Institute of Paper Science and Technology
Atlanta, Georgia

IPST Technical Paper Series Number 626

Pulping with Anthraquinone: Fundamental Chemistry

D.R. Dimmel

September 1996

Submitted to
TAPPI Pulping Conference
Nashville, Tennessee
October 27–31, 1996

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
PURPOSE AND MISSIONS

The Institute of Paper Science and Technology is a unique organization whose charitable, educational, and scientific purpose evolves from the singular relationship between the Institute and the pulp and paper industry which has existed since 1929. The purpose of the Institute is fulfilled through three missions, which are:

- to provide high quality students with a multidisciplinary graduate educational experience which is of the highest standard of excellence recognized by the national academic community and which enables them to perform to their maximum potential in a society with a technological base; and

- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and

- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

ACCREDITATION

The Institute of Paper Science and Technology is accredited by the Commission on Colleges of the Southern Association of Colleges and Schools to award the Master of Science and Doctor of Philosophy degrees.

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

PULPING WITH ANTHRAQUINONE: FUNDAMENTAL CHEMISTRY

Donald R. Dimmel
Professor
Institute of Paper Science and Technology
500 10th Street N.W., Atlanta, GA 30318

ABSTRACT

A review of the collective evidence for the mechanism of action of anthraquinone (AQ) in alkaline pulping systems indicates that a unique set of reactions is governing the chemistry. AQ and its reduced forms, anthrahydroquinone dianion (AHQ^{-2}) and radical anion (AHQ$^{\cdot}$), are mediating reactions in which electrons are transferred from carbohydrates to lignin, causing the former to be oxidized to relatively stable aldonic acid polymer end units, and the latter to be reduced, leading to fragmentation and solubilization. The two effects account for the observed improved pulp yields and faster pulping rates. Experiments indicate that single electron transfer (SET) reactions are more efficient than nucleophilic reactions (soda/kraft systems) in breaking down lignin. The chemistry of AQ, soda, and kraft pulping will be reviewed and evidence for SET reactions presented.

INTRODUCTION

Kraft, the dominant chemical pulping process in the world, uses NaSH and NaOH to degrade the lignin component in the wood. While the process obviously has several advantages, there are also disadvantages, including low pulp yield, odor emissions, and the dark color of the resulting pulp. High levels of bleaching chemicals are needed to brighten the pulp; the resulting effluents contain large amounts of organic material that is an environmental concern. The kraft process on pine affords a pulp yield <50%, with nearly equal losses of carbohydrate and lignin components [1]. Yet, alternative pulping technologies generally can not match the good economics and pulp strength of the kraft process.

Alternatives often involve the use of anthraquinone (AQ): soda/AQ, sulfite/AQ, and alkaline sulfite/AQ/methanol (ASAM). Of course, AQ can also be used in conjunction with kraft; several pulp mills have gone this route in an effort to increase production, reduce sulfur emissions, and/or reduce bottlenecks [2]. There is generally a few % pulp yield increase and faster delignification associated with the use of AQ. However, in the case of soda/AQ, the pulp tear strength is 10-15% lower than kraft [3]. The strength reduction may be related to retention of more hemicellulose fibers and/or to carbohydrate oxidative depolymerization reactions [4].

Anthraquinone exists in several oxidation states during pulping: the oxidized form (AQ); the partially oxidized (partially reduced) semiquinone form, anthrahydroquinone radical anion (AHQ$^{\cdot}$); and the fully reduced form, anthrahydroquinone dianion (AHQ^{-2}).
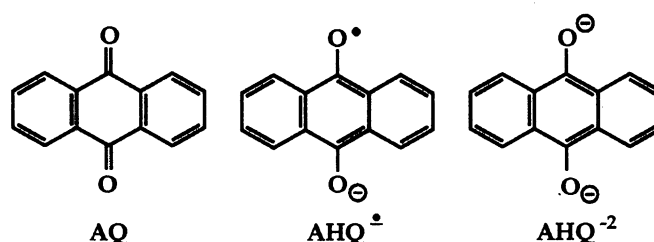
The yield increase with AQ has been attributed to a set of redox reactions (Figure 1). Here, AQ or AHQ$^{\cdot}$ oxidizes carbohydrate aldehyde end units, thereby reducing the extent of alkaline carbohydrate degradation; in the process AHQ^{-2} is formed. The latter reacts with lignin, causing fragmentation of the lignin (a rate increase) and oxidation of the AHQ^{-2} back to AQ or AHQ$^{\cdot}$. These redox reactions account for the large effects observed from a small amount (<0.1%) of AQ that is generally employed.
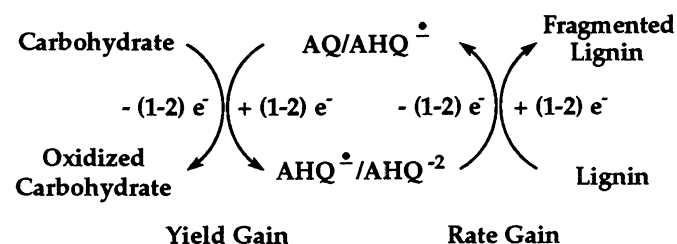

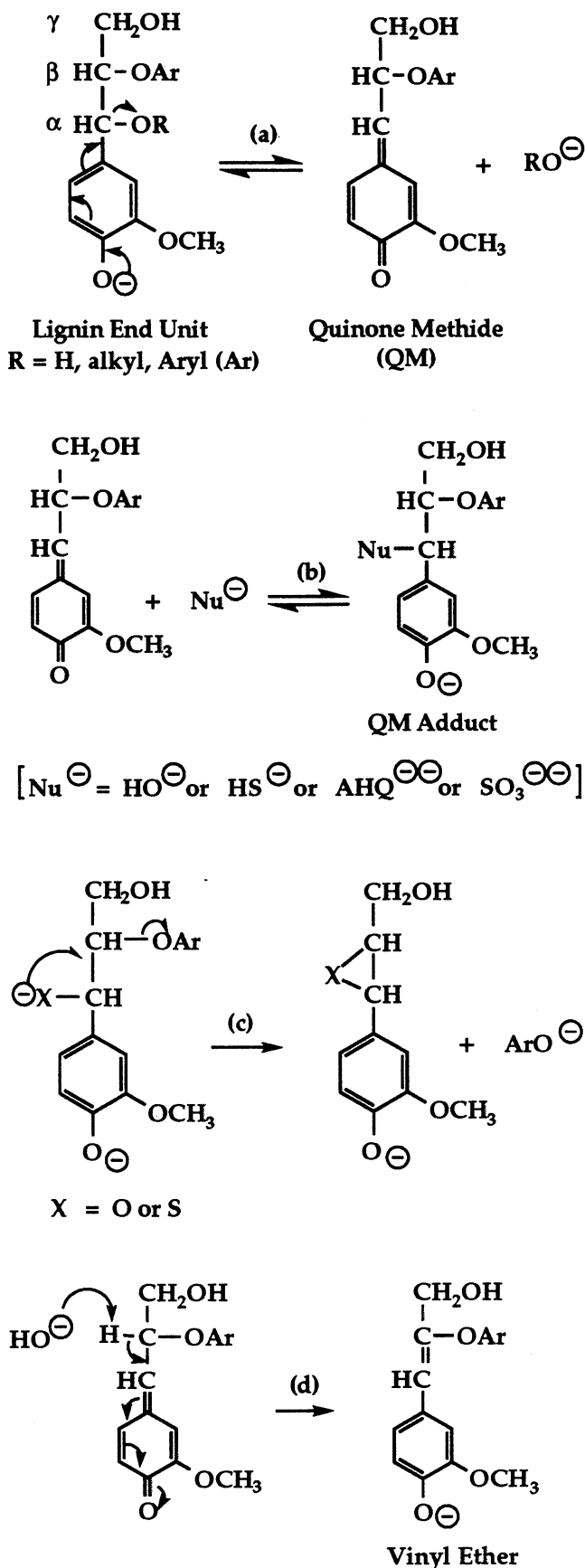Figure 1. Anthraquinone redox reactions with wood components [5].

If we wish to make improvements in, or replace, the kraft process, we need to understand the chemistry associated with the action of the pulping chemicals. To this end, we need to understand how AQ works.

The mechanisms for delignification of wood during alkaline pulping have intrigued wood chemists for decades [6]. This curiosity was heightened when AQ was first introduced in 1977. In many respects, the discovery of AQ as a pulping promoter was because of the greater understanding of how reagents might improve the selectivity of pulping [2]. [Selectivity in this context means the ability to remove lignin from wood without affecting the properties of the fibrous carbohydrate components.]

One of the main difficulties in establishing the detailed chemistry of pulping systems is the dominance of the delignification rate by the first step in the process -- formation of a quinone methide intermediate (Eq. a). The rates of subsequent steps (i.e., Eqs. b and c) in a multistep process are difficult to determine; however, the rates of these steps are critical to the partitioning of the quinone methide towards a productive fragmentation processes, as opposed to undesirable competing reactions, such as vinyl ether formation reactions (Eq. d) [6]. The predominant productive delignification event appears to be cleavage of the abundant β-aryl ether linkages (Eq. c) [6].

Initially, the accepted mechanism of action of AHQ was similar to that proposed for NaSH, namely a nucleophilic addition of AHQ^{-2} to a lignin QM to give an adduct (Eq. b), followed by an elimination reaction that regenerated AQ and led to β-aryl ether cleavage [7]. However, research has shown that the AHQ-QM adduct formation reaction is reversible [8], thus opening up other possibilities for the mechanism of AHQ-induced β-aryl ether fragmentation.

The review paper presented here attempts to establish that the chemistry of AQ pulping is unique and involves a set of single electron transfer (SET) steps (Figure 2). The proposed steps begin with an electron transfer from AHQ^{-2} to a lignin quinone methide (Eq. e). The resulting QM radical anion then breaks down to an ion and a radical fragment (Eq. f). The latter picks up an electron from another AHQ^{-2} to give a second phenolate ion (Eq. g). The AHQ^{-2} ions are regenerated when a carbohydrate is oxidized by $AHQ^{\bullet}$ to an aldonic acid (Eq. h). The sum of these equations, Eq. i, indicates that electrons are transferred (via soluble AHQ ions) from carbohydrates to lignin, causing the former to be oxidized to relatively stable aldonic acid polymer end units, and the latter to be reduced, leading to fragmentation and solubilization. The two effects account for the observed improved pulp yields and faster pulping rates.
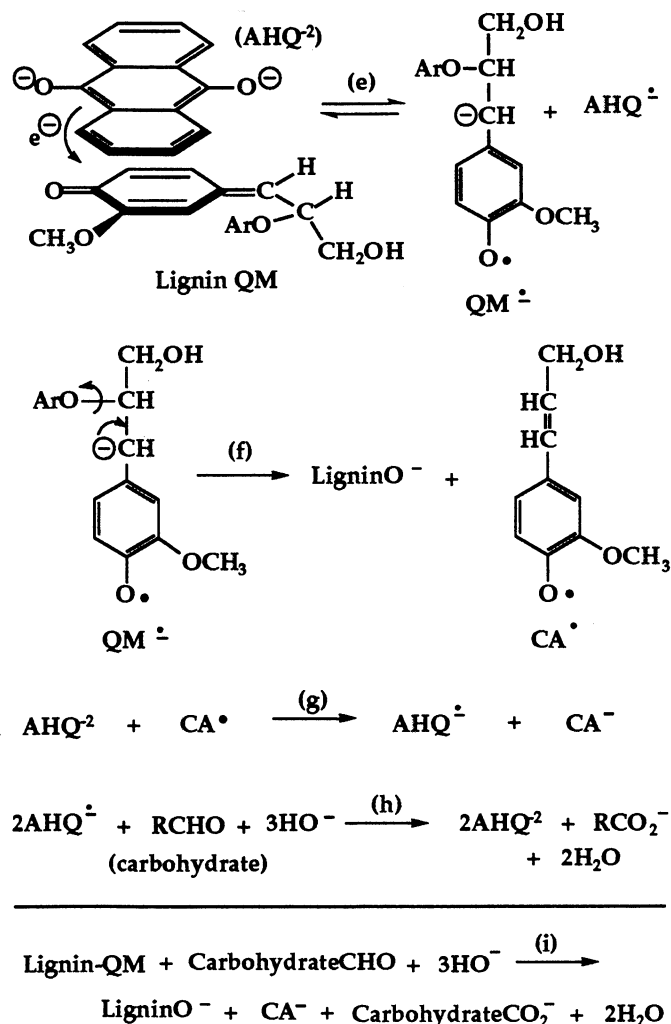
$$\gamma \quad CH_2OH$$
$$\beta \quad HC\text{-}OAr$$
$$\alpha \quad HC\text{-}OR$$

(a)

$$CH_2OH$$
$$HC\text{-}OAr$$
$$HC$$

$$+ \quad RO^{\ominus}$$

Lignin End Unit
R = H, alkyl, Aryl (Ar)

Quinone Methide (QM)

$$CH_2OH$$
$$HC\text{-}OAr$$
$$HC$$

$$+ \quad Nu^{\ominus}$$ (b)

$$CH_2OH$$
$$HC\text{-}OAr$$
$$Nu\text{-}CH$$

QM Adduct

$$[Nu^{\ominus} = HO^{\ominus} \text{ or } HS^{\ominus} \text{ or } AHQ^{\ominus\ominus} \text{ or } SO_3^{\ominus\ominus}]$$

$$CH_2OH$$
$$CH\text{-}OAr$$
$$^{\ominus}X\text{-}CH$$

(c)

$$CH_2OH$$
$$CH$$
$$X\text{-}CH$$

$$+ \quad ArO^{\ominus}$$

X = O or S

$$HO^{\ominus} \quad H\text{-}C\text{-}OAr \quad CH_2OH$$
$$HC$$

(d)

$$CH_2OH$$
$$C\text{-}OAr$$
$$HC$$

Vinyl Ether

Figure 2. Postulated SET reactions between AHQ ions and wood components [5]; CA = coniferyl alc.

The schematic shows:

$$(AHQ^{-2}) \overset{(e)}{\rightleftharpoons} \text{Lignin QM} + AHQ^{-\cdot}$$

$$QM^{-\cdot} \overset{(f)}{\longrightarrow} LigninO^- + CA^{\cdot}$$

$$AHQ^{-2} + CA^{\cdot} \overset{(g)}{\longrightarrow} AHQ^{-\cdot} + CA^-$$

$$2AHQ^{-\cdot} + RCHO + 3HO^- \overset{(h)}{\longrightarrow} 2AHQ^{-2} + RCO_2^- + 2H_2O$$
$$\text{(carbohydrate)}$$

$$\text{Lignin-QM} + \text{CarbohydrateCHO} + 3HO^- \overset{(i)}{\longrightarrow}$$
$$LigninO^- + CA^- + CarbohydrateCO_2^- + 2H_2O$$

RESULTS

Several approaches have been employed to establish the nature of QM/AHQ interactions; some have been inconclusive. One study examined steric effects in QM/AHQ reactions; adduct reactions are subject to steric inhibition, while SET reactions are relatively insensitive [9]. We employed models and AHQ substrates with different strategically placed bulky groups, but changes in the rates of QM formation clouded the interpretation of the results [10]. Studying models with different ring substituents showed us that the β-ring is lost as an anion (not as a radical) [11]. This observation is compatible with either an adduct or SET mechanism. Nevertheless, several studies have demonstrated the existence of SET reactions in the reactions of AHQ and QMs; these are outlined below. The key to studying QM/AHQ reactions is to recognize that the slow rate of formation of quinone methide intermediates will generally mask the rates (and chemistry) of subsequent steps, but that most QM reactions are reversible.

Electrochemistry

We have electrochemically generated AHQ radical anions in select organic solvents and studied their reactions with independently prepared QMs [12]. Quinone methides have a relatively long lifetime in organic solvents [13]. The reduction potential of $AQ + e^- \to AHQ^{-\cdot}$ is -0.92 volts in acetonitrile; the QM 1 had a acetonitrile reduction potential of -1.17 volts corresponding to a $QM + e^- \to QM^{-\cdot}$ transition.
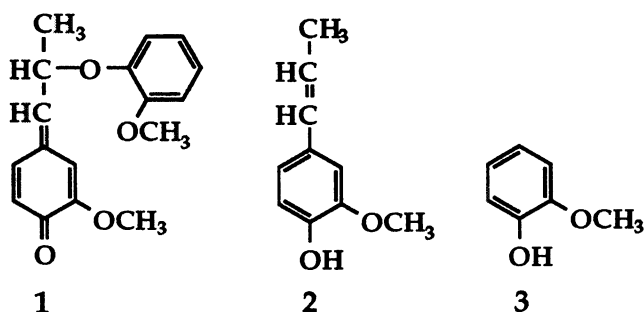
A cyclic voltammogram of a mixture of AQ and QM 1 in acetonitrile/electrolyte showed a enhanced current associated with the -0.9 volt AQ reduction and the absence of a -1.2 volt QM reduction. The observation is consistent with the chemistry shown in Eq. j. The current associated with the reduction of QM 1 is not seen because 1 is rapidly reduced by $AHQ^{-\cdot}$ before the sweeping potential reaches -1.2 volts. The enhanced current for the -0.9 volt signal is due to regeneration of AQ by the QM, effectively increasing the AQ concentration at the electrode surface. The behavior observed is not consistent with an adduct mechanism; the expected adduct had a very different cyclic voltammogram.

$$AQ + e^- \to AHQ^{-\cdot} + QM \to QM^{-\cdot} + AQ \quad (j)$$

A preparative electrolysis of a mixture of AQ and QM 1 in acetonitrile/electrolyte was performed at -0.8 volts. This potential was chosen because it is sufficiently close to the first AQ reduction potential to cause some production of $AHQ^{-\cdot}$, but too low in energy to reduce the QM. In the absence of the QM, the preparative electrolysis immediately produced red colored AHQ ions. In the presence of the QM, the

red color began to appear after about two hours of electrolysis. Analysis of the solution after 2 hours showed the presence of β-aryl ether fragmentation products **2** and **3**, derived from QM **1**. Obviously, the generated AHQ⁻ transferred an electron to the QM, which led to fragmentation.

The above chemistry demonstrates that SET reactions between AHQ and QMs are possible at room temperature in organic solvents. Can this chemistry also operate at 170°C in water/alkali? In order to answer this question, we electrolyzed 1M NaOH solutions of bleached pulp/AQ and wood meal/AQ in a pressure vessel that contained several electrodes [14]. The temperature was increased from 20-165°C while periodically recording cyclic voltammograms. The bleached pulp experiment showed the typical reversible redox currents of AQ. The wood meal showed an enhanced AQ reduction current that lasted for ~30 minutes at 165°C. The wood meal contained lignin and, thus, the experiment suggested that a reduction of lignin and oxidation of AHQ⁻ or AHQ⁻² was occurring under pulping conditions.

Evidence of Radical Intermediates

Another way to establish the existence of an SET mechanism is to show that a radical is produced during reaction. Radicals are known to cyclize to 5-membered rings with 5-hexenyl substrates. Therefore, we studied the reaction of a 5-hexenyl radical probe that could form a QM under soda, kraft, and soda/AQ pulping conditions [15]. The expected SET reactions are shown in Figure 3.

The soda and kraft reactions of radical probe **4** led largely to recovered starting material. In contrast, alkaline AHQ⁻² led to a rapid consumption of **4** and the production of a mixture of **8** and **9**, with the former dominating. Heating **4** in aq. NaOH that contained glucose also gave a mixture of **8** and **9**, but at a slower rate and with the latter dominating. It is apparent that radicals **6** and **7** were formed during both soda/AHQ and soda/glucose treatments. In the AHQ case, **6** was rapidly reduced (a hydrogen atom supplied by AHQ) to give **8**, while with glucose the reduction was slower and more cyclization occurred.

The reduction of QMs by AHQ⁻² to give -CH₂-benzyl carbons has also been observed in the treatment of a β-methoxy phenolic lignin model with AHQ at 150°C [16] and the reactions of syringyl alcohol (**10**) in alkali at 135°C (Figure 4) [17].
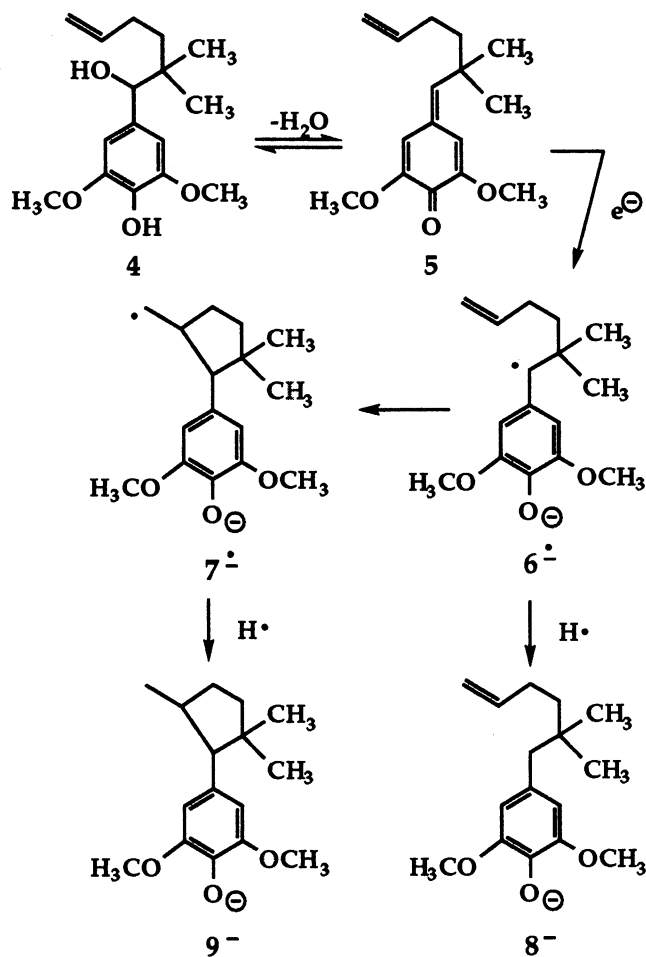

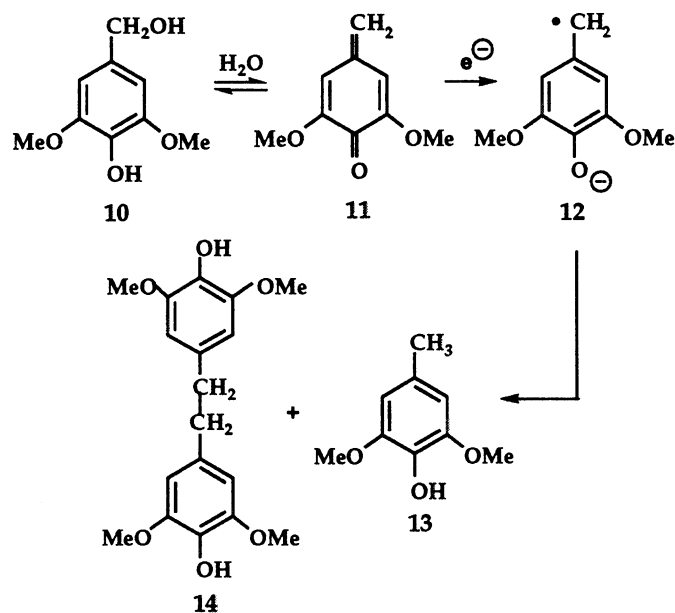Figure 3. SET reactions of compound **4** [15].


Figure 4. SET reactions of syringyl alcohol [17].

A comparison of the reactions of syringyl alcohol with soda, kraft, soda/AHQ, and soda/glucose indicates that only the AHQ and glucose cases led to any significant reduction to syringol (13), presumably by way of SET transfer to the QM 11 to give intermediate radical anion 12. The AHQ case also provided a substantial amount of a dimer product 14, a product that logically results from the coupling of a radical anion with the QM or another radical anion.

Reductions of lignin QMs during pulping would reduce the occurrence of undesirable condensation reactions and may partially account for the effectiveness of AQ as a pulping promoter. [Radical coupling would be deterimental; but might be insignificant due to a low concentration of radicals.]

These observations indicate that AHQ chemistry is different from soda and kraft chemistry; radicals are produced in the AHQ case and not in soda and kraft.

Organometallic/QM Reactions

While not an example of AHQ chemistry, the reactions of organometallic compounds, such as 15, provide additional support that single electron transfer chemistry is possible under pulping conditions. Watson, Wright, and Fullerton (17) report that the β-aryl ether cleavage a lignin model, when reacted with 15, is similar to that observed with AHQ; they argue that the most likely mechanism is SET. The cobalt oxidation state change of II → III for SET reaction is reasonable, but the change of II → IV required to form an adduct is unlikely. In addition, formation of a 15/QM adduct would be unlikely due to the steric bulk of 15.
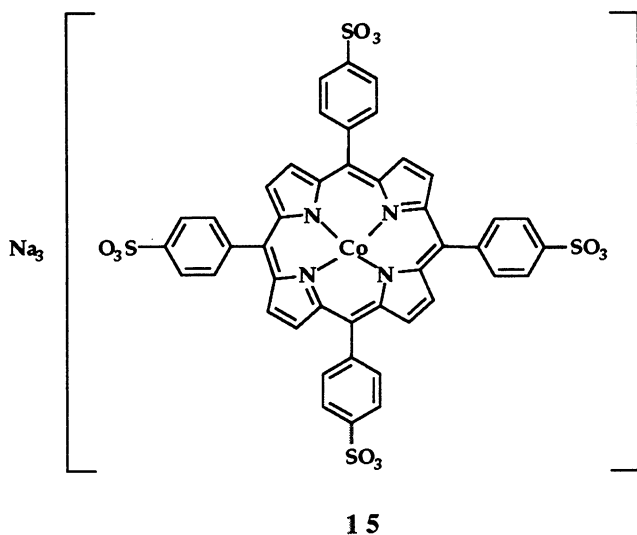
Enhanced Fragmentation by AHQ

Additional supporting evidence for SET anthraquinone reactions comes from a comparative study of the reactions of model 16 under different pulping conditions (19). This model produces quinone methide 17 in alkali at 150°C (Figure 5). The terminal hydroxyl group on the side chain is capable of reacting with the QM intermediate to give cyclic product 18. The rate of QM fragmentation can be "timed" relative to the cyclization event by determining the relative yields of guaiacol (3) and cyclized product 18. Consequently, this "clock" reaction provides information on the relative efficiencies of different pulping additives to fragment a lignin model.
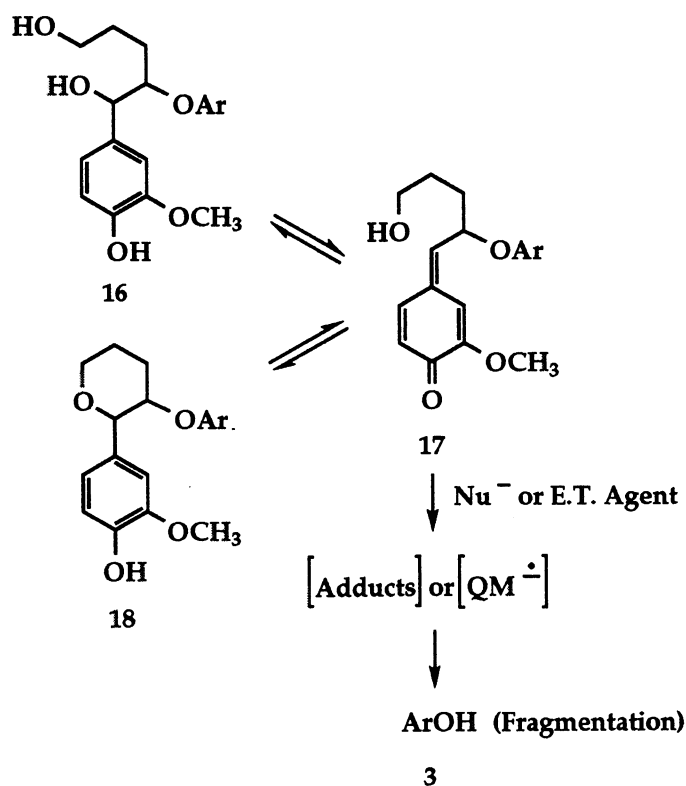

Figure 5. A clock reaction to determine relative efficiencies of pulping additives (19).

Model 16 has been reacted under soda, kraft, and soda/AHQ conditions; in each case the NaOH level was the same, meaning that rate of cyclization should be the same. All experiments showed the same rate of disappearance of 16. This indicates a common slow step, namely quinone methide formation. In terms of product differences, AHQ gave high levels of fragmentation, and little cyclization; soda was just

the reverse; and kraft conditions were in-between. Thus, the fragmentation efficiency (delignification effectiveness) was: AHQ > > kraft >> soda.

Additional studies with organic/water solvent mixtures showed that organic solvents greatly enhanced the model fragmentation reactions with AHQ, but had no effect with soda and kraft.

CONCLUSIONS

Electrochemical studies indicate that AHQ transfers single electrons to quinone methides and that the resulting QM$^-$ readily undergoes β-aryl ether fragmentation. The products obtained from high temperature alkaline reactions of syringyl alcohol and a radical probe lignin model demonstrate that radicals are formed in the case of AHQ but not for kraft conditions. The superior fragmentation efficiency of AHQ, together with an observed synergistic effect between AHQ and organic solvents, indicate that the chemistry of AQ pulping is unique - SET.

REFERENCES

1. (a) Stone, J. E., and Clayton, D. W., *Pulp Paper Can.*, 61(6): T307 (1960); (b) Enkvist, T., *Svensk Paperstid.*, 60(17): 616 (1957); (c) Sjostrom, E., *Tappi*, 60(9): 151 (1977).

2. (a) Holton, H., *Pulp & Paper Can.*, 78(10): T218 (1977); (b) Ghosh, K., Venkatesh, V., Chen, W., and Gratzl, J., *Tappi* 60(11): 127 (1977).

3. MacLeod, J., Fleming, B., Kubes, G. and Bolker, H., *Tappi*, 63(1): 57 (1980); McKenzie, A., *Appita*, 38: 428 (1985).

4. Kibblewhite, R., and Bawden, A., *Appita*, 42: 275 (1989); Teder, A., and Tormund, D., *Tappi*, 64(4): 138 (1981).

5. Dimmel, D., *J. Wood Chem. Technol.*, 5: 1 (1985).

6. Gierer, J., *Wood Sci. Technol.*, 19: 289 (1985).

7. Obst, J., Landucci, L., and Sanyer, N., *Tappi*, 62(1): 55 (1979); Landucci, L., *Tappi*, 63(7): 55 (1980); Gierer, J., Lindeberg, O., and Noren, I., *Holzforschung*, 33: 213 (1979).

8. Dimmel, D., and Shepard, D., *J. Wood Chem. Technol.*, 2: 73 (1982).

9. Miller, J., Calcaterra, L., and Closs, G., *J. Amer. Chem. Soc.*, 106: 3047 (1984).

10. Dimmel, D., and Schuller, L., *J. Wood Chem. Technol.*, 6: 345 (1986).

11. Dimmel, D., and Schuller, L., *J. Wood Chem. Technol.*, 6: 565 (1986).

12. Dimmel, D., Perry, L., Chum, H., and Palasz, P., *J. Wood Chem. Technol.*, 5: 15 (1985).

13. Ralph, J., and Young, R., *J. Wood Chem. Technol.*, 3: 161 (1983).

14. Dimmel, D., unpublished.

15. Smith, D., and Dimmel, D., *J. Org. Chem.*, 53: 5428 (1988).

16. Dimmel, D., Bovee, L., and Brogdon, B., *J. Wood Chem. Technol.*, 14: 1 (1994).

17. Smith, D., and Dimmel, D., *J. Wood Chem. Technol.*, 14: 279, 297 (1994).

18. Watson, P., Wright, L., and Fullerton, T., *J. Wood Chem. Technol.*, 13: 371, 391, 411 (1993).

19. Dimmel, D., Schuller, L., and Apfeld, P., *J. Wood Chem. Technol.*, 7: 97 (1987); Brogdon, B., and Dimmel, D., *J. Wood Chem. Technol.*, 16(3): accepted (four paper series) (1996).