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THE OCCURRENCE AND LIGHT INDUCED FORMATION OF ortho-QUINONOID LIGNIN STRUCTURES IN WHITE SPRUCE MECHANICAL PULP

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ABSTRACT

A sensitive method, based on reaction with trimethyl phosphite, was developed for the determination of ortho-quinonoid structures in pulp. It was used to show that structures of this type are responsible for most of the color of white spruce mechanical pulp and for most of the increase in color associated with light induced yellowing. The untreated pulp contained 3–6 quinone units per 100 lignin G_0 units, which were responsible for about 75% of its color. Upon irradiation with simulated sunlight for 20 hr, the number increased to about 10 and the increase accounted for about 75% of the increase in color. The quantum efficiency of quinone formation was 0.08 moles per mole of photons absorbed.

INTRODUCTION

Increasing wood costs and predicted shortages in future wood supplies have continued to stimulate interest in the production and use of high yield pulps. However, a major problem associated with the use of such pulps, both bleached and unbleached, is that they "yellow" upon exposure to sunlight. This light induced yellowing (or reversion) increases the absorbance of these pulps in the visible region of the spectrum, and hence, decreases pulp brightness. This, in turn, limits their use as substitutes for fully bleached chemical pulps.

The photochemical and chemical reactions involved, while of economic significance, are not fully understood. Results obtained with model compounds (1–6), isolated lignins (7–8), and groundwood pulps (9–10), have led to theories suggesting that ortho-quinonoid lignin structures are formed during the photobleaching process (Fig. 1). It is well known that such structures are highly colored, and their formation would account for at least a part of the color developed when mechanical pulps are exposed to light. In addition, it has been suggested that such structures may account for the natural color of wood and wood pulps (9–10).

The extent of the contribution of these structures to the color of wood pulps, however, has not been quantitatively evaluated. In this work, a method was developed to study both the occurrence and the light induced formation of ortho-quinonoid lignin structures in situ. The method was then used to estimate their contribution to the color of unirradiated and sunlight irradiated white spruce mechanical pulp. It was also used to estimate the quantum efficiency of 312 nm UV light induced ortho-quinone formation.

Method of ortho-quinone Analysis

Since ortho-quinonoid structures in lignin are likely to be strongly colored, the occurrence of only a few of them could account for the color of yellowed high yield pulps. To detect such small amounts in the chemically complex pulp fibers, we sought a method that was both sensitive and specific for these structures.

The method we developed to fill this need is based on the known reaction between ortho-quinones and trivalent phosphorus compounds (11–13). For example, we reacted trimethyl phosphite with 3-methoxy-1,2-ortho-benzoquinone to form, in quantitative yield, the colorless oxophosphorane adduct, I, as shown in Fig. 2 (13). Upon addition of water, I was quantitatively converted to the corresponding cyclic phosphate triester, II (also colorless). These reactions are significant because the ortho-quinone becomes "tagged" with phosphorus, an element foreign to the fiber wall, and one for which sensitive microanalytical techniques are available.

A further advantage of the phosphorus tag is that it allows one to check the assumption that the reagent is specific for ortho-quinonoid structures. This is possible because the phosphorus-31 nucleus is paramagnetic, and its structural environment can, therefore, be characterized by nuclear magnetic resonance (NMR). Thus, the 31P NMR spectrum of the oxophosphorane adduct, I, displayed a single signal at a chemical shift (relative to 85% H_3PO_4) of -45.8 ppm, and the corresponding value for the cyclic phosphate triester, II, was 11.1 ppm. These chemical shifts are characteristic (14); a second reaction with 3,5-di-tert-butyl-1,2-ortho-benzoquinone, for example, gave products with corresponding values of -46.5 and 12.1 ppm.

To further test this method, we oxidized a sample of white spruce mechanical pulp with Fremy's salt (potassium nitrosodisulfonate), which is known to introduce ortho-quinonoid structures into lignin (15,16). When the oxidized pulp was reacted with trimethyl phosphite, it was rapidly bleached, and the resulting pulp produced a single, strong 31P NMR signal at 13.2 ppm, characteristic of a cyclic phosphate triester structure.

Occurrence of ortho-Quinonoid Lignin Structures

We investigated the occurrence of ortho-quinonoid lignin structures by reacting a white spruce mechanical pulp (WSMP) with trimethyl phosphite. As shown in Table 1, the Kubelka-Munk light absorption coefficients of the pulp decreased significantly upon exposure to this reagent. Its 31P NMR spectrum had a strong signal at 12.4 ppm (71.5% of the total signal). A second, weaker signal was observed at 4.2 ppm (28.5% of the total signal). On the basis of the results described above, the signal at 12.4 ppm was attributed to cyclic phosphate triester formation. The origin of the second signal is not known. It appears to be...
Fig. 1 Proposed mechanism for the light induced formation of ortho-quinonoid lignin structures (10). Lignin related, however, since a similarly reacted holocellulose sample produced no clear signals.

Phosphorus microanalysis of three separate samples yielded a value of 0.39 ± 0.056 gram of phosphorus per 100 grams of dry pulp. From the NMR data, the amount of phosphorus associated with naturally occurring ortho-quinonoid structures was calculated to be 0.27%, or 71.5% of the total phosphorus present in the pulp. From this and the Klason lignin content (26.9%) the number of moles of ortho-quinonoid structures per gram of lignin was calculated to be $3.3 \times 10^{-4}$. Assuming a unit weight for spruce lignin of 185 g lignin/mole of C₉ units (17), we then estimated that the pulp contained 5-6 ortho-quinonoid lignin structures per 100 C₉ lignin units.

Table 1. Kubelka-Munk absorption coefficients of WSMP before and after reaction with trimethyl phosphate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kubelka-Munk Absorption Coefficient ((\text{cm}^2/\text{g}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>415 nm</td>
</tr>
<tr>
<td>Unreacted WSMP</td>
<td>141</td>
</tr>
<tr>
<td>Trimethyl phosphate</td>
<td>74.8</td>
</tr>
</tbody>
</table>

The light absorption measurements of Table 1 indicate that these ortho-quinonoid structures contribute significantly to the "natural" color of the pulp. From these measurements, we estimate that their contribution to the absorbance was about 50% at 415 nm, and about 75% at 457 and 520 nm. The formula used in these estimations was

$$\text{contribution to absorbance} = \frac{k - k_b}{k}$$

where \(k\) is the absorption coefficient of the pulp before reaction and \(k_b\) is the absorption coefficient of the pulp after reaction (i.e., bleaching with trimethyl phosphate). Detailed UV-visible spectroscopic analysis (18) indicated that the majority of the reduction in pulp color resulted from...
from the reaction of trimethyl phosphite with ortho-
quinonoid structures and not from the reaction of
trimethyl phosphite with the structure giving rise
to the signal at 4.7 ppm. This was particularly
true for the two longer wavelengths examined.

Sunlight Induced Formation of ortho-quinonoid
Lignin Structures

Upon exposure to simulated sunlight for 20 hours
the WSMP underwent severe yellowing (reversion).
The results presented in Table 2 show that the
associated increases in visible light absorption
were partially reversed when the exposed pulp was
reacted with trimethyl phosphite. The 31P NMR
spectrum of the exposed and reacted pulp had a
strong signal at 12.6 ppm (95% of the total signal)
and a weak signal at 2.1 ppm (5% of the total
signal). As in the two earlier pulps, we attri-
buted the signal at 12.6 ppm to the formation of
cyclic phosphate triesters. The origin of the
second signal is not known; it may have originated
from the same structure found in the unirradiated
and reacted pulp.

Table 2. Kubelka-Munk absorption coefficients of
sunlight irradiated WSMP before and after
reaction with trimethyl phosphite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kubelka-Munk Absorption Coefficient (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>415 nm</td>
</tr>
<tr>
<td>Irradiated WSMP</td>
<td>442</td>
</tr>
<tr>
<td>Irradiated and reacted WSMP</td>
<td>170</td>
</tr>
</tbody>
</table>

The increased formation of cyclic phosphate
triester structures after irradiation shows that
the formation of ortho-quinonoid structures is an
important component of the photoyellowing mechanism.

To confirm that the increased phosphorus incorpora-
tion was a direct result of irradiation, we used x-
ray microanalysis (scanning electron microscopy
with energy dispersive spectrometry, SEM-EDS) to
see how phosphorus incorporation varied with
distance from the irradiated surface of the sheet.
The results (Fig. 3) showed clearly that the sur-
face layers, where most of the radiation is
absorbed, contained most of the cyclic phosphate
triester structures. This shows, in turn, that
ortho-quinonoid structures are formed in an amount
that increases with the amount of UV radiation
absorbed.

Phosphorus microanalysis of the above pulp
yielded a value of 0.47 ± 0.025 gram of phosphorus
per 100 grams of dry pulp. From the NMR data, the
amount of phosphorus associated with the ortho-
quinonoid lignin structures present in the pulp was
calculated to be 0.45%, or 95% of the total phos-
phorus present in the pulp. Calculations similar
to those described above yielded a value for the
pulp of 10-11 ortho-quinonoid lignin structures per
100 Cg lignin units. Thus, we estimate that
these additional structures to the increase in
absorbance of this pulp to be 70-80% when measured
at wavelengths of 415, 457, and 520 nm. The for-
ma equation used in these estimations was

collection to reversion =

\[
\frac{(k_r - k_b) - (k - k_b)}{(k_r - k)}
\]

where

- \(k\) = absorption coefficient of unreverted and
  unreacted pulp
- \(k_r\) = absorption coefficient of irradiated
  (reverted) pulp
- \(k_b\) = absorption coefficient of reacted
  (bleached) pulp
- \(k_{rb}\) = absorption coefficient of irradiated and
  reacted pulp.

Thus, ortho-quinonoid structures are responsible
for most of the color formed when white spruce
mechanical pulp is exposed to simulated sunlight.

Quantum Efficiency

The quantum efficiency of ortho-quinone formation,
defined here as the number of moles of ortho-
quinonoid lignin structures formed per mole of pho-
tons absorbed, is a quantity of both theoretical
and practical interest. If exposure conditions are
known, quantum efficiency values at various wave-
lengt h ranges allow one to predict the extent of
yellowing. Such values would also be useful in the
design of optical brighteners for high yield pulps.

In an attempt to determine this value, we
irradiated sheet samples with known amounts of
nearly monochromatic UV light. We then determined
the number of moles of ortho-quinonoid lignin
structures generated in each sample by reaction
with trimethyl phosphite. It has been shown that
the UV component of sunlight (i.e., light in the
290-400 nm wavelength range) induces yellowing, and
the wavelength range 310-315 nm is most effective
EXPERIMENTAL PROCEDURES

The white spruce mechanical pulp used was prepared in a 12-inch Sprout-Waldron laboratory refiner from fresh chips. It was EDTA treated for 24 hours, ethanol/benzene extracted, and washed with distilled water. Handsheets were then formed according to the procedures described in TAPPI test method T 218 om-83 (basis weight = 160 g/m²) or T 205 Om-81 (basis weight = 30 g/m²) were used as a reference.

Kubelka-Munk absorption coefficients were determined using the method of "black backing" described by Polcin and Rapson (19). Measurements of Rₐ and R₀ were made on a Perkin-Elmer Model 320 spectrophotometer equipped with a Hitachi integrating sphere accessory. Pressed BaSO₄ pellets were used as a reference.

Irradiations were conducted with an ORIEL 1000 watt solar simulator (distance from source = 50 cm, total irradiance 85 mW/cm², roughly equivalent to natural sunlight) or with light from optical equipment designed to provide nearly monochromatic light (18). Both units were located in humidity (50%) and temperature (21°C) controlled labs. "Thick" handsheet samples (basis weight = 160 g/m²) were used in these experiments.

The reaction of trimethyl phosphate with irradiated or unirradiated pulp was performed in anhydrous dichloromethane. Sheet samples were Wiley milled to 20 mesh and dried under vacuum over P₂O₅ for 48 hours. While under dry nitrogen, 0.25-0.30 g of each sample was added to 10 mL of a 10% solution of trimethyl phosphate in anhydrous dichloromethane. The resulting samples were sealed and allowed to react for one week at 20°C. While still under nitrogen, the samples were washed separately with two 500 mL portions of anhydrous dichloromethane and one 1.0 L portion of anhydrous ether. The washed samples were then dried under vacuum and stored under dry nitrogen.

Solid state 31P NMR analyses were performed by Spectral Data Services, Inc. (818 Pioneer, Champaign, IL 61820). An inert environment was maintained during sample preparation and analysis. Microanalyses were conducted by Micro-Tech Labs, Inc. (4117 Oakton St., Skokie, IL 60076). SEM-EDS analyses were conducted by the EM lab at The Institute of Paper Chemistry (P.O. Box 1039, Appleton, WI 54912).

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