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Mechanical and Kraft Pulps: Impact on Photoyellowing

K.-O. Hwang and L.A. Lucia

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NOVEL STUDIES OF SINGLET OXYGEN CHEMICAL MODIFICATION OF MECHANICAL AND KRAFT PULPS: IMPACT ON PHOTOYELLOWING

Ki-Oh Hwang and Lucian A. Lucia

Institute of Paper Science and Technology
500 10th St., NW
Atlanta, Georgia 30318-5794

ABSTRACT

In the pulp and paper industry, singlet oxygen has witnessed few in-depth explorations, yet it has clearly demonstrated a remarkable capacity to react with lignin. From our recent investigations, we determined that it can efficiently degrade the chromophoric constituents in pulp. Since it displayed such proficiency in removing chromophores, we considered the possibility of employing it to modify the chromophores in mechanical pulps and examine subsequent photoyellowing phenomena. The current research therefore examined the photoyellowing response of high-yield BCTMP hardwood pulp and a kraft post-oxygen delignified pulp after a photobleaching stage that consisted of a "singlet oxygen stage." Chemical modification of lignin to inhibit photoyellowing of mechanical pulps is not a new concept. In our work, we found that the distributions of chromophores and photoyellowing response of the pulps were dramatically impacted by singlet oxygen, suggesting a chemical modification of the leucochromophoric structures responsible for yellowing. Singlet oxygen was photochemically generated through direct visible light irradiation of BCTMP pulp suspensions of 10% consistency with a singlet oxygen sensitizer concentration of 0.5% based on the oven dried weight of the pulp. Rose Bengal was used as the sensitizer, acting as the visible light absorber and transferring its excited singlet state energy to molecular oxygen to generate the $^1\Delta_g$ state of oxygen. We photobleached hardwood BTCMP pulp, and observed that its diffuse difference absorbance spectrum displayed one well-defined peak at 420 nm that contrasted sharply with non-photobleached BTCMP pulps, displaying peaks at 360 and 420 nm. TAPPI Brightness measurements indicated that the photobleached BCTMP pulp displays very aggressive photoyellowing properties compared to non-photobleached pulp. SW Kraft pulp showed similar spectral features compare to the BTCMP pulp indicating that singlet oxygen was chemically modifying the lignin structure as reflected by photoyellowing experiments and UV/Vis spectra. Photoyellowing and brightness reversion experiments are discussed in terms of the chemical effect of singlet oxygen on lignin.

INTRODUCTION

High-yield mechanical pulps are high lignin-content pulps that have been explored as an alternative economically feasible source of fiber. They provide a very attractive utilization of precious virgin fiber sources, their production demonstrates reduced environmental impact, and they are a potentially viable market source of pulp.¹⁻¹⁰ Yet, increased utilization of this valuable fiber source is ultimately limited by its intrinsic ability to colorimetrically degrade under light or heat.¹¹⁻¹⁶ This propensity to “yellow” prevents their widespread commercialization and also limits their application primarily to low-grade paper manufacture, such as newsprint. The major component of high-yield pulps responsible for the color degradation of the pulp is lignin, a complex and amorphous biopolymer containing an abundance of phenylpropanoid units. The phenyl units are suspected to engage in yellowing reactions that are characterized by an accretion of visible light-absorbing chemical units. Although no definitive information on the nature and extent of the chromophores responsible for the yellowing is available, quinone-like molecules have been implicated as candidates contributing to the spectral signatures that appear in the near-UV region after photolysis.¹⁷⁻²⁵ Many efforts to compensate for their photoyellowing have been directed at inhibiting their absorption, scavenging radicals responsible for yellowing, or applying whitening agents.²⁶⁻³⁰ Some work has been directed toward chemically modifying the existing leucochromophores to obviate their propensity to photoyellow.^{31,32} Our aim was to conduct a fundamental study of the photoyellowing phenomenon by using a very effective oxidizing agent, namely singlet oxygen, for the chemical modification of leucochromophores and their removal and subsequent comparison of their photoyellowing response to non-treated pulps. We wanted to determine how an active form of oxygen can affect final product photoyellowing response. We had

surmised that singlet oxygen treatment would decrease the photoyellowing response by a thorough oxidation/hydrolysis of the leucochromophoric units that contribute to photoyellowing. The present work was a preliminary investigation that highlighted some of the most fascinating observations in this work.

Singlet oxygen is an extremely potent oxidant that has witnessed a renaissance in its applications in biological and chemical processes.³³⁻³⁵ There has been an inordinate abundance of literature reports that have prominently documented the ability of singlet oxygen to engage in useful, delignifying reactions with kraft pulp.³⁶⁻⁴¹ Nevertheless, its success as a delignification agent has virtually overshadowed its ability to chemically modify lignin to disrupt conjugation. The singlet oxygen molecule is vibrationally excited, electrophilic in character, able to react with electron-rich species such as lignin during a time window of only several microseconds in water. Previous studies with singlet oxygen strongly suggest that it was the primary contributor to the photoyellowing of mechanical pulps.⁴³⁻⁴⁵ It was postulated that it contributed to the formation of colored bodies such as quinones. Other chemical modifications in the domain of mechanical pulps with respect to photostabilizing lignin have not met with success - sodium borohydride being a prime example.⁴⁶ Our strategy was to investigate the ability of singlet oxygen to modify lignin in anticipation of subsequent photolysis experiments and analyze the photoyellowing that ensued.

We used HW BCTMP and SW kraft post-O₂ pulps in the photoyellowing experiments. We hoped to compare and contrast the salient spectroscopic changes observed for these pulps, with a particular interest in correlating the specific spectroscopic changes to common chromophores. For example, photobleached HW and SW pulps displayed similar spectroscopic changes, suggesting that a common chromophore or chromophoric group was responsible for the observed bands. For the

HW sample, however that was not photobleached, we found a completely different spectroscopic signature. In addition to a band centered at 360 nm, we found a shoulder at approximately 420 nm. Absorption in the near-UV band would in all likelihood be directly responsible for increasing the photoyellowing effect since we used near-UV black lamps (output maximum = 350 nm). Our preliminary experiments focused on obtaining UV/Vis spectra and TAPPI brightness to monitor the photoyellowing of the substrates as a function of time. The samples had different levels of lignin, but as will be shown, the levels did not correlate with photoyellowing capacity, perhaps suggesting that photoyellowing is more directly associated with the type of chromophores inherent in the pulp.

The chemistry of the photoyellowing and photobleaching responses of mechanical pulps is likely based on molecular changes in the lignin. For example, it is well known that mechanical pulp lignins respond to near-UV light through a ketyl radical type mechanism, illustrated in Figure 1.⁴⁶ Since 50% of lignin interunit linkages consist of β -O-4 structures (structure 1), the capacity to induce radical type reactions arising from a ketyl mechanism is very high, providing carbonyl-containing products that can absorb visible light (resulting in a colored, “yellow” substrate). Photobleaching, using singlet oxygen as the oxidant, functions along similar pathways, shown in Figure 2, that lead to quinone-type structures.^{47, 48} The quinone structures have been implicated in singlet oxygen chemistry, but based on this work and previous results, lignin removal is hinged upon the occurrence of hydrolytic reactions. An ortho-quinone structure can undergo a ring opening (through an oxygen addition across the 1, 2 dicarbonyl bond) leading to a muconic acid structure that is soluble under alkaline conditions.

The present work will demonstrate the startling contrast between singlet oxygen-treated pulps and untreated pulps after photoyellowing runs.

EXPERIMENTAL

Materials

All chemicals and reagents including Rose Bengal dye (97%) were commercially purchased and used as received. Commercial hardwood (HW) and softwood (SW) bleached chemithermomechanical pulps (BCTMP) were employed for all studies. The HW pulps were prepared employing hydrogen peroxide for the chemical impregnation and bleaching stages. The SW pulps were generously provided by a member company of the Institute of Paper Science and Technology. Cellulosic testsheets were prepared from Whatman #3 filter paper.

Instrumentation

A Perkin-Elmer Lambda 19 UV/Vis/NIR spectrophotometer with a Labsphere RSA-PE-90 reflectance accessory attachment was used to measure all spectra. The reflectance spectra were made relative to a Labsphere standard SRS-99-010. The photolysis of the cellulosic substrates was performed in a Rayonet Photochemical Reactor (RPR-100) using 16 near-UV black lamps (8W) having a Gaussian spectral profile between 300 and 400 nm with a maximum output at 350 nm.

Procedures

The SW kraft and HW BCTMP pulps (along with filter papers) were Soxhlet extracted with acetone for 24 hours and air-dried prior to testsheet formation. The photobleaching experiments were done in a Rayonet Reactor containing sixteen 575 nm “cool-white” fluorescent lamps (8 W each). A pulp slurry at 10% consistency, 0.5% Rose Bengal, and 5% alkalinity was constantly stirred throughout the experiment. After 23 hours of irradiation, the pulp was washed (the Rose

Bengal had been degraded) and air-dried. Testsheets (200 g/m² basis weight) were prepared according to TAPPI procedure T-205 om-88 and air-dried at constant temperature (22.0 +/- 2.0C) and constant relative humidity (50 +/- 2.0%). The TAPPI brightness values (note that this value is a measure of the relative amount of incident light at wavelength 457 nm reflected from a testsheet) for the samples are shown in Table 1.

The diffuse reflectance spectra were performed at 1 nm increments using a 240 nm/min scan rate on a Perkin-Elmer Lambda 19 DM spectrophotometer. The accessory is an optical bench that includes double beam transfer optics and six-inch diameter (154 mm) integrating sphere. All experiments were conducted with the underlying assumption that the scattering coefficients were the same since the handsheets were obtained from the same source. The absorbances (Abs) of the samples were calculated from the diffuse reflectance by applying the following expression derived from the Beer-Lambert Law: $Abs = -\log(\text{Diffuse Reflectance})$. All spectra were averaged from a set of three to four measurements and are displayed as the difference spectra between an irradiated and non-irradiated sample. A Technidyne Brightmeter (Model S-5) was used to measure the brightness of the handsheets. All values were calibrated according to the brightness from a commercially accepted standard.

RESULTS AND DISCUSSION

The current work provides a preliminary account of the unique impact of a photobleach step (singlet oxygen stage) on the subsequent photoyellowing properties of a HW BCTMP pulp. In addition, we used a control HW BCTMP that was not photobleached and compared the spectra of the latter two cases to the spectra obtained from a conventional Southern SW kraft pulp that had undergone both an oxygen stage and a photobleach stage. We were interested in determining how

the development of the chromophores and their distribution affected the rate and efficiency of subsequent photoyellowing.

An important parameter to consider in these studies was the levels of lignin (as determined by the kappa number test, TS 235 cm-85). Table 1 shows the kappa numbers for the pulps that were used in these studies.

TABLE 1. List of Starting Kappa and Brightness Values for the Pulps Used in this Study.

	HW BCTMP	HW BCTMP (photobleached)	SW Post O ₂ SO 15 hour treatment	SW Post O ₂ SO 23 hour treatment
KAPPA	130	50	3.5	4.0
BRIGHTNESS	83	77	80	82

Note that a photobleach treatment of 23 hours on the HW pulp efficiently removes over 60% of the lignin levels, but does not substantially compromise the brightness of the pulp (a drop of approximately 6 units as shown in the table). Although the lignin concentration directly influences its ability to photoyellow, it is only one of the factors that must be considered in this phenomenon. The major factor, of course, is availability of chromophores in the pulp – are chromophores present in sufficient abundance to contribute to photoyellowing given the frequency of light used? Our interpretations of the photoyellowing are based on UV/Visible spectroscopy and Brightness measurements, both of which can give insight into the response of the lignin to the light used in the experiments.

Surprisingly, we observed that the photobleached HW pulp underwent yellowing at a more accelerated rate, almost 30% faster, than did the non-photobleached pulp. Although its lignin levels were more depleted (66%), it underwent more rapid photoyellowing under the same conditions as the control. Figure 3 shows the brightness changes for the two pulps as a function of irradiation time using 350 nm black near-UV lamps. Notice that the photobleached pulp began at a brightness value that was almost 6 units lower than the starting pulp. This was not unexpected since during the irradiation, singlet oxygen generates colored intermediates (see Figure 2) which can undergo hydrolytic reactions culminating in delignified pulp. Thus, the final brightness value is obviously a competition between “photoyellowing” and delignification reactions in the lignin whereas in this case, the delignification reactions were almost 4 times more efficient than the photoyellowing reactions during singlet oxygen photobleaching. Remarkably, singlet oxygen reactions appear to combine the oxidative capacity of oxygen delignification and the bleaching ability of hydrogen peroxide.⁴¹

In order to shed more light on the enhanced photoyellowing kinetics of the photobleached HW sample, we collected UV/Vis spectra for all the samples. A normal HW BCTMP sample typically displays 2 distinct UV/Vis absorption bands, one at 360 nm and the other at 420 nm. Figure 4 illustrates the absorption bands for a HW BCTMP sample at 1 hour of irradiation. Also shown in the figure is the spectrum for a HW BCTMP sample that was photobleached for approximately the same time under the same conditions.

The photobleached HW sample absorbs at lower energy wavelengths, which is very reasonable considering the oxidative changes the lignin sustains in response to singlet oxygen (ortho-quinone structures absorbing in that region are generated and destroyed). The rate of formation of the

chromophores at 360 nm appears to be accelerated by a factor of 2-3 in the non-photobleached sample versus the photobleached sample. This is not unreasonable since the maximum of the irradiating light source is at 350 nm, and the photobleached sample absorbs about 50% less light than its non-photobleached counterpart. Yet, although the photobleached sample chromophore(s) in the 400 nm band grow at an appreciably slower rate than their counterparts, they undergo faster (30%) photoyellowing. This faster photoyellowing may be a consequence of the broadness of the photobleached HW band versus the non-photobleached band. Although a shoulder exists at 420 nm for the non-photobleached band, the band is very shallow compared to its counterpart. Thus, the photoyellowing changes that occur in the photobleached sample will be more pronounced, although the band at 400 does not increase as fast.

The latter results suggest that the chromophores generated in the photobleached sample are more electronically conjugated. The non-photobleached sample has two bands (one at 360 and the other at 420 nm) indicating two distinct chromophore species, which is obviously not the case for the photobleached sample. This conjugation would have significant ramifications for photoyellowing since the energy of the light can be appropriately channeled via electronic communication to induce color changes. The non-photobleached sample would partition the absorbed light unequally between the two absorption bands, as a function of oscillator strength, but probably preferentially to the species that absorb at 360 nm. These species do not contribute to brightness changes, unless they sensitize chromophore changes. Apparently, they do not contribute to color changes as significantly as the photobleached sample.

Of course, the non-photobleached sample has considerably more lignin than does the photobleached sample, but we are comparing only relative trends in spectroscopic and brightness

changes. Since we suggest that conjugated structures may be accounting for the photoyellowing effect in singlet oxygen treated mechanical pulps, we were interested to determine how a condensed and chemically modified lignin would respond in photoyellowing experiments. We chose to photobleach a post-O₂ kraft pulp in hopes of understanding how conjugated structures impact the photoyellowing phenomenon. Shown in Figure 4 is the brightness reversion data for a singlet oxygen treated (23 hours) post-O₂ pulp as a function of irradiation time. The spectroscopic changes versus the HW sample are minor, perhaps due to the paucity of lignin species whose photoyellowing from conjugation effects would not be as pronounced as in a higher lignin-containing sample. Yet, the UV/Vis spectra also show one peak, which is red-shifted by almost 20 nm. This is not altogether surprising, and in fact is expected, since the extensive oxidative sequence more than likely engendered a very modified, condensed, conjugated lignin macromolecule. Unfortunately, since the lignin levels are significantly lower than the HW samples, we cannot say with certainty if the photoyellowing phenomenon would be as fast as the HW photobleached sample. Yet, it is worth noting that the pronounced red-shift and broad spectrum strongly suggests that it may have the potential for enhanced photoyellowing.

CONCLUSIONS

Thus, the preceding study demonstrates that a singlet oxygen treatment of a HW BCTMP pulp engenders chromophoric species that can photoyellow faster than a non-photobleached, more lignin-enriched HW sample. This results strongly indicates that singlet oxygen can accelerate photoyellowing by introducing conjugated structures that will photoyellow at high efficiency. It may be possible to encourage photostability in such pulps in the context of brightness by directly reducing the probability to engender conjugated structures and thus decreasing the propensity for

photoyellowing. Since conjugation reactions occur via radical coupling mechanisms, we believe that radical scavengers should be increasingly studied and promoted to protect against the formation of conjugated structures. Future work will involve examining the structure of the chromophores that are found in such pulps and correlate structure with photoyellowing phenomena.

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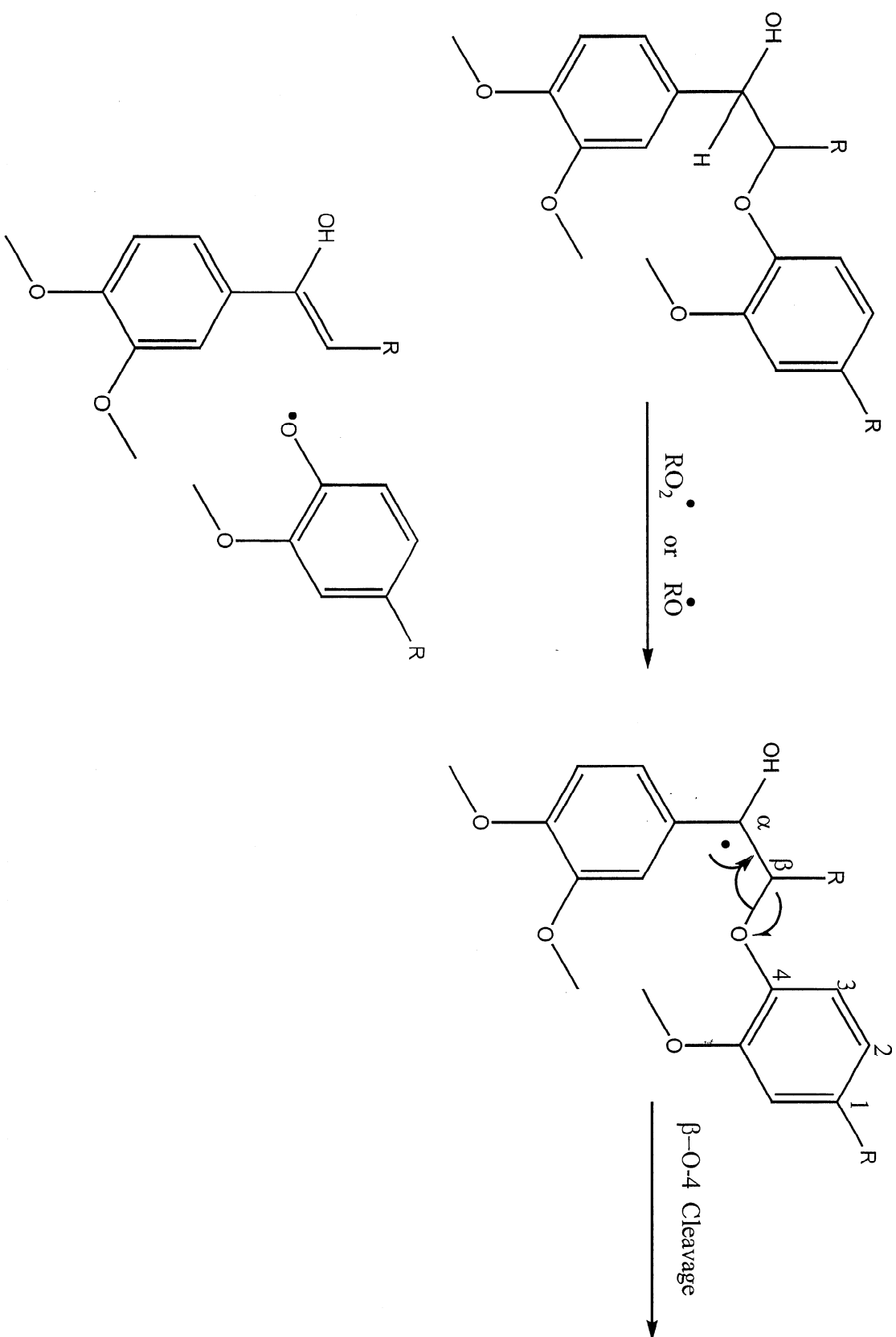
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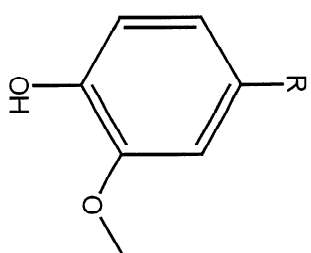
FIGURE 1. Due to UV irradiation of pulps, carbon-centered radicals can react with molecular oxygen to generate radicals that abstract α -protons to initiate the mechanism illustrated above. The resultant phenoxy radical can induce further radical reactions.

FIGURE 2. Mechanism of lignin degradation by singlet oxygen that results in both para and ortho quinones.

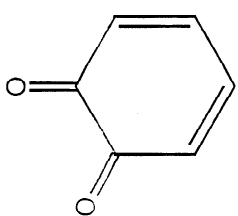
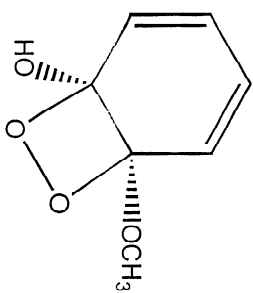
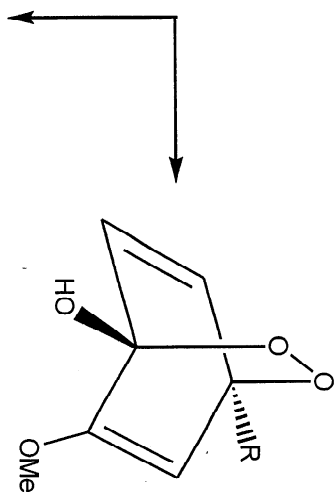
FIGURE 3. Brightness changes for HW nonphotobleached (14 hours, BCTMP, kappa ca. 90) and photobleached (0 hours, BCTMP, kappa ca. 130) samples under ambient conditions as a function of time.

FIGURE 4. Absorbance spectra obtained after 1 hour near-UV irradiation under ambient conditions for HW nonphotobleached and photobleached samples.

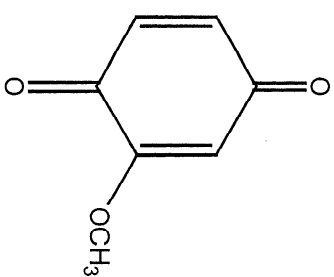
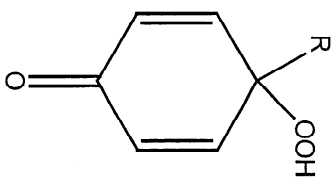




+



O-Quinone



Para-Quinone

