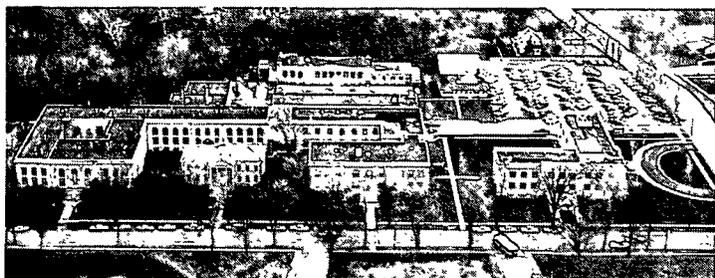THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

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CHARGE-TRANSFER COMPLEXES IN KRAFT LIGNIN. PART 3: IMPLICATIONS ON THE POSSIBLE OCCURRENCE OF CHARGE-TRANSFER COMPLEXES IN RESIDUAL LIGNIN AND IN LIGNIN OF LIGHT-INDUCED YELLOWED HIGH-YIELD PULPS

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ABSTRACT

A study was made of the color contribution of known chromophores in kraft lignin solutions (methyl-cellosolve, DMF). Based on the results, the intensity of the visible absorption band of quinones, as such, contributes only about 1/3 of the color, whereas approximately 2/3 of the light absorption is due to a quinone-phenol charge-transfer interaction. Extended chromophoric systems are ruled out as noticeable light absorbers. The possible implications of such charge-transfer complexes to the color of residual lignin in chemical pulps and to the discoloration of high-yield pulps during yellowing by sunlight are discussed.

INTRODUCTION

The intensive color of lignins in kraft liquor and kraft pulp has been the object of investigations for some time. Recent studies on residual lignin isolated from kraft pulp have shown that in essence residual kraft lignin is similar to kraft lignin isolated from black liquor.

Kraft lignin isolated from a black liquor was chosen for this investigation for a number of reasons. First, the isolation procedure was much less complicated than one to obtain a residual lignin. Secondly, practically all previous investigations, with respect to color, have employed isolated kraft lignins. Therefore, the results obtained in this study can be compared to these previous results. Thirdly, isolated kraft lignins are soluble in a number of organic solvents, allowing spectroscopic investigations of their solutions.

CHROMOPHORIC STRUCTURES IN KRAFT LIGNIN

Early research into the so-called "kraft color" was concerned with the source of the reddish-brown color of kraft pulps. Through the 1920's and 30's, sources of kraft color were proposed including tannins and phlobaphenes, along with the condensation products between tannins and alkali-labile carbohydrates, sulfur dyes, lignin and its reaction products, and carbohydrate degradation products. By 1948 Pigman and Csellak (1) were among the first to pinpoint lignin and its degradation products as responsible for the bulk of the color found in kraft pulps.

Subsequent research has centered on identifying the individual chemical structures which are responsible for this color. Although some of these structures may be incorporated into the lignin macromolecule during the original lignification in the tree, many are known to result from various degradation and condensation reactions that lignin participates in during the kraft pulping process.

The work discussed is based on the results obtained from isolated kraft lignin or from lignin model compound studies. Only chromophoric structures capable of contributing to the visible absorption spectrum of kraft lignin are considered.

Electronic absorption spectroscopy provides a useful instrumental method for examining chromophoric or light-absorbing structures. Some features of such a spectrum (2) which are characteristic for the majority of kraft lignins may be pointed out. These include the phenolic maximum at 280 nm, a shoulder which occurs near 340 nm, and a gradually decreasing absorption above 400 nm. The smooth nature of the curve throughout the visible range may represent the action of several different chromophore systems, including the tails of absorption bands occurring in the near UV spectral region.

Several investigators have attempted to resolve the electronic absorption spectrum of kraft lignin into its component bands (3,4). Norrstrom (4) modeled the lignin spectrum by the use of thirteen overlapping Gaussian bands. He divided these bands into four general groups, categorized by their response to changes in pH. However, no further characterization of these individual bands has appeared in the literature.

Transition Metal Complexes

Various transition metals are found in kraft lignin, iron usually being the most abundant. The metals may be present in the original wood source or may become associated with the lignin from contact with various process waters or machinery. These metals are able to form complexes with certain structures in the lignin molecule (2,5,6), most notably, phenols and catechols. These complexes are considered as potentially important contributors to the color of kraft lignin, since they absorb light in the visible region of the spectrum.

Metal-lignin complexes have been studied by the use of model compounds. Polcin and Rapson (7) determined the absorption spectra of various metal ions with catechol and flavon-type structures. From these spectra they were able to conclude that iron complexes gave longer wavelength absorptions than other metal complexes, including manganese, copper, and aluminum ones. Furthermore, ferric ions were found to be the most effective in color formation, whereas ferrous ions had little or no effect on color. Imsgard et al. (5) and Marton et al. (8) determined the absorption spectra for ferric complexes with various lignin model catechols and phenols and found the absorption maxima to occur between 500 and 590 nm, with molar absorptivities ranging up to 2000 liters/mol-cm.

Several researchers have complexed ferric ions with kraft lignin and have observed subsequent increases in its absorption spectrum, centered at 560 nm (2,5). The magnitude of this increase together with the known molar absorptivities of model catechol complexes were then used to estimate the catechol content of lignin. According to these calculations, kraft lignin contains 6-7 catechol structures per 100 C-9 units.

Another approach has been to remove metal ions from kraft lignin using chelating agents and then

to examine the resulting absorption spectra for decreases in absorbance. Nakano and coworkers (9,10) found iron was the only significant metal present in kraft lignin with respect to a contribution toward its color. Removal of the iron by EDTA chelation resulted in a decrease in absorption of the kraft lignin spectrum centered around 500 nm. The percentage decrease in the absorbance of the lignin was found to be about 5% at 450 nm, approximately 14% at 500 nm, and reached a maximum of about 20% at 700 nm.

The iron content of the kraft lignin used in our study (11) was 37.67 ± 12 ppm. (Chromium, nickel, copper were present in amounts less than 10 ppm, manganese and cobalt in about 0.5 ppm.) The contribution of the metal complexes to the visible absorption spectrum was investigated by removal of these metals. This was accomplished by their chelation with EDTA, followed by the extraction of the metal chelates from the lignin via electrodialysis. The removal of the metals did not result in a decrease in the lignin's absorbance above 500 nm. For comparison, an industrial kraft lignin (Indulin AT, Westvaco, SC) was also investigated. This lignin showed significantly higher levels of metals (iron 176 ppm, manganese 56.7 ppm). Upon the same treatment as above the absorbance decreased in the long wavelength region of the spectrum centered at approximately 520 nm.

The different behavior of the laboratory and industrial kraft lignins indicated the possibility of a threshold level of iron below which removal of additional iron would have no beneficial effect in terms of color reduction.

Conjugated Unsaturated Systems

Kraft lignin contains various unsaturated functional groups, including carbonyls and carbon-carbon double bonds. Individually, these functional groups absorb light in the ultraviolet portion of the spectrum. Absorption bands appearing between 300 and 350 nm are typical for lignin model compounds which contain carbonyl or carbon-carbon double bonds (12). Based on model compounds the shoulder appearing at 340 nm in the kraft lignin spectrum has been attributed to stilbene structures (2). While these individual structures do not contribute to the visible absorbance of kraft lignin, conjugation with other unsaturated structures could lead to extension of the absorption bands into the visible region of the spectrum.

Both o,p' and p,p'-dihydroxystilbene structures have been shown to form from model compounds under kraft pulping conditions (2,13). p,p'-Dihydroxystilbenes have also been isolated from kraft cooking liquors (14). o,p'-Dihydroxystilbenes are formed from phenyl coumaran-type structures via quinonemethide intermediates, while similarly formation of o,p'-dihydroxystilbenes originates from 1,2-diarylpropane-1,3-diol structures.

The dihydroxystilbenes absorb only in the UV portion of the spectrum, but they are readily oxidized to red colored stilbenoquinones upon standing in air (13,15,16). Various metal ions including ferric and cupric ions catalyze this oxidation

(13). Quinonemethides, which are known to be oxidizing agents (2,15), could perform this oxidation in kraft pulping liquors.

From ionization difference spectroscopy, Falkehag et al. (2) estimated there were 7 stilbene structures per 100 C-9 units present in kraft lignin. Similarly the specific amount of p,p'-dihydroxystilbene structures was estimated to be 5 per 1000 C-9 units using a technique employing peroxide oxidation of the lignin in the presence of cupric ions.

Butadiene structures have also been isolated from model compounds subjected to kraft cook conditions. Gierer (13) has found 1,4-bis-(p-hydroxyphenyl)-buta-1,3-diene in the reaction mixture which resulted from the kraft cook of phenolic pinoresinol structures. On oxidation these structural types are expected to yield highly conjugated quinonoid chromophores.

Finally, there is the possibility of two or more chromophores joined together by conjugation to form extended conjugated systems. Such extended systems are also expected to have absorptions in the visible range of the spectrum. In the tentative formulation for kraft lignin given by Marton (17), such an extended chromophoric system is shown.

We examined the color contribution from extended chromophores by hydrogenating their connecting carbon-carbon double bonds (11), thereby interrupting the conjugation in these systems. The hydrogenation was carried out with diimide in order to avoid catalyst poisoning, steric restrictions involved with the approach to the catalyst surface, and nonspecificity of reductions. A large decrease in the lignin's UV absorbance was observed, but no decrease in the lignin's visible absorbance was detected. This leads to the conclusion that extended conjugated systems do not contribute to the visible absorption spectrum of the laboratory produced kraft lignin.

Quinonemethides

Quinonemethides are important intermediates, both during lignin biosynthesis and in pulping reactions. They may play a part in contributing to the color of kraft lignin in one of two ways. First, the role of quinonemethides as possible oxidizing agents for other color precursors (dihydroxystilbenes and catechols) has already been mentioned. Secondly, as Harkin (18) pointed out, resonance stabilized quinonemethides resulting from the dehydrogenation of dihydroxy-diphenylmethane structures are yellow-colored chromophores in their own right and could be responsible for some of the color of kraft lignin.

Free Radicals

In 1960 Rex (19) first demonstrated the existence of stable free radicals in lignin preparations. Several years later Steelink and coworkers (20) found that kraft lignins, as well as other chemically or biologically modified lignins contained increased radical contents compared to native lignins. Steelink and coworkers also showed

various derivatization procedures dramatically altered the free radical content of kraft lignin. This led to the novel proposal of the presence of quinhydrone-type structures in kraft lignin. These structures are complexes between a quinone and its corresponding hydroquinone. Steelink (21) was also able to show syringol derivatives which possessed an α-carbonyl group could be oxidized to remarkably stable radicals in solution. These radical solutions were purple in color and had several strong absorbance bands in the visible region of the spectrum.

Quinones

Quinones are cyclic conjugated diketones which have two absorption bands occurring in the visible region. Quinoidal structures might form in lignin during the original lignification process in the tree (5). Oxygen or hydroxy radicals are capable of adding to phenoxy radicals of guaiacyl or syringyl derivatives. Such additions would lead to demethoxylation and subsequent formation of quinone structures.

Pew and Connors (22) found that simple phenylpropane model compounds underwent phenol dehydrogenation reactions analogous to those taking place during lignin biosynthesis to yield phenyl-parabenzoquinones. Harkin and Obst (23) showed the enzymatic phenol oxidation of 2,4,6-trimethoxyphenol caused the elimination of a methoxy group, leading to a mixture of products containing mostly the para-quinone, 2,6-dimethoxy-1,4-benzoquinone, and a small amount of the ortho-quinone, 3,5-dimethoxy-1,2-benzoquinone. In the authors' opinion, similar reactions with guaiacyl and syringyl structures during lignin formation would introduce quinonoid structures into the lignin macromolecule.

Although these "original" quinone types are significant contributors to the natural coloration of woods, they are not as important when considering the coloration of chemical pulps. Of much more importance for kraft pulps is the formation of a substantial number of quinone precursors during the pulping process. Specifically, catechols are formed by demethylation of lignin structures with hydrosulfide, hydroxy, and methylmercaptan anions. Although the catechols are not colored themselves, they are easily oxidized to red colored orthoquinones. The oxidation can take place in a manner similar to that described for the dihydroxystilbenes.

Although quinones clearly play a major role in the observed color of kraft lignin, determination of the magnitude of this contribution has been hampered by a lack of direct analytical or instrumental methods for the detection of the quinones. Contributing to this problem is the inherently unstable nature of many quinones and the likelihood the quinones are present in kraft lignin in relatively small quantities.

The concentration of quinoidal structures in kraft lignin has been estimated from comparison of spectra obtained before and after treatment of the lignin with a reducing agent such as sodium borohydride or sodium hydrosulfite. The maximum of the decrease in absorbance of the lignin spectrum caused by this treatment can then be related to the quantity of quinones present, making use of average absorptivities from model ortho-quinones. The method assumes spectral properties of isolated model quinones are comparable to quinone structures incorporated within the lignin macromolecule. Using this approach, Ilyama and Nakano (24) estimated softwood kraft lignin contained 3 to 4 orthoquinone structures per 100 C-9 units. This number of quinones accounted for 40 to 45% of the lignin's absorbance in the visible spectrum.

The concentration of quinones in the laboratory produced kraft lignin in our study (11) was determined by a carbon-14 labeling technique. After acetylation of the quinones with pyridine/acetic anhydride the acetylated kraft lignin was reductively acetylated with carbon-14 acetic anhydride/pyridine/zinc dust. The activity of the lignin was, therefore, directly related to the quinone concentration of the kraft lignin. For the laboratory kraft lignin, the quinone concentration averaged 3%.

Indications for Charge-Transfer Complexes in Kraft Lignin

Charge-transfer complexes (CTCs) are molecular complexes formed by the weak interaction between electron donors and electron acceptors. An electron donor may be defined as a molecule possessing a relatively high localized electron density. Oppositely, an electron acceptor is relatively deficient in electrons. CTCs are also termed donor-acceptor complexes.

Electron paramagnetic resonance data were used by Steelink (20) to postulate the existence of a semiquinone radical structure in kraft lignin, coexistent with a diamagnetic quinhydrone moiety. Quinhydrones are known CTCs. A portion of Steelink's data are given in Table 1.

Table 1 Free radical content of lignin derivatives [(spins/g) x 10 (exp 17)]

Yellow Pine	Na Salt	Acidified Salt	Borohydride Reduced	Na Salt of Borohydride Reduced
3.0	100–300	3.0	1.3	22

The untreated yellow pine kraft lignin was found to have a spin content of 3.0 x 10 (exp 17) spins/g, which increased one hundred fold upon basification. This increased radical content was reversible, and upon acidification the initial spin content was again obtained. This type of behavior, wherein a large and reversible change in spin content is caused by pH alone, is also characteristic of quinhydrone-type systems and therefore led to Steelink's proposal. As further evidence for this type of structure, quinone structures in the lignin were removed by sodium borohydride reduction. In this case, basification of the reduced lignin did not produce the same large increase in the free radical content.

Kratzl and coworkers (16) investigated the reductive acetylation of kraft lignin, which reduces

quinones and removes them as chromophores. Neither proton NMR, acetate content determination, nor elemental analysis revealed any difference between the reductively acetylated and a normally acetylated lignin, within the experimental error. These results were obtained even though the reductively acetylated lignin was lighter in color and had a substantially less intensive visible absorption spectrum than the normally acetylated lignin.

CHARGE TRANSFER COMPLEXES
IN KRAFT LIGNIN SOLUTIONS

Only a summarizing outline of the experimental approach and of the results is provided. Details are published elsewhere (11).

The electronic absorption spectrum of kraft lignin is very complex, indicating a number of different chromophores probably present in relatively small quantities. From the evidence available, the most likely type of CTC involves an interaction between a phenol and a quinone. Since the content of CTCs was then assumed to be very small and their effect difficult to determine, a modified kraft lignin rich in ortho-quinone structures was prepared. Side reactions were kept at a minimum during the applied periodate oxidation in order for a useful comparison between the original and the modified lignin to be obtained.

The evaluation of the contribution of various chromophores to color involved the methodical removal of these chromophores from kraft lignin and the determination of their individual effects on the kraft lignin spectrum. Difference spectroscopy was used to great advantage in this regard. Extended chromophoric systems were studied by sodium borohydride reduction of carbonyl groups and diimide hydrogenation of carbon-carbon double bonds. Transition metal complexes were investigated by EDTA chelation and removal of these metals. The contribution of quinones and the separation of their individual contribution from that caused by their participation in CTCs was determined by carbon-14 labeling of the quinones.

Quinones were the major visible light absorbing chromophores which were identified in the studied kraft lignin. The occurrence of CTCs in the various kraft lignin systems was concluded from the acquired data. The CTC interaction appeared to occur between free phenolic and ortho-quinone structures acting as donor and acceptor halves of the complex. Upon sodium borohydride reduction of a laboratory produced kraft lignin, only one-third of the absorbance decrease could be accounted for by the quinones. The remaining two-thirds was assigned to the disruption of CTCs.

THEORY OF CTCs

The discussion which follows will consider CTCs in some detail, providing the basis for the understanding of their possible significance in residual lignin and light induced yellowed high-yield pulp. For both lignin types a solid state CTC interaction between phenolic (donor) and quinonoid (acceptor) moieties has to be considered as a major contributor to the dark color.

Theoretical Treatment

CTCs exist in two states, a ground state and an excited state. In the ground state, the two molecules composing the complex undergo the normal physical forces expected between two molecules which are in close proximity to each other. These forces include London dispersion forces and any electrostatic interactions, such as between dipole moments. In addition to these normal forces, a small amount of charge is transferred from the donor to the acceptor. This contributes some additional binding energy to the complex (25).

The excited state of the complex occurs when the ground state complex absorbs a photon of light having the appropriate frequency. In the excited state, the electron which had only been slightly shifted toward the acceptor in the ground state is almost totally transferred (25). Depending on the structural features of both the donor and acceptor, the wavelength of light absorbed may be in the visible range of the electromagnetic spectrum. In many cases, therefore, CTCs are colored substances.

Mulliken (26) was responsible for the development of what has been the most successful theoretical treatment of CTCs using wavefunctions for the description.

Classifications of CTCs

CTCs may conveniently be classified according to the types of orbitals in the donor and acceptor molecules which are undergoing the interaction. Donor and acceptor molecules may each be divided into three clases (27,28). However, complexes involving π-donors with π-acceptors appear to present the most obvious candidates for CTCs in kraft lignin. Good examples of these structures are phenols and quinones, respectively.

Structural Considerations

CTCs can exist as intermolecular complexes, where the interaction takes place between two molecules, or as intramolecular complexes, where both the donor and acceptor moieties are contained within one molecule. For CT interaction to occur, the donor and acceptor components must be close enough for their differences in electron density to be felt. For unrestrained complexes, distances between the components of 3.0 to 3.4 angstroms, or slightly less than the Van der Waals distance, are common (25).

Most CTCs exist in a 1:1 stoichiometric ratio of donor to acceptor. For some π-π types of complexes, there is evidence for the existence of higher order complexes in equilibrium with the 1:1 complexes (29). The crystal structures of phenol-benzoquinone complexes have been found to have both 1:1 and 2:1 stoichiometries (30).

Many aromatic, crystalline CTCs involving donors and acceptors are found to be composed of infinite chains of alternate donor and acceptor molecules in which the donor acceptor distance is slightly less than the Van der Waals distance (30). Additionally, the aromatic π-π complexes are found to occur in staggered sandwich forms in which the

plane of the donor is parallel to the plane of the acceptor. Ideally, the donor and acceptor molecules are staggered by one-half of their widths in order for their orbital overlaps to be maximized. Direct superposition of an aromatic donor over an aromatic acceptor results in negative parts of one wavefunction overlapping the positive portion of the other wavefunction, giving a net overlap of zero (25).

The amount of orbital overlap between the donor and acceptor plays a critical role in the magnitude of the CT interaction observed. Constraints resulting from steric hindrances are major factors in this regard (31). Synthesis of intramolecular CTCs, which vary in their magnitudes of orbital overlap, has been an active area of research. Intramolecular complexes including para- and meta-cyclophane quinhydrones [Staab and coworkers (32-34); Tashiro and coworkers (35,36)], napthalen-ophane quinhydrones (37,38), oligooxaparacyclophane quinhydrones (39), cyclophane-ortho-quinones (40), and substituted biphenyls (41) have been investigated. The results from these investigations clearly show the overlap between donor and acceptor orbitals has a large influence on both the frequency and intensity of CT absorptions.

Other forces which also influence the orientation of the donor and acceptor to each other, will likewise affect the magnitude of the CT interaction. Included among these other forces are solvation effects on the individual donors and acceptors and hydrogen bonding between donors and acceptors. Large differences are observed in the magnitude of CT for quinhydrone-type complexes in solution and in the solid state (42,43). They are attributed to the hydrogen bonding of the complexes in the solid state.

IMPLICATIONS ON THE POSSIBLE OCCURRENCE OF CHARGE-TRANSFER COMPLEXES IN RESIDUAL LIGNIN AND IN LIGNIN OF LIGHT INDUCED YELLOWED HIGH-YIELD PULPS

Recent studies on residual lignin isolated from kraft pulp have shown that residual lignin is similar to kraft lignin. The major difference is the higher molecular weight of the residual lignin, a higher concentration of vinylether-type structures, and the possible occurrence of covalent bonds to carbohydrates (44-47). Since the same functional groups, although in different amounts, have been found in both isolated kraft lignin and residual lignin, it would appear that residual lignin and kraft lignin contain the same type of chromophore structures.

Although we cannot exclude a contribution of extended chromophoric systems to the color of residual lignin without further investigations, we are certainly correct in the assumption that any CTC interaction between phenolic and quinoidal parts of the lignin will be enhanced in the solid state. Besides intramolecular CTCs, intermolecular CTCs may be contributing due to the lack of interference by any solvent (25,48).

A simple molecular model investigation shows (Fig. 1) that for the formation of an intramolecular CTC between a phenolic and a quinonoid part of

the molecule a minimum of three sp³ hybridized carbon atoms between the donor and acceptor moieties are required for the ideal orbital overlap. However, for intramolecular complexes examples are also known of indirect, through-bond interactions besides the direct, through-space interaction (37,49).
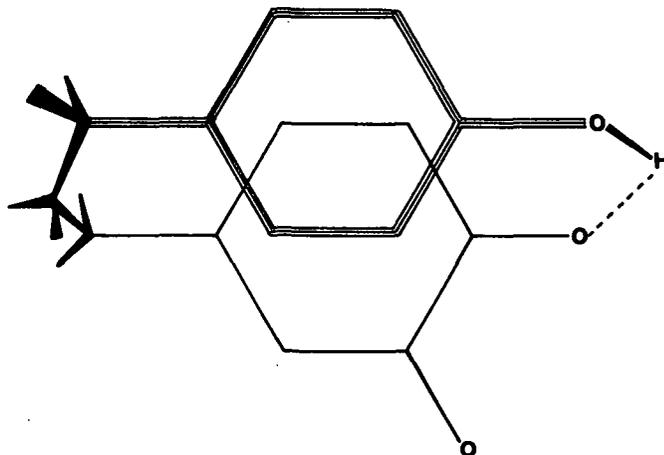

Fig. 1. π-π CTC in lignin.

A similar deduction can be made for the light-induced yellowing of high-yield pulps. We have evidence that small amounts of predominantly ortho-quinones cause the strong brightness loss that is observed when high-yield pulp sheets are exposed to natural or artificial sunlight (Lonsky and coworkers, to be published). Again, CT interaction of quinones with donor species, like phenols or aromatic structures with high electron density, have to be considered as a possibility for the enhancement of the discoloration beyond the contribution of quinones per se.

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