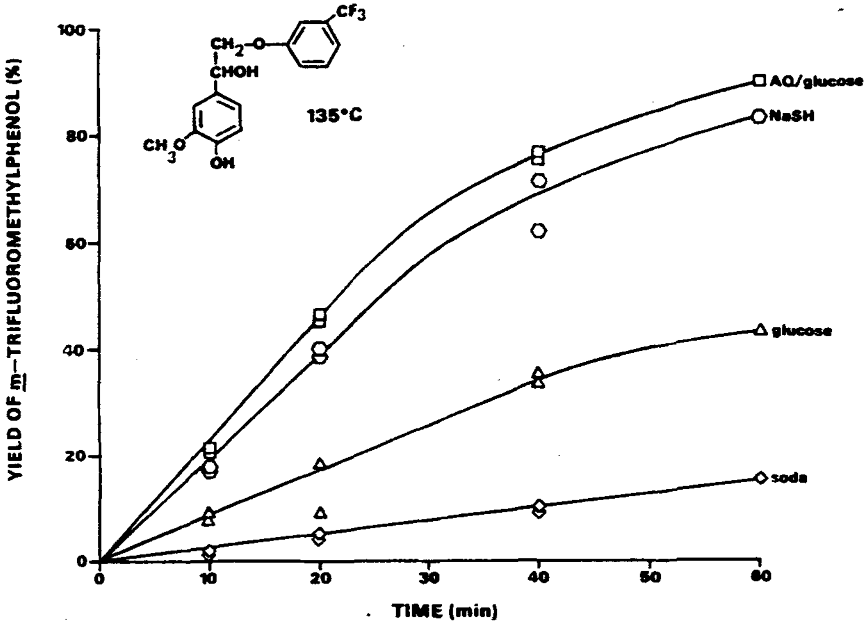


Figure 3. Phenol yield as a function of time for the degradation of model 1D in the presence of different additives at the 5 equiv. level at 135°C.

TABLE 1

Statistical Analysis of the Data from Kraft and AHQ Degradations of Model 1A–D at 135°C[a,b]

| Compound | 1A | 1B | 1C | 1D |
|---|---|---|---|---|
| 1A | 0.997 | 0.705 | 0.133 | 0.922 |
| 1B | 0.485 | 0.730 | 0.360 | 0.946 |
| 1C | 0.137 | 0.412 | 0.910 | 0.511 |
| 1D | 0.336 | 0.185 | 0.540 | 0.995 |

---

[a] The yield vs. time profiles of two runs were compared using a BMDP statistical program.[16] Numbers close to 1.00 indicate a high degree of confidence that the two sets of data are different; generally, any number below 0.90 signifies that the reaction rates are not statistically different.

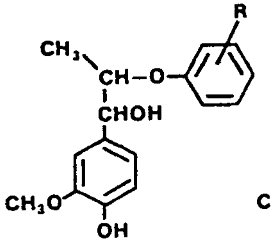
[b] ⬚ AHQ vs. SH □ AHQ vs AHQ ⬚ SH vs. SH.

degree of confidence, in at least two cases, that AHQ degradations cause more fragmentation than $SH^-$ degradations (Table 1, diagonal from upper left to lower right).

Although not shown in the table, data analysis indicated that glucose induced fragmentation yields differ from model-to-model, with the m-$CF_3$ model (1D) being the most reactive and the m-$CH_3$ model (1A) the least reactive. The difference here probably reflects soda degradation contributions. The fact that carbohydrates can cause model fragmentation reactions has support in the literature.[17]

### Degradations of Ring B Analog Models 4A-D

Degradation of the β-methyl model series (4) were performed at 150°C with pairs of models in the same reactor in the presence of excess AHQ. One of the model pairs was generally the m-chloro compound 4B; this provided a check on the consistency of the data. For example, the yield of m-chlorophenol from 4B was 80-83% at an 80 min reaction time in four different runs.



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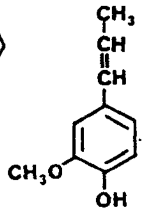

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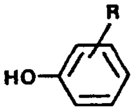


3

| # | R |
|---|---|
| A | m–$CH_3$ |
| B | m–Cℓ |
| C | m–$OCH_3$ |
| D | m–$CF_3$ |
| E | H |
| F | o–$OCH_3$ |

The model fragmentation efficiencies as a function of time, with and without AHQ, are shown in Fig. 4. In the absence of AHQ the models displayed quite different reactivities; the meta substituent order was $CF_3$ > Cl > $OCH_3$ > $CH_3$. A similar order was observed in the soda degradations of models 1A-D.[12] In the presence of AHQ all models reacted at approximately the same rate after applying certain assumptions.

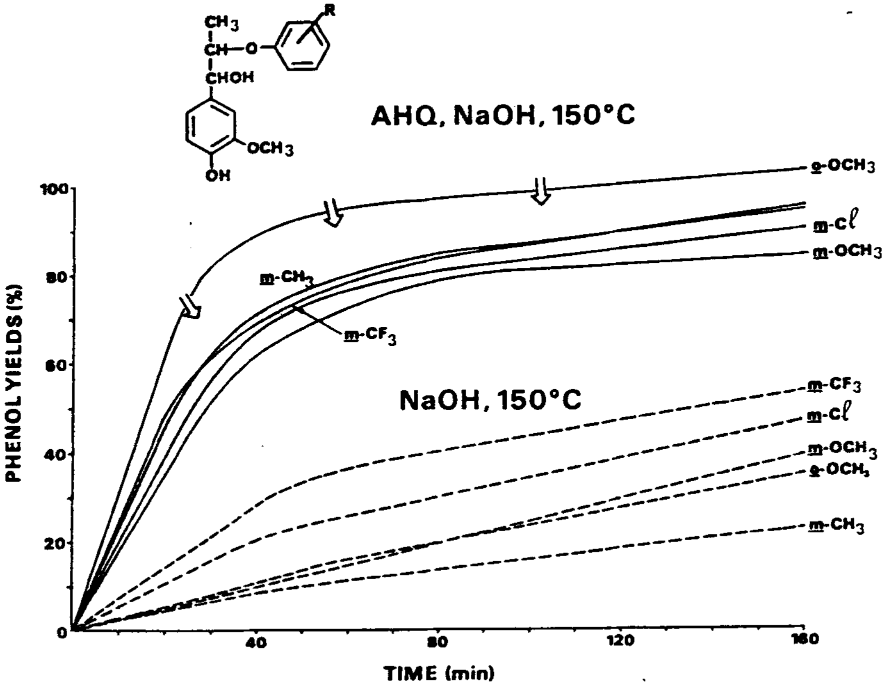


Figure 4. Phenol yields as a function of time (5, 10, 15, 20, 30, 40, 60, 80, and 160 min) for the degradation of models **4A–D,F** (done as 1 equiv. pairs in the same reactor) at 150°C in the presence of 75 equiv. of NaOH and 6 equiv. of AHQ diacetate (——) and in the presence of 50 equiv. of NaOH (– –). Data points have been omitted for clarity reasons.

The main assumption relates to the fact the β-methyl models are relatively pure, but not absolutely pure compounds. Thus, the somewhat lower yields observed with *m*-OCH$_3$ model (**4C**) may be due to impurities in the substrate. The *m*-Cl model **4B** was known to be contaminated with unsubstituted **4E** isomers and its yields were corrected accordingly. Interestingly, the yield of phenol from degradation of the unsubstituted impurity in the *m*-Cl sample matched the other substituted-phenol yields.

The high yields of guaiacol observed in the degradation of the o-$OCH_3$ model 4F can be attributed in part to some guaiacol production from ring A cleavage. Small amounts of guaiacol, which must originate from ring A, were observed in all degradations of B ring models 1A-D and 4A-D; for example, at 150°C, the guaiacol yields increased gradually to roughly 1.5% after one hour for soda and soda/AHQ degradations of 1A and about 9% under soda/NaSH conditions.

Although the β-methyl series has its problems, the data from this series are consistent with those of the non-β-methyl 1 series. The most electron-withdrawing and electron-releasing substituents, $CF_3$ and $CH_3$, respectively, displayed **similar** reactivities in the presence of AHQ and quite **different** reactivities in the presence of only NaOH. The phenol yields in the β-methyl series appear to level off better than the non-β-methyl series at long reaction times, possibly meaning less phenol losses to competing side reactions. [Isoeugenol (5) has less tendency to polymerize and does not appear to cause losses in other phenol products.[13]]

## Degradation of Ring A Model Analogs

Several models differing in their A-ring substituents were also studied. These models would be expected to have quite different reactivities if a step involving the A-ring were the slow step in the mechanism. Several steps in the proposed mechanisms for additive induced fragmentation do involve the A-ring; QM formation and addition of ions or electrons to QMs are examples.

Degradation of ring A model analogs having m-$CH_3$ substituents in their B rings at 135°C in the presence of either AHQ or $SH^-$ showed the following order of fragmentation efficiency: 2',5'-dimethyl alcohol 6B > 3'-methoxy alcohol 1A > unsubstituted alcohol 6A (Fig. 5). Again, it appears that fragmentation yields with AHQ are slightly better than with $SH^-$ (confidence levels of a significant difference were 0.989, 0.997, and 0.725).

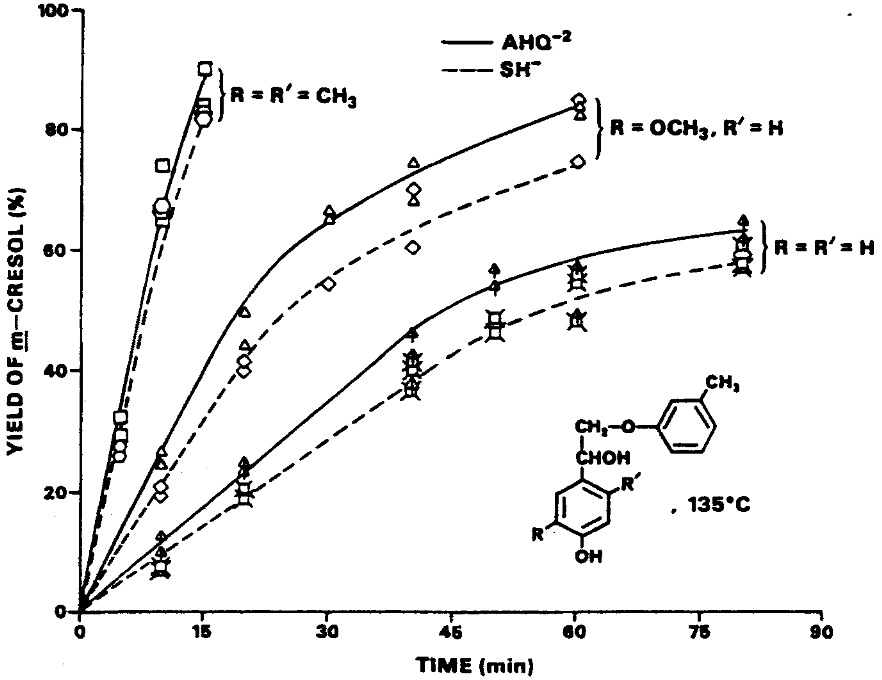
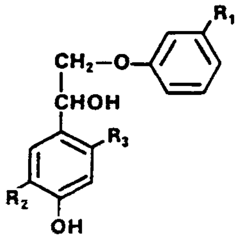


Figure 5. Phenol yields as a function of time for the degradations of models differing in their ring A substituents in the presence of excess levels of AHQ (——) and SH$^-$ (- -) at 135°C in aqueous alkali.



6

| # | R$_1$ | R$_2$ | R$_3$ |
|---|---|---|---|
| 1A | CH$_3$ | OCH$_3$ | H |
| 6A | CH$_3$ | H | H |
| 6B | CH$_3$ | CH$_3$ | CH$_3$ |
| 6C | CF$_3$ | CH$_3$ | CH$_3$ |

The result that we had hoped for, namely a large difference in yields between AHQ$^{-2}$ and SH$^-$ runs, was not realized. Large differences in additive reactivities would have suggested mechanistic differences. One would expect that the quinonemethides from 1A, 6A, and 6B would be quite different in their reactivities toward accepting electrons and fragmenting to radicals (SET mechanism) *versus* adduct formation and fragmenting to ions.

The observed reactivity order rules out adduct formation as the slow step in the mechanism. Adduct formation, which develops a full negative charge in ring A, would be expected to be slow with the 2',5'-dimethyl models because the methyl groups are electron feeding and would destabilize carbanions; also, the 2'-methyl should sterically hinder the reaction. Instead, the 2',5'-dimethyl analogs were the most reactive.

The results point toward a common slow step in the mechanisms of the $AHQ^{-2}$ and $SH^-$ reactions. Most likely this step is QM production. In general, highly substituted QMs are more stable than unsubstituted QMs. Thus, the order we observed for ease of fragmentation fits an order for ease of QM generation. The order does not, however, rule out single electron transfer to the QM as the slow step. The radical nature of $QM^{\dot{-}}$ might derive some stabilization from electron releasing ring methyl groups.

With the proper substituents on the A ring, QM formation may become so easy that this step would no longer be the rate limiting step, and the chemistry of subsequent reactions might be observable. Therefore, the degradations of two 2',5'-dimethyl ring A models, having different ring B substituents (*m*-$CH_3$, 6B, and *m*-$CF_3$, 6C), were compared. As can be seen in Fig. 6, the *m*-$CF_3$ model is more reactive than the *m*-$CH_3$ model (100% confidence level). However, the difference was not substantial and may only reflect differences in NaOH-induced fragmentation (6C > 6B). Again, in this series, AHQ was better than hydrosulfide ion at inducing fragmentation (99.96% confidence of a difference).

## Competitive Model Degradations

Model degradations in the presence of an excess of AHQ or NaSH show similar fragmentation yields, irrespective of the B ring

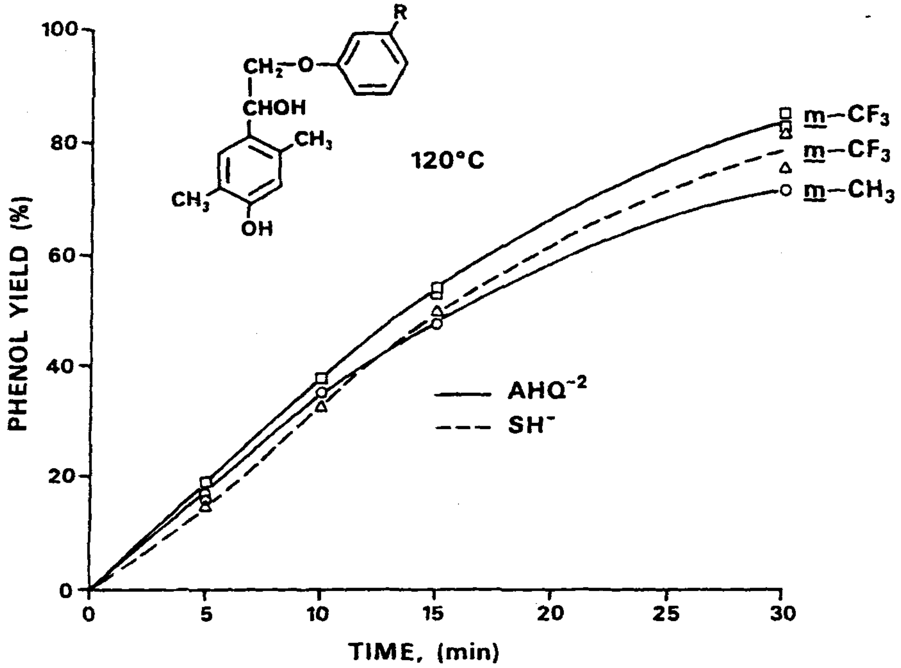


Figure 6. Comparison of phenol yields as a function of time for the 120°C degradation of models **6B** (R=m–$CH_3$) and **6C** (R=m–$CF_3$) in the same reactor in the presence of 25 equiv. of NaOH, 5 equiv. of glucose, and 5 equiv. of AQ (per model), and of model **6C** in the presence of 25 equiv. of NaOH and 5 equiv. of NaSH.

substituent and whether the reactions are competitive or not. However, when limited amounts of additive were used during the competitive degradations of our two most dissimilar B ring models (m-$CH_3$ and m-$CF_3$), significantly different reactivities were observed. This was demonstrated with model pairs **1A**/**1D** and **6B**/**6C**; the former have a methoxy group on their A ring, the latter have two methyl groups.

Data from the competitive degradations of **1A** (m-$CH_3$) and **1D** (m-$CF_3$) are shown in Table 2. The degradations employed 1 equiv. of each model in aq. alkali in the presence of 0.8 equiv. of an

TABLE 2

Phenol Yields from Competitive Model Degradations Performed with Limited Amounts of Additive[a]

| 1D (%) | Time, | Phenol Yield from 1A (%) | | | Phenol Yield from | | |
|---|---|---|---|---|---|---|---|
| Volume[b] | min | $SH^-/OH^-$ | - $OH^-$ | = $SH^-$ | $SH^-/OH^-$ | - $OH^-$ | = $SH^-$ |
| Low | 20 | 25.5 | - 1.1 | = 24.4 | 29.7 | - 5.0 | = 24.7 |
| Low | 40 | 35.7, 34.9 | - 2.6 | = 32.7 | 43.8, 45.7 | - 10.1 | = 34.7 |
| High | 20 | 18.4 | - 0.8 | = 17.6 | 22.6 | - 3.4 | = 19.2 |
| High | 40 | 29.6 | - 1.9 | = 27.7 | 35.2 | - 7.0 | = 28.2 |
| | | AHQ/OH | $OH^-$ | AHQ | $AHQ/OH^-$ | $OH^-$ | AHQ |
| Low | 20 | 16.2 | - 1.2 | = 15.0 | 23.9 | - 4.4 | = 19.5 |
| Low | 40 | 19.4, 18.2 | - 2.4 | = 16.2 | 30.1, 30.6 | - 8.6 | = 21.8 |
| High[c] | 20 | 11.3 | - 1.0 | = 10.3 | 18.1 | - 4.1 | = 14.0 |
| High[c] | 40 | 15.5 | - 2.1 | = 13.4 | 26.8 | - 8.1 | = 18.7 |

---

[a] One equiv. of models 1A and 1D was mixed with 0.8 equiv. of additive and 25 equiv. of NaOH and heated at 135° for 20 or 40 min.
[b] Low and high refer to 1.5 and 3.5 mL volumes.
[c] Fifty equiv. of NaOH were used in this case.

additive ($SH^-$ or AHQ). This level of additive was chosen because it was the best compromise between low additive levels and our ability to conclusively distinguish additive-induced reactions from NaOH-induced reactions. Under these conditions, NaOH-induced fragmentation reactions will compete; therefore, the "net" yield caused by additive induced fragmentation was calculated (columns 5 and 8 of the table).

Both high and low volume reactions were employed to observe how the yields might change with reactant concentration changes. At low volume, the occurrence of reactions between "intermediates" would be more likely. While this could lead to product distribution changes, few effects were observed. There was roughly a 5% yield increase in both phenol products with the volume changes in each case. This result is in agreement with trends observed in the soda degradations.[12]

At reduced AHQ levels, the m-$CF_3$ model (1D) appears to be more reactive than the m-$CH_3$ model (1A) in net yield; with $SH^-$, the difference between 1A and 1D is small, probably within the experimental errors of the measurements. Over a series of six time measurements, 1B (m-Cl) was consistently more reactive than 1A (m-$CH_3$) in net yield in the presence of 0.8 equiv. of AHQ at 150°C.

Finally, competitive degradations of the m-$CH_3$ model 6B and the m-$CF_3$ model 6C were conducted. With these models, lower temperatures can be used, thereby extending the lifetimes of, and allowing better opportunity for the reactions between, the reactive intermediates.

Figure 7 shows a comparison of the phenol yields from models 6B and C when degraded simultaneously at 120°C in the presence of limited amounts of AHQ and NaSH. **The m-$CF_3$ model was substantially more reactive than the m-$CH_3$ model in the presence of the additives.** The data in the figure indicate that AHQ is depleted after about 10-15 minutes and that NaOH-induced fragmentation commences at this time.

The reactivity differences in the presence of AHQ and NaSH cannot be accounted for by differences in soda control rates, which are small at 120°C, or in secondary phenol consumption reactions[13] (as seen in Fig. 2). Secondary reactions would as expected be (a) different for reactions producing 2,5-dimethyl vs. 3-methoxysubstituted styrene by-products, (b) less at 120° vs. 150°C, (c) more apparent at long reaction times, (d) more pronounced with 5 equiv. of AHQ per model (Fig. 6) vs. 0.4 equiv. (Fig. 7) and (e) low in the NaSH case where fewer styrene by-products are formed.[3]

Under the conditions of limited additive levels, $SH^-$ induces more fragmentation than AHQ. The reason for this is not obvious. One possible explanation is that the concentration of $AHQ^{-2}$ is less than anticipated because of non-quantitative reduction by glucose or reaction with residual oxygen; the reactions were per-

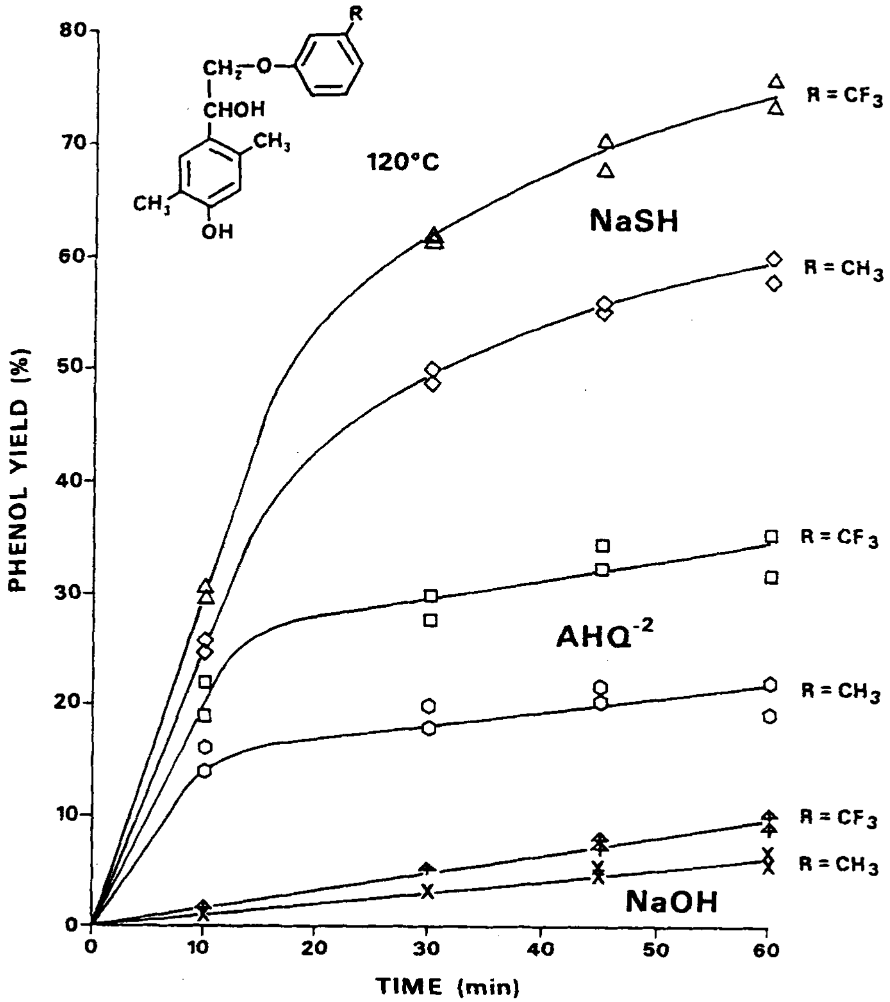


Figure 7. Phenol yields as a function of time for the 120°C degradations of 1 equiv. each of models **6B** and **C** in the same reactor in the presence of 25 equiv. of NaOH and no additive (lower lines), 1 equiv. of AQ and glucose (middle curves) and 1 equiv. of NaSH (upper curves).

formed with extremely low levels of reactants, levels where even trace amounts of oxygen could have an effect. The abilty of NaSH to substantially outperform AHQ at low additive levels should not be taken to reflect what might happen during pulping since the AQ/AHQ redox cycle[1] operates in the latter case.

## DISCUSSION AND CONCLUSIONS

Additive induced model fragmentation reactions appear to have a common slow step, presumably formation of a quinonemethide, which is sensitive to substituents located on ring A but not to substituents on ring B. Our results indicate that the slow step in additive induced fragmentation of lignin model compounds cannot be nucleophile addition to a quinonemethide or fragmentation of the $\beta$-aryl ether bond.

The close similiarities in the rates of AHQ and $SH^-$ degradations, where the additives are used in excess, suggests a common slow step, namely quinonemethide generation. The effectiveness of an additive ($AHQ^{-2} > SH^- >$ glucose) can be accounted for based on the efficiency by which the additive fragments the model vs. competing side-reactions.

### Kinetic Interpretation of Additive Effects

The rate of generation of fragments for a model should obey the following expression:

$$\text{Frag. Rate} = k_{HO}\,[HO^-]\,[\text{Model}] + k_{Add}\,[\text{Add}][\text{QM}] \qquad (6)$$

where $k_{HO}$ and $k_{Add}$ are the rate constants for the soda induced and additive induced fragmentation reactions, respectively, and reactant orders are assumed to be 1. The concentration of the quinonemethide (QM) can be calculated by applying the steady state assumption for reactive intermediates and considering the various reactions available (Fig. 1) to the QM:

$$[\text{QM}] = \frac{k_{QM}[\text{Model}]}{k_{Add}[\text{Add}] + k_{VE}[HO^-] + k'_{VE}[HO^-] + k_{CON}[ArO^-] + k_{-QM}[HO^-]} \qquad (7)$$

where $k_{VE}$ and $k'_{VE}$ are the rate constants for the two reactions which produce vinyl ether by-products, $k_{CON}$ is the rate constant for condensation reactions involving phenols ($ArO^-$), and $k_{QM}$ and $k_{-QM}$ are the forward and reverse rate constants for QM formation and return to the model.

Combining Equations (6) and (7) gives:

$$\text{Frag. Rate} = k_{HO}\,[HO^-]\,[\text{Model}] + k_{QM}\,[\text{Model}] \cdot X \qquad (8)$$

where X is the fraction of reaction which is additive induced fragmentation vs. all other reactions of the QM:

$$X = \frac{k_{Add}[\text{Add}]}{k_{Add}[\text{Add}] + k_{VE}[HO^-] + k'_{VE}[HO^-] + k_{CON}[ArO^-] + k_{-QM}[HO^-]}$$

If the $k_{Add}$ [Add] term is large relative to the other terms in the denominator of the X term, expression (8) reduces to:

$$\text{Frag. Rate} = k_{HO}\,[HO^-]\,[\text{Model}] + k_{QM}\,[\text{Model}] \qquad (9)$$

According to this expression, the rate of fragment generation should be independent of additive concentration above a certain level. We have observed such effects in our studies and others have seen similar effects in kraft delignification systems.[18]

The fragmentation efficiencies which we observed for the reactions of excess with models, namely AHQ > $SH^-$ > glucose, can be accounted for by assuming that X is largest for AHQ and smallest for glucose. This interpretation accounts for the additive yield differences while still maintaining that QM formation is rate determining for the additive reactions. In essence the additive affects the product determining steps, rather than the rate determining step.

## Interpretation of the Competitive Reaction Results

Two soluble, model lignin quinonemethides (QM and QM') present in the same reaction vessel might undergo the following SET reactions:

$$\mathrm{QM} + \mathrm{AHQ}^{-2} \rightleftharpoons \mathrm{QM}^{\bullet -} + \mathrm{AHQ}^{\bullet -} \tag{10}$$

$$\mathrm{QM'} + \mathrm{AHQ}^{-2} \rightleftharpoons \mathrm{QM'}^{\bullet -} + \mathrm{AHQ}^{\bullet -} \tag{11}$$

$$\mathrm{QM} + \mathrm{QM'}^{\bullet -} \rightleftharpoons \mathrm{QM}^{\bullet -} + \mathrm{QM'} \tag{12}$$

$$\mathrm{QM}^{\bullet -} \longrightarrow \mathrm{Ar_AO^-} + \mathrm{Ar_BO\bullet} \tag{13a}$$

$$\mathrm{QM}^{\bullet -} \longrightarrow \mathrm{Ar_AO\bullet} + \mathrm{Ar_BO^-} \tag{13b}$$

$$\mathrm{QM'}^{\bullet -} \longrightarrow \mathrm{Ar_AO^-} + \mathrm{Ar_B'O\bullet} \tag{14a}$$

$$\mathrm{QM'}^{\bullet -} \longrightarrow \mathrm{Ar_AO\bullet} + \mathrm{Ar_B'O^-} \tag{15b}$$

If QM and QM' differ only in their ring B substituents, the rates of quinonemethide formation and the acceptance of electrons by the quinonemethides, Eq. (10) and (11), should proceed at the same rates. Also, the equilibrium constant for Eq. (12) should be 1.0. Many SET reactions are characterized by SET steps between species as part of a chain mechanism;[19-21] therefore, the equilibrium indicated by Eq. (12) should occur. The extent of electron exchange indicated by Eq. (12) may be limited by the expected low concentration of the intermediates; however, roughly 15% QM-QM coupling products have been observed in a closely related systems involving $\mathrm{AHQ}^{-2}$ and reactive QMs.[22]

Fragmentation of $\mathrm{QM}^{\bullet -}$ and $\mathrm{QM'}^{\bullet -}$ would produce the same ring A fragments, but different ring B fragments. The substituent on ring B can now exert its influence and the reaction rates of steps (13) and (14) will differ. It is expected that one of the fragmentation types, [Eq. (13a)/(14a) or Eq. (13b)/(14b)], will predominate. Since QM-AHQ adduct reactions are reversible,[11] similar arguments apply; product distributions from competitive reactions will reflect the stabilities of the resulting ring B phenolate ion fragments.

Experimentally, we observed that the simultaneous degradations of two different sets of models with limited amounts of either $AHQ^{-2}$ or NaSH produced the following result: the models having ring B m-$CF_3$ groups fragmented faster than the ones having m-$CH_3$ groups. This result indicates that interactions between QM intermediates occur and that ring B is liberated as an ion, and not a radical, during the fragmentation step.

If equilibria between quinonemethide intermediates, Eq. (12), do not occur, the yields of m-$CF_3$ and m-$CH_3$ phenols would be the same, because the concentration of quinonemethide intermediate ($QMs^{\dot{-}}$ or QM-adducts) should be the same. However, the yields are different when additive levels are low. Because not all the QMs are converted to $QMs^{\dot{-}}$ or QM-adducts, some are left to participate in equilibrium reactions, such as indicated by Eq. (12), and the most reactive $QM^{\dot{-}}$ or QM-adduct is then able to produce more fragmentation.

Since the predominant product in the presence of low additive levels is the m-$CF_3$ phenol, the most reactive QM intermediate must be the B ring m-$CF_3$ $QM^{\dot{-}}$ or QM-adduct. The high reactivity of this intermediate is due to its ability to generate a relatively stable m-$CF_3$ phenolate ion.

All indications are that $SH^-$ can add reversibly to QMs under pulping conditions.[7,22] Where two different QMs are present, two QM-SH adducts are possible even though the formation of the QMs is the rate determining step. The adduct which fragments the fastest will dominate the product distribution when $SH^-$ is in limited supply. This is what we have observed.

Similar arguments could be made for $AHQ^{-2}$ and QM-AHQ adducts, since these reactions are reversible[11] and should favor production of the m-$CF_3$ phenol. However, the SET mechanism is not ruled out by our results. If the mechanism is SET, fragmentation must proceed in a manner which generates an A ring radical and a B ring ion, Eq. (13b) and (14b). This preference can be rationalized based on a resonance form in which the β-carbon of the A ring styrene fragment is better able to stabilize a radical intermediate than an anion intermediate. The fact that the yields of the styrene products are often very low in AHQ-induced model degradation reactions[3,13] suggests that the styrene is produced as a phenolate radical which subsequently polymerized.

## EXPERIMENTAL SECTION

The synthesis of the compounds, the general degradation procedure, and methods of analysis were previously described.[12] Specific changes in the degradation procedure are described below.

**Degradation Procedure.** Except for AQ and AHQ-diacetate, which had to be weighed into each bomb (small pressure vessel), all reactant solutions, IS solutions, etc., were added to the bombs with an automatic pipette.

Standard solutions of glucose, sodium hydroxide, and sodium sulfide in water, and model compounds and p-isopropylphenol (IS) in aq. NaOH were prepared just prior to use. The models were present in 0.015 mmole amounts, and the other reagents were adjusted to 0.015 mmole = 1 equiv. Generally, this meant the use of 25 equiv. of NaOH and 5 equiv. of additive/model. The amount of NaOH solution used was adjusted to compensate for additive consumption (i.e., 4 equiv./AHQ-diacetate) or additive liberation ($Na_2S + H_2O \rightleftharpoons NaSH + NaOH$).

The appropriate solutions and make-up water were added to the cool bombs. For degradations involving AQ/glucose and AHQ-diacetate, the bombs were prewarmed along with soda controls at 60° for 30 min prior to immersion in the oil bath. This prewarming helped to give a high concentration of $AHQ^{-2}$ prior to immersion. No model fragmentation (even for the most reactive models, 24 and 25) occurred as a result of prewarming in the presence of NaOH or NaOH/additive solutions.

After removal from the hot oil bath, the bombs were immediately cooled in ice-water, opened, diluted with IS solution, and the contents transferred to an Erlenmeyer flask for derivatization, followed by GC analysis.

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