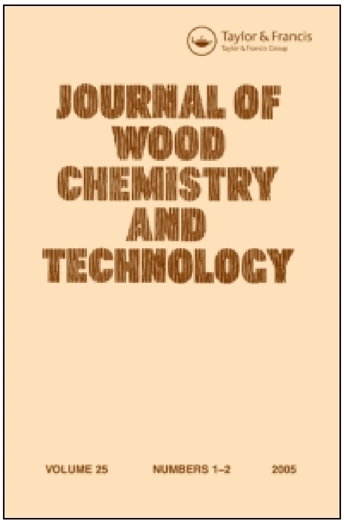

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THERMOMECHANICAL PULP AND LIGHT -PHOTOACTIVITY OF α-CARBONYL GROUP IN SOLID LIGNIN-

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ABSTRACT

Interaction of sunlight and UV light with thermomechanical (TMP) pulps, milled wood lignin (MWL) and various lignin model compounds in solid state was studied. It was found that TMP fibers were sensitive to these lights. During exposure, TMP lost its brightness as a function of irradiation time and increased its yellowness. The α-carbonyl group functioned as a light absorption center to promote photocleavage of C_α-C_β and β-O-4 linkages. Electron spin resonance (ESR) studies demonstrated that free radicals were generated in the interim. Phenoxy radicals appeared to be important radical intermediates that ultimately transformed into o-quinonoid structures.

INTRODUCTION

Rapid development and utilization of thermomechanical (TMP) and chemithermomechanical (CTMP) pulps have attracted considerable attention in the pulp and paper industry in the last twenty years. Much research has been conducted to improve the quality, such as strength and color, of these products. Nonetheless, overcoming discoloration and brightness reversion of TMP and CTMP appear to be a perplexing task. The causes of discoloration and its color stabilization have been extensively studied in the last two decades.[1-3] Due to the nature of the chemical constituents in TMP and CTMP, it is obvious that stabilization of their color is not simple, especially when a high amount of lignin is present. Lignin is a phenolic polymer which manifests light absorbing properties and is sensitive to oxygen. The consequence of the reaction of lignin with light and oxygen is the formation of various chromophores.[4-6] Autoxidation of lignin can also lead to formation of coloring products.[7] Recently, photoinduced discoloration and photodegradation of lignin have been studied extensively.[7-14] Most of the information published is based on photolysis studies of solutions of lignin and lignin compounds, but not based on TMP or solid lignin. In solution, chromophoric or active groups can diffuse together easily and react to produce free radical pairs with high efficiency and participate freely in secondary reactions. In solids, however, diffusion of the active groups is severely constrained. Intermolecular energy transfer is not as efficient as that in the solution. Hence, the tangible photoinduced reaction mechanisms of TMP fiber or lignin may differ considerably from those derived from lignin in solution. Recently Schmidt and his coworkers[15,16] have made observation of light-induced transients in TMP using a diffuse-reflectance laser-flash photolysis technique. Based on their results, the transient was assigned as the lowest energy triplet excited state of a carbonyl chromophore in lignin. They proposed that the carbonyl triplet abstracted hydrogen from the phenolic hydroxyl group, forming a ketyl-phenoxy radical pair. After diffusing away from the ketyl radical, the phenoxy radical was attacked by ground-state oxygen, and led to the formation of colored quinones. In this work, however, no work was done to identify the structures of free radicals. Since lignin readily reacts with light, it is believed that free radical intermediates in TMP are mostly generated in lignin.[5] Small amounts of free radicals may derive from cellulose.[5] Stabilization of these free radicals is likely responsible for the formation of chromophoric groups.[17] Formation of free radicals in lignin solution by light was studied by means of ESR (electron spin resonance) techniques.[9] However, neither well-defined ESR spectra nor detailed free radical structures were determined. In this study, discoloration of TMP, lignin and lignin model compounds in solid state by direct sunlight and artificial ultraviolet (UV) light (λ>300 nm) were studied. Free radicals that were generated in the photoinduced discoloration process were monitored by ESR spectroscopy. Loss of brightness and change in color were also evaluated.

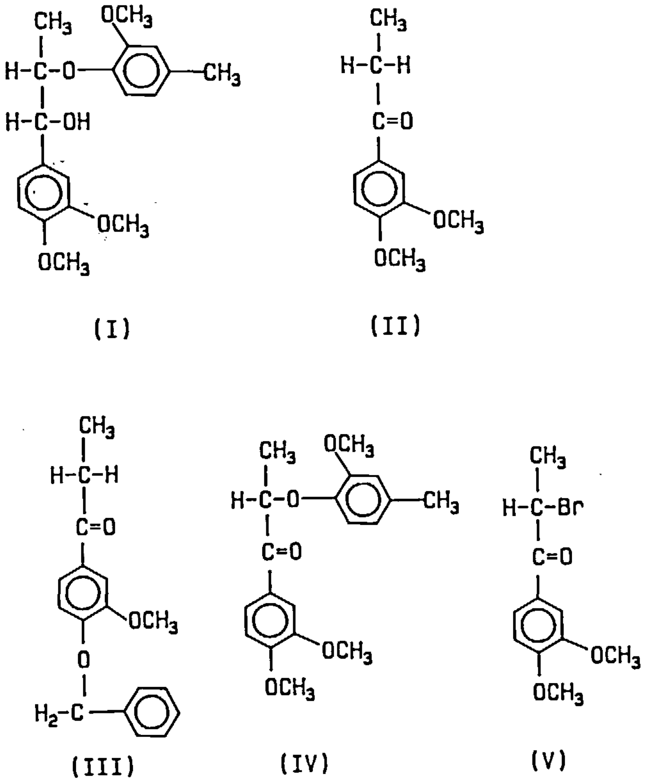
EXPERIMENTAL

Materials

Commercially available unbleached southern pine TMP fibers were used to make handsheets for this study. Bleached TMP was prepared by bleaching it with potassium hypochlorite. Milled wood lignin was prepared based on a modified Bjorkman method.[18,19] Several lignin models were synthesized according to methods described in the literature.[20,21] Their structures are depicted in Figure 1.

Exposure

A high pressure quartz xenon-pact mercury-vapor lamp (ACE-Hanovia, lamp type 6531-12, 200W) with a pyrex window (λ>300 nm) was used for irradiation. Handsheets were either exposed to sunlight outdoors or to UV light from 1 to 96 hrs. The brightness, color and reflectance



(I) (II) (III) (IV) (V)

FIGURE 1. Lignin model compounds used in this study.

spectra were measured by means of a Hunter colorimeter (LabScan II).

ESR Measurement

An electron spin resonance (ESR) spectrometer (Varian E-12) was used to determine free radical structures. TMP handsheets and lignin model compounds were introduced into a high quality quartz ESR sample tube which was then inserted into the ESR cavity.

Samples were irradiated with the UV light for 60 min at 77°K (-196°C). Reactivity of free radicals was monitored by changing temperature of the ESR cavity using a temperature controller.

RESULTS AND DISCUSSION

Effects of Light on Brightness and Reflectance Characteristics

When handsheets of TMP were exposed to the sunlight and UV light, loss of brightness was promptly observed. When the TMP handsheets were exposed to the two exposure systems (i.e., sunlight and UV light), loss of reflectance was observed in the wavelengths ranging from 400 to 700 nm, especially in the range of 400 - 580 nm. This range corresponds to the range of violet - blue - green regions of absorption, which in turn translates into the apparent visible color of yellow - orange - red. Consequently, yellowness/orangeness of the exposed TMP specimens increased sharply. Using unexposed TMP handsheets as the control, the color difference between unexposed and exposed handsheets was also measured. The color difference of sunlight exposed handsheets is shown in Figure 2. It is obvious that a significant change in the color region of 460 - 580 nm took place, indicating that the handsheets were severely yellowed (or browned). A similar magnitude of color change was also observed from handsheets irradiated with the UV light.

ESR Studies

When handsheets were irradiated by UV light at 77°K for 60 minutes and measured at 77°K, a poorly resolved multiplet signal was detected. This signal was transformed into a singlet signal when the sample was kept at 280°K for 1 minute and its ESR signal was measured again at 77°K (Figure 3). This phenomenon

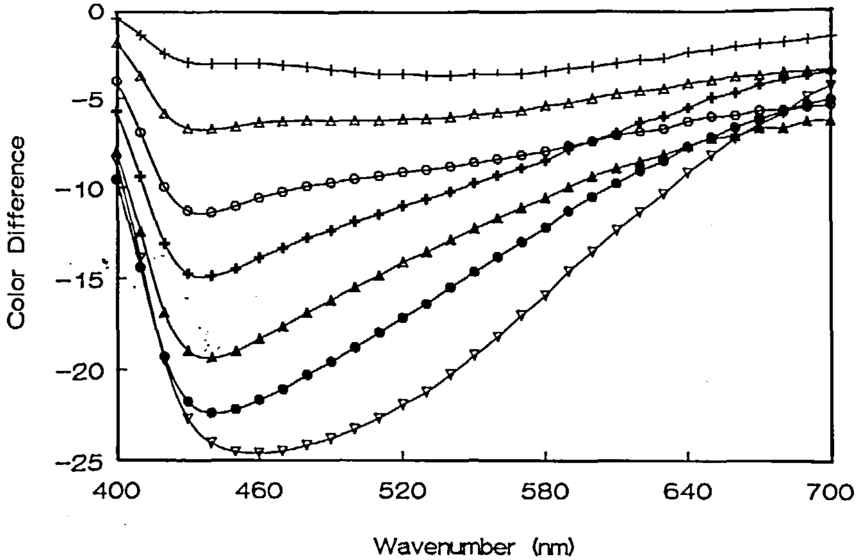


FIGURE 2. Effect of sunlight on the color of thermomechanical handsheets. Irradiation time: (+) 1hr, (△) 3 hrs, (O) 6 hrs, (+) 12 hrs, (▲) 24 hrs, (O) 48 hrs and (▽) 96 hrs.

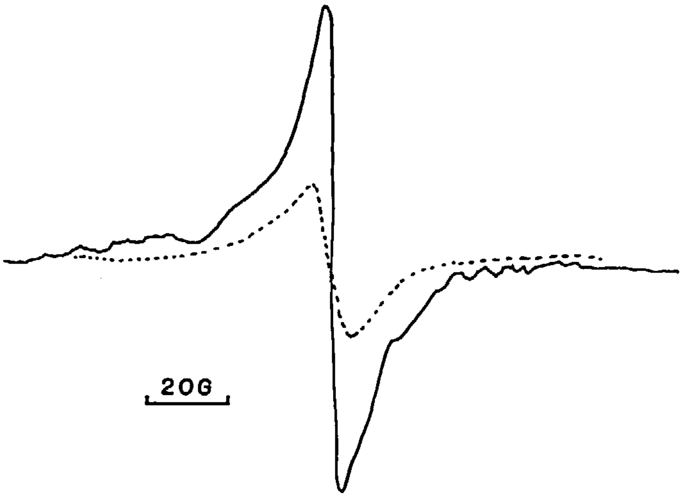


FIGURE 3. ESR spectra of thermomechanical handsheets irradiated with an Ultraviolet light for 60 minutes at 77°K and recorded at 77°K. Dotted line was detected after the irradiated samples were warmed to 280°K for 1 minute and recorded again at 77°K.

suggested that labile free radicals, which contributed to the unstable ESR signals generated in the TMP handsheets, were decayed rapidly at 280°K, and only stable radicals which contributed to the singlet signal were detected. Bleached TMP handsheets and milled wood lignin (MWL) were also photoirradiated under identical conditions. From bleached TMP fibers, a very weak singlet signal was detected, indicating that small amounts of free radicals were generated in cellulose.[5] For MWL, a spectrum with discernible multiplet signals was detected (Figure 4). This suggested that ligninic free radicals are predominantly formed in the exposed TMP surface. Since most of the free radicals and color of TMP were generated in lignin,[3,4,22,23] free radical formation in solid lignin was further scrutinized.

Due to the complexity of lignin structure, it is suspected that various types of free radicals can be generated and contribute to a complex ESR profile (see Figure 4) which is very difficult to interpret. Based on the lignin chromophoric systems which are likely to trigger photoinduced discoloration reactions, several lignin model compounds were synthesized (see Figure 1). They were exposed to UV light and the structures as well as the fate of free radicals generated were studied.

When the model compound (I), a dimer, was irradiated at 77°K, only a diffuse and very weak five-line signal was detected. When the irradiated compound (I) was then warmed to 280°K for 1 minute and recorded again at 77°K, only a singlet signal with a line-width of 16 gauss and a g-value of 2.003 was obtained. Since the line-value and the g-value are identical to that of the phenoxy radical, it is quite obvious that a ß-O-4 ether bond was cleaved (Scheme 1). The radical pair generated at the $C_ß$ position was unstable, they decayed rapidly at 280°K. As the intensity of the signal of compound (I) was weak, it is believed that the dimer with a benzylic alcohol group

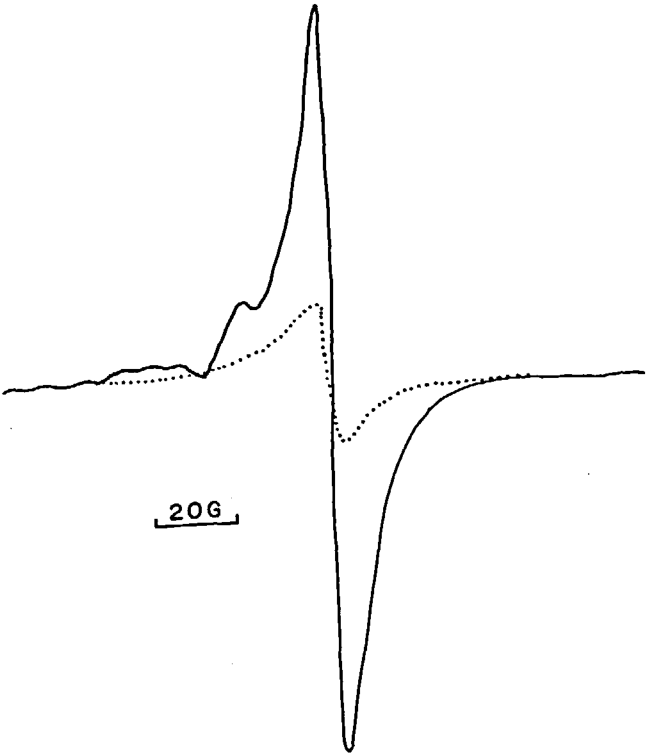
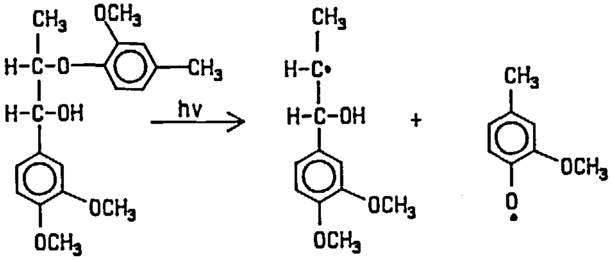


FIGURE 4. ESR spectra of milled wood lignin irradiated with an Ultraviolet light for 60 minutes at 77°K and recorded at 77°K. Dotted line was detected after the irradiated samples were warmed to 280°K for 1 minute and recorded again at 77°K.



(Scheme 1)

in the α position and a ß-aryl-ether was not effectively degraded by light.

It is known that lignin contains about $0.06/OCH_3$ carbonyl groups.[24] These groups may have been formed by various uncontrolled reactions during the biosynthesis or the isolation of lignin.[4,25] The presence of carbonyl groups in lignin seems to play an important role in photodegradation of lignin, as reported extensively in the literature.[1,4,11,22] It has been proposed that the α-carbonyl group was brought to an excited state after absorption of light, which in turn abstracted a hydrogen from the phenol group to generate a phenoxy radical.[9]. The phenoxy radical reacted with oxygen to form coloring products such as quinone.[14] It has also been speculated that the excited carbonyl group transferred its energy to molecular oxygen to produce singlet oxygen, which oxidized a phenol group to one of the yellow chromophoric groups.[26-28]. However, a recent report by Forsskahl and her coworkers[29] claimed that singlet oxygen, generated by microwave discharge, did not discolor stone groundwood or CTMP. Contrarily, they observed a slight bleaching effect due to the singlet oxygen. This discrepancy may be due to the difference in reaction media, i.e., in solution versus in solid. A majority of the mechanisms proposed for lignin discoloration, however, was deduced from the degradation end-products of lignin (model compounds) in solution. The effect of solvent on the energy transfer as well as its participation in the photochemical reactions were not considered. Consequently, the photochemical reactions of lignin and lignin model compounds in solid state and in TMP fiber may differ considerably from those in solution. Moreover, neither intermediate transient species nor the formation of free radicals as the consequence of light absorption by carbonyl groups nor the stabilization of these free radicals that leads to formation of color were

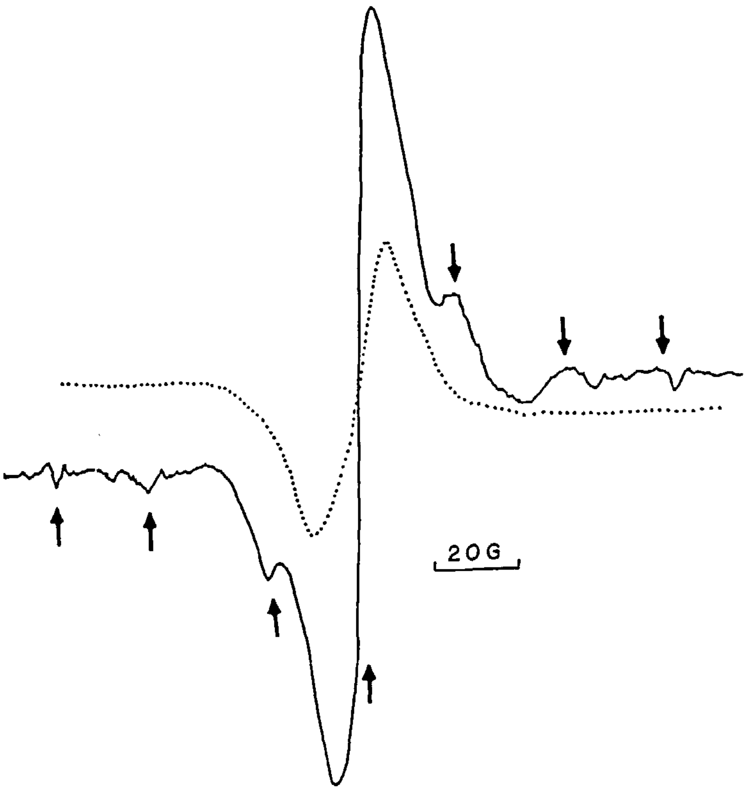
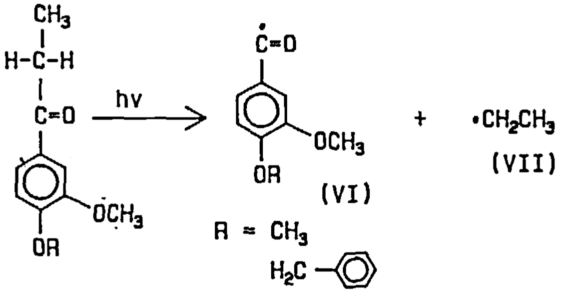


FIGURE 5. ESR spectra of model compound (II) irradiated with an Ultraviolet light for 60 minutes at 77°K and recorded at 77°K. Dotted line was detected after the irradiated samples were warmed to 280°K for 1 minute and recorded again at 77°K.

considered. In order to obtain precise information on free radicals generated in TMP fibers, lignin model compounds with α-carbonyl groups were exposed to UV light in solid state.

The ESR spectrum of compound (II) was detected at 77°K after irradiation for 60 minutes at 77°K, as shown in Figure 5. A poorly resolved seven-line signal was detected. A similar ESR signal with stronger intensity



(Scheme 2)

was observed from compound (III). Since the intensity ratio of the seven-line signal is not the expected ratio for interaction of an electron with six equivalent protons, it is believed that the spectrum detected was not due to a single signal originating from a single radical species. It is more likely a superposition of several signals which derived from several radical species. When the sample was warmed to 280°K for 1 minute, the multiplet signal was transformed into a singlet signal with a line-width of 11 gauss. The g-value was 2.006.

It is known that carbon-carbon bonds adjacent to carbonyl groups are prone to dissociate in photochemical reactions. This reaction is referred to as the Norrish type I reaction.[26] Accordingly, the model compounds (II) and (III) plausibly underwent this type of reaction: the cleavage of C_α-C_β linkage (Scheme 2). In this dissociation, ethyl radicals (VII) would give rise to a six-line spectrum, where acyl (benzoyl) radicals (VI) would give rise to a singlet spectrum. Irradiation of benzyl chloride gave rise to a singlet signal ($\Delta H = 10G$) with a g-value of 2.006, which substantiated the dissociation mechanism. This is anticipated because the carbon halogen bond is readily cleaved by light. When benzyl chloride was irradiated, C-Cl bonds were cleaved and benzoyl radicals were produced. The g-value of benzoyl radicals observed is in agreement with the literature value.[30] Blocking of a phenolic hydroxy group with a bulky group appeared to promote cleavage of C_α-C_β bond. High intensity of the latter implies higher free radical concentration and higher frequency of cleavage. A similar effect was also observed by Schmidt et al.[34] who studied the transient species in TMP pulp using diffuse-reflectance laser-flash photolysis.

ß-O-4 aryl ether adjacent to α-carbonyl groups exhibited different photoactivity. When model compound (IV) was irradiated at 77°K, a prominent five line spectrum was observed as shown in Figure 6. When the sample irradiated was warmed to 298°K for 1 minute and recorded again at 77°K, the five-line spectrum transformed into a singlet signal with a line-width of 15 gauss, and a g-value of 2.003. Since the g-value was lower than that of benzoyl radicals (g = 2.006), and matched the value of phenoxy radicals (g = 2.003), the Norrish type I reaction apparently did not occur in these compounds. Instead, ß-O-4 aryl ether bond was cleaved (Scheme 3). In pursuance to clarifying the reaction mechanism, a different model compound (V) was irradiated under the identical conditions described above. An analogous prominent five-line spectrum was observed. However, when this sample was subsequently warmed to 298°K for 3 minutes and recorded again at 77°K, all signals disappeared. Apparently the five-line signals were derived from free radicals at the C_β due to the cleavage of the C-Br bonds. From these findings, it is evident that the singlet signal from compound (IV) was derived from the phenoxy radical due to the cleavage of the ether bond at the ß-O-4 position, as shown in Scheme 3. The radical pair (C_β, VIII) simultaneously formed was attributed to the five-line component of the spectrum.

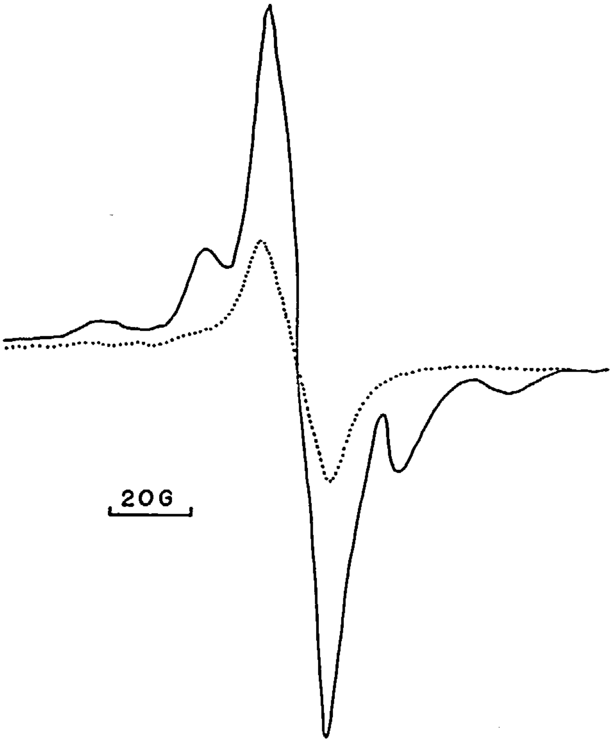
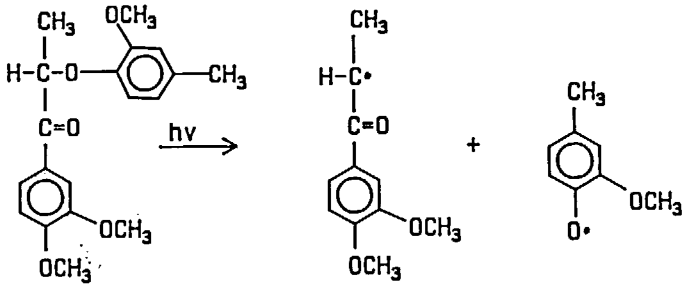


FIGURE 6. ESR spectra of model compound (IV) irradiated with an Ultraviolet light for 60 minutes at 77°K and recorded at 77°K. Dotted line was detected after the irradiated samples were warmed to 280°K for 1 minute and recorded again at 77°K.

Since no aryl-ß-ether bonds were present in compound (V), no phenoxy radicals were detected from it. In comparing the ESR spectra of compound (I) and Compound (IV), the intensity of the former is only 22% of the latter. It would appear that a compound bearing a benzylic hydroxyl group, rather than a α-carbonyl group, has not responded to light effectively.



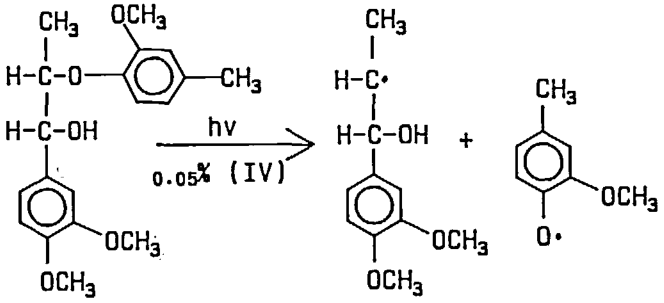
(VIII)

(Scheme 3)

The work of Schmidt and his coworkers[15,16] postulated that carbonyl groups in the triplet excited state that are close to a phenolic hydroxyl groups are likely to be quenched through abstraction of the phenolic hydrogen to produce a ketyl-phenoxy free-radical pair. They also suggested that carbonyl triplets distant from phenolic hydroxyls must be deactivated by a different mechanism. From this study it is evident that the excited carbonyl group is deactivated by energy migration that lead to the cleavage of ß-O-4. No hydrogen abstraction by carbonyl group is necessary.

When 0.05% (w/w) of compound (IV) was mixed with compound (I) and irradiated with light at 77°K, a prominent five-line spectrum was observed. This indicated that the ether linkage of compound (I) was cleaved. This fact suggested that compound (IV) functioned as a photosensitizer and accelerated the photochemical degradation of ß-O-4 linkage (Scheme 4). Brunow and Erikksson[31] also observed that acetoguaiacone that contains α-carbonyl groups was able to sensitize the photodecomposition of phenolic structural units with a saturated side chain.

It is known that phenoxy radicals are readily generated in phenolic hydroxy groups in the presence of



(Scheme 4)

UV light. In addition, the cleavage of ß-O-4 linkages also led to the generation of phenoxy radicals. Stabilization of phenoxy radicals frequently led to the formation of o-quinone.[14] One of the plausible mechanisms is via demethylation.[5] The presence of o-quinonoid structures in yellowed pulp has been confirmed.[32]

CONCLUSIONS

TMP pulps are sensitive to sunlight and UV light. During exposure to either sunlight or UV light, TMP lost its brightness as a function of irradiation time. Color difference studies revealed an increase in yellowness.

Photodegradation mechanisms deduced from this study may have been different from those of earlier studies which were deduced from the degradation products of lignin in solution. ESR studies of TMP, bleached TMP, MWL and various lignin compounds in solid state showed that free radicals were generated. C_α-C_β bonds adjacent to α-carbonyl groups were photodissociated via the Norrish Type I reaction. This reaction did not occur efficiently in those structures with ether bonds adjacent to the α-carbonyl group, i.e., ß-O-4. Energy transfer from a carbonyl group facilitated photodissociation at the ether bond. Blocking of phenolic hydroxy groups with bulky groups appeared to promote photoactivity. Compounds bearing benzylic alcohol groups at C_α did not respond to photoreaction effectively except when other units with α-carbonyl groups or other photosensitizers were also present.

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