FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING: DELIGNIFICATION REACTIONS
Project 3475

Report Three
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

February 3, 1986
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Chemical pulping attempts to remove lignin from wood, while preserving both the native yield and strength of the cellulose fibers. The term "pulping selectivity" refers to how well these goals are met. Project 3475 is concerned with understanding the detailed chemistry of carbohydrate degradation reactions as well as that of lignin fragmentation and of condensation reactions. Related student work has similar goals. With the knowledge gained we hope to improve the rate of delignification, better protect the cellulose fibers, and thereby improve pulping selectivities.

The project has been concentrating on the chemistry of anthraquinone (AQ) pulping; the selectivities here are higher than with other commercial alkaline pulping systems. The general approach taken has been to study the reactions of AQ with wood and model carbohydrates and the reactions of anthrahydroquinone (AHQ) with selected lignin model compounds. Justification for the "models approach" is provided. This report concerns only the lignin reactions part of Project 3475. Its main theme centers on a better understanding of how AHQ causes lignin to fragment and more specifically, on whether or not a new type of chemistry, single electron transfer (SET), explains the high efficiencies of AQ-based pulping systems.

Several approaches have been taken in order to confirm that SET reactions of AHQ and lignin model quinonemethides (QMs) do indeed occur. Some approaches have been successful and others have not. However, even in the
latter cases, we have gathered important mechanistic information on lignin fragmentation reactions. For example, a detailed study of the reactions of typical pulping additives with variously substituted lignin models has shown that model fragmentation rates are determined by the rates of quinonemethide generation.

Fragmentation of lignin appears to be aided by terminal QM units on the polymer, provided that there is an additive present which can direct the QMs toward fragmentation and away from undesirable side reactions. The chemistry of undesirable side reactions, such as condensation reactions and vinyl ether generation, has also been a focus of our recent research. Since these side reactions produce pulping-resistant (residual) lignin, it is important that we understand, and eventually control, the chemistry of these reactions.

Studies on the sodium hydroxide reactions of lignin model compounds having different β-substituents have provided knowledge about the factors governing model fragmentation vs. vinyl ether formation. The latter is more prominent at low alkali levels, is retarded by β-side-chain substituents, and is unaffected by changes in β-aryl ring substituents. The reverse effects apply to soda-induced fragmentation reactions.

The effectiveness of a pulping additive appears to be related to its ability to provide a low energy pathway for QM fragmentation; such is probably the case with SET reactions. Evidence that SET reactions occur between AHQ and QMs, and can cause fragmentation of β-aryl ether models, has been provided by studying the interactions of relatively stable models QMs with anthrahydroquinone ion radicals. The model QMs were synthesized by standard chemical techniques, while the AHQ ion radicals were generated electrochemically in an organic
solvent; both processes were done at room temperature. While the conditions of these initial electrochemistry experiments are quite different from pulping, verification of SET reactions between AHQ ions and QMs in aqueous alkali at 135-150°C has been provided by the research of Ph.D. student D. Smith.

Our cooperative research with electrochemist Dr. H. L. Chum at the Solar Energy Research Institute has provided valuable mechanistic information and suggests an area for future research. High temperature aqueous electrochemistry offers an opportunity to promote, directly or indirectly, SET reactions and to monitor pulping reactions by monitoring QM levels. These areas will be pursued in future research efforts.
INTRODUCTION

It has been nearly six years since the last comprehensive progress report. The research results from work under this project has reached a major milestone and it is now appropriate to present a comprehensive summary of the results and their implications. Since the last progress report we have prepared thirteen manuscripts concerning project research accomplishments for distribution to member companies (as Technical Papers) and for submission to scientific journals; ten have been published and three are still under review for publication. Related student research has led to four published papers and one still under review. Emerging results have also been provided to the IPC membership via twice-yearly status reports.

An extensive review of all this work would make this progress report much too lengthy. Instead, I will present the highlights of our research findings over the last five years and reference our published work for a source of more detailed information. An extensive amount of literature has been published on the practical aspects of anthraquinone (AQ) pulping; this will not be reviewed here. Where appropriate, the mechanistic studies of other researchers concerning AQ pulping chemistry will be reviewed.

PROJECT GOALS

The present project (3475) grew out of another project (3370), whose title was "Promotion of Alkaline Delignification by AQ." While mechanistic AQ studies have been the focal point of the present work, the new project is intended to be of greater scope, including an examination of a variety of pulping systems other than AQ. Our specific goals are to develop a detailed fundamental
understanding of lignin reactions under a variety of conditions and then use this knowledge to develop better pulping and bleaching systems.

Our concentration on AQ stems from the fact that at very low levels of AQ the selectivity of pulping is improved over other conventional techniques. It is advantageous to be able to control pulping selectivity. Understanding the chemistry of AQ pulping systems provides valuable information for improving selectivity.

SELECTIVITY

Pulping selectivity refers to the degree to which lignin is removed and carbohydrates are retained; a highly selective process removes large amounts of lignin, gives a good yield of carbohydrates, and limits cellulose degradation. The material balance for a kraft pulping and chlorine bleaching process is exemplified in Fig. 1; the overall yield of bleached pulp is only about 43% from southern pine wood.

Generally, high selectivity is preferred because the increased pulp yield and reduced levels of bleaching lead to lower operating costs, greater profits, and fewer pollution problems. Improved selectivity also means less cellulose degradation and better strength properties for the products. There are two major ways of improving pulping selectivity. One is to stabilize the carbohydrate components from fragmentation reactions that cause them to dissolve during pulping. The other is to increase the rate at which lignin is dissolved so that less time is available for carbohydrates to be degraded. A consequence of the latter approach is that less energy is needed for pulping and more productivity is realized.
In order to bring about significant improvements in pulping selectivities, we must understand the chemistry associated with carbohydrate and lignin degradation reactions. This is the goal of Project 3475. One sub-project of 3475 is focusing on understanding carbohydrate degradation reactions; the other sub-project, which is the subject of this report, concerns the corresponding lignin reactions.

**DELIGNIFICATION CHEMISTRY - A SIMPLE PICTURE**

Progress in pulping chemistry has been impeded by the structural complexities of the wood components, which are principally polymers. Lignin is a very irregular, randomly cross-linked polymer that is difficult to define accurately. The individual monomer units, phenylpropane units, are held together
by many different types of linkages. Some of these linkages are easily cleaved during pulping; others are very resistant to cleavage by any chemical treatment.

A simplified representation of lignin is given in Fig. 2. In this figure the circles represent lignin monomer units; the thin lines represent weak linkages between units; and the thick lines represent strong linkages. Lignin is not soluble in water, but its fragments, if small enough, are soluble in water. The delignification of wood is simply the fragmentation of the lignin into water-soluble pieces. Our goal is to delignify at a rate considerably faster than the rate of the carbohydrate degradation reactions that are also occurring during pulping.

The soluble lignin fragments recombine to some extent during pulping, generating a new lignin polymer that contains strong linkages between monomer units (Fig. 3). The only way to remove the recombined lignin from wood is through extensive bleaching. Thus, delignification has two conflicting reactions: a
fragmentation type that helps lignin dissolve and a recombination type that retards lignin removal.

Figure 3. A simplified representation of lignin recombination reactions.

Alkaline pulping processes, such as soda and kraft, were developed long before the structures and the nature of the major components of wood were understood. As structural studies on cellulose, hemicellulose, and lignin progressed\textsuperscript{2,3} so did the chemistry of pulping. Theories have evolved which now explain how hydroxide and hydrosulfide ions (OH\textsuperscript{-} and SH\textsuperscript{-}) cause carbohydrate\textsuperscript{2,4-6} and lignin\textsuperscript{3,7} to dissolve during pulping. Most of the theories are based on experiments with model compounds rather than actual wood.
OVERVIEW OF AQ RESEARCH

AQ BENEFITS

In 1977 Holton introduced two new variations of the alkaline pulping processes: soda/AQ and kraft/AQ. In these variations, the liquors contain 0.1% or less AQ. The soda/AQ process gives pulping rates equivalent to kraft, yields products nearly as good as kraft, and produces selectivities higher than kraft. Anthraquinone can be used in several ways: to increase productivity, to lower energy inputs, or to decrease the amounts of sodium hydroxide and/or sodium sulfide used. The commercialization of an AQ-based pulping process is, however, very dependent on economics, i.e., the cost of AQ vs. its benefits.

An important aspect of the AQ discovery was that, unlike the older alkaline systems, the AQ process evolved because the chemistry of pulping was becoming better understood. Yet, much of what AQ accomplished during pulping was a mystery. How could an organic material at a 0.1% level cause the same effects as 6% NaSH (kraft)? Why did AQ processes exhibit better pulping selectivities? The advent of AQ pulping caused a revitalization of interest in pulping chemistry.

REDOX CYCLE

Early in the mechanistic AQ studies came the realization that anthrahydroquinone (AHQ, a reduced form of AQ) played an important role during pulping. There are several types of compounds capable of reducing AQ to AHQ, one being carbohydrates. In a reaction with AQ, carbohydrate end groups are oxidized and are thereby stabilized toward yield-reducing alkaline reactions. Certain lignin groups are also capable of converting AQ to AHQ.
Model compound studies indicate that AHQ probably promotes delignification by a combination of at least two effects: promotion of lignin fragmentation reactions$^{16-22}$ and retardation of lignin condensation reactions.$^{23}$ During the course of these reactions, AHQ is oxidized to AQ, completing one reduction-oxidation (redox) cycle.$^{24}$ Repetition of this cycle explains the catalytic activity of AQ, high pulp yields, and fast delignification rates (Fig. 4).

**Figure 4.** A redox cycle proposal for explaining the catalytic action of anthraquinone during pulping.

The next level of sophistication in the mechanistic studies was to understand the details of each of the redox reactions. In this regard, only the AHQ induced fragmentation of lignin model compounds has received much attention. Lignin fragmentation steps, which are crucial to effective alkaline pulping, are believed to involve quinonemethide (QM) intermediates.$^7$ Two theories have evolved to explain the chemistry of an AHQ and QM interaction that gives rise to efficient fragmentation of lignin: adduct formation and SET reactions.$^{25}$

**ADDUCT vs. SET MECHANISMS**

The first theory proposed in the literature was that anthrahydroquinone dianion (AHQ$^{-2}$ or AQ$^{2-}$, as shown in Fig. 5) collides with a reactive (QM) end
unit of a lignin polymer chain and forms a bond to this unit. The resulting "adduct" then fragments to give AQ, a water-soluble lignin fragment (a simple phenol), and a new lignin polymer end unit (Fig. 5). The latter may be capable of forming new reactive end units, and the process is then repeated.

Figure 5. Hypothetical anthraquinone promoted lignin fragmentation reactions.

The second theory proposes that AHQ\(^{-2}\) (or AQ\(^{2-}\)) approaches a QM lignin end unit and at some remote distance transfers an electron to the QM.\(^{25}\) This transfer gives rise to anthrahydroquinone radical ion (AHQ\(^{+}\) or AQ\(^{+}\), as shown in Fig. 5) and a lignin end unit ion radical. Fragmentation of the latter affords a phenolate radical \((-O)\) or ion \((\cdot O)\) and a new lignin end unit ion or radical. In a subsequent step the radical pieces can accept a second electron from AHQ\(^{-}\) (AQ\(^{+}\)) to give the same product as proposed in the adduct mechanism. [The second electron transfer could be from AHQ\(^{-2}\) (AQ\(^{2-}\)) and, thus, the highly insoluble AQ need not be generated.]
Much of the rest of this report will be concerned with examining the experimental evidence which supports the adduct and single electron transfer (SET) theories. Proof of which mechanism actually exists during AQ pulping is crucial to the development of new pulping strategies. The report will also present my interpretation of the chemistry of lignin fragmentation and condensation reactions in the presence of sodium hydroxide (soda pulping), sodium hydro sulfide (kraft pulping), and anthrahydroquinone (AQ pulping).
THE MODELS APPROACH

ADVANTAGES AND DISADVANTAGES

At present, the best way to understand the chemistry of delignification is through the use of lignin model compounds. These compounds generally contain most of the important structural features of a lignin monomer unit, along with parts of a second monomer unit. An example is shown in the boxed-off region of Fig. 6. This type of model is referred to as a dimer model with a β-aryl ether connecting linkage; this linkage accounts for about 50–60% of the bonds which hold lignin together.  

Figure 6. A chemical formula representation of lignin, in which bold lines represent linkages between individual phenylpropane lignin monomer units, and the designated area represents the structure of a typical lignin model compound.
Unlike actual lignin, the models are well-defined compounds that allow a study of the detailed chemistry of how the major lignin units degrade under pulping conditions. One of the biggest drawbacks of model compounds, however, is that they are small molecules and, therefore, have solubility properties quite different from those of the large polymeric lignin. One way to bridge the gap between small models and complex polymeric lignin is to build and study the chemistry of polymeric lignin models. This is the goal of a current IPC Ph.D. thesis by P. Apfeld. He is attempting to graft a well-defined lignin model compound onto a polymeric material and study its reactions.

To date, lignin model studies have generally provided information that agrees with pulping results. For example, we recently observed that DMSO, an organic solvent produced by the kraft pulping industry, promoted the fragmentation of a lignin model compound. This led us to do some soda-DMSO pulping experiments, and subsequently we have shown that, under identical conditions, soda-DMSO is better than soda and equivalent to soda-AQ for lignin removal from loblolly pine. Unfortunately, fairly large levels of DMSO are needed to match the effects of 0.1% AQ, and a DMSO pulping process does, therefore, not look economically attractive. A few experiments were performed, both under an exploratory project number and this project, which helped to define some of the chemistry of DMSO delignification.

**IMPORTANCE OF QUINONEMETHIDES**

Another example of the usefulness of models is that of defining the importance of quinonemethide (QM) intermediates to the lignin fragmentation process. Phenolic 8-aryl ether dimer models, which are capable of generating QMs at elevated temperatures (Fig. 7), are readily fragmented by kraft pulping
conditions.\textsuperscript{7} Methylation of the phenolic hydroxyl group prevents QM generation and shuts down model fragmentation.\textsuperscript{7} Methylation of wood also severely hampers (initial) delignification.\textsuperscript{27}

\begin{center}
\begin{align*}
\text{CH}_3\text{O} & \quad \text{CH}_2\text{O} \\
\text{CHOH} & \quad \text{CHOH} \\
\quad & \quad \\
\text{OH} & \quad \text{OCH}_3
\end{align*}
\end{center}

Figure 7. Quinonemethide generation QM reactions.

AQ STUDIES

Model studies by Obst, Landucci, and Sanyer have shown that soda/AHQ and kraft are superior to a straight soda system for fragmenting models which are capable of producing QMs (Fig. 8).\textsuperscript{16} These results mimic the pulping efficiencies of these systems.

\begin{center}
\begin{align*}
\text{CH}_3\text{O} & \quad \text{CH}_2\text{O} \quad \text{CHOH} \\
\quad & \quad \\
\text{OH} & \quad \text{OCH}_3
\end{align*}
\end{center}

lignin model

\begin{center}
\begin{align*}
guaiacol & \quad 4\text{-vinylguaiacol} & \quad \text{a vinyl ether}
\end{align*}
\end{center}

\begin{center}
\begin{tabular}{|l|c|c|}
\hline
\textbf{CONDITIONS} & \textbf{YIELDS (%)} \\
\hline
SODA & 23 & 0 & 45 \\
SODA/AQ/PULP & 76 & 32 & 3 \\
KRAFT & 79 & TRACE & 0 \\
\hline
\end{tabular}
\end{center}

Figure 8. Alkaline degradation of a model lignin.\textsuperscript{16}
Note, in Fig. 8, that the AHQ system produces a unique fragment, 4-vinylguaiacol. [The level of 4-vinylguaiacol should equal that of guaiacol; however, the former has a tendency to polymerize under the reaction conditions employed.] Coniferyl alcohol, a compound analogous to 4-vinylguaiacol, has been observed in pulping liquors,\textsuperscript{28} and its level is pronouncedly increased when AHQ is present.\textsuperscript{29} So again, model studies agree with pulping results.

The point is that model studies have provided and probably will continue to provide valuable information on lignin pulping chemistry. They do not, however, always give the right information. For example, 1,4-dimethyl AHQ effectively fragments lignin models as well as AHQ;\textsuperscript{30} yet 1,4-dimethyl AQ is quite inferior to AQ as a pulping catalyst.\textsuperscript{31} Here, solubility differences between the models and wood probably play a major role.
ADDUCTS OF AHQ AND QMs

FORMATION

At about room temperature, AHQ$^-$ can be alkylated in aqueous alkali with a number of substrates, including quinonemethides (Fig. 9). The yield of QM-AHQ adducts (2A) was quite high for unhindered QMs (1A). In aqueous alkali, QMs 1B-D gave low yields of adducts (2B-D), presumably because some of the QMs were being diverted to $\alpha$-hydroxy (3) and vinyl ether (4) products by reactions with hydroxide ion. Other investigators have obtained good yields of hindered adducts, such as 2B and 2C, by using two phase (CH$_2$Cl$_2$/$H_2$O) or single phase organic solvent systems.

Figure 9. Adduct formation and competing reactions.
The lack of good yields of adducts from somewhat hindered QMs in aqueous alkali have been interpreted by us to mean that adduct formation between lignin QM end units and AHQ$^{-2}$ under pulping conditions will not be very favorable. The poor yields could also be due in part to an instability of a hindered adduct once formed. We have not exhaustively studied this point, except in the case of 1B ($R=CH_3$) where an α-OH product (3C), and not adduct degradation products, was recovered from the adduct preparation attempt.

**REACTIONS**

Several research groups have synthesized adducts [Eq. (3)] which contain β-aryl ether groups (5) and have shown that such structures, when warmed with alkali, fragment [Eq. (4)] to liberate AQ and two phenolate ions. Lignin contains large numbers of β-aryl ether linkages. The model studies suggest that rapid pulping rates are a result of AHQ adding to lignin QMs having neighboring β-aryl ether groups and that the resulting adducts fragment.

Adducts of AHQ and acylated milled wood lignin at 10°C have been reported.
A particularly attractive feature of the adduct theory for AHQ induced delignification is its similarity to the mechanism proposed for hydrosulfide-promoted delignification of wood. Here, it is believed that $\text{SH}^-$ adds to $\text{C}_\alpha$ of a lignin QM [Eq. (5)] and then assists in a cleavage of the $\text{C}_\beta$-aryl ether bond by a neighboring group displacement step [Eq. (6)].

There appears to be little doubt that heating a $\beta$-aryl ether QM-AHQ adduct, i.e. 5, causes fragmentation; but what happens when a simple adduct, i.e., 2A, is heated? Several years ago we did some experiments directed at answering this question; the results were given in the last report\(^1\) and, therefore, will be only briefly reviewed here. Above 60°C a simple adduct fragments to its constituent parts (AHQ\(^-2\) and a QM). This was demonstrated by heating an adduct in the presence of a QM of a different structure and observing the production of a new adduct (Fig. 10).\(^{24}\)

![Figure 10. "Crossover" experiment demonstrating the reversibility of adduct reactions.\(^{24}\)](image-url)
Heating of a simple adduct at 100°C in aqueous alkali causes a disproportionation reaction to occur, leading to the production of AQ and a substituted anthrone product (11) (Fig. 11). This oxidation-reduction disproportionation has been interpreted to proceed via SET steps and provides further evidence for the loss and gain of QM units between AHQ molecules.

![Diagram of reaction](image)

Figure 11. Simple adduct reactions at 100°C.

If the 100°C heating of a simple adduct is done in the presence of an excess of AHQ⁻², the product is a QM-anthrone adduct (12) (Fig. 11). Heating anthrone adduct 11 in the presence of AHQ⁻² gives 12 and QM-AHQ adduct 2A (Fig. 11); thus, QM species participate in reversible reactions with both AHQ and anthrone ions. Both mono- and di-QM-anthrone adducts 11 and 12 can be prepared by alkylating anthrone with a simple QM (1A); only a mono QM-anthrone adduct could be prepared when an α-substituted QM (i.e., 1D) was used.

The reactions mentioned above offer an explanation as to how anthrone (found in trace amounts) is formed and AQ is lost during AQ pulping. Because of the "bulk" of lignin QMs, di-QM-anthrone adducts would not be expected.
However, mono QM-anthrone adducts could serve as a reversible source of anthrone and, if stable enough, could lead to possible "dead end" products of AHQ (Fig. 12).

$$\text{AHQ}^2 + \text{lignin QM} \quad \overset{\text{OH}^- \rightarrow \text{H}_2\text{O}}{\longrightarrow} \quad \text{anthrone}^{-1} + \text{lignin QM}$$

![Figure 12. Possible pulping reactions of anthrahydroquinone.](image)

Heating a simple QM-AHQ adduct, such as 2A, in aqueous alkali at 173°C, caused extensive degradation to AQ and a variety of QM condensation products. The yield of AQ was only about 50%; where did the remainder go? A small amount was still present as adduct. Results of this type suggest that adducts between AHQ and lignin QMs which lack fragmentable β-aryl ether linkages may account for a substantial portion of the "lost" AQ observed during pulping.

[Our work on the preparation and reactions of adducts led to the extensive use of nuclear magnetic resonance (NMR) and mass spectrometry (MS) techniques for molecular characterizations; some of the results were reported as separate papers.36,37]
SET REACTIONS OF AHQ

INTRODUCTION

The fact that adducts can dissociate into a QM and AHQ\(^{-2}\) at temperatures where adducts give rise to QM fragmentation products raises some questions. Are adducts on the direct pathway to fragments or a dead end? What other way could QMs and AHQ\(^{-2}\) react to give QM fragmentation products? Is an alternative way, i.e., single electron transfer (SET), more or less efficient than an adduct pathway?

Scheme 1 offers a mechanism of fragmentation in which AHQ\(^{-2}\) and AHQ\(^{2}\) act as carriers in the transfer of electrons from carbohydrates to lignin; no adducts are involved. The soluble electron transfer catalysts AHQ\(^{-2}\) and AHQ\(^{2}\) are mediating a reaction between two insoluble polymers.

The recent organic chemical literature is abundant in examples of reactions which were hitherto thought to be ionic nucleophilic substitutions (SN\(_1\) or SN\(_2\)) but have now been shown in certain cases to be SET reactions. Examples are presented in my recent review article.\(^{25}\) Most of the examples where SET reactions have been observed involve the reactions of highly hindered substances which can also form relatively stable radical intermediates. The generality of SET mechanisms in nonhindered systems is less clear, although examples are known. Also, SET reactions can proceed without radical initiators.

The literature SET examples almost exclusively involve organic solvents and moderate reaction temperatures. The procedures developed for detecting and promoting SET are difficult to extend to reactions in water at 170°C.
SCHEME 1

Proposed Mechanism of Action of AQ Species
Pulping via SET Reactions

\[ \text{AHQ}^{-2} + \text{ArO}^- + \text{CH}_3\text{O}^+ \rightarrow \text{AHQ}^+ + \text{ArO}^- \]

(7)

\[ \text{ArO}^- + \text{AHQ}^{-2} \rightarrow \text{ArO}^- + \text{AHQ}^+ \]

(8)

\[ 2\text{AHQ}^{-2} + \text{RCO}^- + 3\text{OH}^- \rightarrow 2\text{AHQ}^+ + \text{RCO}^- + 2\text{H}_2\text{O} \]  

(Carbohydrate)

(10)

ARGUMENTS FOR PULPING SET REACTIONS

A quinonemethide, which is nonaromatic, would appear to be a good substrate for electron transfer reactions, since acceptance of an electron gives
an extensively resonance stabilized, aromatic QM− species. Anthrahydroquinone radical anion, AHQ−, should also be an excellent partner in electron transfer reactions, since not only is AHQ− extensively resonance stabilized but its oxidized and reduced forms, AQ and AHQ−2, also have good stability.

Besides the plausibility of the reactions outlined in Scheme 1, the arguments for SET mechanisms operating during pulping are extensive. Radicals in general38 and AHQ− in particular39−41 have been observed during pulping. We have observed two cases where AHQ−2 appears to participate in SET reactions. One example is the reduction of adducts by AHQ−2 at 100°C in aqueous alkali.34 The other is the promotion of benzaldehyde Cannizzaro reactions by AQ and AMS (anthraquinone monosulfonate).1 The benzaldehyde Cannizzaro reaction [Eq. (16)] has been shown to involve radical intermediates.42

The reduction potentials for the two steps AQ → AHQ− → AHQ−2 are identical in water;17 thus one molecule of AQ (in its AHQ−2 form) should be capable of initiating two QM → QM2 conversions. This could explain the "square-root dose relationship" found for AQ pulping;43 an adduct mechanism cannot. A "linear-dose relationship" is observed44 for SH−, and nucleophilic substitution mechanisms have been suggested [Eq. (5) and (6)].

If steric hindrance to reaction were to play a significant role during delignification, the SET mechanism would be favored. Electron transfer reactions across distances of 10Å and greater have been reported to occur at astonishingly fast rates.45 In contrast, an adduct mechanism requires two relatively flat substrates to assume a specific geometry for the production of roughly a 1.5 Å bond between C9 of AHQ−2 and Cα of a QM. After bonding, Cα contains two bulky substituents, one of which is the quaternary substituted C9 carbon. Any group on Cβ
(typically a CH$_2$OH group in lignin) would seriously impair adduct formation through a strong gauche strain interaction with the C$_9$ carbon, as shown below:

![Diagram showing adduct formation](image)

Except for possible negative effects due to solubility,$^{46}$ the size and shape of a pulping catalyst seem to have little influence on the effectiveness of the catalyst. Some fairly hindered catalysts, such as the rosindones,$^{47}$ and metal porphyrins,$^{48}$ are as efficient as AQ at low concentrations in delignifying wood and/or fragmenting models. This observation is contrary to what one would expect with an adduct mechanism. Many of the known pulping catalysts, such as AQ, phenazine,$^{49}$ fluorenone,$^{50}$ and metal porphyrins,$^{48}$ would be very suitable electron transfer catalysts.
Poppius and Brunow claim that anthrone causes β-aryl ether cleavage of a lignin model by a pathway not involving an adduct intermediate. A logical explanation of their results is that an anthranol anion transfers an electron to a QM intermediate to give fragmentation of the QM and an anthranol radical. Coupling of two radicals, followed by enolization, then gives dianthranol, an observed by-product.

The lifetimes of the intermediates in both the proposed adduct mechanism and SET mechanism should be extremely short at the high temperatures used in AQ pulping systems. How do we differentiate a momentary bonding-fragmentation mechanism from an electron transfer mechanism? Three major approaches have been taken. One involves electrochemical studies of lignin model QMs and AHQ in organic solvents at room temperature. The other two, a steric effect study and an electronics effect study, are also of lignin model compounds, but the conditions resemble that of pulping, i.e., aqueous alkali at 135-170°C.

**STERIC EFFECT STUDY**

Our first attempt to more accurately define the mechanism of lignin fragmentation reactions caused by AHQ involved the study of steric effects. The chemical literature supports the fact that steric effects will be minimal, or nonexistent, for an SET mechanism. Based on the stereochemistry shown in Eq. (12), steric effects could be large for an adduct mechanism in which close contact (bonding) is required. An example is provided in Fig. 13. Considerable steric congestion will occur when the two *-carbons are brought together to make an adduct. An SET mechanism will probably not require a specific reaction orientation; the electron could be transferred from a side ring of the AHQ reactant to the ring portion of the QM substrate.
While the adduct and SET mechanisms should undoubtedly have different steric requirements, it was not certain that the differences would be noticeable. Evidence being gathered in another study indicated that the energy required to generate a QM was greater than the energies associated with the AHQ-induced fragmentation reactions. Could the relative energies of these two processes change with structural modifications of the QM or AHQ reactant? If the energetics are represented by case A, Fig. 14, 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.
The reactions of three AHQ \textsuperscript{-2} analogs and four models shown in Fig. 15 have been examined. The model fragmentation efficiencies were the same for both sterically hindered and unhindered AHQ analogs in either water or water-organic solvent mixtures (see example, Fig. 16). This result indicates that the reaction mechanism (a) cannot involve a rate determining adduct formation step, (b) is an SET type, where steric effects are minor, or (c) is dominated by a highly energetic QM generation step.

We also observed that 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.
Figure 15. Compounds studied to show steric effects on lignin model fragmentation reactions.

Figure 16. Relative comparison of 4-methylyxringol yields from degradations of the 2-carbon syringyl model (shown in Fig. 21) 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.
ELECTRONIC EFFECT STUDY - SODA REACTIONS

Substituents can influence reaction directions and rates in a number of ways. Their steric size, as just discussed, is one way. Another is their ability to increase or decrease electron densities on attached carbons or groups by a combination of polar and resonance effects. An electronic effect study is one in which an examination of how a substituent's electron-donating or releasing abilities affect the rate of a reaction. The resultant substituent/reactivity relationship can provide valuable mechanistic information - information which might support either an adduct of SET mechanism for lignin fragmentation reactions with AHQ.

Prior to examining the effects which AHQ$^{-2}$ and other additives have on model degradations, we needed to know the NaOH (soda control)/model chemistry. Consequently, models of the type 21 and 22 were treated with different levels of NaOH for different time periods and at different temperatures. Figure 17 gives an example of the results; here we followed the rate of $\beta$-ring phenol being liberated from the model (i.e., the fragmentation rate).

The four models initially showed a large difference in fragmentation rates as a function of structure (the nature of R). After about 20 minutes, the starting materials were consumed and only fragmented products and vinyl ether structures (24) remained. The slow, and nearly identical, fragmentation rates after 20 minutes indicated that the vinyl ether structures also fragmented to give $\beta$-ring phenols and that fragmentation rates did not vary with changes in R. The rates were also strongly dependent on the level of alkali used (Fig. 17) and temperature.
Figure 17. Phenol yields as a function of time in the simultaneous degradation of models 22A-D at 170°C in the presence of 150 equivalents of NaOH (upper four curves) and the single degradation of 22A at 170°C with 12.5 equiv. of NaOH (lower curve).
Data of this type allowed us to conclude that the α-hydroxy models are subjected to competing reactions, namely vinyl ether formation via a quinone-methide intermediate (path a, Scheme 2) and direct fragmentation via a dianion intermediate (22⁻²) (path b). The strong (electronic) effect of the substituent R indicated that cleavage of the β-aryl ether bond (step b₂, Scheme 2) was the slow step in the direct fragmentation of the model. In agreement with this proposal was the fact that variation of the substituents on the A-ring had only a minor influence on the model fragmentation.

SCHEME 2

Modes of Soda Induced Decomposition of Models 22

![SCHEME 2 Diagram]

**ELECTRONIC EFFECT STUDY - ADDITIVE REACTIONS**

The previous study showed that substituent effects can be large (during direct fragmentation) or nonexistent (during vinyl ether fragmentation). Either result gives clues as to which steps are critical in the two fragmentation
reactions. Degradations of α-hydroxy-β-aryl ether models of the type 22 in the presence of AHQ\(^{-2}\) showed identical initial fragmentation rates for the differently substituted models (Fig. 18).

![Graph showing phenol yields over time for degradations of models 22A-D](image)

**Figure 18.** Phenol yields as a function of time for degradations of models 22A-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.

This result means that the ability of the R-substituent to release or withdraw electrons has no effect on the rate because the critical, slow step in the mechanism must not involve a development of charge near ring B; the slow step is probably the quinonemethide generation [Eq. (13)].

\[
\text{AHQ, NaOH, 150°C}
\]

\[
\text{CH-OAr} \xrightarrow{\text{slow}} \text{CH-OAr} + \text{OH}^- \xrightarrow{\text{SET or adduct}} \text{fragments}
\]
Further verification of this conclusion comes from examining the fragmentation rates of models which have different A-ring substituents (Fig. 19). Substituted QMs are generally more stable and, therefore, more easily formed than unsubstituted QMs. The fragmentation of the A-ring models follows this trend.

Figure 19. Phenol yield 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.

Studies of the effect of SH— and glucose on these same models indicated that the critical step in the mechanism of their fragmentation-promoted reactions was also QM formation. These materials are, however, not as efficient as AHQ—2 in fragmenting the models (Fig. 19 and 20).
Even though QM generation dominates the kinetics of these fragmentation reactions, it is still possible to study the chemistry of reactions occurring after QM formation the using conditions where the additive (AHQ$^{-2}$ or SH$^{-}$) is present in limited amount with two substrates. This was the case that was used to obtain the data shown in Fig. 21.

Here we see that with a very limited amount of AHQ$^{-2}$ the two models have quite different reactivities. In contrast, with 5 equivalents of AHQ$^{-2}$ per model, there is practically no difference in reactivities during a simultaneous degradation. The data from sulfide ion degradations were similar to the AHQ$^{-2}$ results. In each case, the preference for fragmentation of the CF$_3$-substituted
model over the CH$_3$-substituted one indicates that the β-ring is fragmenting as a phenolate ion.

![Diagram of molecular structures and reaction kinetics](image)

**Figure 21.** Phenol yields as a function of time for the 120°C degradations of 1 equiv. each of the indicated models in the same reactor in the presence of (a) 25 equiv. of NaOH (lower arrows) and (b) 25 equiv. of NaOH, 1 equiv. of glucose and 1 equiv. of AQ (upper curves).

Losing the β-ring as an ion is compatible with an adduct mechanism [Eq. (4), page 18] and one version of an SET mechanism. The one version is that the OM$^-$ must preferentially fragment [Eq. (15), Scheme 3] to give a β-ring ion and an A-ring radical. The latter could gain another electron from an AHQ ion to
result in a phenolate ion product and/or polymerize. The yield of A-ring phenol
is always lower than B-ring phenol (i.e., Fig. 8, page 15) and we often observe
dimers of the A-ring fragment; both observations support the view that the A-
ring is produced initially as a radical.

**SCHEME 3**

**Delignification via AHQ-Induced SET Reactions**

In summary, the electronic effect studies have not allowed a distinc-
tion to be made between SET and adduct mechanisms for AHQ\(^{-2}\) promoted delignifi-
cation; this is because QM formation proved to be the rate determining step.
Much has been learned, however, about the chemistry of soda and additive-
promoted delignification reactions.
Besides the conclusions already mentioned, it is apparent that the fragmentation step is much easier to accomplish than QM generation; i.e., the system is more like case A, than case B, in Fig. 22. If case B was the true description of the fragmentation pathway, one would expect that changes in β-ring substituents would lead to observable reactivity differences under standard conditions.

![Energy diagram](image)

**Figure 22.** Hypothetical partial energy diagrams for fragmentation of a model by way of a QM.

**SYNTHESIS**

Our steric and electronic efforts studies required a considerable amount of model synthesis work. In this connection, we have developed a new method (methylation without phenol protection) for building a 3-carbon lignin side chain model; two synthesis articles have been published on this method. Scheme 4 outlines the synthesis steps (either paths a or b) for preparing compounds needed for the electronic effect study. Similar chemistry was employed to prepare β-ring guaiacyl and 4-methylsyringyl models containing, 0, 1, or 2 methyl groups on the β-carbon for use in the steric effect study.
SCHEME 4

Steps in the Model Synthesis

\[
\begin{align*}
&\text{CH}_3\text{C}=\text{O} \\
&\text{OAc} \quad \text{Br}_2 \to \text{CH}_3\text{Br} \\
&\text{OAc} \quad \text{K}_2\text{CO}_3 \to \text{CH}_3\text{O-} \\
&\text{Br}_2 \quad \text{DMF} \quad \text{Chrom.} \quad \to \quad \text{CH}_3\text{O-} \\
&\text{OH} \quad \text{OAc} \quad \text{NaOCH}_3 \quad \to \quad \text{CH}_3\text{O-} \\
&\text{OH} \quad \text{OH} \quad \text{NaBH}_4 \quad \to \quad \text{CH}_3\text{O-} \\
&\text{R} \quad \text{Cl} \quad \text{CF}_3 \quad \text{NO}_2 \quad \text{OH} \quad \text{OAc} \quad \text{H} \\
&\text{A} \quad \text{B} \quad \text{C} \quad \text{D} \quad \text{E} \quad \text{F} \quad \text{G} \quad \text{H} \\
&\text{CH}_3 \quad \text{CH} \quad \text{OCH}_3 \quad \text{OCH}_3 \quad \text{CHOH} \quad \text{OH} \quad \text{OH} \quad \text{OAc} \quad \text{H} \\
&\text{14} \quad \text{15} \quad \text{16} \quad \text{17} \quad \text{18} \quad \text{19} \quad \text{20} \quad \text{21} \quad \text{22} \\
\end{align*}
\]

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ELECTROCHEMICAL STUDIES

An electrochemical study was done simultaneously with the steric and electronic effects studies and as a joint project with Dr. Helena Chum, Senior Electrochemist, Thermochemical and Electrochemical Research Branch, at the Solar Energy Research Institute (SERI) in Golden, Colorado, and Dr. Peter...
Palasz, a Postdoctoral Fellow. The SERI personnel are experienced in electrochemistry in general and electrochemistry of biomass derived products (including lignin) in particular.

Electron transfer reactions are the heart of the field of electrochemistry. "Electroactive" substances will either accept or give up electrons at electrode surfaces, depending on the type of voltages applied. In organic solvents, such as acetonitrile or DMSO, AQ accepts one electron at a voltage of roughly -0.8 to -0.9 V to give AHQ$^2-$ and then a second one at -1.5 to -1.7 V to give AHQ$^-2$. [The voltages are relative to a Ag/AgCl reference electrode.] These AHQ ions are relatively stable in the solvent with a N$_2$ atmosphere and can be converted back to AQ by reversing the potential of the working electrode.

We have prepared and examined the electrochemistry of β-aryl ether QMs, such as 25, and found that they are electroactive. For example, QM 25 readily accepts an electron at -1.1 to -1.2 V to give a QM$^2+$; the latter rapidly undergoes a chemical reaction which leads to rupture of its β-aryl ether bond. Mixtures of AQ and QM 25 show current enhancements at the -0.9 V potential of a cyclic voltammogram, indicating electron transfer is occurring between AHQ$^2-$ and the QM.

Preparative electrolysis of AQ in acetonitrile at -0.9 V produced a strong red color (associated with AHQ$^2-$ production). An identical electrolysis of a mixture of AQ and QM 25 exhibited no red color initially, presumably because the electrolytically generated AHQ$^2-$ rapidly reacted with the QM in the solution. When the QM had been consumed, the red color appeared. Analysis of the reaction mixture at that time showed that guaiacol (7) and isoeugenol (26) were present in good yields. Preparative electrolysis of QM 25 by itself at -0.9 V did not produce guaiacol and isoeugenol.
Scheme 5 outlines the chemistry which is probably occurring during the coelectrolysis at -0.9 V. In essence, QM.25 is stable at -0.9 V in the absence of AQ, but readily fragments at this potential in the presence of AQ because electrochemically generated AHQ⁺ is able to SET to the QM and the resulting QM⁻ falls apart. The electrochemical results thus verify that several of the SET reactions proposed earlier (Scheme 1, page 23) are possible under certain conditions.
SCHEME 5

PREPARATIVE COELECTROLYSIS OF AQ and QM 25 AT -0.9 V

\[ 2\text{AQ} + 2e^- \rightarrow 2\text{AHQ}^2^- \quad (17) \]

\[ \text{AHQ}^2^- + \text{CH}=\text{CHCH}_3 \rightarrow \text{AQ} + \text{QM25}^- \quad (18) \]

\[ \text{QM25}^- \rightarrow \text{7}^- + \text{26}^- \quad (19) \]

\[ \text{AHQ}^2^- + 26^- \rightarrow \text{AQ} + 26^- \quad (20) \]

\[ \text{AHQ}^2^- + 2e^- \rightarrow \text{CH}=\text{CHCH}_3 \quad (21) \]
The work on Project 3475 has raised many interesting research questions which have become the basis of master's students' (8 credit) "independent study" research and Ph.D. students' theses. This section of the report briefly highlights some of research done by the many capable students that have worked with me. Generally, the independent study research addresses small problems, and the Ph.D. theses tackle problems of greater scope.

**HIGH TEMPERATURE REACTIONS OF HO⁻ and HS⁻**

Student research projects often address very fundamental questions. For example, Dean Smith's independent study concerned trying to establish how strong of a base is NaOH at 170°C. By means of model compound reactions and NMR analysis, Dean showed that NaOH in water at 170°C could deprotonate organic acids having pKa values of about 35. Since the normal pKa of NaOH is about 16 at room temperature (and pKa values are logarithmic), the ability of NaOH to deprotonate wood constituents is much greater than originally thought. This type of information gives us clues as to what kinds of reactions are possible under pulping conditions.

The basicity of NaOH should depend on the degree of solvation by water molecules. Solvation should decrease with increasing temperature. Unsolvated ions in the gas phase often show remarkably different properties than solution solvated ion. This raises the question as whether the properties of ions in water at 170°C resemble room temperature solvated ions or high-temperature gas phase ions. Gregg Reed, in both his master's and Ph.D. research, is trying to
establish if the relative nucleophilicities of \( \text{OH}^- \) and \( \text{SH}^- \) change with temperature (up to 200°C); answering this question will provide valuable information on the nature of the chemistry in kraft pulping systems.

MODEL EVALUATION

Still along the lines of very fundamental studies is the Ph.D. thesis of Patrick Apfeld. He is attempting to prove or disprove that the chemistry of soluble lignin model compounds represents that of lignin in wood. Mention of this work was made in an earlier section of this report (p. 14).

Specifically, Apfeld has prepared a lignin model dimer containing an extended side chain with a terminal alcohol group, compound 27. This compound has been reacted with trityl chloride to give 28 and with a trityl polystyrene to give a polymer bound product 29. The degradations of 28 and 29 are presently being compared to observe any differences in fragmentation yields based on solubility differences. Should there be no yield differences, the research will support the long assumed proposition that the chemistry of models accurately predicts the chemistry of actual lignin.

![Chemical Structure]

27, \( R = \text{H} \)
28, \( R = \text{CPh}_3 \)
29, \( R = \text{CPh}_2 - \text{polystyrene} \)
HIGH TEMPERATURE AQ REACTIONS

The fate of AQ and the influence of AQ on typical compounds found in pulping liquors has been the subject of several brief student investigations at IPC. A set of students have looked at how AQ interacts with tall oil compounds; except for a small amount of reduction of dehydro to dehydrodehydroabietic acid, the reaction between AQ and resin acids is slight.\textsuperscript{58}

Patrick Apfeld showed, in his master's research, that anthraquinone monosulfonate (a water soluble AQ derivative) oxidized both benzylic alcohols and mercaptans to aromatic ketones and that the rate of the mercaptan oxidation was several hundred times faster than the alcohol.\textsuperscript{59} The results suggest that benzyl mercaptans, a likely structure formed during kraft pulping, could reduce AQ to AHQ and, thus, aid delignification.

The conversion of anthraquinone to anthrahydroquinone was determined by mixing AQ with typical pulping constituents (or models of) in a flow-through cell and filtering while hot.\textsuperscript{60} The very limited solubility of AQ in 1M NaOH at 160°C is increased significantly (by conversion to soluble AHQ\textsuperscript{2}) with glucose, kraft lignin, or sodium sulfide. The flow-through filtering cell was also used by Carola Storgard-Envall to estimate effective methods for reducing AQ and AQ-analogs to AHQ species and to attempt to recover AQ from pulping liquors.\textsuperscript{60} The latter unsuccessful procedure involved contacting hot, spent soda/AQ pulping liquors with oxygen and filtering while hot; under these conditions AHQ should be converted to AQ and the latter collected by filtration.

A student study of AQ pulps and liquors (from the pulping of loblolly pine) by negative chemical ionization mass spectroscopy showed the importance of
this technique for detecting trace levels of condensed aromatic compounds. The observation of compounds 31-33 led us to speculate that these were intermediate compounds formed when AHQ$^{-2}$ is methylated by carbohydrates (Fig. 23).

Figure 24. Possible mechanism for the formation of methyl anthrone (34).

**CONDENSATION REACTIONS**

There has been considerable associated student research work in the area of lignin condensation reactions. The studies of Tom Brown on molecular weight changes of dioxane lignin as a function of AQ, glucose, and AQ/glucose addition helped establish that AHQ interferes with lignin-lignin condensation.
His work and our own work on vanillyl alcohol condensation reactions were explained in detail in the previous project report. These studies demonstrated an effect but did not provide an explanation.

Dean Smith's Ph.D. thesis is concerned with understanding how AHQ\textsuperscript{-2} inhibits lignin condensation reactions. Smith's thesis work is also being followed by the start-up of a new Ph.D. thesis (Bob Barkhau) in this highly important area. The control of condensation reactions could allow us to pulp to much lower lignin levels. Smith's work will be discussed here in greater depth than the other student research because (a) his work is a direct outgrowth of project work and (b) he has demonstrated the existence of SET reactions under pulping conditions.

Our work with vanillyl alcohol (35) was complicated by the fact that 35 has two sites for reaction, C\textsubscript{1} and C\textsubscript{5}, and polymers formed. Syringyl alcohol (36) has only one site (C\textsubscript{1}) for condensation (of the usual type) and, thus, dimers are the biggest molecules possible. Smith's study was therefore of syringyl alcohol; with a simpler product mixture he could quantitate the results of different additives on the syringyl alcohol reactions. The additives under investigation were typical pulping additives and materials which might promote or inhibit radical reactions. The reaction of syringyl alcohol in a 1N NaOH solution at 135°C (henceforth to be referred to as the system) produced five compounds. The expected dimer, disyringylmethane (37), was the major product. Three monomers, syringol (38), 4-methylsyringol (39), and syringaldehyde (40), were produced in moderate yields, and a trace amount of the dimer bisyringyl (41) was also observed.

The mechanism responsible for the formation of 4-methylsyringol, bis-syringyl, and syringaldehyde appears to be radical in nature. This mechanism is
viewed as beginning with the transfer of an electron from a phenoxy anion to a QM resulting in the formation of a benzyl radical and a phenoxy radical (Scheme 6). The resulting benzyl radical can then either form 4-methylsyringol or bisyringyl.

![Chemical structures](image)

35, 36, R = CH₂OH  
38, R = H  
39, R = CH₃  
40, R = CHO  
42, R = CH₂SH  
37, X = -CH₂-  
41, X = -CH₂-CH₂-  
43, X = -CH₂-S-CH₂-

The 4-methylsyringol product obtained from treating α,α-dideutério-syringyl alcohol with alkali was fully deuterated at the benzyl methyl group. This suggests that 4-methylsyringol results from transfer of a hydrogen atom (or deuterium atom) from the benzyl position of syringyl alcohol to the syringyl QM radical anion \(44^a\). Bisyringyl probably is formed by the coupling of two benzyl radicals or the addition of a benzyl radical to a QM and the subsequent acquisition of an electron. Thus, the radical mechanisms can explain some of the reactions occurring during the alkaline reaction of syringyl alcohol; 4-methylsyringol and bisyringyl are the reduction products and syringaldehyde is the oxidation product.

Additional studies of the alkaline reactions of syringyl alcohol were done by adding various compounds to the system. When two molar equivalents of anthrahydroquinone (AHQ) were added, the rate of the consumption of syringyl...
SCHEME 6

Postulated High Temperature Reactions of Syringyl Alcohol
alcohol increased and the product distribution was drastically changed. Production of 4-methylsyringol and bisyringyl was enhanced, while that of disyringylmethane was retarded. Apparently, AHQ was able to transfer electrons to QM's, resulting in an increase in the production of QM radical anions (Scheme 6). The QM radical anions can then form 4-methylsyringol or bisyringyl as previously described. Anthrahydroquinone appears to enhance the radical reactions of syringyl alcohol by increasing the concentration of benzylic radicals.

In order to simulate the presence of carbohydrates, two molar equivalents of glucose were added to the system. The presence of glucose did not change the consumption of syringyl alcohol to an appreciable degree, but it did decrease the production of disyringylmethane by half and that of syringaldehyde entirely. The production of 4-methylsyringol was nearly doubled and that of bisyringyl was also increased. Perhaps glucose or some of its alkaline degradation products can also transfer electrons to QM's and enhance the radical reactions of syringyl alcohol as does AHQ.

When two molar equivalents of sulfide were added to the system, there was an initial rapid consumption of syringyl alcohol followed by a moderate consumption. The rapid consumption of syringyl alcohol was not accompanied by an increased production of disyringylmethane. On the contrary, production of disyringylmethane was decreased; after 85 minutes the amount of disyringylmethane produced was less than half of that produced by the soda system alone. The production of syringaldehyde, bisyringyl, and 4-methylsyringol were also decreased. Analysis of the reaction solution by gas chromatography/mass spectrometry showed the presence of two new compounds, 3,5-dimethoxy-4-hydroxybenzylthiol (42) and di-(3,5-dimethoxy-4-hydroxybenzyl)sulfide (43).
The appearance of these compounds indicates that the hydrosulfide ion in the reaction system can capture QM's to form 42 (Scheme 7). Ionization of 42 allows the capture of a second QM to produce 43. Since all of these reactions are reversible, an equilibrium was probably established early. Thus, the original fast consumption of syringyl alcohol was during the establishment of the equilibrium. As syringyl alcohol was further consumed, the equilibrium shifted in the reverse direction, replenishing the syringyl alcohol and thus providing only moderate decreases of syringyl alcohol. Unlike AHQ and glucose, sulfide appeared to interact with syringyl alcohol by ionic pathways in which hydrosulfide ions add to QM's to produce "adducts."

SCHEME 7

Postulated Reactions of Syringyl Alcohol with Hydrosulfide Ion
Additional proof for the electron transfer reactions involving QM's and pulping chemicals was sought by using radical "probes" built directly into the QM's. The cyclization of 5-hexen-1-yl intermediates (\(\overset{\cdot}{*}\)) to 5-membered rings is taken as proof that radicals (\(\overset{\cdot}{*}\) = \(\cdot\)) existed. [A carbonium ion (\(\overset{\cdot}{*}\) = \(+\)) would cyclize to a 6-membered ring, and a carbanion (\(\overset{\cdot}{*}\) = \(\cdot\)) would not cyclize.] Compound 45 was specifically designed to provide QM 46 when heated in alkali (Scheme 8). Should QM 46 accept an electron in a SET reaction, the resulting ion radical 46\(^{+}\) might cyclize to a 5-membered ring ion radical 48\(^{+}\). Formation of reduction products 47 and 49 would thus indicate that radical intermediates were present.

Heating compound 45 with and without additives present has shown which additives produce radicals via SET reactions. Both AHQ\(^{-2}\) and glucose were quite good at generating radicals; AHQ\(^{-2}\) gave large amounts of 47 and small amounts of 49, while glucose did just the opposite. The yields of open side-chain product 47 and cyclized side-chain product 49 depend on the relative rates of hydrogen atom subtraction vs. cyclization. Soda "pulping" of 45 led only to recovered 45, while kraft "pulping" of 45 gave small amounts of radical derived products. Consequently, the reactions of 45 indicate the possible occurrence of SET reactions in pulping situations.
SCHEME 8

Possible SET Reactions of Compound 45

\[ \text{Compound 45} \xrightarrow{\text{OH}^-} \text{Compound 46} \downarrow \text{e}^- \]

\[ \text{Compound 46} \xrightarrow{\text{H}^+} \text{Compound 47}^- \]

\[ \text{Compound 47}^- \xleftarrow{\text{H}^+} \text{Compound 46}^- \]

\[ \text{Compound 46}^- \xleftarrow{} \text{Compound 48}^- \]

\[ \text{Compound 48}^- \xrightarrow{\text{H}^+} \text{Compound 49}^- \]
This section of the report attempts to correlate literature data with our own data to speculate on the relative energies associated with several important delignification reactions. Specifically, the reactions of phenolic β-aryl ether end units of lignin will be the prime focus. Cleavage of these units probably represents the most prominent reaction occurring during the "initial" phase of pulping and undoubtedly is also an important secondary reaction during "bulk" phase delignification.

Using kinetic and competitive experiments with lignin model compounds, Gierer and Ljunggren\(^6\) have proposed the following relative rates for reactions involving quinonmethides: C\(_8\)-proton abstraction < QM generation < C\(_7\)-formaldehyde elimination < addition of phenolate carbanions to C\(_6\) < addition of SH\(^-\) to C\(_6\). Our recent data indicate that addition of AHQ\(^-2\), or SET of AHQ\(^-2\), to a QM is faster than any of the above reactions\(^3,4,5\) and that the energy for soda-induced model fragmentation is comparable to that of C\(_8\)-proton abstraction.\(^5\) A rough relative order of energy differences (and thus rate differences) for several lignin reactions are given in Fig. 24.

The energy diagram presented indicates that the reaction options for a soda pulping system are poor. The options consist of a high energy fragmentation pathway, condensation reactions and two pathways for generation of vinyl ethers. The condensed and vinyl-ether modified lignins are relatively stable toward further fragmentation and, thus, delignification will be retarded by their presence. The energetics of the undesirable reactions appear similar to the desirable, direct fragmentation reactions; therefore, undesirable competing reactions will occur.
Figure 24. Hypothetical energy diagram for the reactions of phenolic lignin end units.
Straight soda pulping of wood is probably aided by the presence of carbohydrate in the medium. Although less efficient than SH⁻ and AHQ⁻², glucose enhances fragmentation of models containing β-aryl ether linkages. Unless the conditions are quite severe, sodium hydroxide alone is quite poor at fragmenting these kinds of models.

The energy diagram (Fig. 24) pictures that QM formation is lower in energy than NaOH-induced fragmentation. What is needed for fast pulping is the ability to fragment the intermediate QM species. This is what kraft and AQ-based pulping systems do. The active ingredients, SH⁻ and AHQ⁻² ions, attack the QMs and produce new intermediates which readily fragment. The pathways here, which are either "adduct" or "SET" in nature, preclude significant condensation or ether formation reactions.

KINETIC INTERPRETATION OF ADDITIVE EFFECTS

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

\[ \text{Frag. Rate} = k_{HO} [HO^-][\text{Model}] + k_{Add} [\text{Add}][\text{QM}] \] (22)

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 quinonemethide (QM) can be calculated by applying the steady state assumption for reactive intermediates and considering the various reactions available (Fig. 24) to the QM:

\[ [\text{QM}] = \frac{k_{QM}[\text{Model}]}{k_{Add}[\text{Add}] + k_{VE}[HO^-] + k'_{VE}[HO^-] + k_{CON}[ArO^-] + k_{QM}[HO^-]} \] (23)
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 (\( \text{ArO}^- \)), and \( k_{QM} \) and \( k_{QM}^- \) are the forward and reverse rate constants for QM formation and return to the model.

Combining Eq. (22) and (23) gives:

\[
\text{Frag. Rate} = k_{HO} [\text{HO}^-][\text{Model}] + k_{QM} [\text{Model}] \cdot X \tag{24}
\]

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

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

If the \( k_{Add[Add]} \) term is large relative to the other terms in the denominator of the \( X \) term, expression (24) reduces to:

\[
\text{Frag. Rate} = k_{HO} [\text{HO}^-][\text{Model}] + k_{QM} [\text{Model}] \tag{25}
\]

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.\(^6\)

The fragmentation efficiencies which we observed for the reactions of additives with lignin models, namely \( \text{AHQ} > \text{SH}^- > \text{glucose} \), can be accounted for by assuming that \( X \) is largest for \( \text{AHQ} \) 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.
LIGNIN CONDENSATION REACTIONS

At the heart of lignin condensation reactions are quinonemethides. Elimination of such structures would undoubtedly lessen undesirable condensation reactions; however, these structures are also crucial to many beneficial fragmentation reactions of lignin. What is needed for efficient pulping is to maximize the production of QMs which will fragment and minimize the production of condensation-causing QMs. In some cases these will be the same QMs.

Quinonemethides which contain β-aryl ether groups are essential to efficient lignin fragmentation. It is important that these QMs be "pushed" rapidly onto fragmentation pathways before condensation occurs (Scheme 9). The "push" comes from additives such as SH⁻ and AHQ⁻² which either bond, or SET, to the α-carbon of the QMs.

If the additive effect is too slow, phenolate ions (or radicals) can effectively compete to give carbon-Çα (condensed) structures (Scheme 9). The β-aryl ether units in the latter structures probably will be stable to pulping conditions and chemicals. Thus, condensation of this type is very detrimental; both the size of the lignin is increased and potential fragmentation points are lost.

An efficient additive will interact with the lignin QM end units before phenolic condensation can occur and rapidly produce fragments when β-aryl ether groups are present. If fragmentation is not possible, at least the additive may tie up the QMs long enough to decrease the tendency to condense. The "tied-up" structures, i.e., adducts and QMs², may further react to eventually remove the QM structures and prevent condensation. These secondary reactions may be in the form of production of stable adducts or reduced species (Scheme 7).
Some of the Reaction Options of a Lignin Quinonemethide (QM)

1. Condensation: $\text{CH}_3-\text{O}$

2. Fragmentation:
   - $\text{CH}_3-\text{N}\cdots\text{CH}_3$ (unstable adduct)
   - $\text{Add} + \text{QM}$

3. Reduction:
   - $\text{QM} + \text{OH}^- \rightarrow \text{product}$

Add = $\text{H}_{2}\text{S}^-\text{S}^2-$
The Ph.D. research of D. Smith and B. Barkhau, some of which was described earlier in this report, is been directed at studying the mechanisms of condensation reactions, especially with regard to how AHQ⁻² acts and whether or not radicals are involved. Barkhau's studies may also address the question of whether or not AHQ⁻² affects the condensation of formaldehyde with phenols. The latter reaction is believed to occur to some extent during pulping.⁷

The discussion in this section has focused mainly on the reactions of phenolic lignin end units having β-aryl ether or other attached groups. While the chemistry of these units is very important to efficient pulping, other reactions need to be considered. Such reactions as the cleavage of nonphenolic units of lignin are important to "bulk phase" delignification.⁷ These reactions have not yet been studied by us and, therefore, will not be reviewed here.
CONCLUSIONS

The following major conclusions can be drawn from our combined research efforts:

- AHQ^2 can transfer electrons to quinonemethides at room temperature in organic solvents (electrochemical studies) and in aqueous alkali at 135-150°C (Smith's thesis).

- QMs^2 containing ß-aryl ether units fragment to phenolate ions and radicals in organic solvents (electrochemical studies).

- SET mechanisms are as logical as adduct mechanisms for AHQ-promoted delignification reactions (literature and early project work, plus recent steric and electronic effects studies).

- The most difficult step in additive-induced lignin model fragmentation reactions is the formation of the QM (steric and electronic effects studies).

- Additives must function by providing efficient pathways for QM fragmentation in preference to QM condensation and vinyl ether formation reactions. Fragmentation by way of QMs and additives is of lower energy than soda-induced fragmentation reactions (pulping energetics logic).

- Soda-induced lignin model fragmentation is favored by high alkali levels, high temperatures, ß-side-chain substituents, and a good ß-phenoxy leaving group (steric and electronic effects studies).

- Promotion of SET reactions during pulping should benefit lignin fragmentation reactions (electrochemical studies) and interfere with lignin condensation reactions (Smith's thesis), thus providing the opportunity for future pulping process improvements.
FUTURE STUDIES

GENERAL COMMENTS

If the hypothetical diagram proposed in Fig. 24 is correct and the reactions outlined there are important to delignification, how do we proceed to improve pulping rates and to study additive effects? Let's address the last point first.

Any study of additive effects must take into account the fact that QM formation is probably the rate determining step in the chemistry;\(^ {53}\) as such, it will dominate the kinetics. Therefore, simple kinetic studies will likely be uninformative. Experiments will probably have to be devised, such as the competitive model degradations we employed,\(^ {53}\) which will provide information about the steps following the energetically dominating QM generation step. An alternative would be to study the chemistry of stabilized QMs, but the compounds would not be very "ligninlike."

An obvious way to improve the rate of pulping would be to lower the energy required for QM generation by (a) stabilizing the QM with new ring substituents or (b) providing a better leaving group at C\(_\alpha\). Both options appear expensive to accomplish; the latter option has been tried successfully with models.\(^ {66}\) Attempts to specifically functionalize C\(_\alpha\)-OH groups to provide better C\(_\alpha\) leaving groups will be difficult, considering the enormous amounts of carbohydrate OH groups in wood and the accessibility of lignin at moderate temperatures.

As far as improving pulping selectivity, delignification rates would be improved by making the QM fragmentation steps more efficient. This might be accomplished by providing better nucleophiles or SET agents or better conditions.
for promoting the adduct or SET reactions. The concentration of nucleophiles or
SET agents could be increased to provide more efficient capture of the QMs;
again this could be an expensive alternative, if it meant adding more reagent.
Another option would be to maintain the pulping additive in its most active
form. In the case of AQ/AHQ pulping, this would mean rapid reduction of AQ to
AHQ\(^{-2}\) and prevention of reactions which consume AHQ\(^{-2}\) toward the formation of
stable adducts.

Finally, any reactions which interfere with lignin-lignin condensation
reactions will facilitate pulping rates and our ability to pulp to lower residual
lignin levels. The best approaches to accomplish this goal appear to be (a) to
promote lignin fragmentation reactions in order to shorten pulping times and
avoid condensation and (b) to reduce the QMs to stable \(\alpha-\text{CH}_2\) structures. An
oxidative procedure looks less desirable because it would probably be difficult
to selectively oxidize lignin \(\alpha-\text{CHOH}\) groups to \(\alpha-\text{carbonyl}\) groups without oxidi-
dizing some carbohydrate \(-\text{CHOH}\) groups; the latter would adversely affect pulp
properties.\(^{67}\)

SPECIFIC AREAS - LIGNIN

We need to establish the relative importance of SET and adduct mecha-
nisms in lignin fragmentation and condensation reactions. Related to this
question is whether or not SET reactions offer a rate advantage over other types
of pulping reactions. Kinetic studies probably will not provide an answer to
this question, since the rate of QM formation will most likely dominate the
results.

One approach that we have recently initiated for examining the impor-
tance of SET reactions is to study quinonemethides, such as 50, which could
react by (a) intramolecular cyclization with a side-chain OH group; (b) nucleophile addition (adduct formation), or (c) SET (Scheme 10). The latter two pathways could lead eventually to β-aryl ether cleavage, while the cyclization reaction would produce a "dead-end" product. The cyclization, which should be a very fast reaction, will shut down all but extremely fast competing reactions. Theoretically, SET reactions will be faster than nucleophilic addition reactions.

Another model QM which has a built-in "clock" reaction is 51. An SET reaction would produce 51², which now has a choice of cyclization with the side-chain olefin or fragmentation (Scheme 11). Again, the intramolecular cyclization should be a fast reaction; but, will it be faster than fragmentation?

Fundamental studies of this type are needed to conclusively demonstrate that SET reactions are prominent. If we assume, however, that SET reactions are beneficial to good delignification (and at this time the assumption appears valid), how do we exploit this unique kind of chemistry?

Certain ways are known for turning on and off SET reactions in organic solvents; but what about pulping conditions? One possible way is to put electrons into a pulping digester. This idea has led us to investigating high temperature aqueous electrochemistry. The appropriate cell and electrodes are now under development.

It should be possible to promote pulping reactions by either direct or indirect electrolysis. The latter involves using electrochemistry to keep an SET agent in its "active" form. High temperature electrochemistry may also offer ways to monitor the course of pulping. In this regard, QMs are very
**SCHEME 10**

Possible reactions of QM 50

![Chemical structure](image)

**SCHEME 11**

Possible SET reactions of QM 51

![Chemical structure](image)
electroactive species and are important to most lignin reactions, so following their concentration should be both possible and beneficial.

Proposals for outside funding of a joint project with Dr. H. L. Chum at SERI to study high temperature aqueous electrochemistry have been submitted. The proposals concern going from lignin model to wood studies over a 3-year time period. We are enthusiastic over the possible information and pulping benefits that could come out of studying high temperature electrochemistry.

SPECIFIC AREAS - CARBOHYDRATES

The carbohydrate research being done in Project 3475 has been discussed very little in this report. Even though this portion of the project has been undermanned for several years, some value information has been generated which soon will warrant a separate Progress Report.

The project studies have been principally concerned with developing techniques to evaluate carbohydrate molecular weight distribution and thus using the techniques to study cellulose chain cleavage reactions. The investigation is being supplemented by a large amount of student research in the general area of understanding carbohydrate degradation reactions. Chain cleavage reactions cause decreases in the degree of polymerization (DP) of cellulose and thus adversely affect pulp strengths. Understanding the chemistry which causes DP losses should help to devise new ways to improve pulp strength properties.

Project work is presently concerned with assessing the importance of cellulose physical structure (crystalline vs. amorphous) to losses in DP. How AQ affects DP is being actively pursued. Longer range goals will probably be directed toward studying the affects of ionic strength (level of inorganic salts or dead-load) on carbohydrate degradation reactions.
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