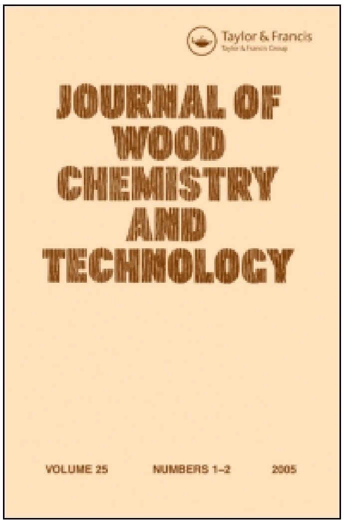

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Light-Induced Yellowing of Mechanical and Ultrahigh Yield Pulps. Part 2. Radical-Induced Cleavage of Etherified Guaiacylglycerol-β-Arylether Groups is the Main Degradative Pathway

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LIGHT-INDUCED YELLOWING OF MECHANICAL AND ULTRA-HIGH YIELD PULPS. PART 2. RADICAL-INDUCED CLEAVAGE OF ETHERIFIED GUAIACYLGLYCEROL-β-ARYLETHER GROUPS IS THE MAIN DEGRADATIVE PATHWAY.

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ABSTRACT

Bleached softwood mechanical pulp was treated with sodium borohydride to reduce carbonyl groups and dimethyl sulphate to block phenolic hydroxyl groups. Upon irradiation with near ultra-violet light, new phenolic hydroxyl groups and aromatic carbonyl groups formed. Existing mechanisms for photoyellowing require that either aromatic ketones or phenolic hydroxyls be initially present in the pulp, and cannot explain these observations. We interpret our results in terms of light-induced breakdown of etherified arylglycerol-β-arylether structures in lignin. Degradation occurs via the corresponding ketyl radicals, which cleave rapidly at the β-O-4 bond to give a phenoxy radical and an acetophenone enol. The enol tautomerizes to a ketone, while the phenoxy radical is oxidized to coloured groups. We believe that the ketyl route is the main lignin degradative pathway, and estimate that up to 70% of the colour formed during light-induced yellowing is attributable to this reaction.

INTRODUCTION

Light-induced yellowing of mechanical and ultra-high yield pulps is a consequence of the photooxidation of lignin. Figure 1 summarizes

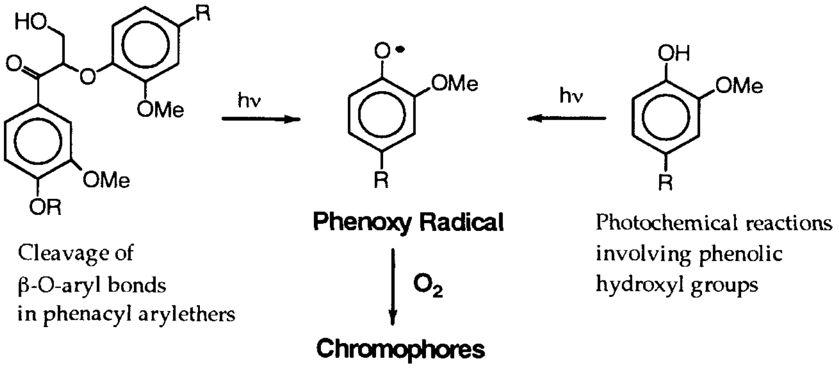

Figure 1: Summary of proposed mechanisms for the light-induced yellowing of mechanical pulps.

previously proposed reaction mechanisms. Considerable evidence[1] implicates the phenoxy radical as a key intermediate species, whose oxidation results in formation of coloured groups in the lignin. The various reactions proposed to account for formation of phenoxy radicals fall into two categories: 1) reactions involving the phenolic hydroxyl groups, 2) cleavage of the β-O-4 bond in phenacyl arylethers, a non-phenolic lignin structure.

We showed earlier[2] that the quantity of phenoxy radicals produced by these pathways is insufficient to account for the magnitude of the increase in absorption coefficient observed during photochemical discolouration of mechanical pulps. If the phenoxy radical is to be retained as a central intermediate, we must identify a lignin structure that can form a significant number of phenoxy radicals, but which does not fall into either of the categories described above. We have also observed the formation of aromatic carbonyl groups during irradiation of mechanical pulps[2], another phenomenon which existing mechanisms cannot explain satisfactorily.

As the title indicates, we feel that the experiments described here suggest that light-induced degradation of etherified guaiacylglycerol-β-arylethers can account for both of these observations.

EXPERIMENTAL

Washed and chelated black spruce TMP was bleached with alkaline hydrogen peroxide (4% peroxide on OD pulp, 60 °C, 2 h, 20% consistency), giving pulp with an ISO brightness of 75%. Pulps treated with a second 4% charge of peroxide had a brightness of 80%.

Bleached pulp was reduced with sodium borohydride (50% on OD pulp) at 1% consistency in a 50/50 volume mixture of water/methanol at 60 °C. Reaction time was typically four hours. The solvent was initially deoxygenated by bubbling with nitrogen, and a gentle stream of nitrogen was maintained during the reaction.

Phenolic hydroxyl groups were methylated as described in previous work[2], using 125 mL dimethylsulphate for 10 g OD pulp. Phenolic hydroxyl contents were determined using the periodate oxidation technique of Lai *et al.*[3]. About 400 mg of sample was extracted overnight with acetone, air dried, and suspended in 7 mL water with 114 mg/mL of sodium periodate. The pulp was left for three days in a refrigerator, and was shaken several times each day. Methanol liberated from the phenolic hydroxyl groups was analyzed by gas chromatography (J&W DB-Wax capillary column, 15 m, 0.025 μm film thickness, 60 °C), using acetonitrile as an internal standard.

Low-basis weight sheets (0.010 kg/m^2) were irradiated in a Rayonet RPR-100 photochemical reactor (Southern New England Ultraviolet) equipped with sixteen 75W blacklight lamps. According to the manufacturer, this arrangement gives 24W of light energy in the 300-400 nm region. All irradiations were performed in an environmental cabinet maintained at 25 °C and 50% relative humidity. Some irradiations were done at lower intensities, using only two lamps in the reactor. Samples used to track the phenolic hydroxyl content as a function of irradiation were of a higher basis weight (0.020 m^2/kg) to obtain sufficient sample for the periodate analysis.

Reflectance measurements over the range 260 - 600 nm were recorded with a Philips PU8800 uv-visible spectrophotometer equipped with an integrating sphere. A computer program written by the authors was used to calculate absorption coefficients from the reflectance data. A more detailed description of the spectral measurements has been published[2, 4].

Plots of absorption coefficient versus time were fitted to a double-exponential function using commercially available software, FitAll version 5.1, MTR Software, Toronto. This program uses the Marquardt non-linear least-squares algorithm.

RESULTS AND DISCUSSION

Contribution of Phenolic Groups

Figure 2 shows the kinetics of the increase in the absorption coefficient K^* at 420 nm during irradiation of peroxide-bleached black spruce TMP, and of bleached TMP which was methylated with dimethyl sulphate. This wavelength was chosen because it is sensitive to chromophore formation, and because increases in the absorption coefficient

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[*] In the Kubelka-Munk[5] theory the unit of absorption coefficient K is inverse pathlength, cm^{-1}. Van den Akker[6] showed that for paper basis weight is a more appropriate characteristic than pathlength, and proposed the designation k to indicate an absorption coefficient with unit of inverse basis weight. However, in this paper we use K to designate specific absorption in units of inverse basis weight, and k to indicate a rate constant.

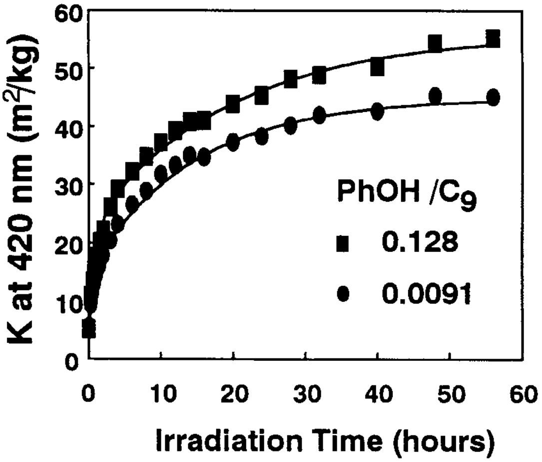

Figure 2: Kinetics of the increase in absorption coefficient at 420 nm for bleached black spruce TMP, unmethylated and methylated, during irradiation with near ultra-violet light.

in this region (λ > 400 nm) correspond to discolouration. These samples were irradiated with a complete set of sixteen 350 nm lamps in the Rayonet reactor.

Both unmethylated and methylated samples behaved similarly: the absorption coefficient initially rose rapidly, and eventually approached a limiting value. The kinetic curves were characterized by fitting to a double-exponential function, equation 1. The values obtained for the fitted parameters are listed in Table 1: K^∞ is the maximum (limiting) value of K, and A_1, A_2 are the pre-exponential factors for the first-order rate constants k_1, k_2.

$$K(t) = K^\infty - A_1\exp(-k_1 t) - A_2\exp(-k_2 t) \qquad (1)$$

The values in Table 1 confirm what one suspects from visual examination of Figure 2: the rate constants for absorption coefficient

TABLE 1

Parameters from Fits of Kinetic Data at 420 nm to Equation 1. Bracketed values are standard deviations for the parameters

Parameter	K^{∞} (m^2/kg)	A_1	k_1 (h^{-1})	A_2	k_2 (h^{-1})
Bleached TMP	56.0 (1.0)	17.3 (2.1)	1.03 (0.20)	33.4 (1.8)	0.051 (0.009)
Methylated Bleached TMP	45.3 (1.5)	9.3 (2.3)	1.32 (0.52)	30.2 (.1)	0.069 (0.013)
Note that $K^{\infty} - K(0) = A_1 + A_2$					

increase (k_1 and k_2) are identical within experimental error for both methylated and unmethylated pulps, while the maximum change in absorption coefficient ($K^{\infty} - K(0) = A_1 + A_2$; Table 1) is lower for the methylated pulp.

Our observation of rapid and slow phases for both unmethylated and methylated pulp differs from recent work by Francis *et al.*[7]. Using a less intense uv-source (sunlight), they observed some inhibition, and zero-order kinetics for methylated, unbleached TMP. They noted that methylation was not as effective an inhibitor for peroxide-bleached pulp, but did not report a kinetic curve.

The values of $K^{\infty} - K(0)$ for methylated and unmethylated pulp, 39.5 and 50.7 m^2/kg, respectively (Table 1), indicate that reactions involving the free phenolic group account for only about 50.7 - 39.5 = 11.2 m^2/kg, about 20%, of the total increase in absorption coefficient for bleached TMP. If one wishes to retain a mechanism which involves phenoxy radicals as intermediates, then non-phenolic sources of phenoxy radicals must be identified.

Contribution of Phenacyl Arylethers

Gierer and Lin[8] first proposed the phenacyl arylether group as a non-phenolic lignin structure that can form phenoxy radicals photochemically (Figure 1), and subsequent work in many laboratories has confirmed that this reaction can occur[9-12]. However, this still cannot explain the magnitude of the increase in absorption coefficient. A generally accepted value for the content of aromatic carbonyl groups in lignin is $0.07/C_9$[13]. Since the 0.13 phenolic hydroxyl groups per C_9 unit result in an increase in absorption coefficient of 11.2 m^2/kg, phenoxy radicals formed by cleavage of phenacyl arylethers account, at best, for an absorption coefficient increase of $(0.07/0.13) \times 11.2 = 6.0\ m^2/kg$.

The small amount of yellowing attributable to the phenacyl arylether group should be eliminated by thorough borohydride reduction, since the corresponding benzyl alcohols do not absorb at wavelengths above 300 nm. However, we and others have found that the rate of brightness reversion is hardly affected by this treatment[2, 14, 15].

It has been reported that pulp treated by borohydride reduction and alkylation maintains stable brightness (*i.e.*, minimal increases in absorption coefficient) during two hours irradiation[7, 16]. We repeated this experiment and confirmed this result (Figure 3). However, for irradiation in excess of two hours the reduced and methylated pulp yellowed as rapidly as untreated pulp, or pulp treated only by reduction or only by methylation.

Figure 4 shows the absorption difference spectra, relative to the original peroxide-bleached TMP, for pulp which has been treated with sodium borohydride, methylated and then irradiated. The spectra indicate clearly that an absorption with λ_{max} = 330 nm, most probably due to aromatic carbonyl groups[2], increased rapidly during irradiation.

The preceding discussion points to two unresolved questions regarding the photochemical yellowing of mechanical pulps: what lignin reactions form the balance of phenoxy radicals required to account for the

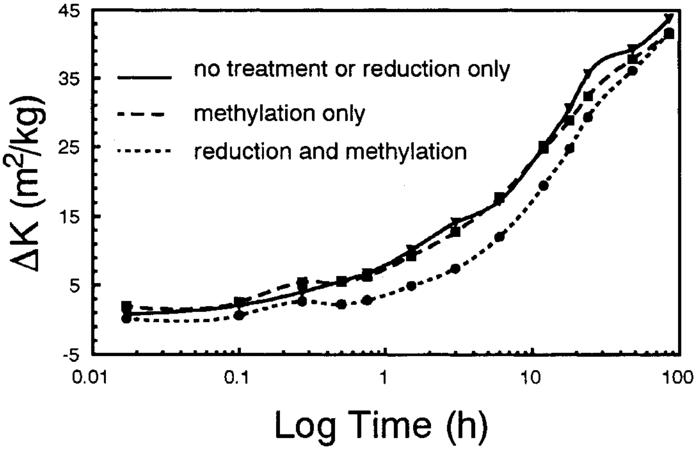

Figure 3: Kinetics of increase in absorption coefficient at 420 nm. Pulp that has been reduced and methylated yellows slower, during the first two hour irradiation, than pulp given only single treatments.

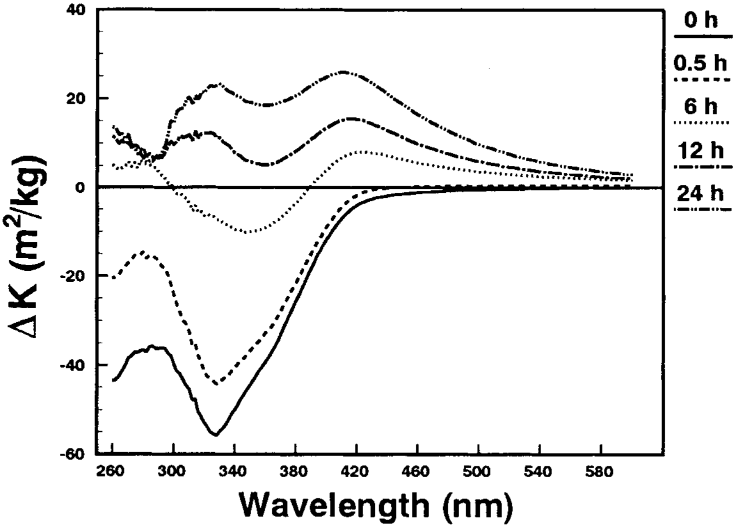

Figure 4: Difference spectra for irradiation of bleached spruce TMP that has been reduced and methylated.

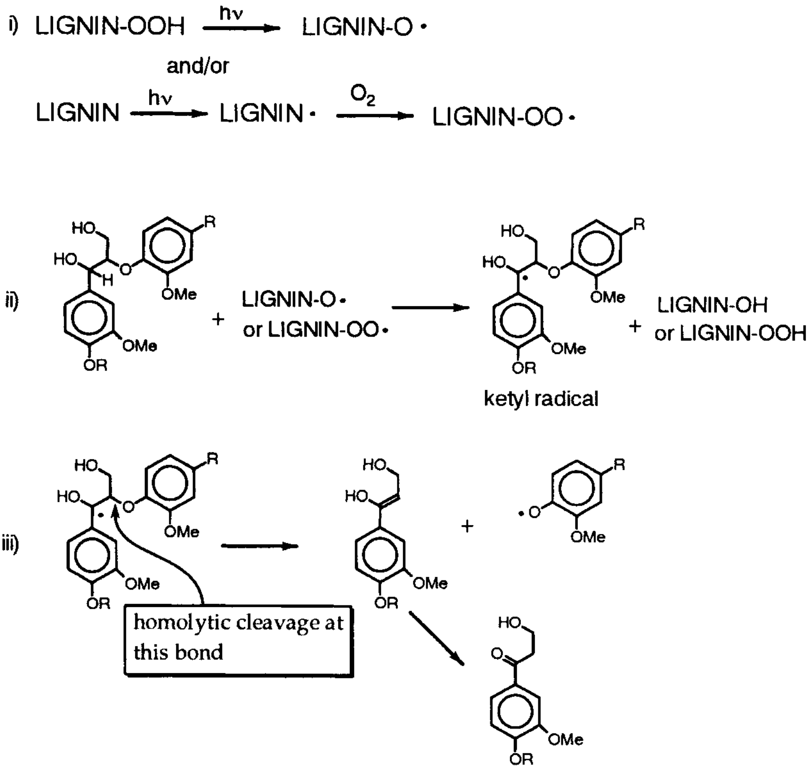

Figure 5: Formation of arylglycerol-β-arylether ketyl radicals, and subsequent cleavage to form phenoxy radicals and aromatic ketones.

total increase in absorption coefficient, and what accounts for the formation of aromatic carbonyl groups?

Phenoxy Radicals From Arylglycerol β-Arylethers

We propose that breakdown of arylglycerol β-O-aryl structures via the corresponding ketyl radical, as shown in Figure 5, neatly explains both the origin of large amounts of phenoxy radicals, and the formation of aromatic carbonyls. Cleavage of the β-O-4 bond forms the phenoxy radical

TABLE 2

Phenolic Hydroxyl Content (/100 C_9) of Pulps After UV Irradiation
Bracketed numbers indicate standard deviations

Sample Treatment	0 h	0.5 h	4 h	30 h	30 h x 8
Untreated	8.62 (0.098)	8.46 (0.076)	8.4 (0.13)	8.39 (0.048)	8.28 (0.086)
Borohydride Reduction	8.79 (0.033)	8.82 (0.14)	8.58 (0.069)	8.31 (0.057)	8.40 (0.058)
Methylation	0.58 (0.065)	0.84 (0.019)	1.13 (0.025)	2.13 (0.006)	3.53 (0.05)
Reduction and Methylation	0.66 (0.081)	0.7 (0.07)	1.01 (0.021)	1.59 (0.049)	2.84 (0.13)

directly from an abundant lignin structure, and the initially formed enol will rapidly tautomerize to the corresponding acetophenone, accounting for the net increase in aromatic ketones.

Published data[17] indicate that ketyl radicals such as those in Figure 5 cleave with a rate constant > 2 x 10^6 s^{-1}, and recent pulse radiolysis experiments have raised this limit to > 2 x 10^7 s^{-1} (J.C. Scaiano, University of Ottawa, personal communication). Rate constants of this magnitude leave little doubt that, once formed in solid lignin, these radicals will cleave virtually instantaneously to the corresponding phenoxy radical and enol. Interestingly, there is also recent evidence for ketyl radical intermediates in the degradation of the phenacyl arylether group[11, 18].

Phenolic Hydroxyl Contents of Irradiated Pulps

Phenolic hydroxyl contents of various pulps as a function of irradiation time are given in Table 2. These experiments were conducted with a different set of pulps than those used for the kinetic experiments. They were bleached twice with hydrogen peroxide to remove any coniferaldehyde groups which may remain in the pulp after a single 4% peroxide-bleaching stage, and irradiation was done with less intense light (only two of a possible sixteen lamps in the reactor) so that any subtle effects early in the reaction would not be missed. One irradiation was done for 30 h with sixteen lamps in the reactor (30 h x 8), to determine the phenolic hydroxyl content in the plateau region of the kinetic curve in Figure 2.

For untreated or reduced pulp there was little, if any, change in phenolic hydroxyl content, even after 30 hours of irradiation with all sixteen lamps in the reactor. Since phenolic hydroxyls are presumably converted to *o*-quinones and other chromophores during photoyellowing, this suggests that phenolic groups are formed, as well as consumed, by photochemical reactions. The formation of new phenolic hydroxyl groups during the irradiation of the methylated pulps confirms this suggestion.

The increase in phenolic hydroxyl content that occurs upon irradiation of methylated pulps is predicted by the mechanism of Figure 5. For pulp which has been both reduced and methylated it provides the most plausible mechanism for the onset of photoyellowing, since all phenolic groups and aromatic carbonyl groups have been eliminated.

The formation of aromatic carbonyls (Figure 4), and the increased phenolic hydroxyl content (Table 2), are evidence that the products predicted for ketyl-radical mediated, β-O-4 breakdown form during irradiation of pulp. Pan *et al.*[19] have confirmed that the β-O-4 structure does, in fact, degrade: after 24 hours uv-irradiation the content of β-O-4 structures in peroxide-bleached spruce TMP decreases almost ten-fold, from 1003 μmol/(g lignin) to 149 μmol/(g lignin). There was little β-O-4 cleavage during the first two hours of the irradiation when, presumably, the free phenolic path of the reaction (Figure 1) is dominating.

TABLE 3

Estimated Contribution of Various Lignin Structures to the Light-Induced Increase in Absorption Coefficient at 420 nm

Structure	Occurrence (/100 C_9)	Contribution to K^∞ - $K(0)$ (m^2/kg)
Phenolic Hydroxyl	13	11.2
β-Arylethers:		
α-carbonyl	7[*]	6.0[†]
α-OH	31[§]	26.7[†]
α-O-alkyl or α-O-aryl	10[§]	8.6[†]
Total		52.5

[*] Reference[20], [§] Reference[21]

[†] Calculated assuming 11.2/13 = 0.86 m^2/kg per phenoxy radical formed

Contribution of Various Lignin Structures to Yellowing

Forty-eight percent of spruce lignin units contain a β-arylether linkage[20]. Seven percent of these have a carbonyl group at the benzylic position (phenacyl arylethers), and can form a phenoxy radical as depicted in Figure 1. Thirty-one percent have benzylic hydroxyl groups[21], and therefore can form a ketyl radical that cleaves to give a phenoxy radical and an enol, as depicted in Figure 5. The remaining 10% of β-arylether structures have either O-alkyl or O-aryl substitution at the α position. A ketyl radical derived from these structures could cleave at the β-O bond to give a phenoxy radical and an enol ether. This is reasonable thermodynamically, but there is little published data on the reactivity of such ketyl radicals.

Table 3 summarizes the estimated contributions of various spruce lignin structures to the increase in absorption coefficient at 420 nm, K^∞ -

K(0). We estimated the increase in absorption coefficient per phenoxy radical formed from the difference in K^{∞} - $K(0)$ between methylated and unmethylated pulp (Table 1): 11.2/13 = 0.86 m^2/kg/phenoxy radical. Degradation of β-arylethers with benzylic hydroxyl accounts for 50% of the observed value of K^{∞} - $K(0)$ (50.7 m^2/kg, see Table 1) in bleached spruce TMP. If one also assumes that β-arylethers with etherified benzylic positions degrade via ketyl radicals as described above, the calculated value of K^{∞} - $K(0)$ is 52.5 m^2/kg, in good agreement with the experimental value. This analysis suggests that up to 70% of the increase in absorption coefficient can be attributed to the breakdown of saturated β-arylether structures.

Formation of Ketyl Radicals

The exact mechanism for formation of the ketyl radicals is not known, but recent work suggests involvement of both oxygen- and carbon-centred radicals. Shkrob *et al.*[22] have shown that direct attack by O_2 at phenoxy radicals does not yield coloured products, as Figure 1 proposes; rather, alkoxyl or perhydroxyl radicals are the active oxidizing species. Oxygen enters the mechanism indirectly, via reaction with alkyl radicals to give peroxyl radicals. Thus discolouration of mechanical pulps implies the presence of alkyl, alkoxyl or perhydroxyl radicals, all of which are capable of abstracting the α-hydrogen from benzylic positions[17, 22]. The initial period of colour stability observed during the irradiation of fully reduced and methylated pulp (Figure 3) can perhaps be explained as an induction period, during which these radicals accumulate to a concentration high enough to allow rapid discolouration.

An unresolved problem is the identity of the key light absorber, and the reactions which lead to initial formation of radicals. Experiments with borohydride reduction indicate that carbonyl groups are not necessary for the initiation of photochemical yellowing, although they may become

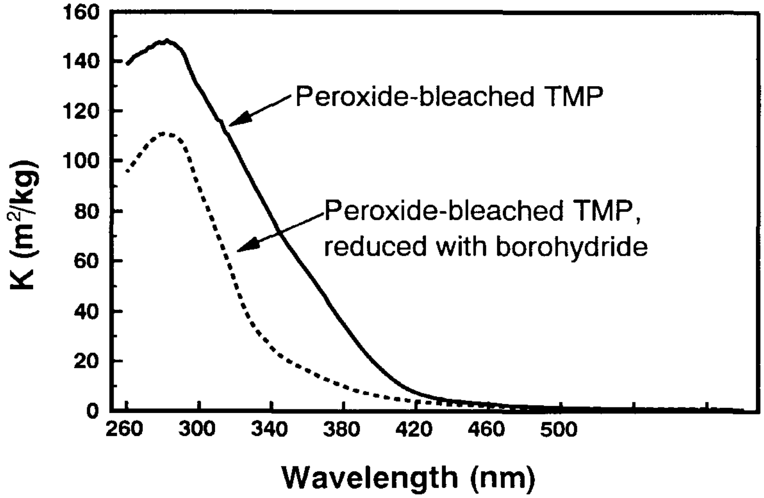

Figure 6: Absorption spectra of peroxide-bleached spruce TMP before and after thorough reduction with sodium borohydride. Significant absorption remains after all carbonyl groups have been reduced.

involved later in the reaction[2, 14, 15]. Figure 6 shows the absorption spectrum (not difference spectrum) of peroxide-bleached spruce TMP, and the spectrum of the same pulp treated with borohydride until no further change is observed. Significant absorption above 300 nm still exists, even though all the carbonyl groups have been removed.

Identification of the groups responsible for this residual absorption would be an important advance. The coniferyl alcohol group is one possibile candidate: it occurs in approximately 6% of lignin units[23], is known to survive pulping and peroxide-bleaching[24], and has an absorption which tails into the $\lambda > 300$ nm region[25]. Another possibility is the stilbene group, which forms during alkaline peroxide bleaching by the reverse aldol reaction of β-1 structures[24].

SUMMARY

Our results indicate that the arylglycerol β-arylether linkage is the major source of coloured groups in photochemical yellowing of mechanical pulps, accounting for up to 70% of the discolouration. We propose that degradation occurs via the corresponding ketyl radical, which cleaves at the β-arylether bond giving a phenoxy radical and an acetophenone enol. The enol can tautomerize to a ketone, while the phenoxy radicals are oxidized to coloured groups. Supporting evidence includes the following: 1) rapid cleavage of ketyl radicals derived from arylglycerol β-arylether model compounds to give phenols and acetophenones[11, 17, 18], 2) formation of aromatic ketones and phenolic groups in irradiated pulps (this work), 3) disappearance of the β-arylether linkage in irradiated pulp[19].

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