

Photoyellowing of lignin-rich paper: interaction of excited states with selected additives

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Abstract

Specific chromophores in bleached thermomechanical pulps (BTMPs) were targeted by fluorescence quenching with cyclohexadiene. The results suggest that fluorophores in BTMPs are mainly conjugated aromatic hydrocarbons (ArH). The observed effect of cyclohexadiene on the photochemical yellowing of BTMPs supports recent work which ascribes a role in lignin photochemistry to ArH chromophores based on stilbene and biphenyl. The relative efficiency of triplet vs. singlet photochemistry was examined by applying a heavy atom agent, lead acetate, to the pulps. It is postulated that α -carbonyl triplets and ArH singlets are important sources of colour reversion. Based on a reconsideration of possible singlet state quenchers, several additives were tested as inhibitors; $(\text{EtO})_3\text{P}$ and Bu_3P were found to inhibit paper yellowing. Results of a tentative mechanistic study point to the reactions of the inhibitors with complex radical intermediates, rather than excited state quenching, as the key process in the observed inhibition.

Keywords: Photoyellowing; Lignin-rich paper; Excited states

1. Introduction

The rapid yellowing of paper composed of lignin-containing mechanical pulps (high yield pulps) when exposed to natural light restricts the use of high yield pulps for high grade furnish. To use forest resources more efficiently in the paper industry (lignin accounts for about 30% of the mass of wood), a large effort has been made to solve the problem of paper yellowing [1]. Various techniques, such as UV-visible [2], Fourier transform IR (FTIR) [3] and nuclear magnetic resonance (NMR) [4] spectroscopy, have been used. The most important mechanisms have now been established [5], and it is widely recognized that the formation of radical intermediates is the key step in the photoyellowing process [1].

Light absorption by lignin chromophores produces singlet and then triplet excited states of the chromophores, which then react to give coloured degradation products. Fluorescence spectroscopy, which detects emission from singlet states, provides a method to study these species [6,7], especially those lignin structures that fluoresce most strongly, e.g. the non-carbonyl conjugated aromatic groups. Further information on the identity of the lignin fluorophores and their involvement in the yellowing process would be very useful, as the

role of these light-absorbing groups in colour reversion is currently being questioned. As part of the work on excited lignin chromophores, we have investigated the effect of heavy atom agents, which suppress processes involving the singlet excited state while promoting triplet processes. Based on the fluorescence data of lignin in high yield pulps, we also suggest a reconsideration of singlet quenchers as inhibitors of paper yellowing. A significant inhibition of paper yellowing was observed for two alkylphosphorus compounds. Possible mechanistic aspects of this inhibition are discussed. To facilitate interpretation of the quenching experiments, the fluorescence spectra presented here were measured on paper sheets immersed in toluene or ethanol, rather than in air. The irradiation of some samples was also performed in this medium.

2. Experimental details

Thermomechanical pulp (TMP) from eastern Canadian black spruce was bleached with hydrogen peroxide according to the method described by Gellerstedt et al. [8]. Fluorescence quenching and monochromatic irradiation experiments were performed in a Spex model-F112 spectrophotometer using a xenon lamp (450

W) as light source. A sample sheet of bleached thermomechanical pulp (BTMP) (20 g m^{-2}) was immersed in the chosen organic liquid in a square UV cell ($1 \text{ cm} \times 1 \text{ cm}$ cross-section) which was placed inside the sample compartment of the Spex spectrometer. A plug was used to fix the sheet and prevent any displacement during irradiation and fluorescence measurements. Quencher was added by means of a microsyringe. The incident light for both excitation and irradiation impinged perpendicular to the sample surface, and fluorescence emission was detected at an angle of 22° with respect to the incident light. For irradiation, the inlet slit was set at 6 mm, giving an impinging light intensity of 10^{17} quanta s^{-1} on a surface section of about 60 mm^2 . The incident wavelength was set at 320 nm. For emission measurements, a single-grating monochromator and a bandpass filter with a cut-off at 385 nm were used on the excitation side to avoid spikes in the spectra, while a double-grating monochromator was used on the emission side. All fluorescence spectra were corrected. Reflectance spectra were measured with the Spex spectrofluorometer using synchronous scanning with no wavelength offset, after allowing the sample sheet to dry at room temperature in the dark.

When studying the heavy atom effect, irradiation of paper sheets was carried out in a Rayonet reactor (model RPR 100, Southern New England UV Company) equipped with four RPR-350 lamps at a temperature of about 35°C . The brightness index and yellowness index (b^*) were measured on a Technibrite Micro TB-1C apparatus. Spectrograde solvents were used as received from Aldrich without further purification. All quenchers and additives (Aldrich) were purified by distillation, under vacuum if necessary. Lignin model compounds were synthesized following the description in the literature [9,10], except for 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethyldiphenyl, which was supplied by Professor N. Weir, Lakehead University, Ontario, Canada.

High performance liquid chromatography (HPLC) measurements were conducted on a Waters-990 apparatus, coupled with a photodiode array detector. A reversed phase Supelcosil LC-18 column was used, with cyclohexane as inner reference. The peak area error range was $\pm 4\%$.

The results of fluorescence quenching, brightness and yellowness measurements are the averages from three TMP sample sheets.

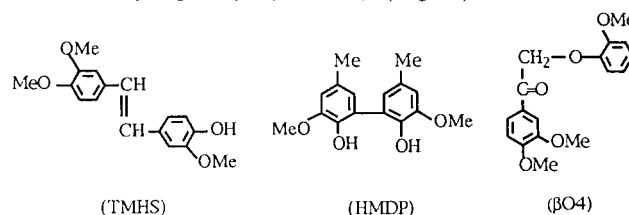
3. Results and discussion

3.1. Diene quenching of fluorescence by complex formation

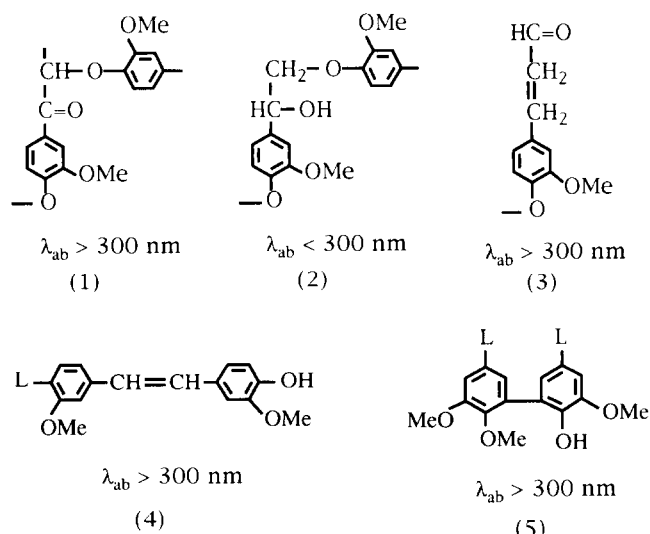
Fluorescence has been observed for extracted mill wood lignin in dioxan solution and for paper handsheets

of BTMP and bleached chemithermomechanical pulp (BCTMP) [6,7]. The relationship between these emissions and the excited species that lead to yellow products has yet to be clarified. Of the lignin chromophores that absorb above 300 nm, the α -carbonyls are generally non-fluorescent [11]. Others, such as coniferyl alcohol, stilbenes and biphenyls, should all be good fluorophores [12]. The α -hydroxyl aromatic structures, on the other hand, are thought to absorb light only below 300 nm, as revealed by their model compounds in solution and on solid substrates such as filter paper.

Conjugated dienes can form charge transfer exciplexes with conjugated aromatic hydrocarbons in their excited states [13], thus quenching the latter via regeneration of their ground states. This is demonstrated on two lignin model compounds, 3,3',4-trimethoxy-4'-hydroxystilbene (TMHS) and 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethyldiphenyl (HMDP) (Fig. 1)



where the fluorescence emission from the model is quenched in the presence of 0.032 M 1,3-cyclohexadiene. Application of 1,3-cyclohexadiene to BTMP immersed in toluene leads to similar quenching results, as shown in Fig. 2. When sheets from mechanical pulps are irradiated, the impact of these quenchers on yellowing can be assessed by measuring the reflectance of the sheet before and after irradiation, i.e. $i_{s,o}(\lambda)$ and $i_s(\lambda)$ respectively. The difference spectrum thus obtained, $\Delta i_s(\lambda) = i_{s,o}(\lambda) - i_s(\lambda)$, reflects the degree of yellowing: the higher $\Delta i_s(\lambda)$ is, the more intense the yellowness.



Scheme 1. Lignin chromophore structures: (1) α -carbonyl; (2) α -hydroxyl; (3) coniferyl; (4) stilbene; (5) biphenyl.

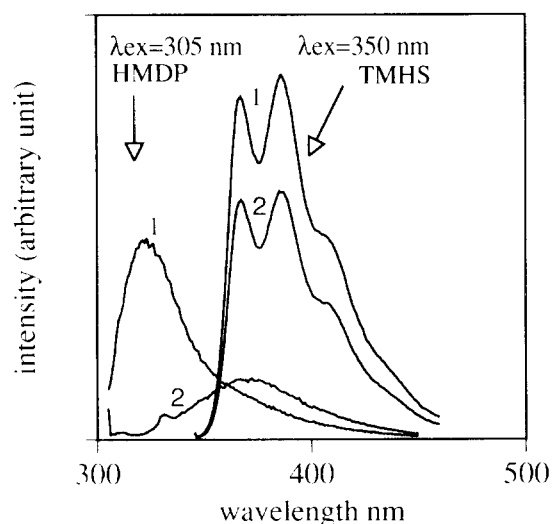


Fig. 1. Quenching of fluorescence of lignin model compounds HMDP (2.05×10^{-4} M) and TMHS (1.79×10^{-4} M) by 1,3-cyclohexadiene in toluene: 1, no diene; 2, $[\text{ene}] = 0.032$ M.

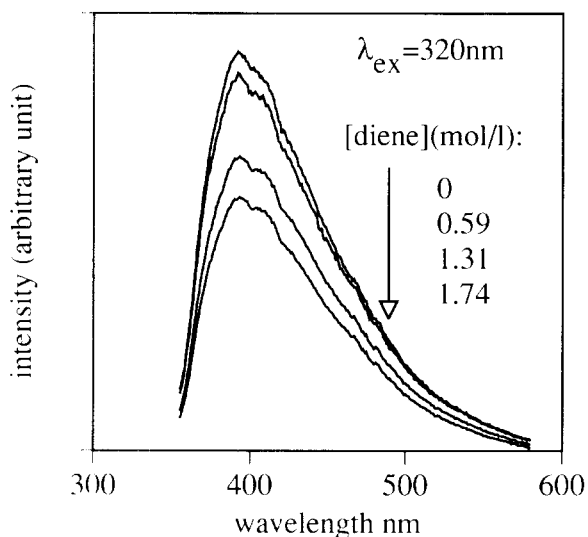


Fig. 2. Quenching of BTMP fluorescence by 1,3-cyclohexadiene. Solvent, toluene.

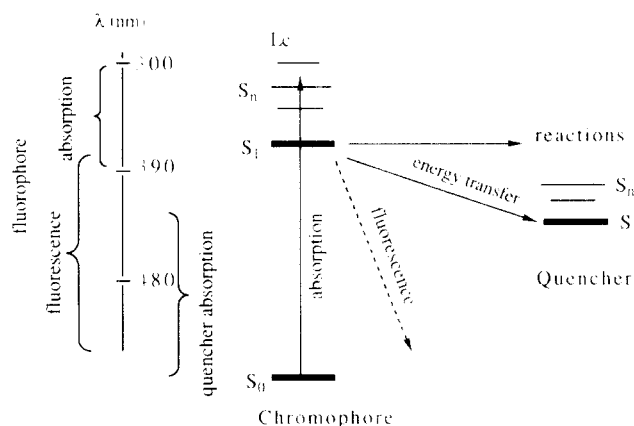
Dividing the ΔI_s data by ΔI_s from the blank experiment without quencher gives the relative difference reflectance spectrum ΔI_s

$$\Delta I_s = \frac{\Delta I_s(\lambda)}{\Delta I_s(\lambda)(\text{blank})}$$

Data for ΔI_s at 457 nm are given in Table 1 for BTMP irradiated in the presence of 1,3-cyclohexadiene. As the emitting species are quenched, a concomitant decrease in the absorption in the visible region of post-irradiated BTMP is observed. Besides singlet quenching (see below), triplet quenching may also exist, as 1,3-cyclohexadiene with $E_T = 54$ kcal mol $^{-1}$ [14] is a good triplet quencher. Solution photoyellowing of a model of an α -aromatic ketone, 3,4-dimethoxy- α -(2'-methoxy-

Table 1
Relative difference reflectance (at 457 nm) of BTMP after monochromatic irradiation (320 nm, 40 min) in the presence of 1,3-cyclohexadiene in toluene

[diene] (mol l $^{-1}$)	ΔI_s (457 nm)
0	1
0.59	0.91
1.31	0.88
1.74	0.69



Scheme 2. Quenching of excited state chromophores by electronic energy transfer, showing schematically the relationship between wavelength (on the left) and energy levels (on the right).

phenoxy)-acetophenone (βO_4), on the other hand, was not affected by 1,3-cyclohexadiene. We postulate that non-carbonyl aromatic conjugated structures in lignin, once excited, also cause yellowing. Diphenyl- and stilbene-type chromophores may be invoked in these cases. They have been shown [10] to undergo photoyellowing reactions in the solid state. New evidence [15] points to the existence of these structures in lignin. Recently, Ragauskas [16] has observed the ability of dienes to slow down the photoyellowing of mechanical pulps in air. The formation of a complex between the singlet excited states of aromatic hydrocarbons and dienes may account for this effect.

3.2. Quenching mechanism

As illustrated in Scheme 2, the use of singlet state quenchers is one of the possible measures to prevent paper from yellowing. Quenching of the excited states of the chromophores takes place by two types of mechanism: electronic energy transfer (to the quencher) and the formation of a complex, so that the excited chromophores are deflected from their normal reaction pathways. The first mechanism requires that the energy of the quencher is lower than that of the chromophore. The excited energy level of lignin chromophores in the pulps can be estimated from the light absorption wave-

lengths which cause the most yellowing, i.e. 300–390 nm (95.3–73.3 kcal mol⁻¹). The energy level of the lowest singlet state, to which higher excited states will relax before undergoing reactions, quenching or emission of fluorescence, is lower, as demonstrated by the red shift of the emission band relative to the absorption band. Consequently, effective quenchers must absorb above 390 nm (or preferably higher), which means that they will probably be coloured themselves. Singlet quenching via energy transfer has the advantage that, according to the selection rules, the dipole–dipole resonance interaction mechanism (Förster mechanism) [11] operates. This type of interaction is effective over a longer distance than the diffusional encounter mechanism, thus making it more attractive in solid state quenching. However, the energy restriction mentioned above virtually rules out the selection of quenchers that work in this way. By contrast, quenchers that work by complexation need not meet energy (and thus absorption) restriction, so that they can be chosen from compounds that do not absorb visible or near-UV light. The drawback to quenching by this mechanism is that, in the solid state with little possibility of diffusion, a higher quencher charge is needed, as only close “contact” between the chromophores and the quencher will result in complex formation. In addition, quenchers will not necessarily inhibit yellowing, as the exciplex may collapse to give new species that may be photolabile and ultimately lead to other new coloured products.

3.3. Singlet and triplet excited states of lignin chromophores in yellowing

Of the light-absorbing lignin chromophores, α -aromatic ketones have been shown [17] to undergo cleavage in solution from both the singlet and triplet excited states, producing phenoxy radicals. For other conjugated aromatic hydrocarbon structures, such as stilbenes and biphenyls, the photoyellowing reactions are not yet well understood. The results given above on the fluorescence quenching of non-carbonyl chromophores and the concomitant decrease in post-irradiation yellowness do not reveal whether singlet or triplet states are more important, since quenching of the singlet also suppresses triplet formation. By providing experimental conditions favouring processes from the triplet state, at the expense of the singlet state, or vice versa, we can evaluate the relative importance of these states in the yellowing process.

Some compounds containing heavy atoms can promote triplet formation via a so-called “spin–orbit” interaction. We have found that lead acetate, Pb(Ac)₂, enhances the phosphorescence from pulps (Fig. 3), indicating an efficient heavy atom effect. Applying Pb(Ac)₂ to pulps at a charge of 2.2% leads to only a slight decrease in the post-irradiation yellowness, in

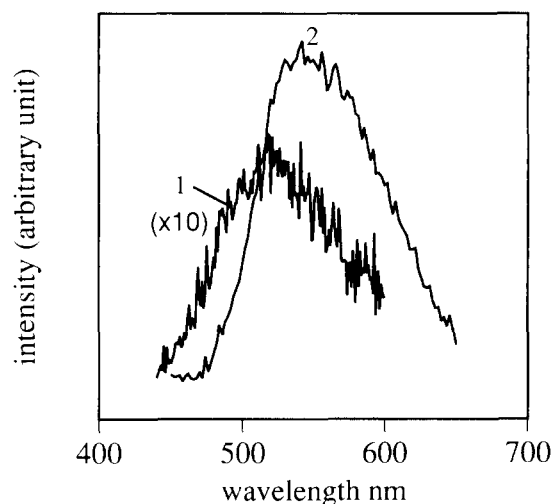


Fig. 3. Phosphorescence spectra of BTMP in dry nitrogen atmosphere: (1) no Pb(Ac)₂, intensity $\times 10$; (2) with Pb(Ac)₂, 1.2% charge. Emission detected 0.1 ms after excitation.

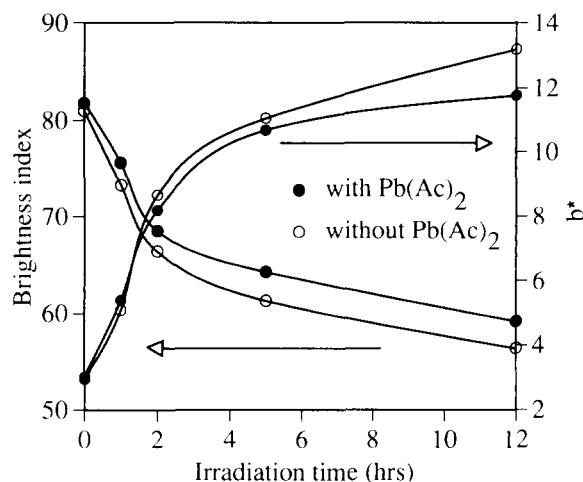


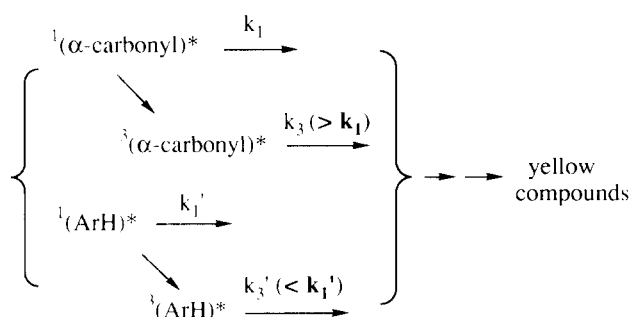
Fig. 4. Comparison of the yellowing of BTMP irradiated in air in the absence and presence of 2.2 wt.% lead acetate.

comparison with a blank, as demonstrated by the brightness and yellowness (b^*) data plotted in Fig. 4. Furthermore, when compound βO_4 , an α -carbonyl model, is tested on filter paper, and submitted to near-UV irradiation (broad band light around 350 nm), it produces deeper yellowing in the presence of Pb(Ac)₂ (see Table 2). No colour reversion is observed when filter paper loaded with an equal charge of Pb(Ac)₂ alone is irradiated. This seems to imply that, in the solid state, the α -carbonyl lignin chromophore possesses activity from its singlet state, although less than that of the triplet. If intersystem crossing of α -carbonyl from the singlet to the triplet is 100% efficient, or if the singlet and triplet possess the same reactivity from the point of view of yellowing, the above results would not have been observed.

For post-irradiated pulp, the slight difference in yellowness observed for the sample loaded with triplet

Table 2
Influence of $\text{Pb}(\text{Ac})_2$ on the brightness index (b^*) of filter papers loaded with model compounds $\beta\text{O}4$ and TMHS, and irradiated with RPR-350 lamps

Compound	b^* before irradiation	b^* after irradiation	Δb^*
$\beta\text{O}4$	1.97	8.61	6.64
$\beta\text{O}4$ + $\text{Pb}(\text{Ac})_2$	2.04	11.69	9.65
Model TMHS	1.81	13.26	11.45
TMHS + $\text{Pb}(\text{Ac})_2$	1.90	8.08	6.18



Scheme 3. The relative importance of singlet and triplet excited state processes of different lignin chromophores to yellowing photochemistry

enhancer can be understood by examining the impact of this enhancer on other non-carbonyl chromophores such as stilbene. Due to the difference in their transition characteristics, the inherent intersystem crossing efficiency of this chromophore is much lower than that of α -carbonyl chromophores. Clearly, from the results included in Table 2, the triplet is less reactive for yellowing formation than the singlet. Thus, in the context of pulp, it presumably acts in opposition to the increase in yellowing reactivity due to the enhancement of the carbonyl triplet, leading to the results shown in Fig. 4. Scheme 3 outlines this explanation.

Generalizing from this one result, we speculate that triplet enhancers, as long as they are chemically neutral, can be applied to pulps with no detrimental effect in terms of yellowing; the excited triplet of lignin chromophores may then become more vulnerable to various types of quenching, including quenching by an additive used in combination with the triplet enhancer.

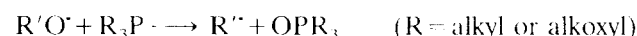
3.4. Yellowing inhibition by $(\text{EtO})_3\text{P}$ and Bu_3P

We have tested some quenchers that may target the excited states of α -aromatic ketone chromophores, whose involvement in yellowing is well known. Several amines [18], phosphines [19] and sulphides [20] have been shown to quench excited singlets and triplets or

aryl ketones via charge transfer-type complexes. We applied the following additives to a mechanical pulp immersed in ethanol (EtOH), followed by irradiation with 320 nm monochromatic light: tripropylamine, diethylamine, dibutylsulphide, tributylphosphine (Bu_3P) and triethylphosphite ($(\text{EtO})_3\text{P}$). All additives are transparent at $\lambda > 300$ nm in EtOH at the concentration used, thus ensuring the absence of any direct photochemical reaction from the additives. In no case was quenching of the pulp fluorescence observed. Only $(\text{EtO})_3\text{P}$ and Bu_3P (denoted by R_3P) showed significant inhibition against pulp yellowing. This inhibition may result from the interaction with (1) excited non-fluorescent chromophores, (2) oxyl radicals, (3) primary yellow compounds or with the final coloured products (see Scheme 4). These possibilities are discussed in turn.

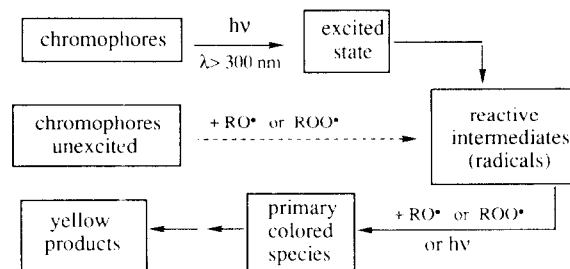
(1) To determine whether quenching of excited carbonyl chromophores by R_3P species occurs in toluene, a study with the model compound $\beta\text{O}4$ was conducted in the same solvent. HPLC analysis of the photoirradiation products showed that the residual concentration of $\beta\text{O}4$ was the same in the absence and presence of R_3P , implying that there was no regeneration of ground state $\beta\text{O}4$ due to quenching. The formation of a complex between excited $\beta\text{O}4$ and R_3P which then collapses to new products cannot be excluded, although no product which could be assigned to such a collapse was identified (see below).

(2) Oxyl radicals, especially peroxy radicals, have recently been recognized as important elements in yellowing. Scavenging of peroxy radicals by phosphites and phosphines has been described [21]



Triethylphosphate ($(\text{EtO})_3\text{PO}$) and tributylphosphine oxide (Bu_3PO) were detected in our inhibition studies on bleached mechanical pulps with $(\text{EtO})_3\text{P}$ and Bu_3P respectively. Thus such scavenging action seems to be justified in the inhibition mechanism.

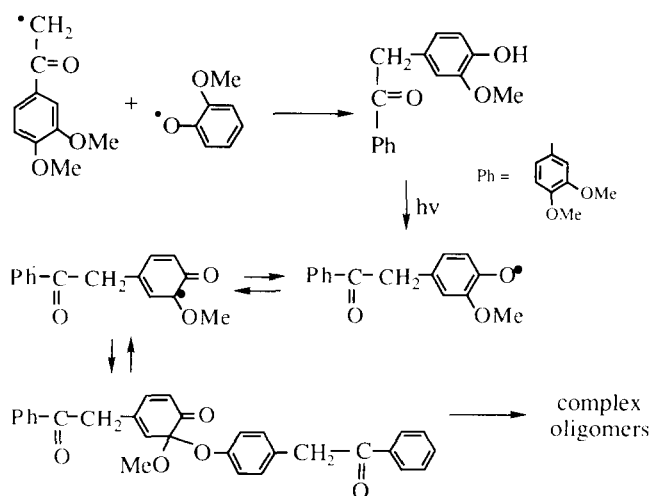
Scavenging of $\text{PhO}\cdot$, which is less reactive towards R_3P because of resonance stabilization of the radical, cannot be ruled out. A slow reaction of phenoxy radicals



Scheme 4. Possible reaction sites of R_3P in an inhibition process.

with phosphites has been invoked [22] for the antioxidant action of some phosphites. Given the relatively long lifetime of PhO^\bullet , scavenging by R_3P may be non-negligible. Reactions of R_3P with secondary photoyellowing products, which may also be radicals, are also possible. This possibility is supported by the strong ^{31}P NMR signal detected from a fraction of non-coloured, very polar composites isolated by column chromatography from βO4 photodegraded in the presence of R_3P .

(3) *o*-Quinones can react with trialkylphosphite to form colourless oxyphosphoranones [23]. We believe, for the following reasons, that if this occurs, it is not the only mechanism that accounts for yellowing inhibition (furthermore, the oxyphosphoranones would undergo further reactions, like *o*-quinones, to give more complex products). (a) *o*-Quinones are certainly not the final yellow compounds, even in the simplified case of irradiated lignin models, such as βO4 . Indeed, when R_3P was added to an irradiated BTMP sheet which was then submitted to further irradiation, very little bleaching resulted. (b) No product assignable to oxyphosphoranones was detected in our study with R_3P and model βO4 . (c) In discussing the formation of *o*-quinones from PhO^\bullet , it is worth emphasizing that many phenoxy radicals absorb light from 300 nm to the visible region [24]. Once excited by light, phenoxy radicals may undergo reactions not possible in thermal conditions. Thus both photochemical and thermal reactions of PhO^\bullet are possible. In the presence of R_3P , the reaction pathways of excited PhO^\bullet could be altered, leading instead to non-quinone, non-coloured products. Recently, Barclay [25] has proposed that structures, such as those outlined in Scheme 5 should account for some of the complex yellow products. It is expected that if R_3P intervenes in such a series of radical reactions,



Scheme 5. Possible structures of the oligomer composites in βO4 -type lignin chromophore photoreactions [25].

the resulting products will be complex and be part of the oligomer composites.

Castellan et al. [26], in a study of yellowing inhibition, argued that inhibitors, such as Rongalit, Blankit or ascorbic acid, did not alter the primary photochemistry of the lignin chromophores. No products associated with these inhibitors were identified other than an inseparable "oligomer" mixture. Obviously, there remains much to be learnt about the nature and formation of the initial coloured products in paper yellowing.

4. Conclusions

- (1) The fluorescence of mechanical pulps was quenched specifically by cyclohexadiene, suggesting that conjugated aromatic hydrocarbons (ArH) contribute to the fluorescence of mechanical pulps. (Castellan et al. [27] have recently shown that coniferyl alcohol, phenylcoumarone and biphenyl biphenol lignin models loaded on cellulose paper give fluorescence spectra that resemble part of the broad emission spectrum of an *Abies* wood sample.) The excited state photochemistry of these chromophores contributes to the formation of yellow products.
- (2) $\text{Pb}(\text{Ac})_2$, which enhances triplet processes in the pulps, does not affect the yellowing result of irradiated pulps. Model compound studies revealed a balancing effect of the heavy atom triplet enhancer towards α -carbonyls and ArH, in that the α -carbonyl triplets and ArH singlets are the most efficient routes to photoyellowing.
- (3) Singlet quenchers that function by trapping the excited energy of lignin chromophores are unlikely to be effective inhibitors of photoyellowing. However, singlet quenchers that quench chemically, by complex formation for example, may be worth investigating as inhibitors.
- (4) $(\text{EtO})_3\text{P}$ and Bu_3P inhibit the photoyellowing of lignin-rich paper, probably by scavenging various reactive radical species formed by excited state photoreactions.

Acknowledgements

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References

- [1] C. Heitner, Light-induced yellowing of wood-containing papers—a review of fifty years of research, in *Proc. 6th. Int. Symp. on Wood and Pulping Chemistry*, Melbourne, Australia, 1991, Appita, Vol. 1, 1991, p. 131.

- [2] J. Schmidt and C. Heitner, *J. Wood Chem. Technol.*, 11 (4) (1991) 397.
- [3] F. Kimura, T. Kimura and D.G. Gray, *Holzforschung*, 46 (1992) 529. F.G.T. St. Germain and D.G. Gray, *J. Wood Chem. Technol.*, 7 (1987) 33.
- [4] T. Kimura, F. Kimura, D.S. Argyropoulos and D.G. Gray, *Holzforschung*, 46 (1992) 331.
- [5] J. Schmidt and C. Heitner, *J. Wood Chem. Technol.*, 13 (3) (1993) 309.
- [6] R.S. Davidson, L.A. Dunn, A. Castellán and A. Nourmamode, *J. Photochem. Photobiol. A: Chem.*, 58 (1991) 349. H. Tylli, I. Forsskahl and C. Olkkonen, *J. Photochem. Photobiol. A: Chem.*, 67 (1992) 117.
- [7] J.A. Olmstead and D.G. Gray, *J. Photochem. Photobiol. A: Chem.*, 73 (1993) 59. J.H. Zhu and D.G. Gray, *J. Photochem. Photobiol. A: Chem.*, 73 (1993) 67.
- [8] G. Gellerstedt, I. Pattersson and S. Sundin, *Sven. Papperstidn.*, 86 (1983) R157.
- [9] C. Vanucci, P. Fornier de Violet, H. Bouas-Laurent and A. Castellán, *J. Photochem. Photobiol. A: Chem.*, 41 (1988) 251.
- [10] A. Castellán, N. Colombo, A. Nourmamode, J.H. Zhu, D. Lachenal, R.S. Davidson and L. Dunn, *J. Wood Chem. Technol.*, 10 (4) (1990) 461.
- [11] N.J. Turro, *Modern Molecular Photochemistry*, Academic Press, New York, 1978.
- [12] K. Lunquist, B. Josefsson and G. Nyquist, *Holzforschung*, 32 (1981) 21.
- [13] L.M. Stephenson, D.G. Whitten, G.F. Vesley and G.S. Hammond, *J. Am. Chem. Soc.*, 88 (1966) 3665. L.M. Stephenson and G.S. Hammond, *Pure Appl. Chem.*, 16 (1) (1968) 125. J. Saltiel and D.E. Townsend, *J. Am. Chem. Soc.*, 95 (1973) 6141.
- [14] D.F. Evens, *J. Chem. Soc.*, (1960) 1735.
- [15] G. Gellerstedt and L. Zhang, *J. Wood Chem. Technol.*, 12 (1992) 387.
- [16] A.J. Ragauskas, *Tappi*, 76 (12) (1993) 153.
- [17] J.A. Schmidt, A.B. Berinstain, F. De Rege, C. Heitner, L.J. Jhonston and J.C. Scaiano, *Can. J. Chem.*, 69 (1991) 104.
- [18] S.G. Cohen and R.J. Baumgarten, *J. Am. Chem. Soc.*, 89 (1967) 3471. R.S. Davidson, in R. Forster (ed.), *Molecular Association*, Academic Press, New York, 1975, and references cited therein.
- [19] R.S. Davidson and P.F. Lambeth, *J. Chem. Soc., Chem. Commun.*, (1969) 1098.
- [20] J. Guttenplan and S.G. Cohen, *J. Chem. Soc., Chem. Commun.*, (1969) 247.
- [21] R. Hiatt, R.J. Smythe and C. McColeman, *Can. J. Chem.*, 49 (1971) 1707. S.A. Buckler, *J. Am. Chem. Soc.*, 84 (1962) 3093.
- [22] J.I.G. Cadogan, in G.H. Williams (ed.), *Advances in Free Radical Chemistry*, Vol. 2, Academic Press, New York, 1967, p. 203.
- [23] S.E. Lebo, Jr., W.F. Lonsky, T.J. McDonough and P.J. Medvecz, *J. Pulp Paper Sci.*, 16 (5) (1990) J139.
- [24] E.J. Land, *Prog. Reaction Kinetics*, 3 (1965) 369.
- [25] R. Barclay, personal communication, 1992.
- [26] A. Castellán, J.H. Zhu, N. Colombo, A. Nourmamode, R.S. Davidson and L. Dunn, *J. Photochem. Photobiol. A: Chem.*, 58 (1991) 263.
- [27] A. Castellán, H. Choudhury, R.S. Davidson and S. Grelier, *J. Photochem. Photobiol. A: Chem.*, 81 (1994) 117.