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**AN ESR AND TIME-RESOLVED CIDEP STUDY OF  
THE LIGHT-INDUCED YELLOWING PROCESSES OF TMP PAPER**

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ABSTRACT

Integral ESR and time-resolved CIDEP techniques applied to the study of the light-induced yellowing of bleached and unbleached TMP samples provide some further insights into the nature and the mechanisms of the processes. The identity of the phenoxy and ketyl free radical intermediates involved in these processes is established and the primary triplet photochemical mechanisms of their formation are characterized. The radical scavenging mechanisms responsible for the inhibition of light-induced yellowing in the TMP system by ascorbic acid and triphenylmethyl thiol are formulated.

INTRODUCTION

In recent years the problems of light-induced yellowing of mechanical pulps have stimulated much interest in the fundamental study of the photochemistry of model lignin compounds and TMP samples. Historically, free radical intermediates have long been implicated in the mechanisms of the light-induced yellowing of paper<sup>1-3</sup>. More specifically, light-induced yellowing of thermomechanical pulp (TMP) is largely attributed to the photochemical reactions of the lignin macromolecules to generate free radicals, such as the methoxy substituted phenoxy radicals<sup>4-6</sup>. Because of the considerable experimental

difficulties dealing with a variety of paper samples, direct and unambiguous spectroscopic characterization of these presumed phenoxy radicals in the paper matrix remains illusive. In the present study we approach this monumental problem by combining both a conventional ESR technique and the customized time-resolved chemically induced dynamic electron polarization (CIDEP) method in order to provide further insights into the photochemical radical processes. We firmly believe that no one single physical or chemical technique, no matter how powerful, is able to resolve such a complex problem. We do hope that our results will bring cross fertilization to other studies with different techniques and emphases.

Electron spin resonance (ESR) when appropriately applied is one of the more convenient and most informative techniques in the direct observations of free radicals in chemical processes in both thermal and photochemical systems. On the other hand, the time-resolved CIDEP technique as applied here is only suitable for gated, pulsed, or flash photolytic studies. An integral approach involving simultaneous operations of both conventional ESR (at 100 kHz modulation) and time-resolved CIDEP (DC detection) has the advantage of being able to sort out the transient polarized radicals formed immediately upon laser excitation from either the background signals or the thermalized radicals produced in the dark. In order to improve the time resolution and the spectral sensitivity of the CIDEP experiments, one normally employs a high-power short-duration pulse laser as the light source. This may lead to double-photon phenomena and other unusual optical conditions which are not typical of common photolysis systems employing conventional light source, including the sun. A more serious implication is that when such a high density of energy is instantly deposited within a very small reaction zone, the transient temperature in this zone may be substantially increased from the ambient conditions. This condition in turn will affect all thermal activation parameters for both primary and secondary reactions within the zone and in the case of paper samples, even the diffusional or other

molecular dynamic properties of the radicals produced in the zone. One does need to exercise caution when comparing results from laser experiments with the observations of light-induced yellowing over a long period of time.

The theories behind the CIDEP techniques are rather sophisticated and mainly deal with fluid systems. It was exactly 20 years ago when we first discovered the phototriplet mechanisms in solution CIDEP systems<sup>7</sup>. Together with the preceding elegant Radical-Pair theory an overall understanding of the CIDEP phenomena in photochemical systems emerged and today time-resolved CIDEP is a popular and convenient tool for photophysical and photochemical studies<sup>8,9</sup>. In the phototriplet CIDEP mechanism the electron polarization of the triplet is initially evolved from the symmetry-governed intersystem crossing between the excited singlet and the sublevels of the triplet. While the polarized triplet is not observable in liquid solution due to relaxation and anisotropy, it is sometimes possible to detect CIDEP of triplets directly in suitable solid solution or crystals at low temperature. For example, we have recently reported the CIDEP spectra of the polarized triplet of  $\alpha$ -guaiacoxylacetoveratrone (GAV) at 77 K<sup>10</sup> and its zero-field splitting parameters are consistent with its lowest triplet state being mainly  $\pi, \pi^*$  in character. Furthermore, indirect evidence of the  $\beta$ -ether cleavage from the singlet excited state of GAV was obtained in low temperature photolysis. For the present paper system which hardly contains any degree of crystallinity, we have not yet been successful in a direct characterization of excited triplets of the macro lignin molecules.

It is noteworthy that our recent studies<sup>10</sup> also show when the carbonyl group in GAV was fully reduced, similar free radical reactions still led to formation of phenols which can subsequently be oxidized to color compounds. Thus, it is important to recognize that aromatic carbonyl groups are not the only precursor to induce the yellowing processes. In the present study, however, we shall focus our attention mainly on the yellowing processes occurring in the presence of GAV.

Aromatic carbonyl compounds generally give an emissively (E) polarized triplet state following intersystem crossing. Before the electron polarization decays via spin-lattice relaxation (usually within  $10^{-7}$  s), the triplet may react to produce a pair of primary radicals which will both be emissively (E) polarized in a manner that all their hyperfine lines are single phased<sup>8</sup>. This conservation of spin memory in the phototriplet reactions renders a powerful, unambiguous finger-printing of the primary triplet reaction mechanism. Obviously, radicals produced by excited singlet state reactions can not lead to radicals with totally emissive polarization. On the other hand, both singlet and triplet reactions leading to radicals can be dealt with by the radical-pair mechanism<sup>8</sup>. Here it is not required that the radicals contain any initial polarization at birth. In most cases simple rules dealing with the most common S-T<sub>0</sub> mixing mechanism of the radical-pair theory provide convenient accounting of radical-pair polarization for geminate pairs (spin correlated pair such as those produced by singlet reactions) and for random pairs (such as pairs produced by triplet reactions). Symmetrical E/A hyperfine pattern (low-field hyperfine lines in emission and high-field lines in enhanced absorption) is exhibited for radicals with triplet precursors and the opposite A/E pattern is displayed for the radicals with singlet precursors. Since the radical-pair theory is developed based on a diffusion model in fluid media, such polarization mechanism will not be efficient in the solid paper matrix as radical diffusion would be greatly restricted. Nevertheless, due to the unusual thermal effect within the reaction zone in laser experiments as mentioned above, limited diffusion of smaller radicals may indeed be possible but not highly probable. Thus, the current CIDEP observations on TMP paper systems are more restricted to triplet reactions and the results are much simpler to interpret. The important advantage of our experiments in observing separately but simultaneously photogenerated phenoxy radicals and any thermally generated and background phenoxy radicals remains a powerful tool in the mechanistic formulation of the radical processes in these systems. Indeed, the present CIDEP

results of a totally emissive (E) phenoxy radical in TMP paper represents a first time observation of polarized radicals derived from the triplet mechanism in a room temperature solid matrix and the results in turn establish the triplet photochemical reactions in pulps.

An important aspect of experimental information, the hyperfine structure of radicals, eluded the paper studies since the small hyperfine splittings of phenoxy radicals are not resolved in such matrices. However, identification of the free radical intermediates is made possible by a comparison of model systems in which known chemicals, including various phenols, are impregnated into the paper matrix and subsequently photolyzed to generate the radicals accordingly.

In the same manner various standard radical scavengers such as ascorbic acid were introduced into the TMP paper matrix and the overall reactions are monitored both with respect to the free radical intermediates and the production of the yellow chromophores.

### EXPERIMENTAL

Black Spruce (*picea mariana*) thermomechanical pulp was washed and chelated with a 0.2% charge of DTPA at 1% consistency at 65 °C for 1 hour, dewatered to 25% consistency and bleached with a 4% charge of alkaline hydrogen peroxide at 60 °C for 2 hours at 20% consistency to give a pulp with an ISO brightness of 75%. Other characteristics of the pulp and the paper samples used in the experiments have been reported in previous studies<sup>11</sup>.

Whatman number 1 filter paper which alone does not give any photo-generated ESR or CIDEP signal when tested in this laboratory, was used as a host paper matrix for the deposition of various phenols. For standard comparative studies, photolysis of these samples led to the observations of the expected, corresponding phenoxy radicals in the paper matrix. The paper samples were cut

into strips of standard size of 0.5 cm x 3 cm and were mounted onto a pyrex plate for ESR measurements. In other series of experiments, paper samples were impregnated with selected lignin model compounds by soaking overnight in their saturated solutions (in ethanol or in 1:1 ethanol/water). The treated paper samples were rinsed with the solvent to remove any surface deposits and then vacuum dried. In a similar manner, acetonitrile solutions containing 200 mg of ascorbic acid and/or thiols were used to introduce these antioxidants into the paper matrix.

ESR and time-resolved CIDEP spectra of the paper samples were recorded by a modified Varian E104 X-band ESR spectrometer which has been described earlier<sup>12</sup>. Irradiation of the paper samples was carried out using either a Lambda Physik EMG-101 excimer laser (308 nm, 150 mJ, 10 ns) or a super high pressure 200 W mercury lamp with a pyrex filter.

## RESULTS AND DISCUSSION

### Standard-Control Experiments with TMP Paper

Both the bleached and unbleached TMP paper are found to contain small amounts of radicals ( $g=2.0039$ ) which can be detected by ESR (Figure 1a). In general, the unbleached TMP samples showed a relatively stronger ESR signal. Upon photolysis, the ESR signal grew in magnitude in both cases (Figure 1b). These ESR signals were broad and unresolved in both cases. The  $g$ -factor of these signals is consistent with an assignment to organic phenoxy radicals. In order to confirm the assignment, a comparison was made of several standard substituted phenoxy radicals<sup>13</sup> generated by UV irradiation of various phenol-impregnated filter papers. It provides further identification of TMP radicals (Figure 1c). It is now possible to conclude that the background ESR signals in TMP paper are likely due to residue- substituted-phenoxy radicals. These

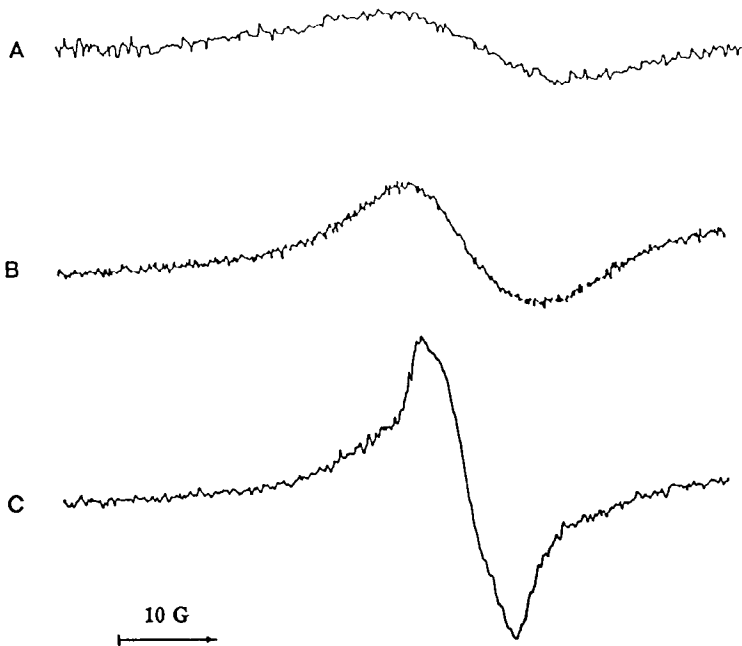


FIGURE 1 ESR spectra of : a) Residue-phenoxy radical signal in unbleached TMP paper samples. b) Signal in unbleached TMP paper after 2 hrs. UV-irradiation with the Hg lamp. c) Signal observed after 2 hrs. UV-irradiation of filter paper sample impregnated with 2,4,6- tri-*t*-butyl phenol.

residue-phenoxy radicals were probably formed and survived through the pulping and paper-making processes. With some caution the results may also suggest that the bleaching processes seem to reduce the content of residue-phenoxy radicals in TMP. Although ESR signal intensities have routinely been related to "radical concentrations", it is noteworthy to point out that ESR measures **only** the number of spins and **not** concentrations. For meaningful comparisons of relatively signal intensities it is necessary to take into account the sizes of the paper samples and the exact positioning of the samples in the ESR cavity.

As far as we are able to determine, the TMP background ESR signals do not change significantly in the dark with age. This fact implies that the residue-



phenoxy radicals in both bleached and unbleached TMP samples are "stabilized" within the paper matrices. The better characterization is that these radicals are persistent in the paper environment, mainly because of kinetic reasons as they are severely limited in diffusion or translational motions. This situation will be drastically changed if the matrix/environment is softened either by localized heating such as high-power laser irradiation, or by localized excitation of the phenoxy radicals. Phenoxy radicals are known to absorb light of wavelength above 300 nm and we have always been aware of the possibility of excitation of these persistent phenoxy radicals when paper is exposed to room light. At this time we do not know the spatial distributions of these radicals in the paper samples but we are working hard on a suitable physical technique which is capable of mapping phenoxy radicals over the sample areas.

### Photolysis of TMP Paper

Upon UV photolysis, both the bleached and unbleached paper samples rapidly yellowed with a concurrent large increase in ESR intensity. Since conventional ESR can not distinguish between the thermalized phenoxy radicals from those freshly formed by UV irradiation, integral simultaneous ESR and time-resolved CIDEP experiments<sup>9,12</sup> were performed to characterize the polarized, photogenerated radicals in the presence of thermalized radicals, detected concurrently. It must be emphasized that these experiments employed the excimer laser as the light source and again caution must be exercised when compared with conventional photolysis studies. Figure 2a shows a typical time-resolved CIDEP spectrum observed for the bleached TMP paper. The totally emissive (E) phenoxy signal can only be formed via a phototriplet mechanism<sup>9</sup> and it therefore contained the finger-prints of a phototriplet reaction. We should point out that photochemically generated phenoxy radicals via an excited singlet mechanism would not have been detected under the present experimental

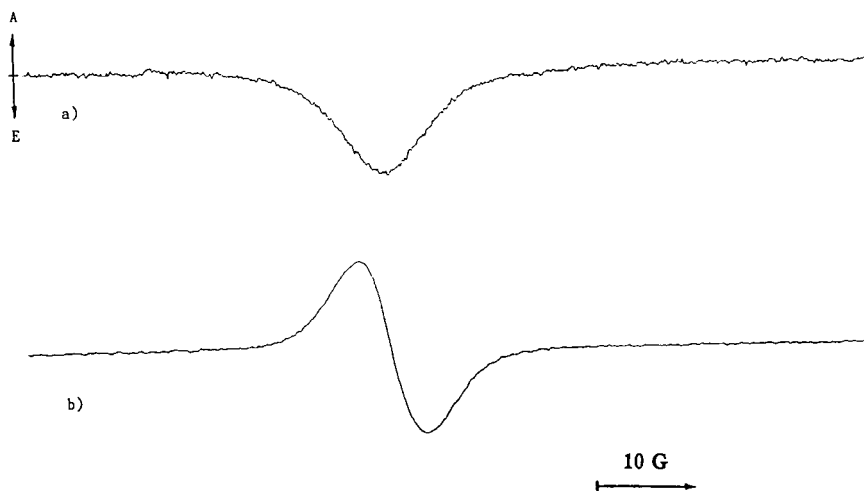
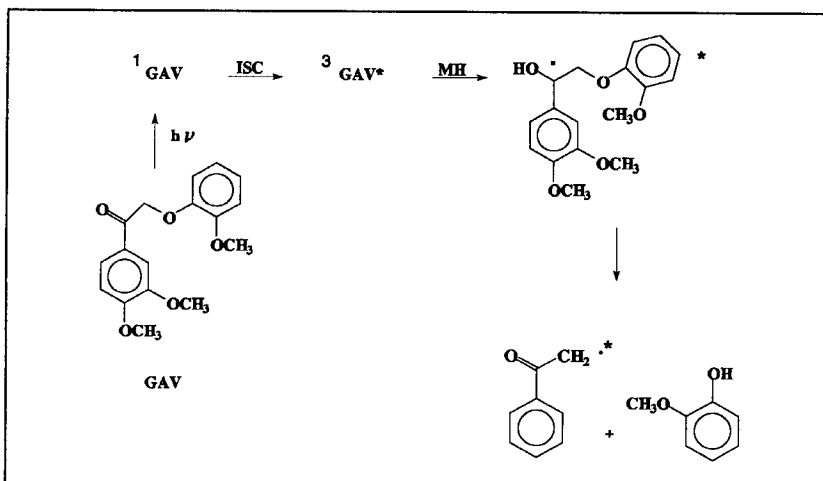


FIGURE 2 Simultaneous measurements of time-resolved CIDEP and ESR of bleached TMP paper. a) CIDEP spectrum at  $2 \mu\text{s}$  after the laser pulse. b) First derivative 100 kHz modulated ESR spectrum.

conditions. Therefore, the CIDEP signal intensities can not be taken as the **total** amount of phenoxy radicals formed within the laser pulse. The 100 kHz modulated ESR spectrum of the simultaneously detected thermalized radicals, including the residue-phenoxy signal, is shown in Figure 2b. It should be noted that the CIDEP signal intensity can not be directly compared or related to the thermal signal but the CIDEP results unequivocally establish the role of an organic excited triplet in the formation of phenoxy radicals in bleached TMP paper. The strongly emissive character of the polarization indicate that the chromophore is very likely an aromatic **carbonyl** moiety of the lignin. In the absence of aromatic carbonyl chromophores such as a filter paper sample impregnated with phenols, laser photolysis did not give any CIDEP signals. In solution studies, there is now a growing recognition<sup>3,14</sup> that for carbonyl compounds such as GAV, the direct participation of the excited singlet state in the photodecomposition leading to formation of phenoxy radical, is also important.

### Photolysis of GAV in Paper Matrix

In recent years, much attention has been focused on the photochemistry of GAV in liquid solutions<sup>14-16</sup> which provide a wealth of valuable information of this particular model lignin. We thought that it would be interesting and informative to study the photochemical reactions of GAV in a paper matrix. Our initial experiments began with standard filter paper for an important reason. We have found that the filter paper samples available in our laboratory show no background ESR signals and they do not produce any appreciable ESR signal nor any degree of yellowing upon photolysis. However, when the filter paper samples were impregnated with GAV, laser photolysis at 308 nm results in the formation of a faint yellow spot. Typical simultaneous ESR and time-resolved CIDEP spectra recorded during the laser photolysis are given in Figure 3. In a previous solution CIDEP study of GAV in various hydroxylic solvents<sup>15</sup> we have shown that the primary GAV triplet reaction is the photoreduction forming polarized ketyl radicals. Subsequent rapid rearrangement of the polarized ketyl radicals by cleavage of the ether link leads to polarized phenacyl radicals and phenol as summarized in the following scheme:



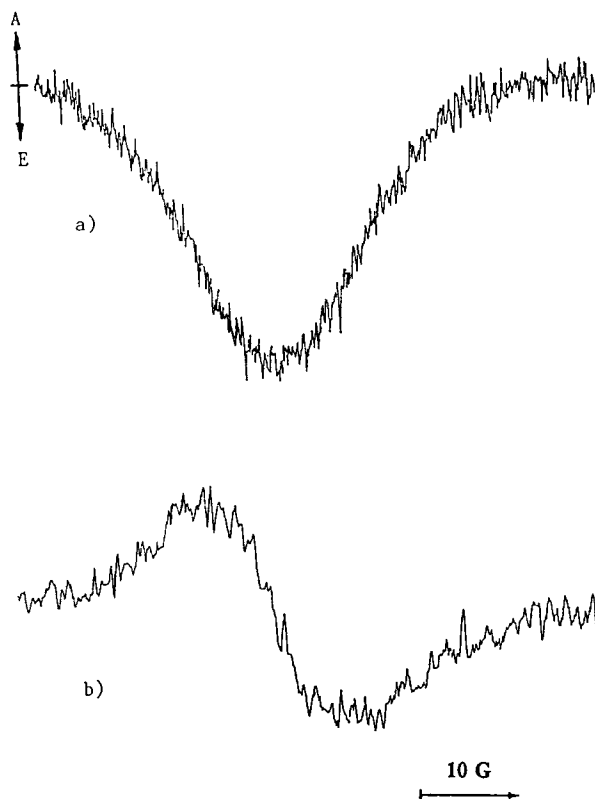


FIGURE 3 Simultaneous measurements of time-resolved CIDEP and ESR of GAV in filter paper. a) CIDEP spectrum at  $2.5 \mu\text{s}$  after the laser pulse. b) First derivative 100 kHz modulated ESR spectrum.

Secondary photochemical reactions of GAV with phenol then produce polarized (designated by a \*) phenoxy radicals. Since the impregnation of GAV into the filter paper sample used an alcoholic solvent, it is inevitable that the matrix would contain some residue packets of solvent molecules and therefore photoreduction of GAV in this experiment is a distinct possibility. It was also pointed out to us by a referee that a distribution in the paper of at least three types of species is expected. These include the monomer + cellulose type; the

monomer + solvent type; and the clusters of monomer type. The interpretation of the CIDEP results in such a complex system encounters further difficulty because of the unresolved spectra. All three types of polarized radicals, the ketyl, the phenacyl, and the phenoxy have similar  $g$ -factors and the broad spectra prevent any absolute identification of the polarized species. As well, the kinetic parameters of all secondary reactions will be very different between liquid and paper systems, particularly among the many types of environments for the impregnated species. Based on our experience with the better resolved solution spectra<sup>15</sup>, it appears that the polarized spectrum in Figure is a better fit for either the ketyl or the phenoxy radical or both, since the superimposition of a phenacyl radical would make a more asymmetric composite spectrum of greater width due to the large hyperfine interaction from the methylene protons. If we assign the polarized spectrum to the primary ketyl radical only, it means that the rearrangement by  $\beta$ -ether cleavage is either absent or it occurs slower than the spin-lattice relaxation rate of the ketyl radical. It is interesting to speculate how such a rearrangement depends upon the molecular flexibility (motions) which might be more limited for the ketyl radical in a solid matrix. We have thus carried out a separate experiment with a frozen alcoholic solution of GAV at 140 °K. The CIDEP observation in this case showed also only a broad structureless spectrum, similar to Figure 3a.

Next, we consider the formation of polarized phenoxy radicals. The direct cleavage of a polarized triplet GAV to phenacyl and phenoxy radicals is unlikely<sup>10</sup>. Two possible routes can be proposed to account for the formation of polarized phenoxy radicals in paper matrix. In the first case the rearrangement of the ketyl radicals actually proceeds in the paper matrix (particularly in the monomer + solvent type of environment) but with a slower rate to produce thermalized phenacyl radicals and molecular phenol. Further reactions of the phototriplet GAV with phenol in the reaction zone would lead to polarized phenoxy radicals and reinitiate the chain reactions. The second possibility is that excited singlet states of GAV directly undergo  $\beta$ -cleavage<sup>14,17</sup> to yield thermalized

phenoxy and phenacyl radicals, followed by polarization transfer from the triplet GAV to the persistent phenoxy radicals in the vicinity. Such a triplet-doublet polarization transfer has been proposed by Obi and coworkers<sup>18</sup>.

In the absence of high resolution CIDEP spectra we are not able to make a definitive interpretation of the CIDEP results in the GAV-filter paper system. Our educated opinion tends toward the middle ground in which both the ketyl and the phenoxy radicals are superimposed in the CIDEP spectrum. This case also illustrates the point that it is much "easier" to start with a well-defined or controlled model system (such as liquid solution) in basic studies than with a real system which is often fraught with uncontrollable implications.

#### Effects of Ascorbic Acid in the Photolysis of TMP Paper

As we are now aware of the fact that there are several routes to the light-induced yellowing of TMP paper, involving chromophores other than aromatic carbonyls<sup>3</sup>, we still believe that the the major part of the photooxidative yellowing processes involve free radical intermediates. Recently, we have demonstrated<sup>19</sup> that in the photooxidation of methoxyphenols, molecular oxygen is not the active reactant. Rather, molecular oxygen is necessary to produce peroxy and alkoxy radicals, RO· and ROO·, which then add onto the phenyl ring to initiate the oxidation processes. The precursor radical R can be derived from many ways via both photochemical and thermal or thermo-mechanical processes. We have therefore directed our attention to the use of established antioxidants/radical scavengers in paper matrix studies.

Ascorbic acid (H<sub>2</sub>A) has long been recognized for its antioxidant activity in many biological systems<sup>20-21</sup> and for its potential ability to inhibit light-induced yellowing of bleached TMP paper<sup>11</sup>. The antioxidant property has been attributed mainly to its ability to scavenge reactive radicals such as peroxy radicals, usually involved in the oxidative chemical processes. In this series of experiments both

bleached and unbleached TMP paper were treated with a saturated solution of ascorbic acid in a 1:1 ethanol/water mixture. Surprisingly, this simple treatment in the dark results in the formation and ESR observation of persistent ascorbyl radical anions ( $\text{HA}^{\cdot-}$ ) in the paper matrix. The ascorbyl radical signal intensity is directly proportional to the ESR signal of residual-phenoxy radicals in the TMP samples before treatment. Bleached and unbleached TMP samples which have been previously UV irradiated to enhance the phenoxy radical signals exhibit correspondingly a higher ascorbyl radical signal intensity upon treatment. The ability of ascorbic acid to quench phenoxy radicals in liquid solutions is anticipated and indeed has been demonstrated for the persistent 2,6-di-*tert*-butyl-4-methyl phenoxy or the 2,4,6-tri-*tert*-butyl phenoxy radicals by ESR studies<sup>22</sup>, although the corresponding ascorbyl radicals are not persistent in liquid solution at room temperature. The present observations show that our method of impregnation of ascorbic acid into TMP paper matrices works rather well. A typical ESR spectrum of the previously UV-irradiated bleached TMP paper after being treated with ascorbic acid is given in Figure 4b. The asymmetry of the spectrum is due to the superimposition of the ascorbyl radicals (the sharper component) and the broader residue-phenoxy radicals, with the ascorbyl radicals having a slightly larger *g*-factor of 2.0051. It is important to note that the same treatment of filter paper in the dark did not produce any ESR signals.

The scavenging reaction thus occurred between ascorbic acid and residue-phenoxy radicals in the TMP paper matrix is a thermal process and can proceed in the absence of light. The bonus observation here is that the resulting ascorbyl radicals are persistent in the paper matrix for direct characterization. This is an unambiguous confirmation of the radical-scavenging process.

The impregnation technique was further examined by flowing an alcoholic solution of ascorbic acid over a previously irradiated bleached TMP paper sample positioned in the ESR cavity. The quenching of the resident-phenoxy radicals in the sample and the corresponding formation of the ascorbyl radical was found to be a slow process over a period of an hour. In this case the rate-controlling step

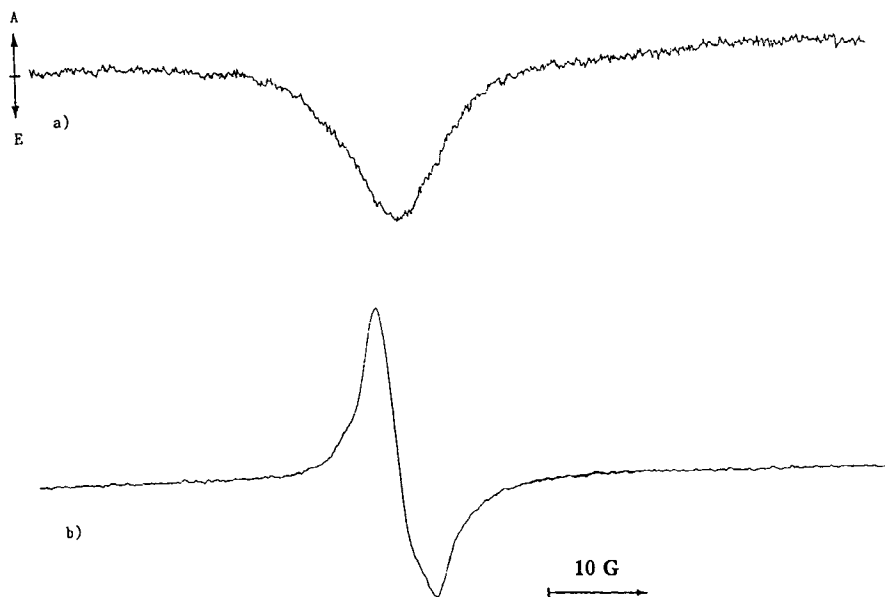


FIGURE 4 Simultaneous measurements of time-resolved CIDEP and ESR of bleached TMP paper treated with ascorbic acid. a) CIDEP spectrum at  $2 \mu\text{s}$  after the laser pulse. b) First derivative 100 kHz modulated ESR spectrum.

is no doubt the very slow diffusion processes (impregnation) of the ascorbic acid into the paper matrix. However, irradiation of the whole system with UV light results in a rapid increase in the ascorbyl radical signal. It is possible that UV irradiation may have produced phenoxy radicals mainly near the surface of the paper and much less time was therefore required for the ascorbic acid to reach the photogenerated radicals near the surface. On the other hand, it is also possible that the ascorbic acid in both the solution phase and paper matrix was photolyzed to yield the corresponding radicals. Indeed, in a separate series of experiments using filter paper impregnated with ascorbic acid, photolysis of the samples clearly produced ESR signals due to the ascorbic radicals.

To understand the nature of the photochemical reactions occurring near the paper surface, a bleached TMP paper sample was exposed to light of different



Table 1. Relative Increase of Ascorbyl Radical ESR Signal in Bleached TMP Paper as a Function of Irradiation Wavelengths.

Irradiation Wavelength (nm)	% Increase in Ascorbyl Radical Signal Intensity $\pm 5\%$
310	104
330	94
410	153
440	91
510	6

wavelengths produced by a super pressure mercury lamp equipped with a scanning monochromator. The results are reported in Table 1.

Irradiation with monochromatic light in the wavelength range between 310 and 440 nm increased the ascorbyl radical ESR signal intensity while excitation at 510 nm produced insignificant changes. Phenols and aromatic carbonyl groups in the pulp matrix absorb light at 310 nm and 330 nm<sup>11,23-24</sup>. These chromophores can undergo photochemical reactions with ascorbic acid to produce more ascorbyl radicals. It should be pointed out that ascorbic acid does not have appreciable absorption of light in wavelengths above 310 nm.

It is expected that in bleached TMP sample most of the ortho-quinone chromophores which absorb strongly in the 410-430 nm region, would have been reduced by alkaline hydrogen peroxide. However, other chromophores such as aromatic ring-conjugated ethylenic double bonds are known to remain upon bleaching<sup>3</sup>. Since the bleached TMP paper sample had been pre-irradiated by UV light of wavelengths above 300 nm, it is quite possible that some of the persistent intermediates such as phenoxy radicals formed near the surface would absorb in the 410-440 nm range<sup>22</sup>. We expect that in the paper matrix a photo-excited

phenoxy radical would be able to overcome part of the energy barrier for diffusion and thus enhance the reaction with ascorbic acid to generate ascorbyl radicals. The photochemistry of excited phenoxy radicals with ascorbic acid and other compounds both in liquid and in paper matrix is our next subject of investigation.

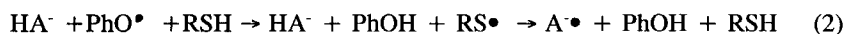
We now turn to the CIDEP studies of the laser photolysis of ascorbic acid-impregnated bleached TMP paper. Figure 4a shows the observed CIDEP spectrum indicating a relatively broad emissive (E) signal. The polarized radicals in this spectrum again can only be generated by the phototriplet mechanism. The broad CIDEP spectrum is likely due to the superimposed components of both the ascorbyl radicals and the phenoxy radicals, as compared with the thermal spectrum in Figure 4b.

#### Effects of Thiols on the Photolysis of TMP Paper

Since solution ESR studies also show that various thiols are capable of quenching the ESR signals of stable radicals due to the weak S-H bond and thus providing a readily abstractable hydrogen<sup>22</sup>, we have carried out a series of experiments using thiol-impregnated TMP samples. Again simple treatments of bleached and unbleached TMP paper with an alcoholic solution of thiols leads to the observations of persistent but anisotropic thiol radical ESR signals. This is indeed a nice feature since thiol radicals are normally too broad to be detected by ESR in liquid solution due to their large anisotropy.

Upon UV-irradiation of the thiol-impregnated bleached and unbleached TMP paper, a rapid increase in the asymmetric thiol radical ESR signals was noted. The time-resolved CIDEP spectrum, however, shows only a single symmetric broad line (E) characteristic of the polarized phenoxy radicals. This observation suggests the quenching reaction by the thiols is a secondary thermal process occurring after the initial triplet photochemical generation of the phenoxy radicals in the normal manner.

In order to examine the synergetic effects of thiols and ascorbic acid, bleached and unbleached TMP paper samples were treated with a solution containing both ascorbic acid and  $\text{Ph}_3\text{CSH}$ . The simple treatment yields a substantial formation of ascorbyl radicals. Two reaction schemes can account for the large formation of ascorbyl radicals under these conditions. The residue-phenoxy radical can directly abstract a hydrogen from ascorbic acid to produce an ascorbyl radical (1). The formation of the ascorbyl radical could arise from a two-step process (2) :



In the two-step process the phenoxy radicals can react first (faster) with the thiol in the initial step and the newly formed thiol radicals then abstract a hydrogen from ascorbic acid in the second step to produce ascorbyl radicals. It is most likely that both processes occur because of the inhomogeneous distribution of the ascorbic acid and the thiol in the paper matrix.

Upon photolysis of the ascorbic acid/thiol treated bleached TMP paper, a much stronger ascorbyl radical ESR signal intensity was produced while the contribution of the thiol radical to the ESR signal became minimal. This suggests that the ascorbic acid quenches both the phenoxy radical and the photo-induced thiol radical efficiently.

On filter paper treated with a combination of ascorbic acid and thiol, a very weak ESR signal was produced thermally. Irradiation of the impregnated paper sample however produced both ascorbyl and thiol radical as shown in Figure 5. The ESR spectra are analyzed in terms of two radicals with overlapping resonances. The sharp feature is mainly due to the ascorbyl radicals and the wide anisotropic spectrum is due to the thiol radicals. The relative

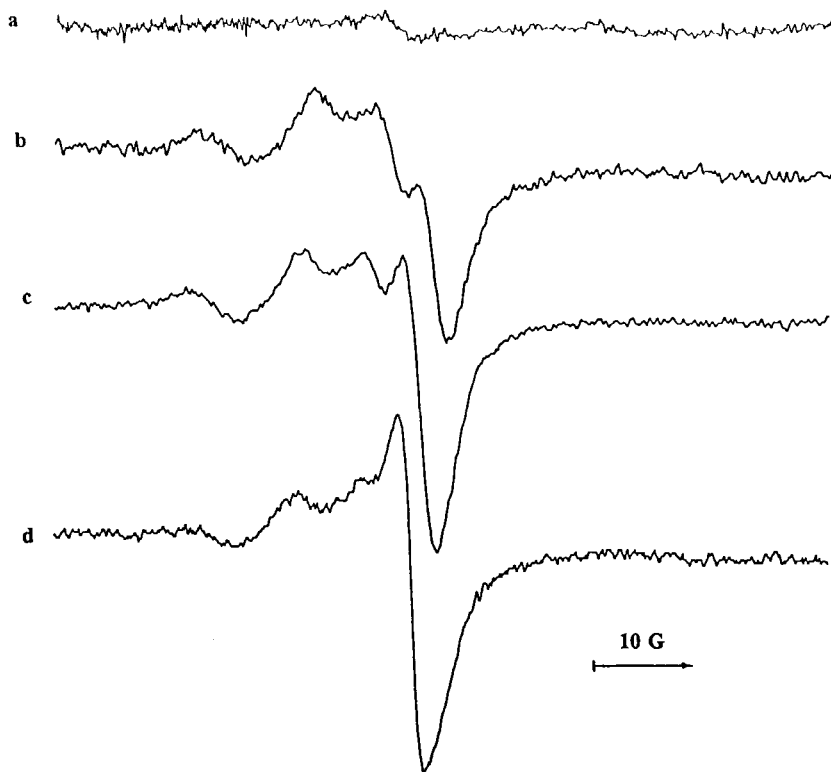


FIGURE 5 ESR signals of filter paper samples treated with  $\text{Ph}_3\text{CSH}$  and ascorbic acid. a) 0 min. UV-irradiation, b) 30 min. irradiation, c) 60 min. irradiation, d) 180 min. irradiation.

intensity of the two radicals changed with increasing irradiation time, with the ascorbyl radical component becoming more intense relative to the thiol radicals during irradiation. It is expected that photodecompositions of thiols under the experimental conditions would proceed faster than ascorbic acid. The overall results are consistent with the thermal reactions scheme formulated above.

### CONCLUSION

The results reported here make possible the identification of **some** of the radical intermediate steps in the light-induced yellowing of TMP paper. The unambiguous confirmation of the role of aromatic carbonyl triplet states of some macrolignin molecules in TMP paper in the production of radicals such as phenoxy radicals would help to understand some day the complete chemistry of light-induced yellowing of TMP paper. The establishment of ascorbyl and thiol radicals in TMP samples provide further insights into the radical mechanisms of these important antioxidation processes.

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