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Photoreactivity of lignin model compounds in the photobleaching of chemical pulps

2. Study of the degradation of 4-hydroxy-3-methoxy-benzaldehyde and two lignin fragments induced by singlet oxygen

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Abstract

The degradation induced by singlet oxygen (sensitized by methylene blue) of 4-hydroxy-3-methoxy-benzaldehyde (vanillin) and two lignin fragments (from rice husks and *Eucalyptus grandis* wood) in methanol solution was investigated. For vanillin, a kinetic study was performed using three different pH values. The rate of degradation of vanillin was highly dependent on the pH due to the ionization of phenol groups. In addition, the physical quenching of singlet oxygen by vanillin was more sensitive than the chemical reaction to an increase in pH. The degradation of lignin under the influence of singlet oxygen was influenced by the existence of free phenol groups. Conjugated carbonyl groups were formed and their quantity was higher than that expected from the consumption of phenols during irradiation. This was attributed to the participation of benzylarylether structural elements in the photodegradation process. © 1997 Elsevier Science S.A.

Keywords: Bleaching; Lignin; Photodegradation; Sensitization; Singlet oxygen

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1. Introduction

The involvement of singlet oxygen in many oxidative processes is well known; however, its role in lignin degradation remains unclear, although several studies have been performed [1–8].

Singlet oxygen ($^1\Delta_g$), which is an excited state of molecular oxygen, displays an accentuated electrophilic character [7], and reacts with electron-rich groups, such as olefinic and aromatic derivatives [7,9]. For unsaturated molecules, the mechanism involves charge transfer between the electron-rich compound and singlet oxygen, with the formation of an intermediate exciplex. The latter may yield dioxetane, endoperoxide and hydroperoxide structures [10]. Carbonyl derivatives are sometimes formed.

Singlet oxygen appears to be a potential delignifying agent for the destruction of lignin during the bleaching of chemical pulps, and may possibly be used to replace noxious electrophilic chlorine derivatives. We have initiated studies to evaluate its ability to bleach chemical pulps and have reported an efficient, three-stage, photochemical bleaching process involving methylene blue as singlet oxygen sensitizer [11].

Lignin is a highly complex composite, and the use of lignin models is very valuable for the determination of certain mechanistic aspects of its photodegradation and reactivity [1–6,12]. In this paper, we report the action of singlet oxygen on 4-hydroxy-3-methoxy-benzaldehyde (vanillin) and two lignin fragments (from rice husks and from an organosolv lignin isolated after acesolv pulping of *Eucalyptus grandis* wood) [11]. The studies were performed in solution for vanillin and for one of the lignin fragments. The other fragment was examined supported on a solid matrix.

2. Experimental details

The oxidative degradation of vanillin and lignin fragments extracted from rice husks (RHL, $\bar{M}_w \cong 390$ Da [13]) and

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from *Eucalyptus grandis* wood (EOL, $\bar{M}_w \equiv 5600$ Da [14]), under the influence of singlet oxygen, was studied. The experiments were performed in solution and in the solid state (for RHL; supported on a glass plate). For the solutions, the concentrations used varied between 50 and 100 mg l^{-1} for the lignin fragments and between 150 and 1500 mg l^{-1} for vanillin. The solution experiments were performed using methanol. The effect of pH on the performance of the reaction was evaluated on EOL and vanillin by the addition of sodium hydroxide.

Singlet oxygen was generated directly in the reaction medium using methylene blue (MB) as sensitizer. In addition, sodium azide, a known singlet oxygen quencher [7], at a concentration around 10^{-4} M, was used to quench singlet oxygen in some experiments. During the experiments, oxygen was continuously bubbled into the reaction mixture. The sensitizer was selectively excited by a tungsten lamp, surrounded by a Pyrex envelope, around which was circulated a 2% potassium dichromate solution, allowing the transmission of light with $\lambda > 550$ nm. In these conditions, almost all of the incident light was absorbed by the sensitizer. The lamp was placed 4 cm from the reactor. Singlet oxygen was generated according to

$$^{1}AM^{+} \xrightarrow{h\nu} {}^{1}AM^{+*} \xrightarrow{ISC} {}^{3}AM^{+*}$$

$$^{3}AM^{+*} + {}^{3}O_2 \rightarrow {}^{1}AM^{+} + {}^{1}O_2$$

The experimental procedure used to study the mechanism of singlet oxygen action was similar to that described previously [9,15].

The electronic absorptions of the solutions (280–290 nm for lignin and 270 nm for vanillin) were used to monitor the photodegradation [16]. The phenol content before and after irradiation of lignin fragments was estimated using absorption spectroscopy [17]. A Hitachi U2000 spectrophotometer was used for this purpose.

The degradation of RHL in the solid state was performed by supporting RHL on a glass plate fitted in front of another plate containing MB in agar–agar. The distance between the two plates was fixed at 0.9 mm. The incident radiation for excitation of the sensitizer was filtered by a 2% dichromate aqueous solution to avoid UV and IR components. Between the plates, a continuous air flux was maintained during the reaction. The relative carbonyl content was monitored by following the changes occurring in the band at 1660 cm^{-1} [18] using a Bomem MB102 Fourier transform IR (FT-IR) spectrometer.

The degradation of vanillin was followed by gas chromatography using a Shimadzu GC14-A chromatograph equipped with a phenylmethylsilane (5% phenyl) capillary column. The concentration of vanillin was estimated from the peak areas; a fluctuation of less than 5% was observed in these measurements. Although the pH is difficult to estimate in methanol, it was evaluated using a combined glass electrode calibrated with buffered methanol solutions. The pH value assigned was that expected for aqueous solutions. The reactivity index β_0 (see Section 3) was estimated for different pH values. The oxidation quantum yields were estimated by measuring the consumption of vanillin by gas chromatography and the light intensity using Reinecke's salt as chemical actinometer [19].

3. Results and discussion

3.1. *Kinetic study of the degradation of vanillin and lignin fragments in solution*

3.1.1. *Vanillin*

The degradation of vanillin induced by singlet oxygen was studied under three different conditions by monitoring the absorbance of the solutions at 270 nm (Fig. 1).

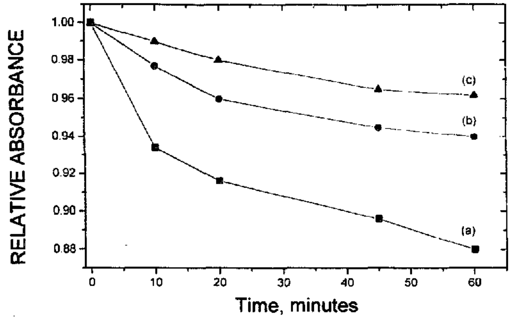


Fig. 1. Effect of sensitizer concentration and $[N_3^-]$ on the reaction involving vanillin (detection, $\lambda = 270$ nm; $[Van] = 1 \times 10^{-3}$ mol l^{-1}): (a) $[MB] = 1 \times 10^{-6}$ mol l^{-1}; (b) $[MB] = 1 \times 10^{-5}$ mol l^{-1}; (c) $[MB] = 1 \times 10^{-6}$ mol l^{-1}; $[N_3^-] = 1 \times 10^{-4}$ mol l^{-1}.

Although MB is a good sensitizer for the generation of singlet oxygen [7,20], it also suppresses its action. As the MB concentration is increased, the degradation of vanillin is partly suppressed (comparison of curves (a) and (b)). This can be considered as evidence for the involvement of singlet oxygen in the reaction. The addition of sodium azide, a known physical quencher of singlet oxygen [9], reduces the rate of degradation (curves (a) and (c)).

The lignin fragments behave similarly to vanillin when sodium azide is added to the solution and when the concentration of the sensitizer is increased (curves not shown).

The measurement of the degradation of lignin and phenolic lignin models by UV–visible spectroscopy only provides an approximate view of the consumption of phenol groups, because α-carbonyl, phenol, α,β-olefinic and aromatic groups exhibit absorption in the same region of the electronic absorption spectrum [16]. Therefore it is difficult to distinguish their individual participations. For this reason, and due to the high accuracy of measurement of the conversion rate of vanillin by gas chromatography, the kinetics of photodegradation of vanillin were studied using this technique.

The reactions between singlet oxygen and the different substrates involve competition between physical and chemical quenching [7]. Usually, for phenols, physical quenching is dominant [21].

The mechanism shown below is proposed to interpret our kinetic data on vanillin photodegradation

$$^1\mathrm{MB}^+ \overset{h\nu}{\rightarrow} {}^1\mathrm{MB}^{+*} \overset{\mathrm{ISC}}{\rightarrow} {}^3\mathrm{MB}^{+*}$$

$$^3\mathrm{MB}^{+*} + {}^3\mathrm{O}_2 \overset{k_1}{\rightarrow} {}^1\mathrm{MB}^+ + {}^1\mathrm{O}_2 \quad v = I_a\gamma_\Delta$$

$$^1\mathrm{MB}^+ + {}^1\mathrm{O}_2 \overset{k_s}{\rightarrow} {}^1\mathrm{MB}^+ + {}^3\mathrm{O}_2$$

$$\mathrm{Q} + {}^1\mathrm{O}_2 \overset{k_Q}{\rightarrow} \mathrm{Q} + {}^3\mathrm{O}_2$$

$$\mathrm{Van} + {}^1\mathrm{O}_2 \overset{k_r}{\rightarrow} \mathrm{product}$$

$$\mathrm{Van} + {}^1\mathrm{O}_2 \overset{k_p}{\rightarrow} \mathrm{Van} + {}^3\mathrm{O}_2$$

$$^1\mathrm{O}_2 \overset{k_d}{\rightarrow} {}^3\mathrm{O}_2$$

where ISC denotes intersystem crossing, I_a is the number of photons absorbed by the solution per time unit, γ_Δ is the efficiency of singlet oxygen production, Q is the singlet oxygen quencher (sodium azide), Van denotes vanillin and MB denotes methylene blue.

All the experiments were performed using solutions saturated with oxygen. A stationary concentration of singlet oxygen is probably established during the photochemical process ($d[^1O_2]/dt = 0$). The stationary state approximation of the singlet oxygen concentration gives

$$[^1\mathrm{O}_2] = \frac{I_a\gamma_\Delta}{k_d + (k_r + k_p)[\mathrm{Van}] + k_s[\mathrm{MB}] + k_Q[\mathrm{Q}]} \tag{1}$$

The rate law for the consumption of vanillin is expressed by

$$-\frac{d[\mathrm{Van}]}{dt} = k_r[\mathrm{Van}][^1\mathrm{O}_2] = v_{ox} \tag{2}$$

By substituting Eq. (2) into Eq. (1), the rate v_{ox} and quantum yield ϕ_{ox} of oxidation of vanillin by singlet oxygen are obtained. They are given by Eqs. (3) and (4) respectively. It is more useful to express v_{ox}^{-1} vs. $[\mathrm{Van}]^{-1}$ where a linear correlation is expected (Eq. (5))

$$v_{ox} = \frac{k_r[\mathrm{Van}]I_a\gamma_\Delta}{k_d + (k_r + k_p)[\mathrm{Van}] + k_s[\mathrm{MB}] + k_Q[\mathrm{Q}]} \tag{3}$$

$$\phi_{ox} = \frac{k_r[\mathrm{Van}]\gamma_\Delta}{k_d + (k_r + k_p)[\mathrm{Van}] + k_s[\mathrm{MB}] + k_Q[\mathrm{Q}]} \tag{4}$$

$$v_{ox}^{-1} = \frac{1}{\gamma_\Delta}\frac{(k_r + k_p)}{k_r}\frac{(k_d + k_s[\mathrm{MB}] + k_Q[\mathrm{Q}])}{k_r}\frac{1}{[\mathrm{Van}]} \tag{5}$$

A plot of v_{ox}^{-1} vs. $[\mathrm{Van}]^{-1}$ allows the reactivity parameter β to be obtained

$$\frac{\mathrm{Slope}}{\mathrm{Intercept}} = \frac{k_d + k_s[\mathrm{MB}] + k_Q[\mathrm{Q}]}{k_r + k_p} = \beta \tag{6}$$

When the concentration of MB and quencher Q become very low, the limit reactivity term β_0 can be given by the relationship

$$\beta_0 = \frac{k_d}{k_q} \tag{7}$$

$$k_q = k_r + k_p \tag{8}$$

where k_d is the rate constant for the decay of singlet oxygen only under the influence of the solvent. In methanol at 25 °C, $k_d = 1 \times 10^{-5}\ \mathrm{s}^{-1}$ [22]. The rate constant k_q represents the two possible quenching routes due to the interaction of the vanillin molecule with singlet oxygen, one giving products (k_r) and the other self-quenching (k_p).

The reactivity parameter β_0 corresponds to the ratio of the rate constant of the natural decay of singlet oxygen to the rate constant of decay due to all other species present in the solution [23,24]. From β, the second-order constant k_q can be determined.

Fig. 2 shows the relationship $[\mathrm{Van}]^{-1}$ vs. v_{ox}^{-1} for $[\mathrm{MB}] = 1 \times 10^{-6}\ \mathrm{mol\ l^{-1}}$ for three different pH values. Linear correlations are obtained which are in good agreement with the proposed mechanism. Because the [MB] and [Q] values were sufficiently low to consider $\beta = \beta_0$, the ratio of the slope over the intercept allowed β_0 to be obtained; the results are reported in Table 1 for the different pH values. Also indicated are the values of k_q calculated by Eq. (7).

In the conditions presently used ([MB] and [Q] sufficiently low to consider $\beta = \beta_0$), the reaction rate constant k_r can be evaluated by measuring the quantum yield of oxidation of vanillin sensitized by MB (Eq. (4)) according to a quantum yield of production of singlet oxygen γ_Δ equal to 0.5 [22]. The values are reported in Table 1.

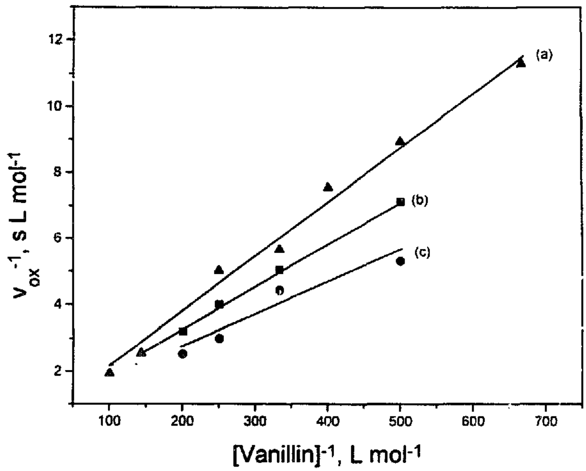


Fig. 2. Plot of v_{ox}^{-1} vs. [Van]$^{-1}$ for three different pH values: (a) pH 5.4; (b) pH 6.3; (c) pH 7.7.

Table 1
Kinetic data related to studies on solutions containing vanillin at different pH values

pH	$\beta \times 10^2$ (mol l^{-1})	$k_q \times 10^{-6}$ (l mol^{-1} s^{-1})	$k_r \times 10^{-6}$ (l mol^{-1} s^{-1})	$\alpha = k_r/k_p$
5.40	4.35	1.96	0.345	0.214
6.30	3.13	2.84	0.362	0.146
7.70	1.27	7.46	0.405	0.057

The productive deactivation of singlet oxygen by vanillin giving photoproducts, estimated by the ratio $\alpha = k_r/k_p$, was also calculated (Table 1).

The value obtained for k_q is typical of singlet oxygen quenching by phenols [7,23]. This is also seen in the α ratio (Table 1). In other words, physical quenching is the major process of deactivation of singlet oxygen by vanillin at high pH. An increase in pH from 5.4 to 7.7 results in an increase of less than 20% in k_r. In contrast, k_p increases by at least 340%. This is in accordance with other studies on the interaction between singlet oxygen and phenols [21,25,26]. Moreover, this must be compared with a recent study on the photochemical action of hydrogen peroxide and MB/O_2 in alkaline methanol solution on 1-(3,4-dimethoxyphenyl)-2-(3′-methoxyphenoxy)-1,3-dihydroxypropane, where the addition of hydrogen peroxide on one benzene ring was observed [27]. Superoxide anion, generated by the deactivation of singlet oxygen by hydroxyl ions [28], was proposed as the reactive species [27].

3.1.2. *Lignin fragments*

Because singlet oxygen is generated by MB (methanol solution) in a photosensitized reaction with a rather high quantum efficiency [22], and probably at a high rate, the concentration of singlet oxygen may be considered as constant during stationary irradiation. Then, a pseudo-first-order rate constant can be proposed derived from Eq. (2)

$$v_{ox} = k^1[\text{Van}] \tag{9}$$

When EOL was irradiated under similar conditions to those used for vanillin, a decrease in absorbance at 280 nm was noted. The pseudo-first-order rate constant was calculated and plotted vs. the concentration of hydroxyl ions (Fig. 3).

From the variation in k_r for vanillin and k^1 for EOL (Fig. 3) as the medium becomes more basic, it might be concluded that bleaching in basic medium would not be very successful. From the photochemical bleaching of chemical pulps in three stages [11], we have shown that the addition of sodium hydroxide (3% of the weight of the dried pulp) in the second stage (involving singlet oxygen) results in good delignification after the third stage. This quantity of base is dependent on the residual lignin content of the cellulosic pulp (in the situation under study, close to 10%). In the singlet oxygen delignifying stage, we believe that the residual lignin suffers changes that improve the rate of delignification in the third stage, with a substantial reduction in the consumption of hydrogen peroxide and other chemicals [11,29].

Another technique which can be used to follow lignin photodegradation is to monitor the phenol content by ionization absorption spectroscopy. Fig. 4 shows a comparison

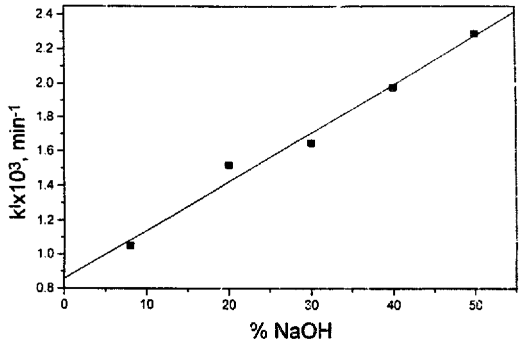


Fig. 3. Effect of alkalinization on the rate of degradation of the lignin fragments (EOL) sensitized by MB (1.00×10^{-5} mol l^{-1}) Pseudo-first-order rate constant of the degradation of EOL vs. the concentration of sodium hydroxide. The irradiation was set to 30 min to limit the conversion rate.

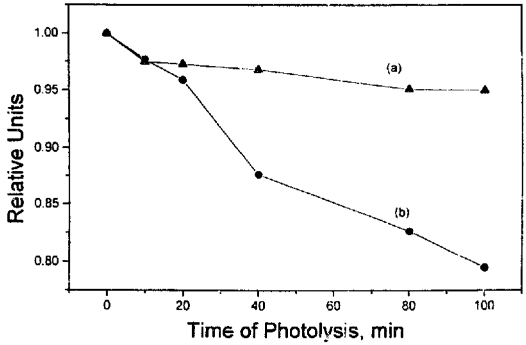


Fig. 4. Photodegradation of EOL fragments sensitized by MB in the presence of sodium hydroxide (8%), measured by the absorbance at 280 nm (a) and by the free phenol content (ionization absorption spectrometry) (b).

of the two methods on EOL in the presence of sodium hydroxide (8%).

The photodegradation of the phenolic part of lignin, given by the pseudo-first-order constant k^1, is at least five times higher than that obtained by measurement of the absorbance at 280 nm (Fig. 5). Because functional groups other than phenol interfere with the UV spectrum of lignin [15] at this wavelength, the determination of the free phenol group content is preferable if quantitative data are desirable to evaluate the degradation.

An enhancement of the quenching of singlet oxygen (k_q) with increasing number of ionized species present in the reaction medium was observed for vanillin (Table 1). Therefore, in solution, some of the ionized species, which correspond to hydroxyl ions, suppress the action of singlet oxygen molecules on the phenolate ions converting them to superoxide ions according to the equation [28]

$$^1O_2 + HO^- \rightarrow O_2^{\cdot -} + HO^{\cdot}$$

Although the reactivity represents only a minor part of the quenching, the rate constant k_r for singlet oxygen quenching at a particular pH can be considered as the sum of the respective rate constants for the undissociated molecule and phenolate ion [30,31]. Therefore, as the pH increases, the participation of phenolate ions in the photodegradation process becomes dominant. A good electrophile, such as singlet oxygen, if not deactivated by hydroxyl ions, should interact with phenolate ions by a charge transfer mechanism, resulting

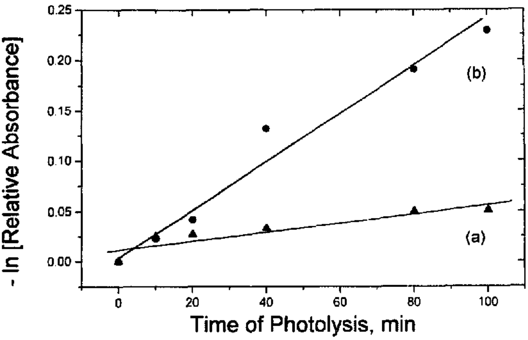
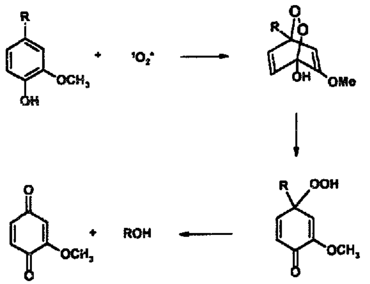


Fig. 5. Comparison of the pseudo-first-order plot: (a) absorbance at 280 nm ($k^1 = 4.28 \times 10^{-4}$ min^{-1}; $r = 0.913$); (b) measurement of the phenol content ($k^1 = 2.33 \times 10^{-3}$ min^{-1}; $r = 0.985$).



Scheme 1. Mechanism of degradation of the lignin phenol structures by singlet oxygen according to Nimz et al. [32].

in the formation of an exciplex intermediate, which can give products [7,9]. At a pH value lower than the pK_a value of the phenols, the mechanism proposed for the action of singlet oxygen on free phenol groups is probably based on the abstraction of the phenolic hydrogen, which generates phenoxyl radicals and, subsequently, quinonoid species [7]. However, Nimz et al. [32] have proposed the formation of an endoperoxide, leading ultimately to *p*-quinones (Scheme 1). The content of free phenol groups in the lignin fragments under study was estimated to be equal to 0.54% for EOL and 2.6% for RHL. The low value found for EOL possibly occurs by virtue of the process of extraction. This lignin was extracted from the liquor by an acesolv pulping process [33] during which some of the free phenol groups were acetylated. In contrast, RHL is a milled wood lignin extracted from rice husks using a mixture of dioxane, water and hydrochloric acid [34]. This process generates phenols by β-O-4 bond cleavage [18].

Differences in structure and function are observed for these two lignin fragments. EOL is a macromolecule with a large molecular weight ($\bar{M}_w \cong 5600$ Da [13]), and has a complex structure. Of the different functional groups present, some were generated by the pulping process, increasing its complexity. In contrast, RHL presents a very low molecular weight ($\bar{M}_w \cong 390$ Da [12]), and seems to be a mixture of dimeric fragments.

3.2. Degradation of lignin on a solid support

The formation of conjugated carbonyl groups, monitored by the increase in intensity in the band at 1660 cm^{-1} and the consumption of free phenol groups, was calculated during the degradation of RHL deposited on a solid surface. An increase in the conjugated carbonyl content was observed (Fig. 6). This may be associated with the formation of quinonoid species during the reaction induced by singlet oxygen. Under our experimental conditions, singlet oxygen acts on the gas–solid interface. Its permeability into lignin was not evaluated. A very similar tendency was observed for studies related to the photo-oxidation of lignin polymer in solution [5]. In parallel, the phenol content was measured (Fig. 6). A clear destruction of phenol groups was observed. The increase in carbonyl group content exceeds, by approximately 100%, the decrease observed in the content of phenol hydroxyl groups. This indicates that other oxidation routes, based on singlet oxygen, lead to the formation of carbonyl structures in parallel with that involving the consumption of free phenol groups. A probable secondary route is the cleavage of the β-O-4 arylether linkages. Considering the mean size of the polymer, we may expect that some β-O-4 ether linkages are present in RHL fragments. Recently, Crestini and D'Auria [35] demonstrated the occurrence of β-O-4 bond cleavage induced by singlet oxygen on lignin dimeric

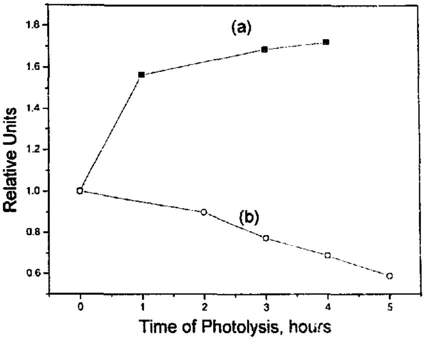


Fig. 6. Formation of conjugated carbonyl groups (a) and consumption of free phenol (b) when RHL fragments are oxidized by singlet oxygen in the solid state.

models (phenoxyacetophenone derivatives), resulting in quinonoid species in addition to other photoproducts. This mechanism is in accordance with the observation of the anomalous increase in the conjugated carbonyl content observed during the degradation of RHL. Thus, phenoxyl radicals, formed from free phenol groups and ether cleavage, can yield quinonoid species during the propagation of the reaction. This is shown by the increase in intensity of the conjugated carbonyl band in the FT-IR spectrum of RHL.

4. Conclusions

From the results obtained in this study on vanillin and lignin fragments, and the data available on the action of singlet oxygen on other functional groups [7,23], free phenol groups can be identified as the main part of lignin responsible for the initiation of the degradation chain mechanism based on singlet oxygen. This degradative process can be improved by the ionization of these groups, facilitating the charge transfer process resulting in the exciplex intermediate [9]. Deactivation of singlet oxygen by hydroxyl ions, added to ionize the phenol groups, probably produces superoxide ions. Moreover, the alkalinization of the reaction medium, which is detrimental for reactions induced by singlet oxygen, is very important for the photodelignification of cellulosic pulps in three stages [11]. This procedure probably activates other important degradative routes. In addition, the results obtained with RHL show that other functional groups participate in the degradation of the polymer induced by singlet oxygen. One of the most probable is β-O-4 bond cleavage, according to a recent article published by Crestini and D'Auria [35] on substituted acetophenones. A better knowledge of the structure of lignin would be useful, and a continuation of the systematic investigation of model compounds will facilitate the evaluation of the decomposition promoted by singlet oxygen and other active species.

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