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Effects of ultraviolet absorbers on rates of anaerobic coloration of lignin model compounds

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Abstract

The long-wave ($\lambda \geq 295$ nm) anaerobic photochemistry of two frequently used lignin model compounds, i.e., I (3,4-di-methoxy-α-(2-methoxyphenoxy)-β-hydroxypropiophenone) and II (1-(3,4-dimethoxyphenol)-2-(2-methoxyphenoxy)propan-1,3-diol) was studied in the presence of three UV absorbers (Tinuvin P, Tinuvin 213 and 2,4-dihydroxybenzophenone), the additives being incorporated into thin films of I and II. Reactions were followed by rates of formation of new, long-wave chromophores (coloration). All of the additives reduced not only the rates of increased absorption, but also the extent of coloration. The most effective additive was Tinuvin P. The relationship between rates of inhibited reactions and concentration of additive was nonlinear, but best represented by the Perrin equation, suggesting that these compounds are not acting simply as UV absorbers, but also as quenchers of excited states of I and II.

Keywords: Long-wave photochemistry; Anaerobic; Coloration; Quinones; UV absorbers; Quenching

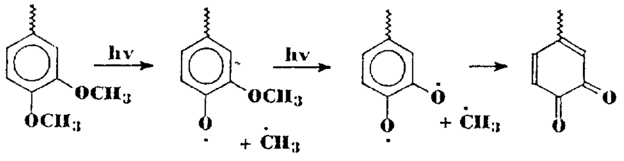
1. Introduction

Coloration, commonly referred to as color reversion, occurs when lignin-rich pulps, and paper are exposed to terrestrial sunlight; i.e., to wavelengths greater than 295 nm in air. Although it is generally recognized that the coloration process involves photo-initiation, followed by a number of concurrent photo and oxidative reactions, no unequivocal mechanism, which can reconcile all of the experimental data, has yet been proposed.

Not only are the constituent reactions complex and not necessarily homogeneous, but also lignin itself is complex and largely intractable. As a consequence, most studies of coloration have been made on plausible model compounds (e.g., α-keto-β-*O*-4 compounds, such as α-aryl-oxyacetoveratrones). On UV irradiation, these compounds undergo rapid β-scission from both singlet and triplet states to form phenoxy radicals [1]. In addition, photoreduction of triplet carbonyls of these compounds gives rise to ketyl radicals, which decompose readily to generate phenoxy radicals [2]. For example, photolysis of α-guaiacoxy-β-hydroxy-propioveratrone results in the formation of a ketyl radical that has a lifetime in the ns range, and which decomposes to form a phenoxy radical [3].

It is now generally agreed that phenoxy radicals are key intermediates, undergoing oxidation in air to form quinones, the highly colored species that have been [4], and are associated with color reversion [5,6].

However, coloration has also been observed when a variety of dimethoxylated aromatic compounds (e.g., poly(3,4 dimethoxy-acrylophenone), α-guaiacylacetoveratrone, and 3,3′,55′ tetra-methoxystilbene) are irradiated with long-wave ($\lambda \geq 300$ nm) UV under anaerobic conditions. It was suggested that, once again, phenoxy radicals, which were formed by direct photolysis of these compounds, i.e., by O–CH_3 fission, were the precursors of the *o*-quinones [7,8]. However, in the absence of O_2, conversion to the *o*-quinone involves the absorption of a second photon by the phenoxy radical, and the fission of a second O–CH_3 bond, i.e.,



The resulting bi-radical then rearranges to form the *o*-quinone. Clearly, the probability of absorption of a photon by a phenoxy radical depends critically on its lifetime. Pre-

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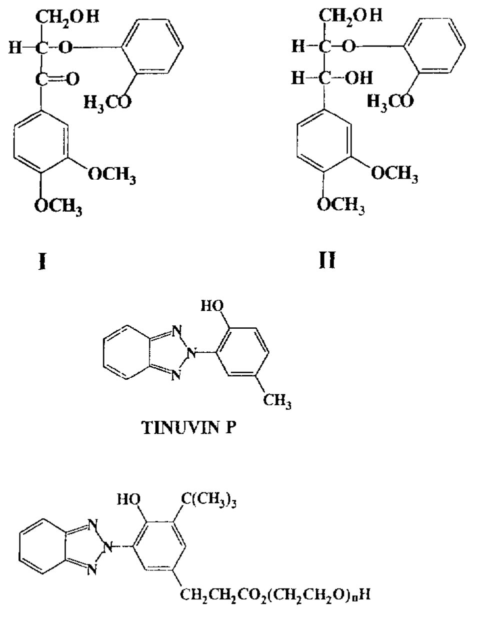

I

II

TINUVIN P

TINUVIN 213

Fig. 1. Structures of compounds I and II and the Tinuvins.

vious work has shown that the lifetimes of phenoxy radicals in the solid state are much longer (the order of days) than those in solution; thus, they are sufficiently long-lived to undergo photolysis [9,10]. More recently, it has been demonstrated that such two-photon processes can occur, *o*-quinones being formed from 2-methoxyphenols upon laser irradiation at 248 nm [11].

The adverse economic consequences of coloration of high-yield pulps have been a stimulus to find a means of inhibiting, or at least minimizing the effects of coloration. For example, it has been shown that rates of photo-yellowing of pulps containing UV screens such as 2,4-dihydroxybenzophenone, are significantly reduced [12,13]. In addition, these effects are enhanced when the UV screens are used in combination with reducing agents [14,15] and thiols [16].

The realization that anaerobic coloration also occurs is relatively recent, and it is therefore understandable that no attempt has yet been made to inhibit it. The purpose of the work described below was to investigate the effects of UV screens (i.e., Tinuvin P, Tinuvin 213 and 2,4-dihydroxybenzophenone) on rates of photo-yellowing of two frequently used lignin model compounds, i.e., 3,4-dimethoxy-α-(2-methoxyphenoxy)-β-hydroxypropiophenone (I) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) propan-1,3-diol (II) (Structures of I and II and the Tinuvins are shown in Fig. 1). These were used in preference to lignin (or pulp) on the grounds that their photochemistry is already well known, and that they and their reaction products are much more tractable materials.

2. Experimental

2.1. Materials

Compounds I and II were synthesized using previously described methods [15–17]. Spectroscopic characteristics (i.r., NMR, and UV) were consistent with the expected structures. Tinuvin P and 213, which were gifted by Ciba-Geigy, Basel, were recrystallized from CH_2Cl_2. 2,4-dihydroxybenzophenone (Aldrich) contained colored material; and repeated crystallization (from CH_2Cl_2) was necessary to produce a colorless sample, which according to spectroscopy, was pure.

2.2. Photochemical methods

The compounds were irradiated at 1×10^{-6} Torr and 25 ± 1°C in the form of thin films (5×10^{-3} mm thick), which were formed by solvent (CH_2Cl_2) evaporation on the faces of anaerobic quartz cells (International Crystal Lab.). The various UV screens were incorporated into the films by co-dissolution in CH_2Cl_2. All samples were rigorously degassed (at 1×10^{-6} Torr) before irradiation, the completeness of the process being indicated by mass spectrometry. The wavelengths of the incident UV radiation, which was produced by a medium pressure Hg arc (200W Hanovia) were restricted to those in the terrestrial sunlight region, i.e., $\lambda\geq295$ nm) by the use of Schott Glass filters (WG 295) that were mounted in front of the cells. More details of the experimental setup are published elsewhere [17].

2.3. Analytical methods

Coloration of films was investigated by UV and visible spectroscopy (Perkin-Elmer Lambda 11), the anaerobic cells being removed from the UV source and placed in the sample compartment of the spectrometer. The use of such cells as reaction vessels avoided the necessity of removing irradiated films from a vacuum environment (and inevitably exposing them to O_2) and placing them in other cells for spectroscopic determination.

3. Results

3.1. UV spectra

The UV spectra of I and II are shown in Fig. 2A and B, respectively. The absorptions in the long-wave region are attributable to $n\rightarrow\Pi^*$ and $\Pi\rightarrow\Pi^*$ transitions in I and II, respectively, these being red-shifted considerably by methoxy substitution of the phenyl group. Also shown in Fig. 2 are the effects of anaerobic irradiation (1.5 h). While the aromatic regions of the spectra are relatively unchanged, new, broad structureless bands appear in the long-wave region, and these not only increase in intensity with increasing exposure,

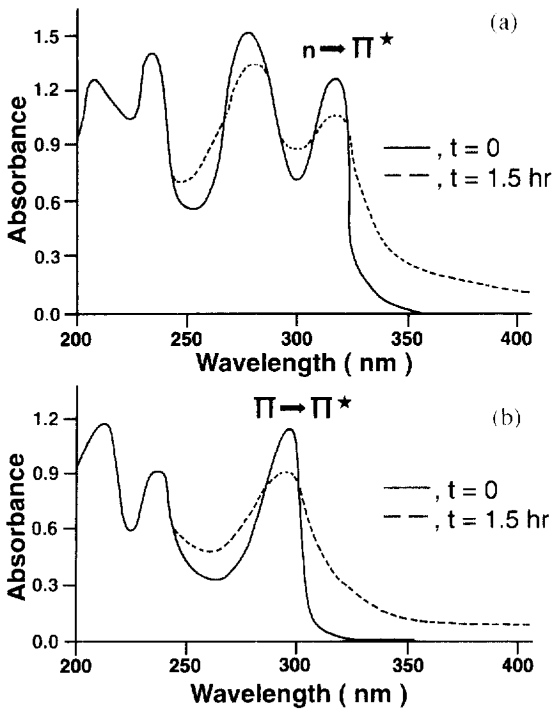

Fig. 2. UV spectra of films I and II (A and B, respectively) and changes brought about by irradiation ($\lambda_{irrad} \geq 295$ nm, $p = 1 \times 10^{-6}$ Torr at 25°C).

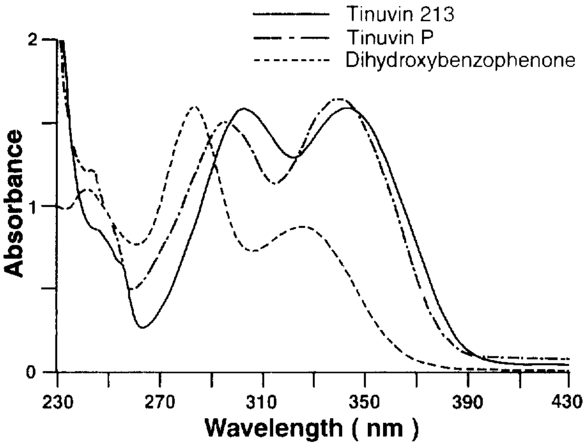

Fig. 3. UV spectra of UV screens (1×10^{-4} M in CH_2Cl_2).

but also become progressively red-shifted, and the films appear yellow.

Spectra of the additives are shown in Fig. 3, and it can be seen that in all cases, their long-wave absorptions coincide with those of I and II. Thus, each has the potential to act as a photo-stabilizer for I and II.

3.2. Spectral changes

The characteristics of increasing long-wave absorption by I are shown in Fig. 4. The 360-nm absorption was chosen on the grounds of greatest sensitivity. However, increased absorptions in the 400–440 nm (indicative of yellow coloration) followed the same qualitative pattern. The effects of the various UV screens are also shown, and all as expected, reduce the rates of the photo reactions, Tinuvin P being the most effective.

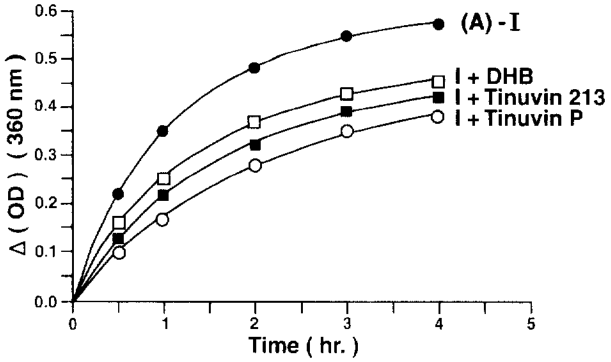

Fig. 4. Time dependence of increased long-wave absorption by I (A) and the effects of UV screens on it: increasing optical density (Δ (OD)) at 360 nm as a function of exposure time ($\lambda_{irrad} \geq 295$ nm, $p = 1 \times 10^{-6}$ Torr), DHB = 2,5 dihydroxybenzophenone.

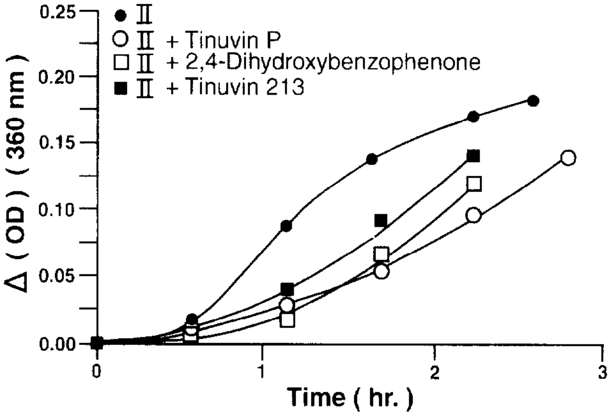

Fig. 5. Characteristics of increasing long-wave absorbance by II alone and with UV absorbers (Δ (OD) at 360 nm as a function of time of anaerobic irradiation).

Corresponding data for II are shown in Fig. 5. The kinetics of the coloration reactions are clearly different from those of I, in that there appears to be an induction period. However, all of the additives reduce the post-induction period rates, and again Tinuvin P is the most effective. The nonlinear character of increasing absorptions (and coloration) of I and II resembles that of polymers; in which case, it was attributed to an optical filtering effect, the newly formed colored chromophores absorbing the incident UV in competition with the substrate [18].

Tinuvin P is the most effective inhibitor in both cases, and as such it was chosen for further investigation of the effects of additives. However, from a kinetic point of view, Tinuvin 213 and 2,5-dihydroxybenzophenone (DHB) behave qualitatively similarly.

The inhibiting effects of various concentrations of Tinuvin P on the reactions of I and II are shown in Figs. 6 and 7, respectively. It can be seen that the rates of coloration decrease, but not linearly, with increasing Tinuvin P concentration, and this is confirmed by the data shown in Figs. 8 and 9 (for I and II, respectively), in which rates of increasing

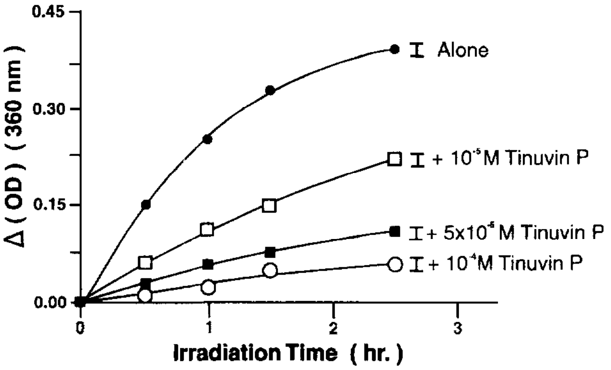

Fig. 6. Effects of concentration of Tinuvin P on the characteristics of increased long-wave absorption by I (anaerobic irradiation: $\lambda_{irrad} \geq 295$ nm and $p = 1 \times 10^{-6}$ Torr).

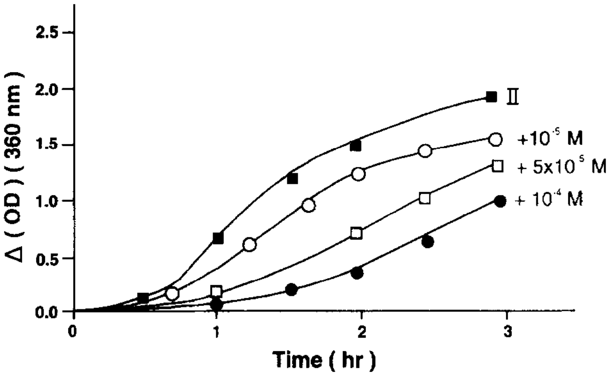

Fig. 7. Effects of concentration of Tinuvin P on characteristics of increased long-wave absorption by II (anaerobic irradiation: $\lambda_{irrad} \geq 295$ nm and $p = 1 \times 10^{-6}$ Torr).

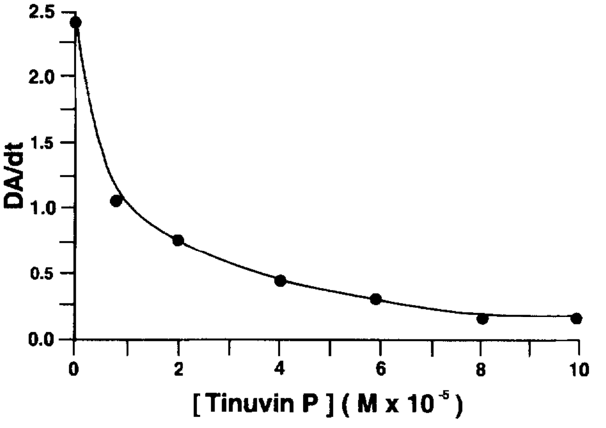

Fig. 8. Effect of Tinuvin P concentration on dA/dt, the rate of increased absorption at 360 nm: anaerobic irradiation of I.

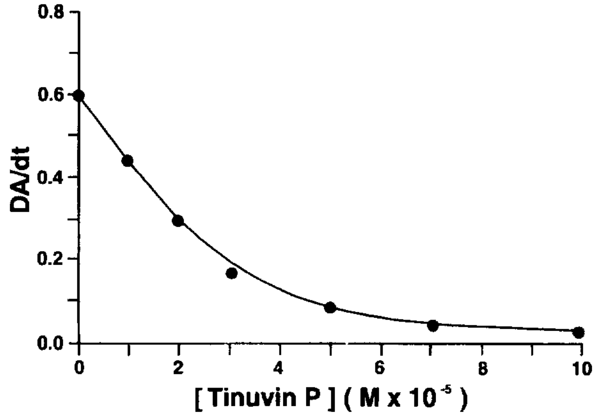

Fig. 9. Effect of Tinuvin P concentration on dA/dt, the rate of increased absorption at 360 nm: anaerobic irradiation of II.

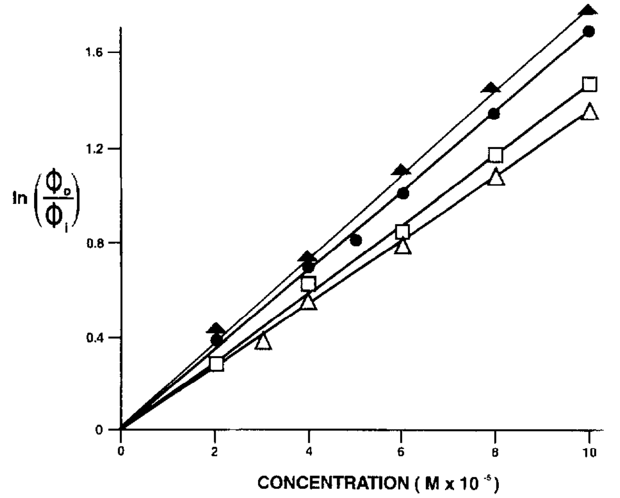

Fig. 10. Reductions in rates of coloration of I and II analyzed in terms of the Perrin equation. ●: I+Tinuvin P, □: I+DHB, △: I+Tinuvin 213, ▲: II+Tinuvin P.

absorption (dA/dt) (coloration) are shown as a function of concentration of Tinuvin P. This type of correspondence suggests that quenching of the excited species may be occurring. In order to test this proposition, the rate data for I (with all additives) and those for II with Tinuvin P (which were the most reliable and reproducible) were plotted in a form that tests the validity of the Perrin equation:i.e.,

$$\ln\left(\frac{\Phi_o}{\Phi_i}\right) = N_A V[Q] \tag{1}$$

in which Φ_o and Φ_i are, respectively, the quantum yields of the uninhibited and the inhibited reactions, N_A is the Avogadro number, V is the volume of the active quenching sphere and $[Q]$ is the concentration of the quencher. This equation has been shown to represent quenching in the solid state more adequately than the Stern–Volmer equation [19]; and it can be seen (Fig. 10) that the data for both compounds conform well to Eq. (1).

4. Discussion

The coincidence of the long-wave absorptions of I and II (Fig. 2) with those of all of the additives (Fig. 3), suggests that the latter have the potential to reduce the quantum yields of the photoreactions of I and II, (e.g., quinone formation, as described in Section 1) [8,11] which are, in turn brought about by absorbance of UV in the 295–320 nm region. The data shown in Figs. 4 and 5 bear this out, both extent and rates of increasing absorbance (and coloration) of I and II being reduced when the additives are present. The initial stages of the reactions of II appear to be different. However, this may be attributable to the uncertainty of the data, which is directly attributable to the much smaller rate of absorption of quanta by II in the 295–320 nm region. On the other hand, the apparent induction period could be associated with a time when more highly absorbing products are being formed; i.e., transformation of II into ketonic or quinonoid species would result in a higher extent of long-wave absorption.

If these compounds are acting as UV screens, it is possible to predict their effects.

The rate of an uninhibited reaction, R_o, in a film of thickness, L, is as follows: $R_o = \phi I_A$, where ϕ is the quantum yield and I_A is the rate of absorption of quanta.

$$R_o = \phi I_o\{1-\exp-(\varepsilon CL)\} \qquad (2)$$

where I_o is the incident intensity and ε and C are the absorption coefficient and concentration, respectively, of the substrate. When more than one absorbing molecule is present in the film, the total rate of absorption, $I'_{A'}$ becomes

$$I'_{A'} = I_o\Sigma\{1-\exp-(\varepsilon_i C_i L)\} \qquad (3)$$

Thus, when a UV absorber (X) is present, the effective rate of absorption by the substrate, I_X, is decreased, and is given by

$$I_X = I_A - I_o\{1-\exp-(\varepsilon_i C_X L)\} \qquad (4)$$

Since ε, C and L values are small, Eq. (3) can be expressed as:

$$I_X = I_o L(\varepsilon C - \varepsilon_X C_X) \qquad (5)$$

The reaction rate, R_X, now becomes

$$R_X = \phi I_o L(\varepsilon C - \varepsilon_X C_X) \qquad (6)$$

While competitive long-wave UV absorption by the additives is undoubtedly occurring, its influence on the quantum yields of the photoreactions is clearly not a dominant one, linear decreases in rates predicted by Eq. (6) not being observed (Figs. 8 and 9). An alternative explanation is that the additives are also acting as quenchers, deactivating excited states of I and II, thereby reducing quantum yields of the initial photoreactions, like O–CH_3 fission. Support for this proposition comes from the linearity of the data plotted in Fig. 10 (Perrin plot). Kinetically, solid-state quenching is best represented by the Perrin Eq. (1) [19] and the data for both I and II (Fig. 10) conform reasonably well to Eq. (1). An analysis of the quenching data shows that radii of the effective quenching spheres range from $R = 17$ Å for Tinuvin 213 to $R = 25$ Å for Tinuvin P. Previously, such 'high' values of R have been associated with polymers, in which energy migration along the chains is occurring [19]. In this case, however, the high R values are likely to be associated with the low quencher concentrations used, the probability of there being an acceptor molecule within the quenching sphere of the donor being correspondingly lower.

In a number of instances, phenolic UV absorbers have been found to act also as radical scavengers [20]. It is therefore conceivable that the additives could scavenge some of the phenoxy radical precursors of the quinones, and thus retard the formation of the long-wave absorbing species. No evidence to support this possibility was obtained. Indeed, retardation has been satisfactorily represented by the Perrin equation, and not by an inverse relationship of the form $\Phi_o/\Phi_i = f[Q]$, which would be valid if competitive scavenging were occurring.

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