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Protection Mechanisms of Novel Photoyellowing Inhibitors

by

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A thesis submitted to the faculty of Graduate Studies and Research in Partial fulfillment of the requirements for the degree of Master of Science

November 1999 Department of Chemistry McGill University Montreal, Quebec, Canada

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ABSTRACT

The long wave aerobic photochemistry of two frequently used lignin model compounds ie. I (3,4-dimethoxy- α -(4-methyl-2-methoxyphenoxy)- β -hydroxypropriophenone) and II (4-hydroxy-3-methoxyphenol)-2-(2-methoxyphenoxy)propan-1,3-diol) were studied in the presence of three UV absorbers 2,4-dihydroxybenzophenone (DHB), an aminated DHB (MDHB), a benzotriazole derivative (Tinuvin P) and an antioxidant; the additives being incorporated into thin films of I and II were applied on filter paper. Several products were identified and quantified using a combination of GC-MS and GC-FID techniques. The photodegradation mechanisms of I and II were found to be consistent with the phenacyl and ketyl pathways from which products were generated *via* oxidation, heterocoupling, H-abstraction and homocoupling reactions. In the presence of the inhibitors, some of these reaction pathways were minimized and others eliminated. In decreasing order, the Tinuvin P/Tempo pair were the most effective in protecting the models against photodegradation followed by MDHB and DHB. A synergistic photostabilization effect was also observed between Tinuvin P and the antioxidant, but was not retained during irradiation, probably due to the low regeneration rate of Tempo on the matrix.

The photostabilization effectiveness of MDHB can be related to the cooperative action of its UV absorbing, hydrogen donating and oxygen scavenging functionalities. However, the separation of product 12 from MDHB was not possible by GC and the photo-chemical fate of MDHB remains undetermined. No synergism was found between MDHB and Tempo. DHB displayed good UV absorbing characteristics but no other photostabilization properties were found to cooperate with it.

RESUME

La photochimie de deux modèles de lignine ie. I $(3,4-diméthoxy-\alpha-(4-méthyl-2$ méthoxyphénoxy)-B-hydroxypropriophénone) et II (4-hydroxy-3-méthoxyphénol)-2-(2méthoxyphénoxy)propan-1,3-diol) par le biais de la lumière UV fut étudiée en présence de trois écrans solaires, 2,4-dihydroxybenzophénone (DHB), un derivé aminé de DHB (MDHB), un derivé de benzotriazole (Tinuvin P) et d'un antioxidant: ces additifs étant incorporés dans de mince films de I et II et déposés sur du papier filtre. Les produits de décompositions ont été identifiés et quantifiés par la chromatographie en phase gazeuse combinée à un détecteur SM et un détecteur DIF. Les mécanismes de dégradations par la lumière de I et II sont conformes aux chemins de jaunissement phénacyl et kétyl d'où des produits ont été formés via des réactions d'oxidations, d'abstraction d'hydrogènes, de couplages homo- et hétéronucleaire. En présence des inhibiteurs, ces chemins de jaunissements ont été ou bien reduits ou bien éliminés. Par ordre décroissant, le couple Tinuvin P et Tempo fut le plus efficace pour contrer la dégradation des modèles de départ, suivit par MDHB et DHB. Un effet de synergie entre l'antioxidant et Tinuvin P a été observé, par contre, l'effet n'est pas permanent probablement à cause du faible taux de régénération de Tempo.

L'efficacité de MDHB pour contrer la décomposition accélérée des modèles de lignine, peut être rattachée à l'action combinée de ses groupes fonctionnelles agissant en temps que filtre UV, donneur d'hydrogène et possiblement accepteur d'oxygène. Par contre, la réactivité de MDHB n'a pus être étudiée par CG, parce qu'il partage avec le produit 12, le même temps de rétention. De plus, aucune synergie ne fut établie entre MDHB et Tempo. DHB démontra une excellente aptitude à filtrer la lumière UV mais aucune autre fonction protectrice ne fut établie.

FOREWARD

In recent years, the use of mechanical pulps has increased substantially, due largely to economic and environmental considerations. However, photoyellowing of these pulps remains a perennial problem which limits their use in high-value products. Extensive research on additives that would block or at least delay for a significant period of time the photoyellowing process, is the long-term goal actively pursued by both academic and industrial interest groups.

Significant progress in the search of enhanced photoyellowing inhibitors was achieved recently, however, their precise photoyellowing inhibition mechanisms on lignin remains unclear. This thesis summarizes an investigation of the photostabilization mechanisms of these inhibitors using appropriate lignin model compounds on a cellulose support. The work is presented in four chapters. The first chapter is a general introduction which is sub-divided into four main sections: The first section provides an extensive review reflecting the current knowledge on the photoyellowing process occurring in lignin-rich pulps. More specifically, the structural identity of the chromophores and the reaction mechanisms leading to their formation are considered. The second section outlines the strategies aimed at suppressing the photoyellowing process and the relative performance of the inhibitors on mechanical pulps. The third section accounts for the recent progress made in this field and emphasize on the enhanced effectiveness of the novel photostabilizers applied to mechanical pulps. It ends with a summary of the aims of the work. The principles of the analytical protocol and the synthesis of the additives are described in the second chapter. Qualitative and quantitative determinations of the photodegradation of models I and II are presented in Chapter 3 with much emphasis on the reaction mechanisms leading to the formation of the various products. In Chapter 4, the photostabilization mechanisms of the inhibitors are assessed by examining their photoreactivity and their influence on product distribution. The thesis closes with some concluding remarks and suggestions for further work.

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Chapter 1

General Introduction

1.1 Introduction

Lignin is the second most abundant polymer encountered in nature. It is defined as an amorphous, aromatic, three-dimensional cross-linked network polymer based primarily on substituted phenylpropane units which are mainly interconnected to one another by ether bonds. It's function is to provide strength and rigidity to trees and plants and plays an important role in the transport of water and nutrients¹.

The process of converting wood into pulp is referred as pulping. This conversion is achieved either by chemical or mechanical means yielding chemical pulp and mechanical pulp respectively. The purpose of adding chemicals during chemical pulping, is to selectively remove lignin and extractives from the raw material without degrading the carbohydrate matrix: Less than half of the original wood by weight is converted to pulp². Essentially cellulose and hemicelluloses remains after this delignification process. In contrast, mechanical pulps, by nature of their production, preserve more than 90% of the components initially present in wood and therefore are classified as high-yield pulps. This means that most of the cellulose, hemicelluloses, lignin, extractives and inorganic compounds are retained in unbleached pulps after the mechanical pulping process³.

Traditionally chemical pulps have been used in the production of high-grade papers because of their strength, high brightness and brightness stability. The fibers in mechanical pulps are stiffer and slightly yellow which have limited their use to short-life, low-cost papers such as newsprint and advertising inserts. Nevertheless there is a growing interest from both the Pulp and Paper Industry and public interest groups⁴ to manufacture quality papers made from mechanical pulps:

The high-yield conversion of wood into mechanical paper implies a more economically favored utilization of the wood supply compared to chemical pulping. Furthermore, producing chemical pulps requires significantly higher amounts of chemicals compared to the mechanical process, which is one of the major sources of production costs. A lower amount of wood residues generated during pulping and a lower chemical demand translates into lower pollution levels and thus lower expenses associated with the treatment of mill effluents. On a different front, the Pulp and Paper Industry would benefit a great deal by enhancing it's tarnished image as a major environmental polluter.

To address these issues, a joint academia-industry partnership, *The National Center of Excellence* (NCE) was created in 1990. As a result, the physico-chemical properties of high-yield pulps have been improved considerably due to a better understanding of the chemistry of papermaking and the development of new equipment, non-polluting bleaching chemicals and novel bleaching sequences⁵.

Another approach consists of substituting part of the chemical pulp with high-yield pulp. It has been reported recently⁵ that a high quality paper was produced with a recorded brightness of 81% ISO by replacing half of the chemical pulp content with hydrogen peroxide bleached stone groundwood pulp for which the physical properties (density, tensile index, tear index and bending force) are similar to paper made from a 100% chemical pulp. The commercial benefit of using this mixture of pulps is very significant: It has been estimated that the production costs would decrease by 85\$ US per ton of paper!.

Despite these major improvements, there are still some important issues to be addressed before mechanical pulps may be used in the commercial production of high-grade papers. For example, all types of high-yield pulps tend to discolor when exposed to light⁶ or heat⁷. In contrast to chemical pulps, this phenomena occurs rapidly in mechanical pulps due to the high lignin content. In other words lignin is the key producer of colored molecules under such conditions. Light and more precisely it's ultraviolet portion in aerobic conditions is the most detrimental factor causing surface discoloration, a process better known as photoyellowing. The photoyellowing process has the potential to decrease the brightness of mechanical pulps by 30 points or more over a short period of time. Under identical experimental conditions chemical pulps such as kraft pulps experience a brightness loss of no more than 3 points⁸.

Obtaining a high brightness level is as important as a good brightness stability. The longterm goal actively pursued by both academic and industrial interest groups is to find an additive or mixture of additives that would completely suppress the photoyellowing process. Since this process is more complex than originally foreseen⁹, pulp buyers and producers would settle for a less ambitious effectiveness on the part of photoyellowing inhibitors: They have defined a minimum period of time for which the paper should be efficiently shielded against color reversion: It has been suggested⁸ that if the above process is halted for at least 36 months, then the market demand for high-grade papers made from mechanical pulps would increase from 0.6 to 2.2 million tons per year; if an additive can be found that disables permanently discoloration, the demand would increase to 2.6 million tons per year!

In order to find an efficient additive that will inhibit the photoreversion process, the identity of chromophores in lignin and the mechanisms of chromophore formations must be well understood.

1.2 The Identity of Chromophores in Lignin

The quest for elucidating the native structure of lignin is still underway because, to this day, all methods of lignin isolation resulted in it's alteration or degradation. Nevertheless, degradative and non-degradative methods of lignin analysis have contributed significantly to the elucidation of it's complex structure:

Lignin is defined as a three dimensional highly branched biopolymer consisting of phenylpropane units bonded with each other *via* ether linkages. There are three kinds of lignins: Guaiacyl lignins, syringyl lignins and para-hydroxyphenyl lignins. These structures are presented in Figure 1.1.



Guaiacyl ligninSyringyl ligninpara-Hydroxyphenyl ligninFigure 1.1: Structure of the basic phenyl propanoid building blocks in lignin¹.

Softwood is mostly comprised of guaiacyl lignins whereas hardwood is a mixture of these three types of lignins.

In an effort to portray the complexity of lignin structure, a 2-D schematic of softwood lignin is shown in Figure 1.2.¹. $H_{2,COH}$



Figure 1.2: Computer generated 2D schematic of softwood lignin¹.

Lignin-rich paper appears yellow because lignin contains chromophores that absorb the near-UV and visible portion of daylight. Chromophores are defined as atoms or groups of atoms that shift the near-UV absorption spectrum toward the visible region (red shift): For example carbonyl¹⁰⁻¹¹ and ethylene bonds undergo respectively $n\pi^*$ and $\pi\pi^*$ electronic transitions upon absorption of near-UV light which results in intense bands of longer wavelengths.

Non-conjugated chromophores in lignin do not participate to the overall color of pulp because their $n\pi^*$ and $\pi\pi^*$ absorption bands do not tail into the visible region (<380 nm). However, in a conjugated system such as lignin, their absorption bands extend into the visible region (>380 nm) thus imparting yellow color to pulp.

The main functional groups in lignin responsible for absorption of near-UV and visible light are conjugated aromatic carbonyl groups, aromatic α -, β - unsaturated aldehydes, quinonoid groups, stilbenes, phenyl coumarans and coumaryl alcohols. The extent by which each of these structures contribute to the overall color of unbleached pulp is not clear. This is attributed to the low concentration of these units in lignin and the lack of sensitivity in detecting and quantifying them.

Figure 1.3³ display the major chromophore units in lignin. The absorption maxima for each of them were measured in simple monomeric or dimeric systems.



Figure 1.3: The major chromophores and leucochromophores in lignin³.

The non-conjugated structures shown in Figure 1.3 exhibit their absorption maxima under 380 nm. However, when part of a conjugated system such as lignin, the absorption maxima of each units are likely to be shifted to longer wavelengths resulting in some cases to render non-absorbing molecules to color contributing molecules:

• Coniferaldehyde structures account for about 10 to 20 % of the total amount of light absorbed by chromophores at 457 nm¹². Their absorption maxima are located in the near UV-spectral region, around 340 nm; taken alone these types of structures are transparent in the visible region. Pew *et al*¹³ have demonstrated that when part of a cellulose matrix, their absorption maxima are shifted sufficiently to the right to make them absorb in the visible region. However hydrogen peroxide cleaves readily the double bond of coniferaldehyde groups in lignin during the bleaching stage, thus explaining the lack of light absorption at 350 nm in peroxide-bleached mechanical pulps.

- *o-* and *p-* Quinones structures have been reported to contribute for about 30 to 65% of the total absorption of lignin at 457 nm¹⁴. They are stable structures when bonded to neighboring structural units in lignin.
- o- and p- Quinone methide structures are intermediates during the polymerization of lignin precursors and hence are present in lignin. Since their absorption maximas are within the lower limit of the visible spectral range (380 - 400 nm respectively), they absorb in the visible region¹⁵.
- Stilbene quinone structures are contributing to the overall color of the lignin matrix because their absorption maximas are well within the limits of the visible spectral range (478 nm)³.
- Phenolic structures, in the form of syringyl moieties are highly reactive because of the free phenolic hydroxyl group which is readily oxidized to phenoxyl radicals when exposed to UV-light. These phenoxyl radicals are covalently bonded to neighbouring lignin units and have the ability of resonance stabilize. Under sufficiently high concentration, they contribute to the color of pulp since their absorption maxima orbits around 400 nm. More importantly, they are readily converted to quinones in an oxygen environment¹⁶.
- Conjugated monomeric phenols were shown¹⁷ to absorb moderately at wavelengths greater than 300 nm.

Another class of molecules which does not absorb in the visible region, has the potential to contribute to the overall color of pulp. They are called leucochromophores (Figure 1.3); although they are not colored in the present form, they can easily be converted to chromophores. Four kinds of leucochromophores have been identified:

- Hydroquinone and catechol groups are readily oxidized to o- and p- quinone structures in the presence of oxygen, hydroxyl radicals or certain transition metals³.
- Dihydroxystilbene structures are subjected to mechanical action during refining or ball milling and are converted to stilbenequinone structures³.
- Catechol groups do not absorb in the visible spectral region, but when chelated to a metal ion like Fe⁺² their absorption maxima are shifted in the 550 to 580 nm range,

rendering them visible. Their contribution to the overall color of pulp doesn't exceed $1\%^{14}$.

• Diphenylmethanes are easily oxidized to *o*-quinone methide structures *via* a hydrogen abstraction reaction³.

1.3 The Mechanisms of Chromophore Formations During the Photoyellowing Process

Forman¹⁸ was the first to acknowledge the role of lignin in the photoyellowing of wood and unbleached pulps. The exposure of wood meal sheets to near-UV light resulted in an initial phase of substantial brightness loss over a short period of time followed by a second phase where the extent of brightness reversion is less pronounced.

The extraction with organic solvents of these irradiated sheets decreased the lignin content from 27.5 to 18 per cent while the cellulose content didn't exhibit any substantial changes. This experiment confirmed the central role played by lignin during the photoyellowing process. Other factors such as humidity, temperature and metal content¹⁹ also contributed to increase the rate of brightness reversion.

Both Van den Akker *et al.* and Leary⁶ proved that the presence of oxygen affects the rate of brightness reversion. The irradiation of newsprint in vacuum or in the presence of nitrogen or carbon dioxide didn't cause any significant yellowing for up to 500 hours.

These observations suggest that the photooxidation of lignin is a major reaction in the yellowing of lignin-rich materials.

The next major advancement in understanding the photoyellowing process can be attributed to Kringstad *et al.*²⁰ who showed, using electron spin resonance (ESR) spectroscopy, that the photo-induced degradation of lignin is governed by radical reactions. Lignin model compounds studies suggested that the nature of these free radicals are of the phenoxyl type.

Three distinct reaction pathways were identified yielding phenoxyl radicals:

• The homolytic splitting of light absorbing molecules containing a free-phenolic group (Scheme 1.1).



Scheme 1.1: The Phenoxyl Pathway²⁰

• The reaction between excited aromatic ketones such as phenacyl- α -O-arylether compounds with non-absorbing phenolic moieties²¹ results in the formation of ketyl and phenoxyl radical intermediates (Scheme 1.2).



Scheme 1.2: Photochemical reaction involving a phenacyl ether and a phenolic hydroxyl group²¹

• In the solid state, carbonyl groups are not always in the vicinity of non-absorbing phenolic units; therefore, the reaction depicted in Scheme 1.2 is no longer valid. Upon absorption of UV-light, excited aromatic α -carbonyl groups release their excess energy by direct scission of β -aryl ether linkages³ yielding phenoxyl and phenacyl radical²² intermediates as shown in Scheme 1.3. The phenacyl radical is further reduced to the corresponding ketone *via* a hydrogen abstraction reaction.



Scheme 1.3: Photolysis of β -O-aryl bond in phenacyl arylether units²².

Free phenoxyl radicals are reactive intermediates which are converted to colored species: Leary²³ was the first to suggest that the identity of these chromophores are quinones, quinone methides and cyclohexadienones. Direct evidence for the formation of these quinonoid-like structures in mechanical pulps was provided by the work of Lebo *et al.*²⁴ by the selective labeling of these chromophoric species with trimethyl phosphite followed by the recording of ³¹P NMR spectra. This procedure was later refined by Argyropoulos *et al.*²⁵

The mechanism of formation of quinonoid structures from phenoxyl radicals is still under debate. Overwhelming evidence^{26-27,88} is pointing toward oxygen as the active participant

in the formation of quinone structures. However, there are still conflicting opinions about the identity of the oxygen species involved. Researchers have identified several pathways leading to the formation of quinone structures from phenoxyl radicals implicating molecular oxygen, singlet oxygen, hydroxyl radicals or hydroperoxide radicals²².

As presented in Scheme 1.4, oxygen may combine with a phenoxyl radical (path 1) to give a peroxyl radical which in turn abstracts a hydrogen from another free phenolic hydroxyl group resulting in the formation of hydroperoxide.



Scheme 1.4: Reaction mechanism between reactive oxygen species and phenoxyl radicals²².

The latter is easily photolysed to hydroxyl and hemiketal radicals. Following hydrogen abstraction and demethoxylation reactions, *o*-quinones and methanol are produced. Supporting evidence for this reaction mechanism is provided by the work of Leary⁶ who observed that the loss of methoxyl groups from irradiated newspaper is proportional to the extent of discoloration.

Alternatively, phenoxyl radicals may react with hydroxyl (path 2) or hydroperoxyl radicals (path 3) yielding the corresponding intermediates and subsequent formation of *o*-quinones.

Until recently, singlet oxygen was considered to be a key player in the formation of quinones; it was hypothesized (Scheme 1.5)⁸ that an excited carbonyl structure transferred its energy to ground-state oxygen to form singlet oxygen which in turn abstracted a hydrogen from a phenolic hydroxyl group to produce phenoxyl radicals:



Scheme 1.5: Suggested role of singlet oxygen in the formation of quinones⁸.

However, two separate studies conducted by Forsskahl *et al.*²⁸ and Takagi *et al.*²⁹ demonstrated that the exposure of lignin-rich paper to singlet oxygen did not induce color reversion.

In light of the above reaction mechanisms governing the photooxidation of lignin, the complete removal of the radical precursors by chemically modifying the structure of lignin should, in theory, block the photoyellowing process. It follows that the reduction of carbonyl groups and alkylation of the free phenolic hydroxyl groups in lignin should suppress the formation of phenoxyl radicals and subsequently the formation of quinone structures. Through absorption studies³⁰, the brightness stability of reduced and

methylated pulps was studied. They observed that the treated pulps were stable for a period of two hours, after which the photoyellowing process occurred at rates similar to those of untreated pulps.

Furthermore, by considering the relative abundance of free phenolic groups and carbonyl groups in TMP, their contributions to the overall increase in absorption coefficient at 420 nm accounts for a total of 30-40% of the photochemistry of TMP yellowing.

These data suggest that other UV absorbing groups leading to at least one more photoyellowing pathway has yet to be identified. Since photooxidation still occurs in reduced and methylated pulps, it follows that the structure of the absorbing lignin units do not possess α -carbonyl or free phenolic hydroxyl groups.

Research efforts by Scaiano *et al.*³¹ and more recently Schmidt *et al.*³⁰ have been crucial in order to elucidate what was judiciously called "the missing link", the major photoyellowing pathway: By studying the photo-behavior of guaiacylglycerol- β -arylethers in the presence of a peroxide-based compound (Scheme 1.6), they discovered that the initiation reaction is the photolytic scission of a peroxide bond to form peroxyl or alkoxyl radicals.



Scheme 1.6: The Ketyl Pathway³¹.

These radicals then abstract a benzylic hydrogen from the α -hydroxyl of β -O-4 phenyl ether units to form a ketyl radical which in turn fragments to enol and phenoxyl radicals. The enol rapidly tautomerizes to the corresponding aromatic ketone and the phenoxyl radical to quinone structures. Supporting evidence in favor of this reaction mechanism as well as the identity and the contribution of the reactants involved in the photodegradation process, originates from UV spectroscopic studies³⁰:

• β -arylether structures bearing a benzylic hydroxyl group accounts for 30% of the building units in lignin³².

- It has been estimated that 70 % of the increase in the absorption coefficient of reverted papers, can be attributed to the fragmentation of these β-arylether structures yielding ketyl radical intermediates³⁰.
- The large increase in absorption accounts for the formation of quinones ($\lambda = 410$ nm) and aromatic ketones ($\lambda = 330$ nm) in reduced and methylated pulps³³.

Unfortunately, the identity of the sensitizer and the reaction mechanism responsible for the formation of alkoxyl or peroxyl radicals remains unknown.

As stated earlier, the long term goal pursued by scientists is to develop economically marketable additives that would efficiently retard the photodegradation of lignin in mechanical papers. Failure of the known additives to retard efficiently this process originate from their inability to permanently block all the major pathways leading to photodegradation. The outcome of the latter point is well illustrated by Ingegerd Forsskahl⁹ from *The Finnish Pulp and Paper Research Institute*:

"Even if one major reaction path to yellowing can be blocked completely, another reaction path, which played a minor role as long as the first reaction was uninhibited, may now become involved in the yellowing process to a much larger extent. In other words, the pulp still yellows, but via another channel."

1.4 Inhibition of the Photoyellowing Process

For an additive to be recognized commercially as an "ideal photoyellowing inhibitor", its physico-chemical properties must satisfy stringent conditions:

- Long-term effectiveness against the photo-induced degradation of lignin
- No alterations of the physico-chemical properties of papers coated with the inhibitor
- Economically viable
- No adverse environmental effects

Based on the photoyellowing mechanisms described in the previous section, various strategies are available to inhibit the degradation of high-yield pulps:



Scheme 1.7: Different strategies aimed at inhibiting the photoyellowing process of mechanical pulps

The first possibility to interact with the process (Scheme 1.7) is to chemically modify or eliminate the chromophores residing in lignin. This approach was proven to be very effective against the photodegradation of lignin although, none of the methods developed to date are cost effective. These include alkylation of lignin phenols by methylation or acetylation, borohydride reduction of α -carbonyl groups and catalytic hydrogenation of lignin aromatics.

The purpose of alkylating lignin is to block the production of phenoxyl radicals formed via the free phenoxyl pathway. Leary³⁴ showed that methylating lignin has a limited inhibition effect because the photoyellowing process still occurs through other pathways. In contrast, acetylation³⁵ substantially retards discoloration because of it's non-selective reaction with hydroxyl groups in lignin. The free phenoxyl and the ketyl pathways are blocked due to the acetylation of free phenolic and α -hydroxyl groups. However, the

etherification reaction is non-specific to lignin and thus hydroxyl groups in cellulose are also acetylated resulting in poor physico-chemical properties of the paper.

Borohydride reduction of α -carbonyl groups followed by methylation of free phenolic groups³⁶ temporarily delays the photo-induced degradation of lignin by preventing the formation of quinonoid structures *via* the free phenoxyl and the phenacyl pathways. However, the major ketyl pathway is not suppressed by these treatments and chromophores are formed through this reaction mechanism.

According to Gierer *et al.*²² the catalytic hydrogenation of ethylene bonds in lignin coupled to borohydride treatment halted permanently the photoyellowing process. Unfortunately, this strategy will not be applicable until a small catalyst capable of diffusing into the fibers and catalyzing the hydrogenation of the pulp matrix is discovered.

A second possibility of interaction with the photoyellowing process (Scheme 1.7) involves a class of additives that shields lignin against the harmful wavelengths of light. By definition, UV-screens are transparent in the visible region and have the ability to absorb near-UV radiation (290-400nm) and then dissipate the energy in a manner that does not lead to photo-sensitization of lignin chromophores. Therefore the application of UVscreens to lignin-rich papers should, in theory, block all the photo-reaction pathways leading to the formation of colored chromophores. Fifty years ago, Nolan³⁷ first acknowledged the effectiveness of UV-screens in order to retard discoloration of mechanical papers. Since then a wide variety of derivatives have been tailored to photostabilize various kinds of light sensitive materials:

Derivatives containing a 2-hydroxybenzophenone or a 2-hydroxy-phenylbenzotriazole skeleton (Figure 1.4) are currently the most effective classes of photostabilizers available for commercial use³⁸:



Figure 1.4: 2-Hydroxybenzophenone(A) and 2-hydroxy-phenylbenzotriazole(B)-type structures³⁸.

The recognized photoprotection mechanism of these UV absorbers³⁹⁻⁴⁰ resides in their ability to form reversible intramolecular hydrogen bonds (six member hydrogen-bonded ring system) between an *o*-hydroxyl group and a heteroatom such as oxygen (2-hydroxybenzophenone) or nitrogen (2-hydroxy-phenylbenzotriazole). Upon absorption of UV-light (Scheme 1.8), a π -electron is promoted to an excited singlet state and *via* intersystem crossing, to an excited triplet state followed by ESIPT⁴¹ (Excited-State Intramolecular Proton Transfer) or "enolization" with proton transfer taking place along the intramolecular hydrogen bond.



Scheme 1.8: Tautomerism mechanism of 2-hydroxybenzophenone and 2-hydroxyphenylbenzotriazole-type of structures (planar conformers)⁴¹.

The quinonoid intermediate tautomerizes through a rapid non-radiative relaxation process (heat) and return proton transfer, thus regenerating the original ketone. The exceptional photostability of these two families of UV-absorbers is attributable to the rapid pathway for deactivating triplet-state ketone groups called the "keto-enol tautomerism mechanism".

In addition, 2-hydroxybenzophenone derivatives have been reported to exhibit additional photo-protection properties. Picket⁴² demonstrated that the stabilizing effectiveness of these UV absorbers goes beyond the pure light filter. In this regard they have been classified as⁴³ hydrogen donors for the termination of alkoxyl and hydroxyl radicals produced in the photolysis of peroxide species and also as triplet-state carbonyl quenchers⁴⁴. The major drawback associated with the use of UV absorbers is the high amount required (2-8%) to significantly photostabilize high-yield pulps thus rendering this approach commercially not feasible.

The third method of reducing the photooxidation rate of the lignin matrix (Scheme 1.7) is achieved by deactivating the excited state of lignin chromophores, precursors of radical intermediates such as phenoxyl, phenacyl and ketyl radicals. Ragauskas⁴⁵ and later Harvey *et al.*⁴⁶ investigated the quenching potential of several unsaturated dienes with appropriate lignin model compounds and BCTMP in solution and in the solid-state respectively. They observed that the photostabilization efficiency of the dienes is dependent upon their structural features: *trans, trans*-2,4-hexadien-1-ol was found to be the most effective quencher of triplet-state carbonyl groups in lignin. The quenching mechanism includes a high-rate transfer of the excess energy from the excited carbonyl to hexadienol followed by its photo-sensitized isomerization yielding all four geometric isomers. *trans, trans*-2,4-Hexadien-1-ol confers a temporary protection to high-yield pulps because the quenchers are eventually consumed leaving the way open for the photoyellowing process to resume. Furthermore, hexadienol has been reported to promote thermooxidative reactions.
The fourth method of counteracting discoloration of lignin (Scheme 1.7), concerns the stabilization of highly reactive radical intermediates by a class of additives known as radical scavengers. Since radicals are generated in high-yield pulps upon exposure to light or heat, they should, theoretically, offer a broader protection against the detrimental effects of weather compared to other classes of inhibitors⁴⁷. In order to be efficient stabilizers, they must successfully compete with lignin for scavenging indiscriminently all light- and heat-induced radicals.

Extensive research efforts have proven that thiol derivatives⁴⁸ and ascorbic acid⁴⁹ are efficient photoyellowing inhibitors when applied to high-yield pulps. The primary photostabilization mechanism relies on their ability to transfer labile hydrogen atoms to free radicals thus restricting radical intermediates such as phenoxyl and ketyl radicals from converting to chromophores. Their effectiveness was found to be strongly dependent upon molecular structure: For example, thiol derivatives bearing α -carbinol or α -carboxylic groups⁵⁰ provided superior photo-stabilization compared to their β -derivatives.

In addition to their inherently high oxidation potential, certain antioxidants exhibit other anti-yellowing properties:

Lignin model compound studies⁵¹ have confirmed that the bleaching effect observed when thio-additives such as 1-thioglycerol and glycol dimercaptoacetate are applied to mechanical pulps, is attributed to a reductive, Michael-type addition reaction between these and pre-existing or light-induced quinone structures.

On the other hand, a light-induced bleaching reaction was observed on pulps treated with ascorbic acid. Schmidt *et al.*³³ proposed that this effect can be ascribed to the photochemical reduction of ketone groups.

The main disadvantage of using this class of additives is that they offer a temporary protection against photooxidation reactions in lignin; once they are consumed, discoloration reactions proceeds with rate similar to those found in untreated pulps. Furthermore, ascorbic acid⁵² and other thiols additives were shown to promote thermal-oxidative reactions.

The fifth and last method of intervention (Scheme 1.7) addresses the problem after the chromophores are formed. Two strategies have shown some success in reversing the effects of post-oxidative yellowing reactions:

- Eliminate the molecules imparting yellow color to the pulp by chemical means
- Offset the yellow color of mechanical papers with fluorescent whitening agents (FWA)

Attempts to chemically eliminate chromophores in yellowed pulps include the removal of quinones by borohydride treatment or adding radical scavengers such as thiols and ascorbic acid for their bleaching properties. However Leary⁵³ reports that these efforts were not successful in restoring pre-existing pulp brightness levels.

Fluorescent brightners (Scheme 1.7) are part of the UV-screen family in the sense that they absorb UV light and re-emit the energy at longer wavelengths. Since the yellow color imparted to irradiated high-yield pulps is caused by a drop in absorbance in the blue spectral region⁵⁴, adding FWAs (Fluorescent Whitening Agents) which have the ability to re-emit the absorbed energy in this range (420-500 nm), will increase the reflection of light and thus make the paper appear more "white". Diamino stilbene disulphonic acid was shown to significantly enhance the brightness of mechanical papers. Unfortunately this FWA and others⁵⁵ were found to be unstable when exposed to UV-light and quickly lost their effectiveness as brightening agents.

1.5 Recent Progress in Inhibiting the Photoyellowing Process in High-Yield Pulps

From the material covered above, the general conclusion which can be drawn is that no single inhibitor meets all the requirements (see conditions in Section 1.3) to be used at an industrial level.

A patent was sought⁵⁶ in 1998 for the inhibition of the photoyellowing of lignin-rich papers by applying a diol in conjunction with clay or zeolite (fillers). The surface of these fillers contains acidic sites which provides the required acidic environment for the diols to

form ketals with the carbonyl groups in lignin. The best photostabilization performance were obtained by combining neopentyl glycol (diol derivative) and montmorillonite (a filler).

Recent studies have demonstrated that specific combinations of additives have been found to work synergistically in inhibiting the yellowing process. Their combination photostabilizes lignin more significantly than the sum of their individual inhibitory effects. The joint efforts of diethyleneoxythiols, with efficient UV-screens such as 2hydroxybenzophenone or hydroxyphenylbenzotriazole derivatives are showing enhanced photostabilization performance⁵⁷. The synergistic nature of this association is ascribed to their complimentary properties to protect lignin and each other from degradation reactions: Thiols are shown to protect the phenolic UV-screens against radical-initiated degradation reactions and in turn, the UV-screen filters the harmful wavelengths that would otherwise decompose the radical scavengers.

This combination of inhibitors substantially retards the rate of photooxidation reactions in lignin, even at low concentrations, but it does not permanently block them. The limitation of this binary system originates from the thiol derivative being consumed while protecting both the UV-screen and lignin against radical reactions. When the radical scavenger reserves are exhausted in the pulp, the UV-screen and lignin are subjected, once again, to radical-initiated oxidation reactions.

It follows that a permanent solution against the photoyellowing process of lignin-rich papers involves the long-term synergistic action of:

- A photostable UV-screen such as 2-hydroxybenzophenone or hydroxyphenylbenzotriazole derivative.
- A radical scavenger which is able to regenerate itself.

Developing a binary mixture which complies fully with the above conditions would greatly benefit the paper industry. Low charges of inhibitors would be required to effectively photostabilize high-yield pulps, thus lowering the cost associated with these additives. Hindered amine light stabilizers or HALS are an efficient class of radical scavengers which are widely used to retard light and heat-induced degradation of synthetic polymers³⁸. Only recently has this class of stabilizer been studied on high-yield pulp. Amongst the various kinds of commercially available HALS, 2,2,6,6-Tetramethylpiperidine-*N*-oxyl is a stable free radical⁵⁸ capable of scavenging radical species without being consumed in the process. The antioxidant-regenerative mechanism of this nitroxide is best known as the "Denisov Cycle" depicted in Scheme 1.9:



Scheme 1.9: The Denisov Cycle³⁸.

This class of stabilizer has only recently been studied on high-yield pulp. Amongst the various kinds of commercially available HALS, 2,2,6,6-Tetramethylpiperidine-*N*-oxyl is a stable free radical⁵⁸. The nitroxide first traps carbon-centered radicals of the alkyl-type, resulting in the formation of hydroxylamine ether. From ESR spectroscopic studies⁵⁹, the scavenging reactions for different alkyl derivatives in solution were found to proceed at high rates, 10^7 - 10^9 M⁻¹s⁻¹. The hydroxylamine ether then reacts with peroxyl or acylperoxyl radicals yielding nitroxide, ketones, alcohols and carboxylic acids depending on the molecular structure of the peroxyl radical. In a polypropylene matrix, there is strong evidence suggesting that this regeneration reaction proceeds quite rapidly.

Recently the photostabilization performance of a nitroxide derivative combined to a watersoluble benzotriazole derivative was assessed on high-yield pulps. McGarry *et al.*⁶⁰ observed that the photostability of treated lignin-rich papers was comparable to that of fully-bleached kraft papers over a period of 250 days. The enhanced performance of this synergistic binary system over a long period of time can, without a doubt, be attributed to the catalytic action of the radical scavenger.

Another promising photostabilization approach which was explored around the same time, consisted of incorporating antioxidant functional groups into efficient

UV-screen molecules.

Alkylated amines have been shown⁶¹ to significantly photostabilize polymers by scavenging oxygen-based radicals.

Using the aforementioned strategy, tertiary amine functional groups were incorporated into the meta position of the phenolic ring in 2, 4-dihydroxybenzophenone (DHB) (Figure 1.5).





2,4-Dihydroxybenzophenone or DHB

3-(dimethylaminomethylene)-2,4-dihydroxybenzophenone or MDHB

Figure 1.5: Structures of DHB and MDHB⁶²

The photostabilization performance of these DHB derivatives were evaluated on BCTMP handsheets⁶² and a photostabilization mechanistic attempt was provided in a later study⁶³. Figure 1.6 demonstrates the enhanced stabilization performance of 3- (dimethylaminomethylene)-2,4-dihydroxybenzophenone (MDHB) over the original DHB.



Figure 1.6: Plots of PC Number as a function of irradiation time for CTMP treated with DHB, and MDHB(1)⁶².

Since the absorption maxima and the extinction coefficient for these compounds was not affected by the nature of the substituent, it follows that the superior inhibitory performance of MDHB could be attributed to the protection action of the tertiary amino group.

These recent advances in the photostabilization of high-yield pulps have been exciting in the sense that a permanent solution which can be implemented at the industrial scale is now conceivable. Due to the recent nature of the last two strategies cited above, two essential questions remains unanswered:

- What are the photostabilization mechanisms of these new inhibition systems when applied on lignin-rich pulps?
- Which are the specific photoyellowing pathways affected by these inhibitors?

Most researchers rely on fundamental studies performed on polymers to answer such mechanistic questions. Unfortunately nature is not so cooperative and research has shown that the photoprotection mechanism of an inhibitor may be different depending on the kind of polymer studied. The later point is well illustrated by Gugumus who stated in an earlier report⁶⁴:

"The degradation mechanisms or the relative importance of different mechanisms vary with polymer structure. Hence, some stabilizers may protect one polymer mainly according to one mechanism and another polymer mainly by another mechanism."

The objective of this research is an attempt to define the precise photostabilization mechanisms of these novel inhibition systems. Insight into their inhibition mechanisms is sought by investigating the changes in product distribution of a mixture of lignin model compounds.

1.6 Aims of the Thesis

The photostabilization mechanisms of two inhibition systems which were proven experimentally to be very effective, were investigated by monitoring their photostabilization action on lignin-like molecules.

Specifically, the experimental work was sub-divided into two sub-objectives:

The first consisted of investigating the photoreactivity of the two lignin model compounds and the degradation products recovered after irradiation. To do so, an experimental protocol was designed to obtain qualitative and quantitative reproducible data. The experimental protocol consisted of different procedures, which ensured that the samples remained unaltered when exposed to chemical or physical treatments before and after irradiation. These include procedures for applying and drying the chemicals, solid-state irradiation of the samples, in a controlled environment (temperature, humidity, oxygen level), extracting, isolating and derivatization of the photoproducts.

The second sub-objective was that of monitoring any possible photochemical interactions that may occur between the novel inhibitors and two lignin model compounds. The two lignin model compounds were irradiated in the presence of the inhibitors in aerobic conditions. The inhibitory effects of the additives were monitored with respect to the chemical changes occurring in photoproduct distributions. These experimental results constitute the basis for the elucidation of the photoprotection mechanisms of the inhibition systems applied to high-yield pulps.

Chapter 2

Materials and Methods

2.1 Materials

The model compounds selected to mimic the photoyellowing reactions taking place in lignin are α -guaiacylacetoveratrone (model I) and guaiacylglycerol- β -guaiacyl ether (model II):



Model II

The photostabilization mechanisms of the following inhibitors were studied:

- 2,4-Dihydroxybenzophenone (DHB). •
- 3-(Dimethylaminomethylene)-2,4-dihydroxybenzophenone (MDHB) alone and in • conjunction with 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxyl (Tempo).
- Tinuvin P with 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxyl. •



2,4-Dihydroxybenzophenone or DHB



3-(dimethylaminomethylene) 2,4-dihydroxybenzophenone or MDHB



All reagents, unless otherwise stated, were supplied by Aldrich Chemical Company and used without further purification. All solvents were of HPLC grade in order to avoid organic and inorganic contamination of the samples. Tinuvin P and Tempo[•] (2,2,6,6-tetramethyl-4-hydroxypiperidine-N-oxyl) were kindly provided by Dr. C. Heitner (PAPRICAN).

2.1.1 Irradiation and Recovery of the Additives.

Mixtures of the additives (lignin model compounds with/without inhibitors) were homogeneously solubilized in an acetone-water (80:20 v/v) solution; with the exception of Tinuvin P which was solubilized in chloroform due to its low solubility in acetone and/or water. Equimolar amounts of the model compounds comprising approximately 30% of the weight of the cellulose sheets were used in order to mimic the lignin content in mechanical papers. In addition, a 1% charge (w/w) of UV-screens and 0.2 % (w/w) charge of the radical scavenger were applied when required to the testsheets.

The homogeneous solutions of additives were impregnated with a syringe on one side of a 2×2 cm² Whatman filter paper. Special care was taken to apply the mixture evenly on the surface of the sheets and to remove (using fresh portions of solvent) any reagent adhering to the surface of the syringe. The impregnated sheets were dried under partial vacuum in a dark desiccator for 12 hours. The samples were then weighted and suspended in the cavity of a photochemical reactor equipped with a 450 watt high pressure quartz mercury-vapor UV lamp (Ace Glass Inc.). The lamp emitted UV light covering a spectral region ranging from 222 nm to 366 nm. A pyrex glass sleeve was used to filter out the wavelengths below 300 nm. The impregnated side of the filter papers was irradiated for a period of 4 hours

under a continuous slow flow of air at ambient temperature and constant humidity levels. After irradiation, the products were recovered by exhaustively extracting the papers with an acetone-water mixture (80/20 v/v). An additional chloroform extraction step was carried out on Tinuvin P samples. The organic solvents were then evaporated under reduced pressure, and the water was removed by freeze-drying the samples for 6 hours. In order to obtain precise quantitative analytic data, each experiment was performed in triplicate.

2.1.2 GC/MS and GC/FID Analyses.

GC/MS analyses were carried out on a Hewlett Packard 5972 mass spectrometer interfaced to a Hewlett Packard 5890-A gas chromatograph equipped with a DB-5 $30m \times 0.25mm$ packed silica capillary column. The injection port temperature was $280^{\circ}C$ and the oven temperature program was $100^{\circ}C$ to $250^{\circ}C$ with a gradient of $10^{\circ}C/min$. The products were analyzed after silylation with N,O-bis(trimethylsilyl)acetamide and they were identified by comparison of their mass spectra with those of commercially available or independently synthesized authentic samples. The evaluation of product ratios was carried out by using 3,4-dimethoxy phenol as the internal gas chromatographic standard. The GC response factors relative to the standard were determined for each of the products by mixing known volumes of this product with standard solutions, followed by measurements of GC areas.

The GC/MS fragmentation patterns for the products originating from models I and II were as follows: -m/z (rel. intensity): Lignin model compounds: I: 316(23), 165(100), 151(16), 137(8), 107(8), 106(5), 91(8), 79(11), 78(6), 77(12); II: 536(1), 299(11), 298(26), 297(100), 181(6), 166(9), 74(5), 73(62); Product 1: 196.05(19), 181(21), 167.9(4), 167(14), 166(100), 150.95(24), 135.9(16), 73(5); 2: 210.1(19), 195.05(12), 182(5), 181(18), 180(100), 165(9), 149.95(9), 148.95(9); 4: 224(30), 209(45), 194.05(100), 180.9(11), 178.9(6), 166(38), 150.9(11), 137(9), 135.9(11), 124(10); 5: 238.05(6), 225(6), 224(16), 223(100), 207.95(36), 206.95(12), 179.9(13), 178.95(7), 165(26); 6: 254(44), 240(12), 239(71), 196.9(5), 196(16), 195.1(100), 180.9(6), 166(10),

165(92), 148.9(5), 136.9(9), 122(8), 121(6), 119.7(7), 119.2(7), 106.9(10); 7: 312(66), 297(100), 282(33), 268(27), 267(85), 253(58), 223(58), 210(7), 192.9(24), 180.9(5), 166.7(7), 162.9(6), 140.9(10), 137.9(6), 134.9(7), 126.1(33), 106.9(7), 97.9(10), 86.8(6), 78(9), 73(68); 8: 282(4), 267(7), 254(26), 239(42), 223(10), 196(11), 180(10), 165(72), 156(8), 149(26), 123(5), 119(8), 92(6), 79(66), 75(100), 73(47); 9: 325.1(6), 299.1(10), 298.1(24), 297(100), 223(9), 209.1(6), 75(6), 74.1(8), 73(47); 10: 420(12), 419(29), 418(85), 403(36), 388(44), 373(10), 358(7), 241(11), 195(8), 180(9), 149(9), 134(9), 78(20), 73(100); 12: 298(10), 297(26), 192(100), 181(6), 166(6), 73(46); 13: 464(1), 227(6), 226(18), 225(100); 15: 446(30), 387(15), 386(33), 385(100), 359(7), 356(9), 233(5); 17: 388(13), 373(7), 193(6), 166(10), 165(100), 77(5), 73(11); 18: 460(100), 445(5), 147(28), 136(5);

Inhibitors: DHB: 358(1), 345(12), 344(31), 343(100), 271(7), 164(11), 105(12), 77(13), 73(37); MDHB: 415(43), 400(66), 384(9), 373(9), 372(29), 371(52), 357(96), 355(42), 341(24), 299(7), 295(17), 283(30), 105(23), 73(100); Tinuvin P: 297(1), 227(8), 226(49), 212(9), 211(52), 105(6), 79(5), 75(12), 74(9), 73(100); Tempo: 316(1), 244(6), 188(22), 158(18), 157(13), 144(14), 143(100), 131(6), 130(9), 109(5), 101(5).

2.2 Synthesis of Reagents.

2.2.1 Synthesis of 3-(Dimethylaminomethylene)-2,4-Dihydroxybenzophenone (MDHB).

The reaction mechanism depicting the synthesis of MDHB starting from DHB is illustrated in Appendix A.1.

This compound was synthesized according to the method developed by Allen *et al*⁶⁵. The reaction mechanism depicting the synthesis of MDHB from DHB is illustrated in Appendix A1. Several modifications to the original method were made: An equimolar amount of concentrated hydrochloric acid was added after the 24h reflux and the hydrochloride salt of MDHB precipitated out of the ethanolic solution. The white crystals were filtered under vacuum and washed with fresh portions of cold ethanol. The neutral form of MDHB was

obtained by dissolving the water-soluble crystals in a bicarbonate solution followed by a chloroform extraction step. The solvent was evaporated under reduced pressure and slightly yellow crystals were obtained. Yield: 91%

2.2.2 Synthesis of α -guaiacylacetoveratrone (model I).

3-methoxy-4-Benzyloxybromoacetophenone (0.47g), guaiacol (0.5g) and powder potassium carbonate (0.5g) were refluxed in acetone (4 ml) for 6 hours under a nitrogen blanket. Product formation was monitored by TLC using a mixture of ethyl acetate: hexane (2:3) as eluents. The reaction mixture was filtered to remove the solid potassium carbonate and concentrated. Purification of model I was carried out by column chromatography on silica gel using the same mixture of eluents. Following the isolation of the fractions containing model I, the solvent was evaporated under reduced pressure yielding a white solid. Yield 99%.

2.2.3 Synthesis of guaiacylglycerol- β -guaiacyl ether (model II).

Model II has been synthesized according to the method developed by Fumiaki *et al.*⁶⁶. No modifications were made. Yield: Not determined.

Chapter 3

Irradiation of the Lignin Model Compounds: Product Studies

In order to mimic the photodegradation reactions which take place when lignin is exposed to light, appropriate models must be chosen. Previous studies have emphasized the key role played by conjugated α -carbonyl and α -hydroxyl β -O-4 phenyl ether units during the photoyellowing process. As such, α -guaiacylacetoveratrone (model 1) and guaiacylglycerol- β -guaiacyl ether (model II) are suitable lignin model compounds since their kinetic behavior resembles closely high yield wood pulps²².

Under simulated sunlight, free radicals are formed by the homolytic fragmentation of model I which in turn induce the photodegradation of model II *via* a hydrogen abstraction reaction⁶⁷. Thus, by monitoring the precise photo-chemical interactions occurring between the novel inhibitors and a mixture of these lignin model compounds (models I + II), an indepth understanding of their enhanced photostabilization mechanism(s) toward lignin-rich materials can be obtained.

A systematic approach of irradiating the additives on cellulose, identifying and quantifying the photo-products was adopted to elucidate the various reaction mechanisms operating during the irradiation process. In total nine distinct experiments were carried out:

- 1. Model I by itself.
- 2. Model II by itself.
- 3. Models I and II.
- 4. DHB by itself.
- 5. Models I and II in the presence of DHB.
- 6. MDHB by itself.
- 7. Models I and II in the presence of MDHB.
- 8. Models I and II in the presence of MDHB and Tempo'.
- 9. Models I and II in the presence of Tinuvin P and Tempo.

3.1 Photochemistry of Lignin Model Compounds in the Solid State

3.1.1 Product Studies of Irradiated Model I

The photochemical reactivity of model I adsorbed on cellulose was investigated in order to gain a basic understanding of the reaction mechanisms governing its photolysis.

The color of the oily samples after irradiation was a dark orange indicating that model I photodegraded to form a mixture of chromophoric moieties. Even though the recovery yield was 100%, not all the products were extracted from the irradiated testsheets. The light yellow color imparted to the cellulose indicated that some chromophore entities remained covalently bonded to the surface.

The results of the major photoproduct analyses are shown in Table 1.

\mathbf{I} ADIC \mathbf{I} . \mathbf{I} HULUIV315 DI VUULLS II VIII HIVUCI	Table	1:	Photolysis	products	from	model l
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Compound	2 ⁽²⁾	3,4-dimethoxyphenyl ethanone	6 ⁽²⁾	Model I	17 ⁽²⁾		
GC % ⁽¹⁾	7.97	Trace	3.90	6.12	4.52		

1. Relative amount of products compared to internal standard

2. See Scheme 3.1 for compound identification

6% (w/w) of the starting material I was recovered which indicates that dimeric conjugated α -carbonyl structures are very reactive when exposed to UV light. In total, five products were identified and quantified which represent all the major peaks in the chromatogram. The nature of the products analyzed were either monomeric or dimeric; the structural identities of the products were found to partially support the phenacyl pathway illustrated in Scheme 3.1.



Scheme 3.1: The identity of the various products formed from model I after four hours of irradiation

The photochemical reactions previously described by Gierer *et al*²² leading to the formation of monomeric moieties cannot explain adequately the other class of products isolated. For example, in addition to the monomeric compounds (2 and 6), compounds (10) and (17) were obtained most likely *via* radical coupling reactions⁶⁸. Previous discussions⁶⁹ on the various parameters affecting the photolysis of α -GAV (Model I derivative), have emphasized the key role of efficient hydrogen donating molecules in the formation of the ketyl radical intermediate. In the presence of an aprotic environment such as benzene, negligible amounts of ketyl and phenacyl radicals were detected which

resulted in low quantities of photoproducts. It follows that in a solution with a low radical content, homo-or heterocoupling reactions are unlikely events.

Upon absorption of UV light by a conjugated α -carbonyl unit¹¹, an electron from the π molecular orbital is promoted to the next higher orbital π^* ($\pi \rightarrow \pi^*$ transition). The carbonyl is said to be in a singlet excited state⁷⁰ from which different relaxation pathways are available: Direct homolytic cleavage of the β -O-4 bond or change of multiplicity are occurring simultaneously. In the presence of hydrogen donors, an efficient *intersystem crossing* to the triplet phenacyl ether⁶⁹ followed by the photoreduction of the carbonyl group to a ketyl radical has been shown to be the predominant pathway. Unimolecular decay involving bond-breaking reactions is responsible for the relaxation mechanism of the ketyl radical: Intramolecular β -aryl bond cleavage is thermodynamically favored (lower activation energy) due to the stabilization by resonance of the radicals generated²². The phenoxyl and phenacyl radical intermediates seek to produce stable products through the following processes:

- The predominant process is for the radical fragments (A and B in Scheme 3.1) to abstract hydrogens from adjacent hydrogen donor molecules: 1-(3,4-Dimethoxyphenyl) ethanone and creosol are formed through this reaction mechanism. Creosol (2) constituted the major monomeric stable product while 1-(3,4dimethoxyphenyl) ethanone was found in extremely low quantities (Table 1). It is well known that aromatic ketones are photosensitizers⁷¹ and may initiate oxidation reactions resulting in their decomposition through secondary reactions.
- Radical intermediates became stable via homocoupling reactions i.e.: Two guaiacoxyl radicals (B in Scheme 3.1) may join by C-C coupling to form dicreosol 10 (Scheme 3.1). Only trace amounts of this dimeric product were detected due to the low mobility of the guaiacoxyl radicals in the solid medium. Solid-state photolysis studies demonstrated the occurrence of condensation reactions involving coupling of phenolic radicals in lignin applied on a cellulose support⁶⁷⁻⁷².
- Alternatively, a guaiacoxyl radical (B in Scheme 3.1) and a phenacyl radical (A) may also recombine through a heterocoupling mechanism resulting in the formation of product 17 (Scheme 3.1). The amount of 17 detected indicates that this reaction

pathway is the second in importance due to the low diffusion rate of the radical species in the cellulosic matrix. Such β -5 structures have been detected before in the photodegradation of MWL⁷³ and shown to play an important role in the photoproduction of colored oligomeric materials⁷⁵. Furthermore no α -carbonyl β -1 structures⁷⁴ were formed owing to the methyl group blocking the 1-position of the guaiacoxyl radical from undergoing coupling reactions⁶⁷.

The structural features of product 6 (Scheme 3.1) indicate that the radical intermediate (B) was oxidized. There is no evidence suggesting that oxygen influenced the magnitude of β-aryl bond cleavage during irradiation, however, the structure of the products were greatly affected by its presence. Significant amounts of 3,4-Dimethoxyphenyl benzoic acid (6) were detected due to the high diffusion rate of oxygen in the cellulose fibers. These results are consistent with the photochemical studies performed by Vanucci⁷⁵ and Argyropoulos⁶⁷ on model I under aerobic conditions. A plausible reaction mechanism for the formation of compound 6 is depicted in Scheme 3.2.



Scheme 3.2: Oxidation reaction mechanism of phenacyl radical to 3,4-dimethoxy benzoic acid (6)⁷⁵.

Molecular oxygen is a diradical and combines with the phenacyl intermediate (A in Scheme 3.2) to produce a peroxyl-type radical (19) which is rapidly converted to hydroperoxide (20) in the presence of a hydrogen donor molecule. Through a Norrish type II reaction, the γ -hydrogen is abstracted by the ketone yielding an unstable hydroxydioxetane structure (22) which is swiftly converted to product 6 and formaldehyde (23).

3.1.2 Product Studies of Irradiated Model II

A slight discoloration of the solid cellulose samples impregnated with II was observed after irradiation. The extraction process failed to isolate the chromophores responsible for the light yellow color imparted to the cellulose sheets. The recovery yield was found to be 100% and GC analysis of the extracted samples indicated that no degradation products were generated during irradiation, yielding model II molecules only. In order to elucidate the origin of these chromophoric structures, cellulose sheets (control) were irradiated under the same experimental conditions in the absence of additives. The same degree of discoloration was observed and no products were retrieved suggesting that the slight yellowing may be ascribed to the mild photodegradation of cellulosic fibers⁷⁶. Thus, the contribution of cellulose in the photodegradation of the lignin model compounds is considered negligible.

On the other hand, it was not surprising to confirm the photostability of model II, since the UV spectra of similar structures such as 1-(4'-hydroxy 3'-methoxyphenyl)-2-(2"-methoxyphenoxy)ethanol were shown to absorb light at wavelengths under 300 nm⁷⁴. Furthermore, ESR studies⁷⁷ demonstrated that β -O-4 dimers bearing α -hydroxyl groups were not effectively degraded except when hydrogen abstracting units are in the vicinity.

3.1.3 Product Studies of Irradiated Models I and II

In an effort to unambiguously trace back the photoproducts to their original lignin models, the rings of each model contained different substituents (see Section 2.1 p.42).

After irradiation, a dark oily mixture in gravimetric yield of 100% was obtained. A light brown color remained on the cellulose sheets which suggests that chromophores other than those observed when cellulose is irradiated alone, were formed. Unfortunately repeated attempts to extract these colored molecules with a mixture of acetone and water were unsuccessful. It was hypothesized that the identity of these molecules are condensed structures⁷⁸.

The color of the oily mixture obtained was darker compared to that generated during the irradiation of model I alone. This provides direct evidence that model II in the presence of model I photodegraded to form amongst others, new chromophores.

The identity and amounts of the major photoproducts formed during the irradiation of equimolar amounts of models I and II are reported in Table 2.

Table 2: Photolysis products from models I and II.

Compound ⁽²⁾	1	Ш	1	2	4	5	6	7	8	9	10	12	15	17	18
GC% ⁽¹⁾	0.85	32.80	0.24	1.67	0.69	0.38	1.61	0.20	0.18	0.07	0.22	1.05	1.09	1.64	1.12

1. Relative amount of products compared to internal standard

2. See Scheme 3.3 for compound identification

In total, 13 products were identified and quantified which represent all the major peaks in the chromatogram of Figure 3.1 (Appendix A2 p.97).

3.1.3.1 Influence of Model II on the Photodecomposition of Model I

The identity and the amounts of products originating from the photodecomposition of model I (Table 2) have not been substantially altered by the presence of model II. This proves that the formation of compounds 2, 6, 10 and 17 is consistent with the reaction pathways discussed above and illustrated in Scheme 3.1. A very significant finding of this

work is that two new products were formed: It is the first time that compounds 8 and 18 (Scheme 3.3) are observed amongst the photolysis products of lignin model compounds. Unfortunately, the precise reaction mechanisms accounting for the formation of the α -keto acid 8 and the β -5 coupling product 18 remains unclear.



Scheme 3.3: The identity of the various products formed from model I in the presence of model II after 4 hours of irradiation

Alkoxyl or peroxyl radicals have been reported to selectively abstract α -hydrogen from etherified guaiacylglycerol- β -Arylether groups which represents more than half of the

lignin units³⁰. Since these radical intermediates are generated during the photolysis of model I, they will react with hydrogen donating molecules in order to form stable products. In contrast to 2, product 20 has not been detected because it is a reactive intermediate in the formation of 6 as shown in Scheme 3.2. Model II units offer an additional source of hydrogen from which these radicals may undergo H-abstraction reactions. The photochemical reaction mechanism of alkoxyl and peroxyl radicals in the presence of model II is depicted in Scheme 3.4.



Scheme 3.4: Photochemical reaction mechanism of alkoxyl and peroxyl radicals in the presence of model II

3.1.3.2 Influence of Model I on the Photodecomposition of Model II

Analysis of the seven products originating from the radical-initiated decomposition of model II shows that monomeric and dimeric compounds were formed mainly *via* the ketyl pathway (Scheme 3.5). Another reaction pathway involving the abstraction of a hydrogen at the γ -position will be covered later.



Scheme 3.5: The identity of the various products formed from model II in the presence of model I after four hours of irradiation

Alkoxyl and peroxyl radicals generated by the photolysis of model I (Scheme 3.4), may oxidize model II at the α -C position yielding a ketyl radical (Scheme 3.5). Fragmentation of the ketyl radical proceeds through the homolytic scission of the β -aryl bond producing

an enol and a phenoxyl radical (Scheme 3.5, C and D). These intermediates seek to produce stable products through the following reaction mechanisms:

- The enol intermediate (C) is readily tautomerized to the corresponding ketone (E in Scheme 3.5). As with all the aromatic ketones (model I or products) encountered in these experiments, they are readily consumed *via* secondary reactions due to their high photoreactivity. However, indirect evidence of the initial existence of the ketone intermediate (E in Scheme 3.5) is provided by the by-products of secondary reactions:
- Oxidative cleavage of the C_α-C_β bond from the aromatic ketone (E) produced vanillin
 4 and ethanol. A tentative rationalization of the reaction mechanism leading to the formation of 4 is given in Scheme 3.6:



Scheme 3.6: Light-induced oxidation and reduction reactions resulting in the formation of products (4) and (9).

Through a direct excitation of the aromatic ketone (E), the carbon-carbon bond adjacent to the carbonyl dissociated *via* a Norrish Type I reaction followed by hydrogen abstraction⁷⁷. In the presence of oxygen, product 4 may be further oxidized to vanillic acid 7. Table 2 shows that significant amounts of oxidation products were formed due to the high mobility of oxygen radicals. Similarly, the irradiation of MWL⁷³ and TMP⁷⁸ generated, amongst the decomposition products, the largest

quantities of vanillin (4) and vanillic acid (7). Apart from their characteristic odor, they do not cause yellowing since their absorption maxima do not exceed 280 nm.

- Another pathway for the deactivation of the excited state of the aromatic ketone (E) is to undergo photoreduction in the presence of H-donating molecules (Scheme 3.6). The corresponding ketyl radical achieves stability by abstracting another hydrogen yielding 4-Hydroxy-3-methoxyphenyl propanediol 9.
- Phenoxyl radicals are stabilized by a hydrogen abstraction mechanism yielding guaiacol

 monomers (Scheme 3.5). In addition, they may be involved in secondary photo oxidation reactions as a source of hydrogen which sustains photoreduction reactions
 of the triplet state of model I.
- Phenylcoumaran structure 15 (Scheme 3.5) was formed most likely *via* an intramolecular rearrangement mechanism. It was suggested⁶⁷ that a coupling reaction between a quinone methide C_{β} radical and the C_{5} centered radical originating from a phenoxyl radical might be accountable for the formation of such products. Previous photostudies⁷⁶ have shown that phenylcoumarans are leucochromophores (no significant absorption above 300 nm) which are readily converted to chromophores. Castellan *et al.*⁶⁸ proposed that the first step in the formation of these colored molecules consisted of an energy transfer process from a photosensitizer (such as an aromatic ketone) to the phenylcoumaran unit 15. This would cause the α -ether bond to cleave and induce the fragmentation of the molecule into a benzyl and a phenoxyl radical. Through a rearrangement mechanism the radical intermediates might couple to form a light-sensitive phenolic stilbene structure. Unfortunately these colored molecules were not detected in the present work.

Hydrogen abstraction reactions from alkoxyl and peroxyl radicals are not restricted to the benzylic position. The γ -C-H is also prone to H-abstraction reactions (Scheme 3.5). The structure of Product 12 implies that cleavage of β -O-4 bonds is not the only pathway, instead the homolytic scission of the C_B-C_y bond seems to be responsible.

Alkoxyl or peroxyl radicals may in turn abstract an α -hydrogen from 12 yielding a ketyl radical (24). β -Aryl ether cleavage follows resulting in the formation of a phenoxyl radical (1) and an enol (25). The enol is tautomerized to the corresponding ketone (5), 4-hydroxyl-3-methoxyphenyl ethanone. A tentative rationalization of the reaction mechanism leading to the formation of 5 is illustrated in Scheme 3.7.



Scheme 3.7: Photooxidation reaction of product 12 to 4-hydroxy-3-methoxylphenyl ethanone (5)

Although the photodecomposition of model II via γ -C-H abstraction reactions cannot be compared to the magnitude of the ketyl pathway, substantial amounts of products 5 and 12 combined were formed.

From Table 2, it is clear that heterocoupling, H-abstraction and oxidation reactions constitute the predominant modes of radical stabilization. Due to their low diffusion rate in

the solid state, the radical pairs generated by the homolytic cleavage of β -aryl ether bonds of models I or II tend to stay in close proximity. Hence, the probability that these reactive species recombine is quite important thus explaining the high amounts of heterocoupling products 15 (Scheme 3.5), 17 and 18 (Scheme 3.3). In contrast, oxygen by virtue of its state at room temperature (gas), is a radical which has a high diffusion rate in the cellulosic fibers. Thus radicals generated by the photodecomposition of models I or II will readily react with oxygen to form large quantities of oxidation products 6 and 7 (Scheme 3.3 p. 55 and Scheme 3.5 p.57 respectively).

Model II exhibited a lower photoreactivity compared to model I with a conversion yield of only 61.5 %(w/w). The high amount of model II remaining after irradiation can be explained by the lack of interactions between the two models caused by the distance separating them in the solid state⁷⁸. In addition model II is not the only supplier of hydrogen radicals and must compete with other H-donating entities in order to form a ketyl radical.

Interestingly, the photoreactivity of model I was enhanced by the presence of model II: 98.9% (w/w) of the starting material was converted to products compared to 94% (w/w) when model I was irradiated alone (see also Figure 4.1 p.64). The presence of model II provides an additional pathway from which triplet state model I molecules may undergo hydrogen abstraction reactions (from the phenolic group). Wan *et al.*⁶⁹ showed that the photodecomposition of α -GAV into ketyl and phenacyl radicals was greatly enhanced in a protic environment. In addition, photolysis by-products such as guaiacol and creosol are good hydrogen donors and can participate in the photoreduction of more model I (Scheme 1.2 p.22).

The recovery yield for the mixture of models I and II was close to 100%, yet lower amounts of decomposition products originating from model I were detected (Tables 1 and 2). This is attributed to the formation of oligomers which are not GC detectable due to their low volatility. This result is in agreement with the work of Pan *et al.*⁷⁸ who observed

an increase in condensed structures during the irradiation of various kinds of mechanical pulps.

The identity, amounts and reaction mechanisms of products generated during the photolysis of an equimolar mixture of models I and II have been determined. Four main pathways resulting in the photostabilization of the radicals intermediates were identified. These include:

- 1. Heterocoupling reactions with the concomitant formation of products 15, 17 and 18.
- 2. Oxidation reactions responsible for the formation of products 4, 5, 6, 7 and 8.
- 3. Hydrogen abstraction reactions from which 1, 2, 9 and 12 were formed.
- 4. Homocoupling reactions yielding product 10.

These reaction pathways constitute a fine recreation of the photoyellowing process in lignin-rich materials. By monitoring, at a molecular level, the chemical interactions occurring between an equimolar mixture of the lignin models and the photoyellowing inhibitors, their underlying photostabilization mechanisms may be elucidated.

The specific photodecomposition reaction pathways of models I and II as affected by these inhibitors and the photochemical fate of the additives will now be investigated in the next chapter. **Chapter 4:**

Photostabilization Properties of the Inhibitors

Having elucidated the detailed photodegradation mechanisms of a mixture of models I and II, the protective action of the photoyellowing inhibitors may be investigated. By monitoring the precise photo-chemical interactions occurring between the novel inhibitors and a mixture of these lignin model compounds (models I + II), an in-depth understanding of their enhanced photostabilization mechanism(s) toward lignin-rich materials can be obtained.

4.1 Photochemistry of Lignin Model Compounds in the Presence of Photoyellowing Inhibitors.

4.11 Photoreactivity of the Models in the Presence and Absence of the Inhibitors

Compared to the control (mixture of models I and II), the addition of the inhibitors markedly improved the photostability of model I against direct photolysis. The protective action of the inhibitors on model I is shown in Figure 4.1.



Figure 4.1: Amounts of model I remaining after 4 hours of irradiation in the presence and absence of various inhibitors

DHB was found to be the least effective of the other inhibitors, in protecting model I from direct photolysis. The application of DHB preserved model I by 86 %(w/w/) more compared to the control (I and II). The best photostabilization performance was provided by the pair Tinuvin P/Tempo which preserved model I by close to nine times, compared to the control. MDHB and MDHB/Tempo offered a lower UV protection by preserving model I two times more compared to the control.

UV spectral analysis has shown⁶² that DHB and MDHB strongly absorb in the near UV region. Furthermore these UV studies proved that the tertiary amino group did not affect the extinction coefficients of MDHB with respect to those of DHB in the 280-400 nm region. This implies that in addition to its UV absorbing ability, MDHB photostabilized model I via other channels involving undoubtedly the tertiary amine group.

The degree of photostabilization of model I in the presence of MDHB was unaffected by the application of Tempo. This result indicates that the later does not possess a wide UV filtering ability which is not surprising since no carbonyl or ethylene bonds are part of its structure. As a corollary, the exceptional photostabilization performance of Tinuvin P in tandem with Tempo, might be attributed to the UV filtering property of the benzotriazole derivative. In order to ascertain the individual contribution of Tinuvin P and Tempo in shielding model I against direct photolysis, separate experiments in the presence and absence of the lignin model compounds should be investigated in future studies (see "Suggestions for Future Work").

The difference in photoprotection performance between benzotriazole and DHB or its aminated derivative has been anticipated. Figure 4.2 shows that⁷⁹ DHB displays lower extinction coefficients in the near UV spectral range compared to Tinuvin P under the same conditions.



Figure 4.2: UV Spectra of UV screens⁷⁹.

In addition, the Tinuvin P offers a broader protection against UV light because it absorbs slightly further into the red part of the spectrum.

Alternatively, the lower photostabilization efficiency of the o-hydroxybenzophenone derivatives may not be uniquely related to extinction coefficients but also to a solvent effect⁸⁰. The excellent UV screen properties of benzotriazole and hydroxybenzophenone originates from their ability to selectively absorb UV light and dissipate it as heat via an excited state intramolecular proton transfer followed by a rapid internal conversion to the ground state. The prerequisite for this catalytic relaxation mechanism to occur is related to the planar form of these UV screens, which favors the formation of this intramolecular hydrogen bond between the carbonyl group (DHB) or the triazole nitrogen (Tinuvin P) and their ortho-hydroxyl groups. An equilibrium is reached between the planar and nonplanar conformations of the UV screen which can readily be disturbed if the solvent possess the ability to form hydrogen bonds⁸¹. Chloroform, the solvent used for Tinuvin P, does not interfere in the distribution of the conformers since it is unable to create hydrogen bonds with the hydroxyl group of Tinuvin P. On the other hand, the benzophenone derivatives were solubilized in a mixture containing water which is able to create hydrogen bonds. Thus the equilibrium between planar and non-planar conformers has been disturbed resulting in higher amounts of the non-planar conformer. Since this

conformer is incapable of intramolecular hydrogen bonding, the photostabilization characteristics of these UV-screens is greatly reduced.

Previous experiments have underlined the key role of alkoxyl or peroxyl radicals in the photooxidation of model II. Since the flux of light was significantly reduced by the incorporation of the inhibitors in the handsheets, lower amounts of these oxygen-based radicals were formed. Figure 4.3 shows that in the absence of inhibitors, 61 % (w/w) of model II was degraded due to radical-initiated reactions.



Figure 4.3: Amounts of model II remaining after 4 hours of irradiation in the presence and absence of various inhibitors

In the presence of the inhibitors, at least twice the amount of II remained unreacted. DHB treated handsheets displayed the lowest protection of all, yielding 73% (w/w) of the starting material II. In contrast, the Tinuvin P/Tempo system offered the best performance with almost no decomposition. The improved efficiency of MDHB over DHB in protecting model II (81 % (w/w) remaining) is evidence that the introduction of an amino group confers an additional protection property to the UV screen: Since radical-attack is responsible for the fragmentation of model II, the tertiary amine must function as a mild antioxidant. Through a H-donation mechanism, MDHB successfully competes with model II molecules in reducing alkoxyl and peroxyl radicals. Similar findings by Allen *et al.*⁶⁵

showed that the amino group in MDHB acted as a chain-breaking donor for the termination of alkoxyl and hydroxyl radicals produced during the photolysis of hydroperoxides in polyolefin films. More recently, Argyropoulos *et al.*⁶³ have observed that the irradiation of MWL samples mixed with MDHB showed less tendency to form condensed structures compared to those treated with DHB. The superior photostabilization performance of MDHB was credited to the tertiary amine groups, scavenging phenoxyl and possibly other types of radicals.

Surprisingly, the presence of Tempo in MDHB-treated samples was found to be completely ineffective in protecting model II. At this stage in the discussion, no satisfactory explanation can be forwarded although Allen⁸² observed that under UV light, Tempo-H did not protect 2- and 4-hydroxybenzophenone from hydroperoxide attack in polypropylene films.

In contrast, Tempo was found to be highly effective in neutralizing alkoxyl and peroxyl radicals when used in conjunction with Tinuvin P. From Figure 4.1, roughly 1.1% (w/w) of model I remained unreacted in the presence of Tinuvin P/Tempo, which means that significant quantities of these oxygenated radicals were generated *via* the phenacyl pathway. Nevertheless, in the presence of Tinuvin P and Tempo, model II was completely shielded against radical attack as shown in Figure 4.3. Since Tinuvin P is not an antioxidant, Tempo must have reacted with these radicals. Strong evidence supporting this reaction mechanism is given by the high photoreactivity of Tempo during irradiation in the presence of Tinuvin P: Only trace amounts of Tempo were detected.

4.1.2 Product Studies of Irradiated Models in the Presence and Absence of Inhibitors

Figures 4.4 to 4.7 (Appendix A3) reveal that low amounts of products 1, 7, 9 (Scheme 3.5) and 8 (Scheme 3.3) were formed during the irradiation period in the absence of inhibitors. However, the presence of these inhibitors eliminated the occurrence of such products. Since the inhibitors blocked the reaction pathways leading to their formation with the same efficiency, the action of the amino group or Tempo cannot be accounted for
the photostabilization mechanism. Instead, the UV absorbing properties of the obenzophenone derivatives and Tinuvin P are most likely responsible.

Figure 4.8 illustrates the influence of the inhibitors in the formation of creosol (Scheme 3.3 p.55). The production of creosol was significantly affected by the presence of Tinuvin P and Tempo. Compared to the control, 40 % less creosol was formed. Since creosol is formed through the photolysis of model I, the decrease can be attributed to the excellent photostabilization characteristics of Tinuvin P.

The combination of MDHB and Tempo also proved to efficiently reduce the formation of creosol offering a 33 % decrease in the amount of creosol produced in the absence of the inhibitors.



Figure 4.8: GC% of creosol (2) generated during irradiation in the presence and absence of various inhibitors

The photooxidation pathway leading to the formation of product 4 (Scheme 3.5 p.57)was seriously affected by the nature of the inhibitors. The addition of the inhibitors in all cases caused a significant decrease in production of 4 as shown in Figure 4.9. DHB and Tinuvin P/Tempo are responsible for a 45% reduction in yield of 4 while MDHB in the presence or absence of Tempo blocked completely its formation. Clearly, the inhibition is due to MDHB which must interfere in the oxidative cleavage of the C_{α} - C_{β} bond of the aromatic ketone (intermediate E in Scheme 3.5).



Figure 4.9: GC% of 4 generated during irradiation in the presence and absence of various inhibitors

The benzophenone derivatives in the presence or absence of Tempo were all successful in reducing the formation of product 6 (Figure 4.10) (Scheme 3.3 p.55). In contrast, Tinuvin P and Tempo promoted its formation. It is interesting to note that a net decrease in the formation of monomeric products bearing carboxylic acid groups (products 6 and 7) was monitored especially in the presence of MDHB but also with DHB. Similar results were observed by Peng *et al.*⁶³ on MWL adsorbed on filter paper.



Figure 4.10: GC% of 6 generated during irradiation in the presence and absence of various inhibitors

The combination of MDHB and Tempo was responsible for a 35 % drop in the formation of 6 compared to 20 % for MDHB by itself. It seems that Tempo interfered with the production of this product. In addition, the photostabilization performance of MDHB is better than DHB which confirms that the tertiary amine is involved in the inhibition of this oxidative reaction pathway.

The coupling reaction pathway leading to the formation of product 10 (Scheme 3.3 p.55) was completely suppressed by the Tinuvin P/Tempo pair (Figure 4.11). This result is of great significance since photochemical condensation reactions are a significant cause of color reversion in high-yield pulps⁸.



Figure 4.11: GC% of dicreosol generated during irradiation in the presence and absence of various inhibitors

In contrast, MDHB/Tempo stimulated its formation. In their presence, more than twice the amount of 10 was generated during the irradiation compared to the control. Since MDHB by itself showed no significant increase over the control (I + II) in the production of 10, on the rate of formation of this product, the inhibition properties of Tempo seem to depend on the nature of its coadditives. DHB and MDHB in the presence or absence of Tempo effectively blocked the photooxidative pathway leading to the formation of 5 (Scheme 3.5 p.57). Tinuvin P and Tempo were also shown to reduce this reaction pathway as depicted in Figure 4.12.



Figure 4.12: GC% of 5 generated during irradiation in the presence and absence of various inhibitors

The C_{β} - C_{γ} cleavage of model II resulted in the formation of product 12 (Scheme 3.5 p.57). The combination of Tinuvin P and Tempo was observed to be the most effective in reducing the yield of 12 by 72 % compared to the control (I + II)(Figure 4.13). A slight reduction in the formation of 12 was also observed for the DHB-impregnated sheets.



Figure 4.13: GC% of 12 generated during irradiation in the presence and absence of various inhibitors

Unfortunately, MDHB and product 12 are eluted from the GC column at exactly the same retention time. Repeated attempts to separate the two compounds by changing the GC temperature gradient program were unsuccessful. As a result, the peak corresponding to 12 is a mixture of the product and the chemically unreacted form of MDHB. A dramatic increase of this peak was monitored in the presence of MDHB and Tempo.

The reaction pathway resulting in the formation of phenylcoumaran (15) (Scheme 3.5 p.57) is seen to be seriously hampered by the presence of the inhibitors as shown in Figure 4.14.



Figure 4.14: GC% of 15 generated during irradiation in the presence and absence of various inhibitors

The benzophenone derivatives by themselves were shown to be the most effective in blocking this reaction mechanism with a 65 % reduction in the amount of product 15 being formed. In the presence of Tempo, the UV screens reduced by half the formation of 15. Since phenylcoumaran units are precursors to the formation of stilbenes, inhibiting this reaction pathway should have a very significant impact in counteracting the photoyellowing processes.



MDHB with or without the assistance of Tempo reduced by 30 % the formation of

Figure 4.15: GC% of 17 generated during irradiation in the presence and absence of various inhibitors

Compared to the control, the Tinuvin P/Tempo pair did not affect this rearrangement mechanism which confirms the ineffectiveness of Tempo toward inhibiting this reaction pathway. In addition, the difference in the performance between DHB and MDHB indicates that the tertiary amine group is largely responsible for the inhibition of this reaction pathway.

The reaction pathway resulting in the formation of product 18 (Scheme 3.3 p.55) was profoundly affected by the action of the inhibitors (Figure 4.16).



Figure 4.16: GC% of 18 generated during irradiation in the presence and absence of various inhibitors

The UV screens in the presence of Tempo were the most effective, which resulted in the complete inhibition of this product. An approximate measure of the influence of Tempo can be evaluated by examining the amount of **18** formed in the presence of MDHB by itself. Since the latter reduced the yield of **18** by 68 %, Tempo contributed to the inhibition of this reaction pathway by 32 % which is not surprising since Tempo reacts with alkyl radicals (Scheme 1.9 p.36). Furthermore, DHB reduced the formation of this product by 30 % which shows that the amino group in MDHB is implicated to a large degree in suppressing this coupling reaction.

4.2 Photostabilization Mechanisms of the Inhibitors

The influence of the various inhibitors on the photoreactivity of the lignin models and on the changes occurring in product distribution has been elucidated in the last section (4.1 p.64). The photochemical behavior of the inhibitors was investigated in this section which provided a more complete understanding of their photostabilization mechanisms.

4.2.1 Photostabilization Mechanism of DHB

4.2.1.1 Photostability of DHB on Cellulose

It was essential to monitor the photochemical behavior of DHB on cellulose in order to assess its stability toward UV light.

DHB did not photodecompose during the irradiation period, and also prevented the cellulose sheets from photoyellowing (see Section 3.1.2 p.53). The recovery yield was found to be 100%, which demonstrates the remarkable photostability of this molecule toward UV light and its ability to dissipate the absorbed light in a manner which is not detrimental to the cellulose.

4.2.1.2 Photochemical Fate of DHB in the Presence of Models I and II

A significant improvement in the final color (visual observation) of the cellulose sheets was observed with respect to the control. The recovery yield of DHB was found to be 100% (w/w), suggesting it has not been subjected to light or radical-induced degradation reactions. This result contradicts previous studies on the photostability of DHB⁵⁸ which showed that alkoxyl and peroxyl radicals are capable of abstracting *o*-hydroxyl hydrogen from DHB, thus rendering the tautomerism mechanism inoperable. The discrepancy between the results can be ascribed to the medium generating less of these oxygenated radicals: The high amount of model II unreacted substantiates this rationalization.

From product studies, the photostabilization mechanism of DHB is based on its UV absorbing characteristics. Lower amounts of products were generated compared to the control, due to a drop in the flux of light reaching the lignin models. There was no conclusive evidence suggesting that it may function through other protection mechanisms.

4.2.2 Photostabilization Mechanisms of MDHB

4.2.2.1 Photostability of MDHB on Cellulose

The cellulose sheets didn't experience color reversion during irradiation which shows that MDHB efficiently shielded cellulose against photo-oxidation reactions. The extracted solutions remained colorless and GC analyses indicated that no photodegradation products were formed. Thus the tertiary amino group in MDHB does not interfere with the keto-enol tautomerism mechanism responsible for the keto-enol tautomerism mechanism (Scheme 1.8).

4.2.2.2 Photochemical Fate of MDHB in the Presence of Models I and II

The color of the irradiated cellulose sheets and the extracted solutions was somewhat less intensely colored compared to those originating from DHB. This suggests that fewer condensed structures and photooxidation products were formed confirming the better effectiveness of MDHB in acting as a UV filter. Unfortunately, the recovery yield of MDHB could not be evaluated by GC since it shares the same retention time with product 12 (see Section 3.1.3 p.54). However, if the assumption is made that both *o*-hydroxybenzophenone derivatives have the same inhibition efficiency, than the "excess" of product 12 may be assigned to the amount of MDHB remaining after irradiation.

When models I and II were irradiated, the product distribution changed significantly in the presence of MDHB. These data clearly demonstrated that the addition of a tertiary amine

group enhances the photoprotection characteristics of the starting material (DHB). Higher amounts of model II were recovered in the presence of MDHB, which suggests that the tertiary amino group functioned as a chain breaking donor for the termination of alkoxyl and peroxyl radicals (Scheme 3.3 p.55). The photodegradation pathways leading to the formation of products 5 (Figure 4.12 p.72), 7 and 8 (Appendix A3) were completely blocked while the one resulting in product 6 (Figure 4.10 p.70) was hindered. The detailed investigation of the reaction mechanisms governing the formation of these products, showed that oxygen is the common factor. Consequently, the tertiary amino group is responsible for the scavenging of oxygen molecules. A similar conclusion was also reached by Allen et al.83 who observed that amino groups grafted to acrylate resins, enhanced their photostability by scavenging oxygen. Scheme 4.1 illustrates the possible additional photostabilization protection procured by the tertiary amino group linked to a DHB molecule: The tertiary amino group may operate as a labile hydrogen donating site for the termination of alkyl or alkoxyl radicals produced during the photolysis of models I and II (see Schemes 3.3 and 3.5). The radical on the α -carbon to the nitrogen will then be attacked preferentially by oxygen thus protecting the lignin. No product studies, however, support it and future work should emphasize the use of an alternative analytical tool for the separation of the products originating from the photodecomposition of the lignin model compounds (see Section 5.2 p.85 "Suggestions for Future Work" for more details).



Scheme 4.1: Proposed oxygen scavenging mechanism of MDHB⁶⁵.

Furthermore, a closer examination of Figure 4.1 reveals that slightly higher amounts of model I remaining after irradiation were recovered in the presence of MDHB compared to DHB. Thus, the UV absorbing effectiveness of MDHB is at least as good as that of DHB. It suggests that the free amine does not interfere with the reversible keto-enol tautomerism mechanism.

As a result, the cooperative action of UV absorbing, hydrogen donating and oxygen scavenging functionalities of MDHB accounts for the enhanced photostabilization of BCTMP handsheets: Since the photooxidation of phenoxyl radicals is responsible for the formation of quinonoid structures (Scheme 1.4 p.24)⁸⁴, the lower discoloration observed in MDHB-treated pulps may be attributed, in part, to the scavenging of oxygen molecules.

4.2.3 Photostabilization Mechanisms of MDHB and Tempo

4.2.3.1 Photochemical Fate of MDHB/Tempo in the Presence of Models I and II

No noticeable difference in the color of the impregnated sheets, or the extracted solutions was observed compared to those originating from MDHB-treated samples. It suggests that MDHB in the presence of Tempo protected models I and II at least as efficiently as MDHB by itself, against photodegradation reactions. Surprisingly, the protection of model II against alkoxyl and peroxyl attack was rather disappointing: It was expected that these radicals would be scavenged *via* the Denisov Cycle (Scheme 1.9 p.36) thus increasing the recovery yield of model II.

Tempo seems to have a positive effect on the reduction of certain products but no conclusion could be made concerning the photodegradation pathway(s) affected by its presence: As shown earlier, products 10 and 18 (Scheme 3.3 p.55)are both formed through a coupling mechanism. While a dramatic increase in the yield of 10 (Figure 4.11 p.71) was recorded, Tempo significantly reduced the formation of 18 (Figure 4.16 p.75). However, the presence of Tempo had a positive effect on the recovery yield of MDHB: A 200% increase in peak area corresponding to product 12 (Figure 4.13 p.72) was

monitored in the presence of MDHB and Tempo compared to MDHB by itself. It would indicate that Tempo shielded MDHB from radical attack.

The low recovery yield of Tempo (35 % (w/w)) revealed that the catalytic regeneration process was inoperative or that its regeneration rate was low. This data may also imply that Tempo is being consumed by coupling with radicals generated during irradiation. Lucki *et al.*⁸⁵ have reported that nitroxyl derivatives are readily neutralized by alkyl radicals to form stable products thus preventing the ether derivatives from regenerating to their initial form.

Despite the mild protection ability of Tempo on MDHB against radical-induced degradation, their application on lignin-rich pulps could not be characterized as synergistic.

4.2.4 Photostabilization Mechanisms of Tinuvin P and Tempo

4.2.4.1 Photochemical Fate of Tinuvin P and Tempo in the Presence of Models I and II

The irradiated handsheets treated with Tinuvin P and Tempo displayed the lowest levels of discoloration. After extraction, the cellulose sheets retained only a small amount of colored chromophores. These observations are not surprising since models I and II experienced the lowest degrees of photodegradation amongst the inhibitors studied.

As expected, Tinuvin P displayed the best photostabilization performance compared to the other UV screens studied, due to its enhanced absorption properties in the near UV region. In addition, Tempo effectively blocked alkoxyl and peroxyl radicals from attacking model II at the C_{α} and C_{γ} positions. However, the most remarkable attribute displayed by this pair of inhibitors is their ability to suppress the formation of condensed structures. This result provides insight into the exceptional protection efficiency witnessed on high-yield pulps⁶⁰.

On the other hand, the photostabilization performance of Tempo is highly sensitive toward the nature of the UV screen "mate": In the presence of Tinuvin P, the photodegradation pathways targeted by Tempo are well defined with a high level of hindrance. In contrast, Tempo in the presence of MDHB was not selective in blocking any photodegradation pathways, which could explain its disappointing photostabilization performance.

Since only 60 % (w/w) of Tinuvin P was recovered after irradiation, this suggests that it was subjected to photodegradation reactions. Previous inquiries⁸⁶ on the factors governing the decomposition of benzotriazole additives, have determined that its photoreactivity originates from the non-planar conformer which is readily susceptible to radical attack in the presence of UV light. UV light by itself is not sufficient to cause the fragmentation of the UV screen but it is necessary in order to promote the non-planar conformation to an excited state which is then prone to radical attack. Also, it was reported that a moderately polar environment (such as lignin) is required. Presumably a polar environment would shift the equilibrium toward the non-planar conformation by promoting the creation of intermolecular hydrogen bonds with the α -hydroxyl group of the benzotriazole. More importantly, as the non-planar conformation is being consumed from radical-initiated fragmentation reactions, more benzotriazole in the planar conformation would be converted to non-planar in order to maintain the equilibrium established by the polarity of the medium. It was also found⁸⁶ that Tinuvin P (the non-planar conformer) is readily attacked by peroxyl radicals in the presence of UV light. Since Tempo in the presence of Tinuvin P was shown to be an efficient peroxyl scavenger, the benefits of combining both are becoming clearer: Tempo is protecting Tinuvin P from radical attack thus increasing the life span of the UV screen. In turn, Tinuvin P is able to effectively shield model I from direct photolysis for a longer period of time. However, only trace amounts of Tempo were recovered which indicates that the regenerative Denisov Cycle (Figure 1.9) might not be operating in this medium or that the regeneration rate might be low. As soon as Tempo's reserves on the cellulose sheets are depleted, the photodegradation mechanisms leading to the gradual disappearance of Tinuvin P and to discoloration of the lignin model compounds would follow. In order to determine the precise photostabilization mechanism of Tinuvin P, an additional experiment must be performed involving the irradiation of Tempo in the presence and absence of the lignin model compounds (see "Suggestions for Future Work").

This set of data shows that a synergistic photostabilization effect was observed between Tempo and Tinuvin P, but was not retained during irradiation. Applied to mechanical pulps, McGarry's team⁶⁰ observed a true synergism between the additives. The apparent conflicting results may be a consequence of the different light source employed to conduct these experiments⁸⁷.

5.1 CONCLUSIONS

The present work provided an insight into the protection mechanism(s) of photoyellowing inhibitors: An equimolar mixture of models I and II were irradiated in the presence of oxygen. The degradation products were identified and quantified and reaction mechanisms leading to their formation have been suggested. The results of this study have shown that Tinuvin P combined with Tempo were most successful in preventing models I and II from photodegradation reactions, followed by MDHB and DHB.

The prerequisite for an inhibitor to block the photodegradation of the lignin model compounds is that model I must be effectively shielded against the harmful wavelengths that would have caused otherwise its photosensitization. In other words, the more an inhibitor hinders the phenacyl pathway from operating, the lower the amount of radicals being generated. The Tinuvin P/Tempo pair displayed the best performance at shielding model I from UV light. In addition, alkoxyl and peroxyl radicals were effectively blocked by this pair of inhibitors, resulting in almost no radical-induced fragmentation of model II. In addition, they suppressed the formation of condensed structures. Since trace amounts of Tempo were detected after irradiation, the synergistic effect occurring between Tinuvin P and Tempo is most likely temporary. However more experiments are needed to confirm these results.

The incorporation of a tertiary amino group into DHB did not interfere with its keto-enol UV absorption mechanism. The net result is an enhancement of its photostabilization properties. In addition to its UV absorbing characteristics, MDHB was shown to act as a labile hydrogen donor for the termination of radical intermediates. Furthermore, it may also act as an oxygen scavenger, inhibiting the formation oxygenated radicals. This result may be translated into lower amounts of quinones formed in MDHB-treated mechanical pulps during daylight exposure and accounts for its enhanced photostabilization performance over DHB.

The combination of MDHB and Tempo did not procure a superior photostabilization protection such as the one observed in the presence of Tinuvin P. The photostabilization performance of MDHB in the presence or absence of Tinuvin P was found to be similar. In addition, low amounts of Tempo were recovered thus strengthening the concept that the antioxidant was being consumed during the irradiation period.

DHB was found to be the least effective inhibitor compared to the others. Nevertheless DHB was shown to greatly improve the photostability of model I compared to the control, revealing its excellent UV filtering ability. In turn, lower amounts of products were generated but, no specific reaction pathways were targeted: The photostabilization mechanism of DHB may be ascribed solely to a drop in the flux of light reaching the lignin models.

5.2 SUGGESTIONS FOR FUTURE WORK

- 1. The protection mechanisms of the inhibitors warrant further investigation. The reactivity of MDHB in the presence of radicals generated during irradiation remains largely unknown since it shares the same retention time with product 12. Furthermore the photochemical fate of MDHB, Tinuvin P or Tempo have not been elucidated, probably because of coupling reactions with other radicals yielding condensed structures. Since GC is incapable of eluting higher molecular weight products, another separation technique is required from which isolation of the products does not rely on their respective boiling points: Although the separation efficiency of GC is about 10 times that of HPLC, the principles of separation of the latter are based primarily on the polarity of the individual products. Liquid chromatography coupled to an MS detector would provide information about the structure of condensed products. As such the fate of the inhibitors when exposed to radical attack could be elucidated. Coupled to a UV detector, quantification of the unreacted MDHB after irradiation may be assessed. In addition, by varying the wavelength of the detector, the identity of the color contributing products (λ =350 nm) would be easily distinguished from non-absorbing products (λ =280 nm).
- 2. A more complete understanding of the role of Tinuvin P and Tempo in the photoprotection of the lignin model compounds is desirable. Irradiation of each inhibitor in the presence and absence of a mixture of I and II would bring about vital information on their photostabilization mechanisms. In addition, kinetic studies on the photobehavior of Tempo in the presence of the model compounds, would provide insight into its regeneration rate and whether or not true synergism exists between Tinuvin P and Tempo in this medium.
- 3. In order to avoid the contribution of secondary reactions in the photodegradation of the lignin model compounds, a shorter irradiation time or a weaker light source is recommended. After 4 hours of irradiation, only 1 % of model I remains unreacted and the products, especially those originating from model I, were shown to undergo extensive secondary reactions. The light source or the irradiation period should be

reduced accordingly so as to achieve less than 20 % (w/w) photodegradation of model I.

4. Substituting the cellulose matrix with a glass support would eliminate the formation of coupling moieties occurring between cellulose and the models or the inhibitors. This experiment would provide a better understanding of the mechanism by which the pair Tinuvin P/Tempo operates to hinder condensation reactions.

5.3 REFERENCES

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Appendix

REACTION MECHANISM DEPICTING THE SYNTHESIS OF MDHB





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Figure 4.4: GC% of 1 generated during irradiation in the presence and absence of various inhibitors



Figure 4.5: GC% of 7 generated during irradiation in the presence and absence of various inhibitors

98



Figure 4.6: GC% of 8 generated during irradiation in the presence and absence of various inhibitors



Figure 4.7: GC% of 9 generated during irradiation in the presence and absence of various inhibitors