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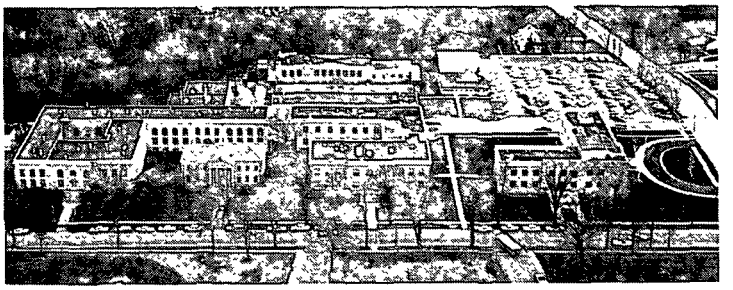

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ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (I): THEORY AND APPLICABILITY TO ANTHRAQUINONE PULPING

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GENERAL SUMMARY

Institute Project 3475 has been concerned with developing a fundamental understanding of the reactions occurring during pulping and bleaching. One phase of this project research has involved a detailed investigation of the mechanism of action of anthraquinone (AQ) as a pulping catalyst. The attached article presents a concise review of AQ pulping chemistry and introduces a new view of explaining AQ's delignification reactions. The article is the first in a series of articles aimed at demonstrating the possible importance of single electron transfer reactions in pulping systems.

ELECTRON TRANSFER REACTIONS IN PULPING SYSTEMS (I): THEORY AND APPLICABILITY TO ANTHRAQUINONE PULPING

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ABSTRACT

A key step in the delignification of wood is the breakage of the β-aryl ether bonds of lignin. Two mechanisms are discussed for how anthrahydroquinone (AHQ) brings about this particular fragmentation. The "adduct" mechanism involves bond formation between lignin quinonemethide (QM) intermediates and AHQ, followed by fragmentation. The other mechanism ("SET" mechanism) involves a single electron transfer between AHQ and a lignin QM followed by fragmentation. The literature concerning adducts and SET reactions is reviewed and analyzed. The SET mechanism must be considered as a viable alternative to one based entirely on adduct formation.

INTRODUCTION

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.[1] As structural studies on cellulose, hemicellulose, and lignin progressed[2,3] so did the chemistry of pulping. Theories have evolved which now explain how hydroxide and hydrosulfide ions (OH^- and SH^-) cause carbohydrate[2,4-6] and lignin[3,7] to dissolve during pulping. Most of the theories are based on experiments with model compounds rather than actual wood.

The advent of anthraquinone pulping in 1977 revitalized interest in pulping chemistry.[8] How could an organic material at a 0.1% level cause the same effect as SH^- at a 6% level? Why did AQ processes exhibit better pulping selectivities (the amount of lignin removed vs. the amount of carbohydrates removed)? Would an understanding of AQ's chemistry provide new insights into improving

pulp yields, decreasing pulping reaction times, altering the structure of "residual" lignin, and developing innovative processes? Only a detailed understanding of AQ's chemistry will provide answers to these questions.

Early in the mechanistic AQ studies came the realization that anthrahydroquinone (AHQ, a reduced form of AQ) played an important role during pulping.[9-11] 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.[12] Certain lignin groups are also capable of converting AQ to AHQ.[13,15]

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. 1).

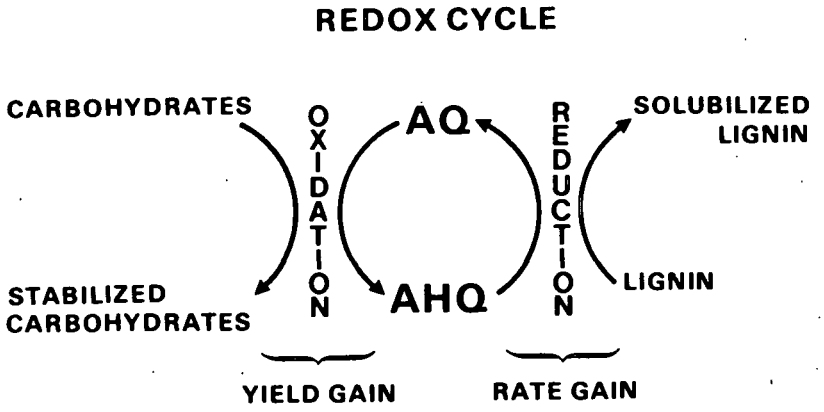


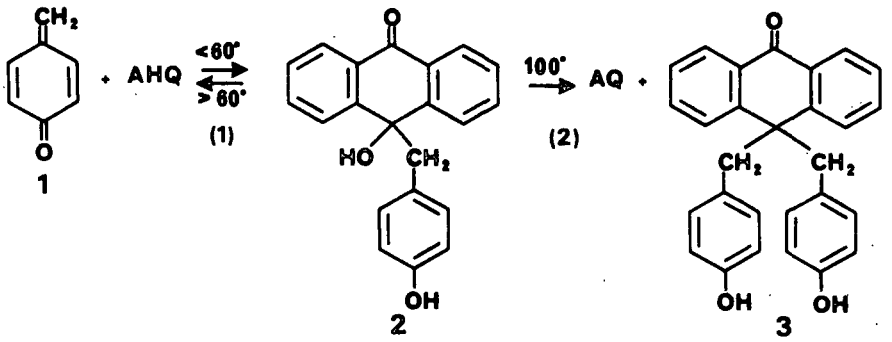
Figure 1. A redox cycle proposal for explaining the catalytic action of anthraquinone during pulping.

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.

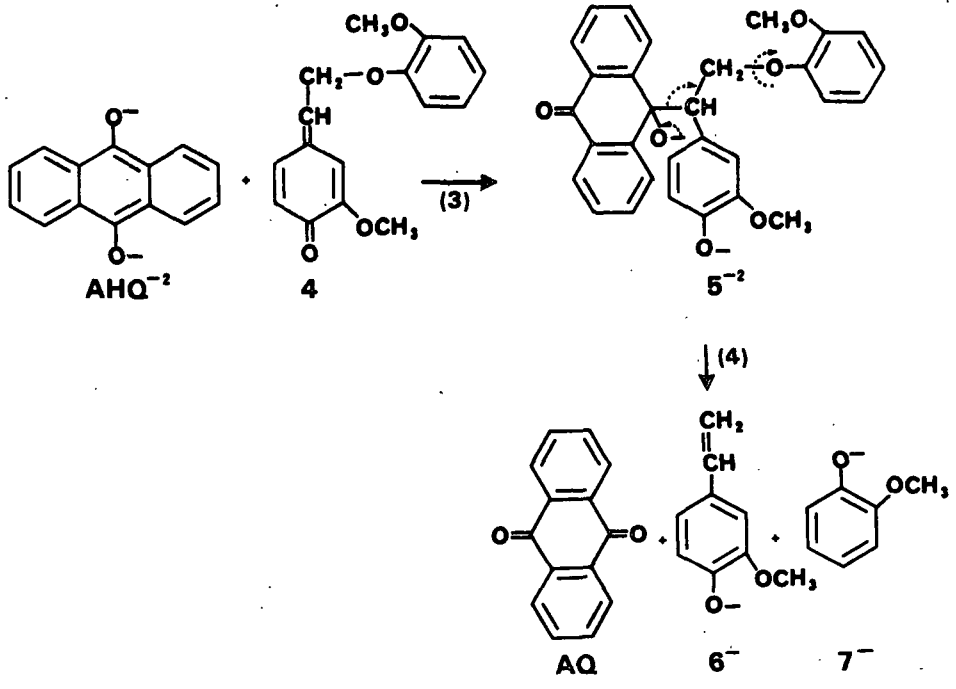
ADDUCT MECHANISM THEORY

At temperatures below 60°C, AHQ couples with simple QMs to give high yields of "adducts."[24] An example is shown below. At about 60°, the reaction of AHQ with a simple QM (1) is reversible.[25] At 100°C, simple adducts such as **2** disproportionate to AQ and an anthrone product **3**.[25] This latter oxidation-reduction reaction has been interpreted as involving single electron transfer (SET) steps.

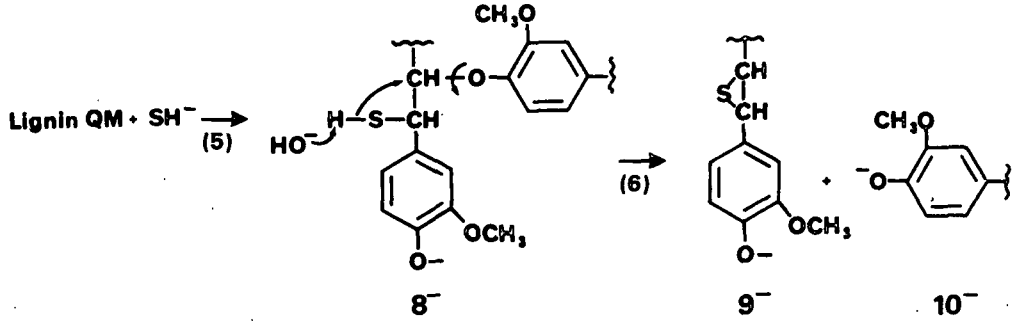


Several research groups have synthesized adducts [Eq. (3)] which contain β-aryl ether groups (5) and have shown that such structures, when warmed with alkali, fragment [Eq. (4)] to liberate AQ and two phenolate ions.[16-19] Lignin contains large numbers of β-aryl ether linkages.[3] The model studies 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.[16-18] Adducts of AHQ and actual lignin at 10°C have been reported.[26]

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 SH^- adds to C_α of a lignin QM [Eq. (5)] and then



assists in a cleavage of the Cβ-aryl ether bond by a neighboring group displacement step [Eq. (6)].[7]

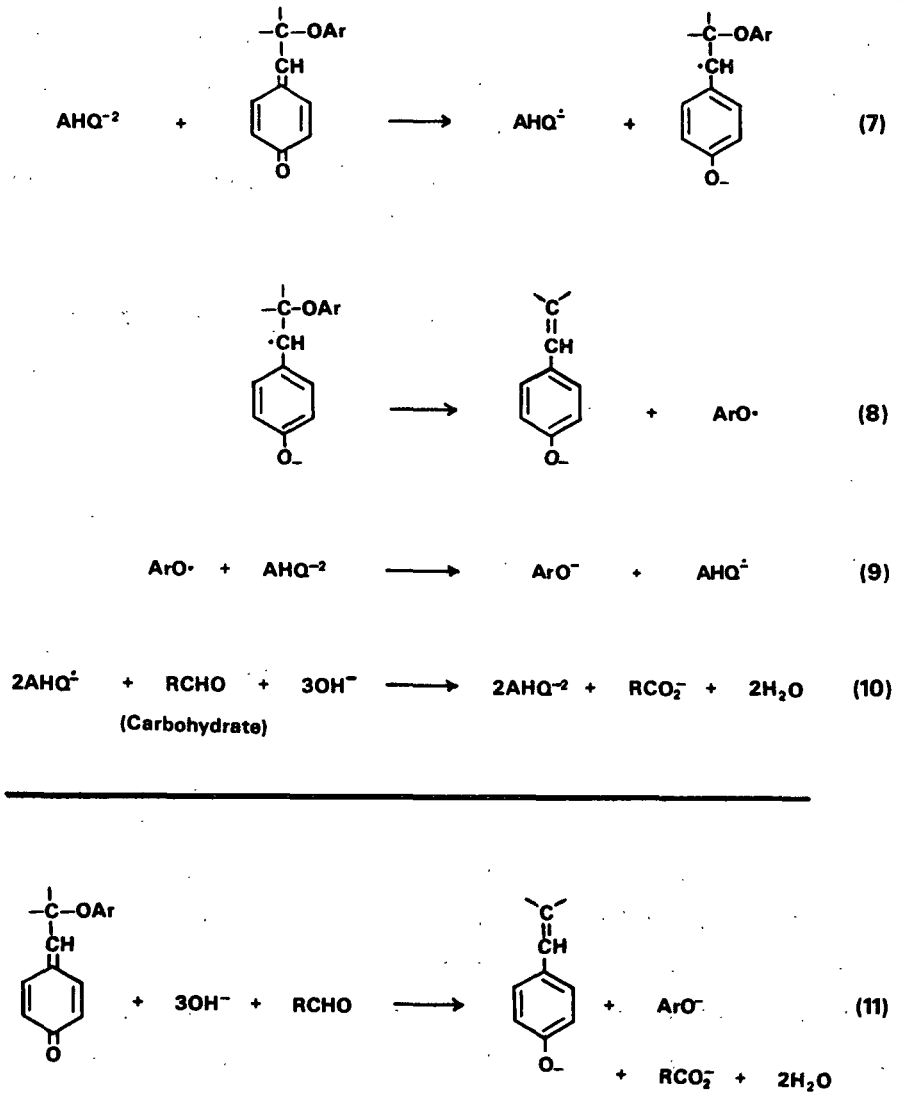


ELECTRON TRANSFER MECHANISM THEORY

Could a β-aryl ether fragmentation reaction, such as that outlined by Eq. (3) and (4), proceed without the production of an adduct intermediate? Scheme 1 offers a mechanism of fragmentation in which AHQ^{-2} and $AHQ^{\cdot -}$ (anthrahydroquinone dianion and radical anion) act as carriers in the transfer of electrons from carbohydrates to lignin; no adducts are involved. The soluble electron transfer catalysts AHQ^{-2} and $AHQ^{\cdot -}$ are mediating a reaction between

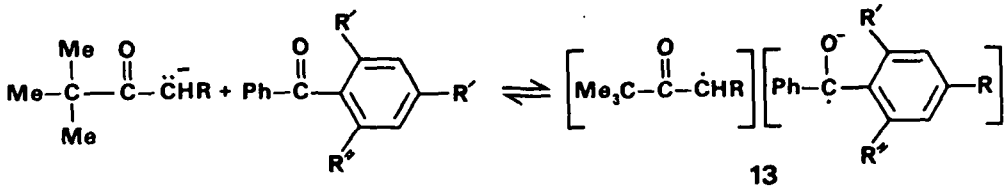
two insoluble polymers; analogous chemistry is known in biological systems.[27]

SCHEME 1



The recent organic chemical literature is abundant in examples of reactions which were hitherto thought to be ionic nucleophilic substitutions (S_N1 or S_N2) but have now been shown in certain cases to be single electron transfer reactions. Some of these examples will be presented here in an attempt to define the scope of SET reactions and their applicability to pulping chemistry.

Electron spin resonance (ESR) studies have shown that some Aldol and Claisen condensation reactions proceed *via* SET mechanisms.[27,28] For example, radical pairs of the type **13** are formed prior to production of products **14** during the aldol condensation reactions of **11a** or **11b** with **12c**, **12d** or **12e**.[28] The intensity of the ESR signal, which is proportional to the level of radicals produced, was the greatest for the most hindered, slow-reacting partners.



11

a, R = H

b, R = Me

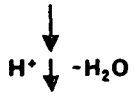
12

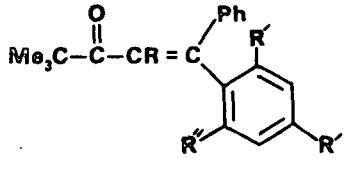
a, R′ = R″ = H

b, R′ = Me, R″ = H

c, R′ = R″ = Me

13

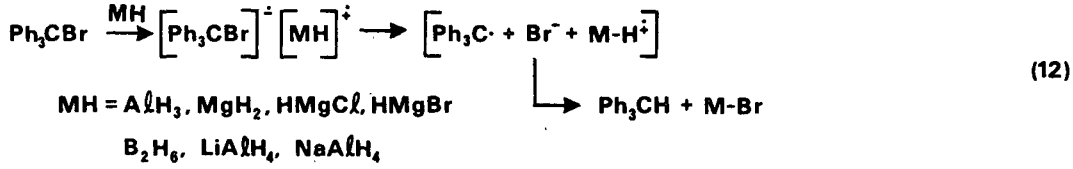


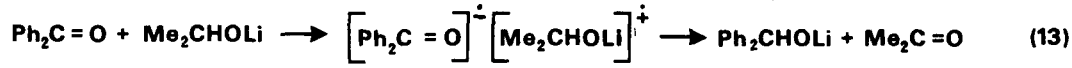


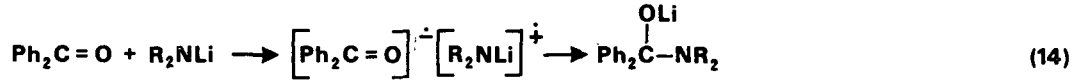
14

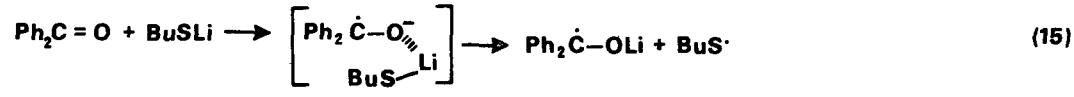
Ashby and coworkers have also observed radicals in the reactions outlined in Eq. (12)-(16).[30] Most of the reactions where SET mechanisms have been observed involve the production of relatively stable radicals such as trityl radicals ($Ph_3C\cdot$) and benzophenone radical anions ($Ph_2\dot{C}\text{-}O^-$). Analogous, simpler systems probably would react *via* standard substitution mechanisms or react so rapidly by radical pathways that detection of radical intermediates would be difficult.

A characteristic of SET reactions is their insensitivity to steric bulk at the reaction site and on the nucleophile. For example, Scheme 2 outlines one of the many examples generated by Kornblum and coworkers and shows the initiation [Eq. (17)] and propagation steps [Eq. (18)-(20)] for the coupling of two hindered reactants, **15** and **16**, in a series of electron transfer reactions









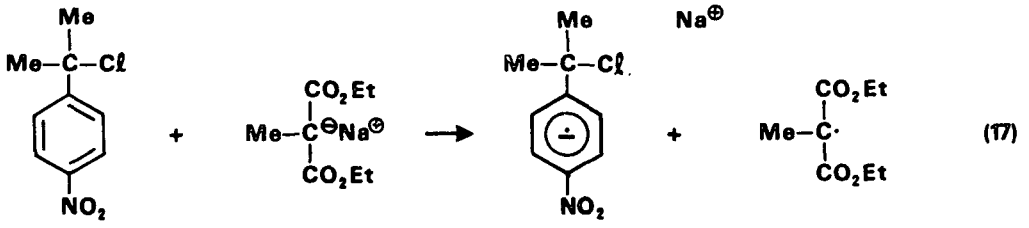
which lead to product **18.**[31] Russell and coworkers have shown that similar mechanisms operate for many substitution reactions of hindered aliphatic nitro compounds.[32]

In summary, SET reactions appear to be the favored mechanism for 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.[30e, 33-35] The examples cited here also point out that SET reactions can proceed without radical initiators.

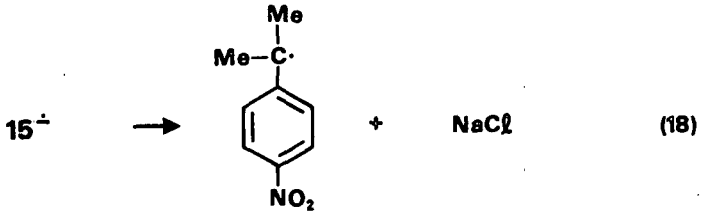
A quinonemethide, which is nonaromatic, would appear to be a good substrate for electron transfer reactions, since acceptance of an electron gives an extensively resonance stabilized, aromatic $QM^{\cdot-}$ species. Anthrahydroquinone radical anion, $AHQ^{\cdot-}$, should also be an excellent partner in electron transfer reactions, since not only is $AHQ^{\cdot-}$ extensively resonance stabilized but its oxidized and reduced forms, AQ and AHQ^{-2}, also have good stability. In the accompanying article,[36] we demonstrate that (a) SET reactions between QMs and $AHQ^{\cdot-}$ occur and (b) appropriately substituted β-aryl ether $QM^{\cdot-}$ compounds fragment, as indicated in Eq. (8).

Besides the plausibilty of the reactions outlined in Scheme 1, the arguments for SET mechanism operating during pulping are

SCHEME 2

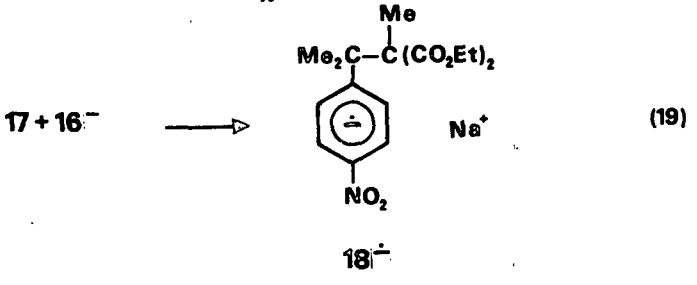


15 16^- $15^{\cdot-}$ $16\cdot$ (17)



$15^{\cdot-}$ + NaCl (18)

17



$17 + 16^-$ Na^+ (19)

$18^{\cdot-}$

$18^{\cdot-} + 15 \longrightarrow 18 + 15^{\cdot-}$ (20)

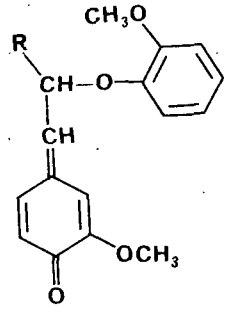
extensive. Radicals in general[37] and $AHQ^{\cdot-}$ in particular[38-40] have been observed during pulping. We have observed two cases where AHQ^{-2} appears to participate in SET reactions. One example is the reduction of adducts by AHQ^{-2} at 100°C in aqueous alkali.[25] The other is the promotion of benzaldehyde Cannizzaro reactions by AQ and AMS (anthraquinone monosulfonate).[41] The benzaldehyde Cannizzaro reaction [Eq. (16)] has been shown to involve radical intermediates.[30e]

The reduction potentials for the two steps AQ ⟶ $AHQ^{\cdot-}$ ⟶ AHQ^{-2} are identical in water;[17] thus one molecule of AQ (in its AHQ^{-2} form) should be capable of initiating two QM ⟶ $QM^{\cdot-}$ conver-

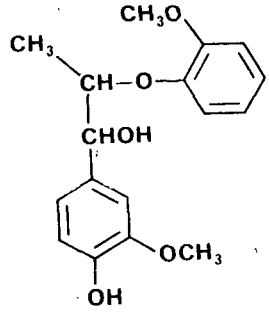
sions. This could explain the "square-root dose relationship" found for AQ pulping;[42] an adduct mechanism cannot. A "linear-dose relationship" is observed[43] for SH^-, and nucleophilic substitution mechanisms have been suggested [Eq. (5) and (6)].

A consideration of the stereochemistry of the interaction of AHQ^{-2} with lignin QMs argues for SET mechanisms. High yields of adducts can be achieved by reacting simple QMs (i.e., **1**) with AHQ^{-2} in water,[24] moderately hindered QMs (i.e., **4**) with AHQ^{-2} in a two-phase water-organic system,[17] and hindered QMs (i.e., **19**) with AHQ in pure organic solvent systems.[44] However, the more hindered QM **20** gave only a poor yield of adduct when reacted with AHQ in organic solvents.[44] Water and alkali seriously impair the yields of adducts between AHQ^{-2} and α-substituted QMs, such as α-methyl, α-ethyl, or α-aryloxymethyl.[24,45]

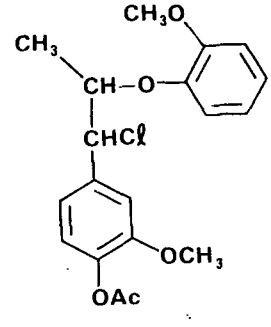
We have been unsuccessful in preparing an AHQ adduct of QM **19** in the presence of water. Two methods were tried: (a) conversion of the α-hydroxy lignin model **21** to α-chloroacetate **22** and then treating the latter with AHQ^{-2} in aqueous alkali and (b) treatment of **21** with $BrSiMe_3$ and $NaHCO_3$ to get a stable solution of QM **19** in $CHCl_3$ and then mixing the latter solution with aqueous AHQ^{-2}. Significant amounts of α-hydroxy compound **21** were recovered in each case. Apparently, the reaction of hindered QM **19** with solvent or alkali occurs in preference to adduct formation.



4, R = H
19, R = CH_3
20, R = CH_2OH

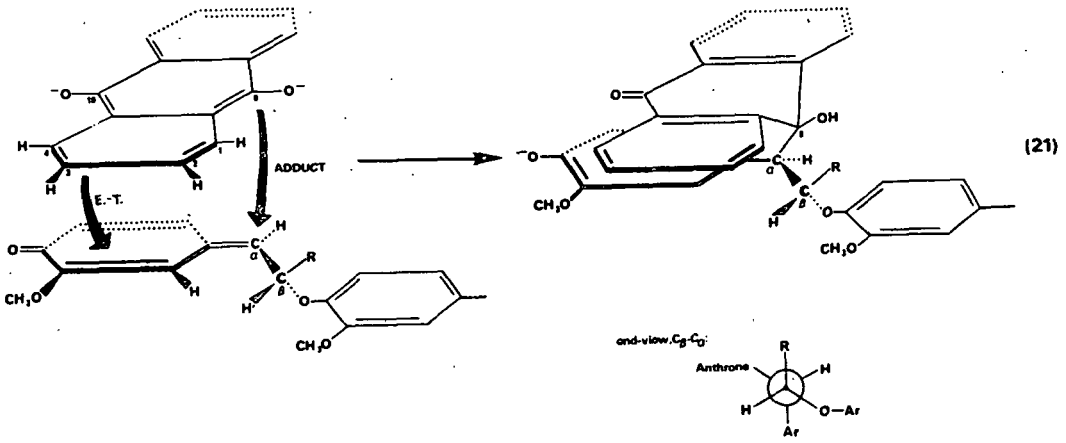


21



22

Quinonemethides **19** and **20** probably represent the absolute lower limit for the least crowded QM found in lignin. Yet, in aqueous alkali (the medium used in pulping), adducts could not be made with QM **19**. A specific geometry is needed to bind AHQ^{-2} to a lignin QM [Eq. (21)]. The resulting adduct of the polymeric material should be highly crowded around the C_α and C_β positions; one of the substitutions on C_α is a quaternary substituted C_9 carbon. In contrast, the distance between reactants and the stereochemical constraints should be much looser in the case of a SET mechanism. For hindered QMs, such as those of lignin, a SET mechanism may be preferred over an adduct mechanism.



(21)

Some fairly hindered pulping catalysts, such as the rosindones, are as efficient as AQ at low concentrations.[46] This observation is contrary to what one would expect with an adduct mechanism. Wright and Fullerton have recently demonstrated that metal complexes of porphyrin structures are efficent pulping catalysts.[47] It is easy to visualize a SET mechanism for this catalyst; an adduct mechanism appears unlikely.

Poppius and Brunow claim that anthrone causes β-aryl ether cleavage of lignin model **21** by a pathway not involving an adduct intermediate.[48] A logical explanation of their results is that anthranol anions transfer electrons to QM **19** intermediates to give

fragmentation of the QM and anthranol radicals. Coupling of the radicals, followed by enolization, then gives dianthranol, an observed by-product.

Previous studies have not established that lignin QM-AHQ adducts are *on the reaction pathways* of fragmentation. For example, the conversion of adduct **5** to AQ and phenols **6** and **7** has been interpreted in terms of a set of electron shifts as shown in Eq. (4);[17] analogous fragmentation reactions are known.[49] However, since adduct formation reactions are reversible,[25] warming an adduct in alkali will give AHQ^{-2} and a QM [i.e., the reverse of Eq. (3)] which may then react by a SET mechanism to give the observed products.

The recent report[26] that adducts of AHQ^{-2} and actual lignin are produced at 10° and can be observed by ^{13}C-NMR also does not establish that the adducts are reactive intermediate in the fragmentation process; they could be deadend by-products. The ^{13}C-NMR spectra do not provide much information about the nature of the "lignin adducts." Corresponding ^{1}H-NMR spectra[26] surprisingly did not show one of the characteristics of adducts, namely an aromatic methoxyl signal at about 3.4δ.[44,50] Also, the molecular sizes of the "lignin adducts" were not well defined,[26] especially *in lieu* of unusual absorption effects which can occur with gel filtration techniques.[51]

CONCLUSIONS

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? We are attempting to tackle this difficult problem. We feel that the mechanisms by which AHQ accelerates pulping rates are not settled. Electron transfer mechanisms offer an attractive alternative to the generally accepted adduct mechanisms.

What difference does it make if the mechanism of AHQ delignification is adduct or electron transfer? A definitive distinction

may lead to improvements in present pulping systems and the development of new systems. We will know (a) whether to promote adduct reactions (or SET reactions) or discourage them and (b) whether to develop new pulping catalysts which will be good nucleophiles or good SET reagents.

EXPERIMENTAL

Two methods were attempted for the preparation of the adduct of AHQ^{-2} and QM **19**; both methods failed. Each method used the dithionite procedure[24] for the preparation of AHQ^{-2}.

Method 1. A stable solution of QM **19** in $CHCl_3$ was prepared by the method of Ralph and Young.[52] Confirmation of the presence of QM **19** was provided by recording the NMR spectrum of **19** in $CDCl_3$.[52] The $CHCl_3$/**19** solution was added to a cold aqueous alkaline solution of AHQ^{-2} and stirred at 0°C for 1 hour. The reaction mixture was then acidified (3M HCl) and the $CHCl_3$ layer separated. The $CHCl_3$ solution was combined with additional $CHCl_3$ extracts, dried (Na_2SO_4), and evaporated. The residue was dissolvd in $CDCl_3$ and an NMR recorded. The signals expected for an adduct[44,50] were absent, only AQ and compound **21** were detected.

Method 2. The chloroacetate **22**[53] dissolved in a small amount of dioxane was added to an ice-cold aqueous solution of AHQ^{-2} and alkali. After stirring at room temperature for 30 minutes, the solution was acidified with HCl and the precipitate collected by filtration. A NMR of the solid dissolved in $CDCl_3$ showed none of the expected adduct signals,[44,50] just AQ and compound **21**. Analysis by GC/MS confirmed these results.

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