



On the homogeneous catalysis of the photochemical and thermal O₂-degrading of lignin in aqueous solution. Mechanistic observations on the processes catalyzed by Al^{III}(phthalocyaninetetrasulfonate)³⁻ and Co^{III} dimethylglyoximate complexes

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ABSTRACT

We have explored in this work the photo- and thermally-induced degradations of water soluble lignin in aqueous homogeneous media. Coordination complexes, Al(III) phthalocyaninetetrasulfonate ([Al^{III}(tspc)]³⁻ and tspc⁶⁻ = phthalocyaninetetrasulfonate) and Co^{III} dimethylglyoximate (dimethylglyoximate = DMG⁻) were used as catalysts of degrading processes with different mechanisms. The photodegradation was induced with visible light, $\lambda_{exc} \geq 470$ nm, and [Al^{III}(tspc)]³⁻ as the photosensitizer of the (³Σ_g⁻)O₂ to (¹Δ_g)O₂ conversion. (¹Δ_g)O₂ was the primary active species of the degrading process. [Co(DMG)₂(SO₃)₂]³⁻ and [Co(DMG)₂Cl₂]⁻ in the presence and absence of SO₃²⁻ were used as catalysts of the thermal lignin degrading process. Differences in the mechanisms of the photo and thermally induced processes lead to some diversity of products. Adducts formed in solutions containing [Al^{III}(tspc)]³⁻ and lignin have the absorption spectrum of phthalocyanine oligomers and could be located in pockets of the lignin. Under a steady state irradiation, the attack of lignin by (¹Δ_g)O₂ was followed by changes in the spectrum of the solution and by the formation of various products. The participation of O₂⁻ radicals in the mechanism photodegrading process was investigated with the pulse radiolysis technique. Different lignin radicals were produced when pulse radiolytically generated O₂⁻ and N₃⁻ radicals reacted with lignin. The Co^{III} dimethylglyoximate catalyzed lignin degrading process was investigated in the presence and absence of SO₃²⁻. Although the presence SO₃²⁻ in the medium is not essential, it accelerates the degrading process. This observation shows the participation of inorganic S(V) radicals, e.g., SO₃⁻, as active species in the mechanism when SO₃²⁻ is present. Moreover, the pulse radiolysis experiments demonstrate that O₂⁻ can be an active species when SO₃²⁻ is absent.

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1. Introduction

For many decades numerous chemical processes for the degradation of lignin, many using transition metal compounds, have been investigated and the subject is still a matter of major efforts. Different motivations explain the great attention that these processes receive [1–8]. The bleaching of the lignin in the paper pulp industry, water detoxification and the production of strategic products from the lignin oxidation are some examples. A great number of the studies of the lignin degrading processes have been made using model compounds which mimic phenolic groups in the lignin's structure [3–5]. On the basis of the work done with these model compounds, it has been shown that the lignin's degrading

processes can be catalyzed with complexes of the transition metal ions. Among these catalysts, the phthalocyanines [6,9] and the cobalt complexes with Schiff base ligands [3] have shown promising reactivities.

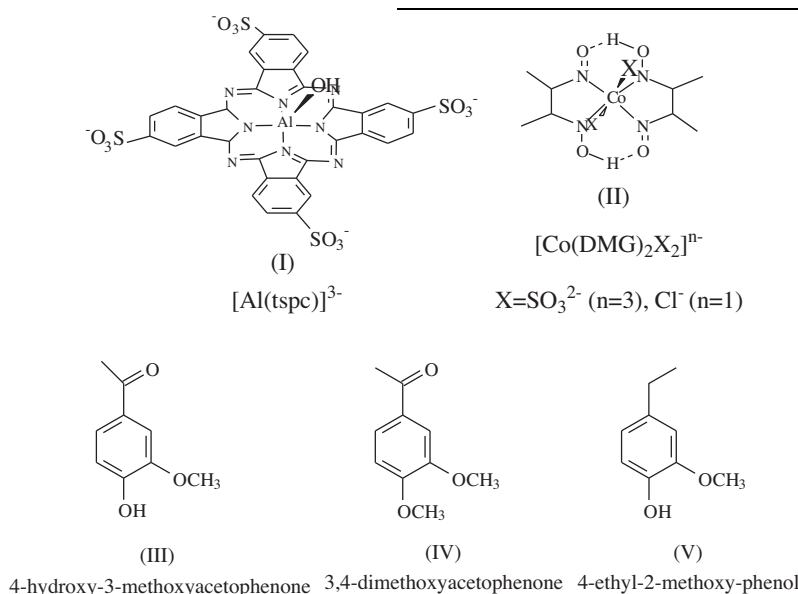
We have recently shown that aqueous solutions of a Al(III) phthalocyanine-decorated polymer photogenerate O₂⁻ radicals under visible light illumination [10]. The radicals degraded lignin and oxidized phenolic compounds preserving the polymer from decomposition. Mechanistic observations on the photochemical and thermal O₂-oxidative degradations of lignin catalyzed respectively by Al^{III}(phthalocyaninetetrasulfonate)³⁻ and Co^{III} dimethylglyoximate complexes were made in this work. To use visible light, i.e., $\lambda_{exc} \geq 470$ nm where the absorption of light by the lignin is weak, the formation of (¹Δ_g)O₂ from the ground state (³Σ_g⁻)O₂ was photosensitized with Al(III) phthalocyaninetetrasulfonate, phthalocyaninetetrasulfonate = tspc⁶⁻ (I), [10]. The thermal

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and photochemical oxidation of SO_3^{2-} to S(V) radicals, e.g., $\text{SO}_3^{\cdot-}$, in solutions of $\text{Co}^{\text{III/II}}$ dimethylglyoximate complexes (II), dimethylglyoximate = DMG^- , has also been communicated in previous works [11]. Because $\text{SO}_3^{\cdot-}$ radicals are converted to $\text{SO}_4^{\cdot-}$, $\text{SO}_5^{\cdot-}$ radicals the presence of O_2 , mechanistic observations on their participation in a lignin degrading process in aqueous solution were also made in this work.

of a known volume of solution in the presence of a well established amount of air in the cell. Vacuum line techniques were used for the manipulation of the gas. The concentrations of lignin were calculated on the basis of the lignin's M_w and an estimated $\text{C}_{10}\text{H}_{11}\text{O}_5\text{X}$ structure, F.W. 2.3×10^2 , designated from herein as the repeating unit. Blanks were made with solutions kept in the dark but having otherwise the same composition of those used for the actual



2. Experimental

2.1. Materials

The water soluble lignin (lignin, alkali, low sulfonate content, $M_w = 6 \times 10^4$ and $M_n = 1 \times 10^4$) was obtained from Aldrich. The elemental analysis of the lignin revealed a total absence of S. The contents of other elements (% C 51.01% H 4.79% O 35.78) correspond to an approximate minimum formula $\text{C}_{10}\text{H}_{11}\text{O}_5$ with an additional 8.4% of other elements. $\text{Na}_3[\text{Al}^{\text{III}}(\text{tspc})]$, (I), $\text{Na}_3[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]$, (II), $\text{Na}[\text{Co}(\text{DMG})_2\text{Cl}_2]$, (II), were available from previous works [10,11]. The purity of the complexes was assessed by means of the UV–Vis absorption spectrum.

Other material were reagent grade and used without further purification.

2.2. Continuous photolysis

Solutions containing appropriate concentrations of $[\text{Al}^{\text{III}}(\text{tspc})]^{3-}$ and lignin and various blanks devoid of lignin or $[\text{Al}^{\text{III}}(\text{tspc})]^{3-}$ were irradiated with polychromatic light simulating solar light. Light from a 250 W Osram Xenophot HLX lamp, placed in an Oriol universal housing, was filtered through a cutoff filter transmitting light of wavelengths $\lambda \geq 470$ nm and focused onto the solutions. HPLC–MS and GC with a flame ionization detector were used for the analyses of the products of the lignin degradation. The solutions used for these analyses were saturated with O_2 or air prior to the experiment and kept under 1 atm of the corresponding gas during the photolysis. Solutions were stirred with magnetic bars to insure the homogeneity of the medium and to maintain constant the concentration of O_2 during the photolysis. The consumption of O_2 was investigated in a different set of experiments. To evaluate by GC the consumption of O_2 during the photolysis, a gas tight cell was used for the photolysis

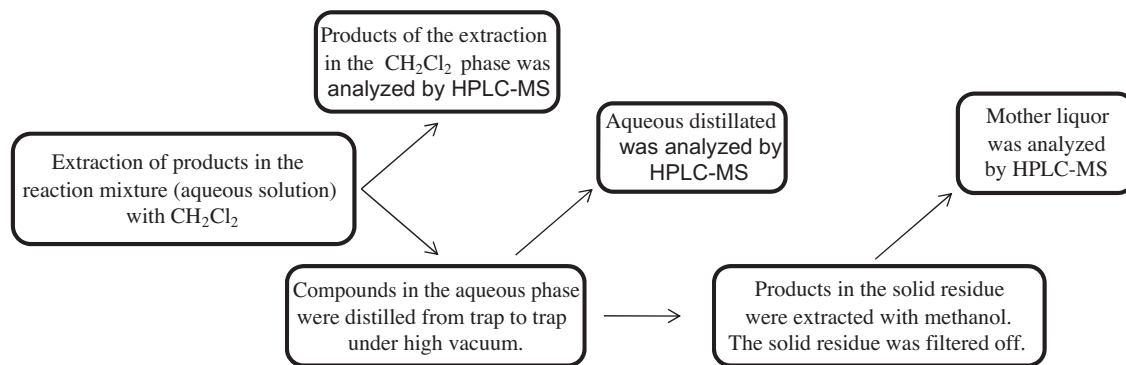
determination of the products of the lignin degrading process. Blanks were made also with solutions saturated with N_2 instead of O_2 . A blank was also made with the liquor obtained from filtering a well shaken suspension of lignin in CH_2Cl_2 .

2.3. Flash photolysis

Absorbance changes, ΔA , occurring in a time scale longer than 1 μs were investigated at room temperature with a flash photolysis apparatus where 15 ns flashes of 532 nm light were generated with a Continuum Powerlite Nd Yag laser. The intensity of the laser flash was attenuated to values equal to or less than 35 mJ by absorbing some of the laser light in a filter solution of $\text{Ni}(\text{ClO}_4)_2$ having the desired optical transmittance, $T = I_t/I_0$ where I_0 and I_t are respectively the intensities of the light arriving to and transmitted from the filter solution. The transmittance, $T = 10^{-A}$, was routinely calculated by using the spectrophotometrically measured absorbance, A , of the filter solution. A right angle configuration was used for the pump and the probe beams. Concentrations of the chromophore in the solution were adjusted to provide homogeneous concentrations of photogenerated intermediates over the optical path, $l = 0.5$ cm, of the probe beam. To satisfy this optical condition, solutions were made with an absorbance equal to or less than 0.1 over the 0.2 cm optical path of the 532 nm pump. Other conditions for these measurements are commented elsewhere in the Results section.

2.4. Pulse-radiolysis procedures

The instrument for the pulse radiolysis experiments and the computerized data collection for time-resolved UV–Vis spectroscopy and reaction kinetics have been described elsewhere in the literature [12]. The solutions were saturated with streams of the O_2 -free N_2O or with the mixtures of O_2 and N_2O required for



Scheme 1.

the experiment. Partial pressures of O_2 and N_2O in the gas mixtures were used for the estimation of the dissolved O_2 concentration. The oxidants $O_2^{\cdot-}$ [13–16], and $N_3^{\cdot-}$ [17] were pulse radiolytically generated following specific procedures in the literature. Experimental conditions were optimized on the basis of the reaction kinetics communicated in the literature for these radicals. The concentrations of $NaHCO_2$ or NaN_3 necessary for the generation of the $O_2^{\cdot-}$ and $N_3^{\cdot-}$ radicals respectively were chosen to prevent reactions between the lignin and the radicals, OH^{\cdot} , H^{\cdot} and e^-_{sol} produced by the radiolysis of H_2O .

2.5. Thermal reactions of lignin with O_2

Solutions used for a study of the $[Co(DMG)_2(SO_3)_2]^{3-}$ or $[Co(DMG)_2Cl_2]^-$ catalyzed degrading of the lignin were treated as indicated for the continuous photolysis experiments, except that their exposure to light was minimized. Lignin solutions devoid of the Co catalysts were used as blanks.

2.6. Analytical procedures

A complex scheme, Scheme 1, was followed for a partial separation and analysis of the products.

To demonstrate that the products were not produced by a spontaneous degrading of the lignin, the reaction mixtures and the corresponding blanks were analyzed in parallel. Moreover, model compounds of the lignin, (III)–(V), were used in preliminary experiments as the substrates of the catalyzed thermal and photochemical reactions. In these reactions, the model compounds were treated in the manner indicated above for the lignin.

3. Results

The lignin model compounds (III)–(V) were initially used instead of the lignin to test the photochemical and thermal reactions respectively catalyzed by $[Al(tspc)]^{3-}$ and Co^{III} dimethylglyoximate complexes. They also were used to obtain experimental information that due to bad optical conditions could not be obtained when lignin was the substrate of the lignin degrading reactions.

3.1. Reactions of the model compounds

Photolysis of oxygenated solutions containing $[Al(tspc)]^{3-}$ and a decimolar concentration of a model compound were carried out with polychromatic light of $\lambda_{exc} > 470$ nm. Products of the reaction were separated by the methods indicated in Scheme 1 and analyzed using the LC–MS and GC techniques. Similar products were obtained when solutions containing 10^{-2} to 10^{-3} M $[Co(DMG)_2(SO_3)_2]^{3-}$, 10^{-1} to 10^{-2} M concentrations of the model

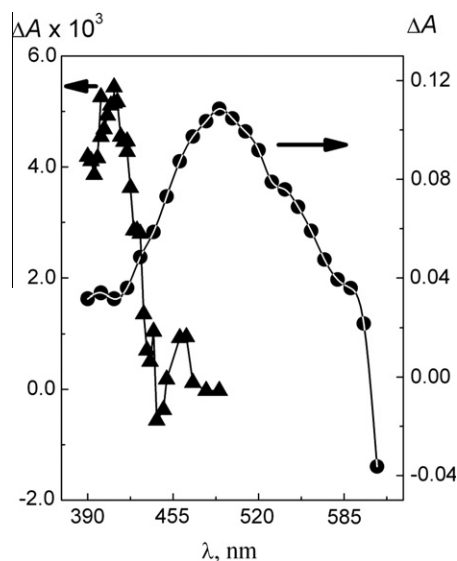


Fig. 1. Transient spectra of the 4-hydroxyl-3-methoxyaceophenone radical (\blacktriangle) and the triplet excited state of $[Al(tspc)]^{3-}$ (\bullet) produced respectively when aqueous aerated and deaerated solutions of the compounds were flash photolyzed at 351 nm. Other experimental conditions are given elsewhere in the text.

compounds and 10^{-2} M SO_3^{2-} were kept under 1 atm of air for periods ranging from 3 to 24 h. The quinone products obtained with (III) and (V), i.e., mainly 2-methoxy and 2,5-dimethoxy para-benzoquinones, were consistent with the proposed formation [3] of phenoxyl radicals in the course of the thermal and photochemical reactions. In contrast, (IV) experienced little if any transformation in the thermally and photochemically catalyzed processes. This experimental observation is consistent with the literature communicated inability of the fully methoxylated phenols to form phenoxyl radicals [3]. It also suggests that partially methoxylated phenylpropanoid groups in the lignin's structure, i.e., *p*-hydroxyphenyl, guaiacyl and syringal, will be the points of attack in the reactions induced with the $[Al(tspc)]^{3-}$ and Co^{III} dimethylglyoximate catalysts.

O_2 -saturated aqueous solutions containing $\sim 6 \times 10^{-4}$ M $[Al(tspc)]^{3-}$ and 10^{-2} M model compound (III), 4-hydroxy-3-methoxyaceophenone, were flash irradiated at 351 nm. The typical transient spectrum of the 4-hydroxyl-3-methoxyaceophenone radical, Fig. 1, was observed at the end of the flash irradiation. When the concentration of model compound was halved to 5×10^{-3} M but the concentration of $[Al(tspc)]^{3-}$ was 6×10^{-4} M, the photogenerated concentration of the phenoxyl radical was the same concentration produced in the preceding experiment. This experimental observation shows that $[Al(tspc)]^{3-}$ functions as the photosensitizer

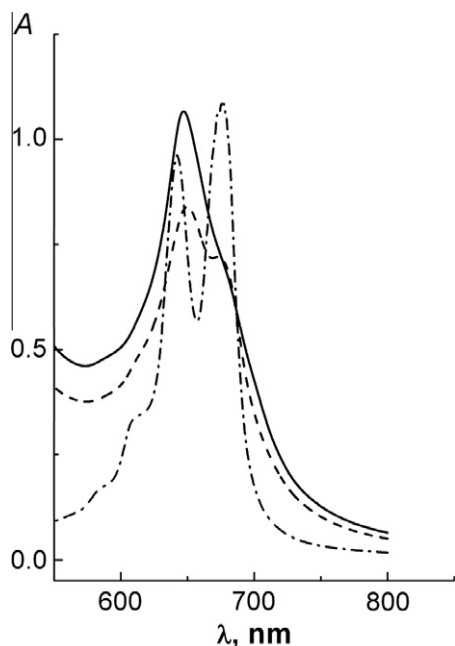


Fig. 2. Optical spectra of the lignin- $[\text{Al}(\text{tspc})]^{3-}$ adduct recorded immediately after elution from the GPC column (solid line) and after 6 h equilibration (dash line). The spectrum of $[\text{Al}(\text{tspc})]^{3-}$ (dash-dot line) is added for comparison purposes.

and that $(^1\Delta_g)\text{O}_2$ is trapped quantitatively at either concentration of the model compound. The point was further verified with blanks consistent of deaerated solutions containing 10^{-4} M $[\text{Al}(\text{tspc})]^{3-}$ and 10^{-2} M model compound. Only the transient spectrum of the $[\text{Al}(\text{tspc})]^{3-}$ triplet excited state was observed when the blanks were flash photolyzed.

3.2. Formation of complex-lignin adducts

The visible absorption spectrum of solutions containing millimolar concentrations of $[\text{Al}(\text{tspc})]^{3-}$ or $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ and

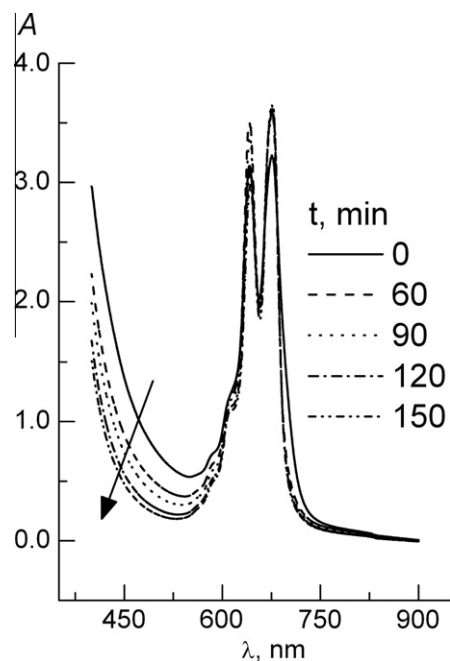


Fig. 3. Changes in the spectrum of a solution containing 0.12 g of lignin and 9.3 mg of $[\text{Al}(\text{tspc})]^{3-}$ in 10 cc of H_2O when is irradiated with polychromatic light, $\lambda_{\text{exc}} > 470$ nm. The sense of the change (arrow) and exposure times are indicated in the figure.

1.8×10^{-2} M repeating units (400 mg of lignin in 100 cc) revealed the formation of adducts between the lignin and the complexes. Since the adduct between the lignin and $[\text{Al}(\text{tspc})]^{3-}$ was sufficiently stable and slow to dissociate into $[\text{Al}(\text{tspc})]^{3-}$ and lignin, it was separated by size exclusion chromatography. The adduct eluted in a fraction by itself while free lignin and $[\text{Al}(\text{tspc})]^{3-}$ eluted later in two other fractions. Inspection of the fraction containing the adduct by means of the visible spectrum showed that it changed over a period of several hours, Fig. 2. The spectroscopic changes were consistent with the liberation of $[\text{Al}(\text{tspc})]^{3-}$ from the adduct and it was indicative of the adduct reaching a new equilibrium position with free lignin and $[\text{Al}(\text{tspc})]^{3-}$ in the solution.

3.3. Homogeneous photocatalysis by $[\text{Al}(\text{tspc})]^{3-}$ of the lignin degrading process

An oxygen saturated aqueous solution of 0.12 g of lignin ($\sim 5.4 \times 10^{-4}$ repeating units) and 9.3 mg of $[\text{Al}(\text{tspc})]^{3-}$ in 10 cc of H_2O was used for the investigation of the photocatalyzed polymer degrading process. The polychromatic irradiation of the solution at $\lambda_{\text{exc}} > 470$ nm caused a progressive bleaching of the absorption bands of the lignin at $\lambda < 450$ nm, Fig. 3. In contrast, no changes in the spectrum of the lignin were observed during the photolysis of a solution containing 0.12 g of lignin in 10 cc of O_2 -saturated H_2O . This is the expected photochemical result because, under the optical conditions of these experiments, the polychromatic light used for the irradiation of the solutions, $\lambda_{\text{exc}} \geq 470$ nm, is almost completely absorbed by $[\text{Al}(\text{tspc})]^{3-}$.

The $[\text{Al}(\text{tspc})]^{3-}$ -photocatalyzed degrading of the lignin was also followed by means of the O_2 consumption. In these experiments a solution containing 3.05 mg of lignin ($\sim 1.3 \times 10^{-5}$ repeating units) and 1 mg of $[\text{Al}(\text{tspc})]^{3-}$ in 10 cc of H_2O and blanks made of solutions containing 3.05 mg of lignin in 10 cc of H_2O were saturated with air instead of O_2 . Chromatographic analyses of the gas mixtures remaining after the solutions were photolyzed for periods equal to or less than 4 h showed a progressive increase of the N_2 : O_2 molar relationship relative to the corresponding blank. and a decrease of the solutions' pH. At the end of a 72 h photolysis, 7.7 mmol of O_2 were consumed per 178 mg ($\sim 8.0 \times 10^{-4}$ repeating units) of lignin. This mass of lignin corresponded to a formula, $\text{H}_{10}\text{C}_{10}\text{O}_3$, very close to the average phenolic unit in the lignin structure. Consistent with the photoinduced consumption of O_2 , numerous products of the lignin degrading process were detected using the LC-MS and GC techniques with both the distillates and the extracts from the reaction mixture. Because these peaks correspond to masses below the 350 range, they must arise from the degradation into fragments associated with one aromatic ring in the lignin structure. Some tentative structural assignments of the light fw products, based only on the mass peaks, are shown in Fig. 4. Small fractions of products with higher masses, i.e., fw > 350, were also detected and tentatively assigned to products derived from groups in the lignin structure containing two or more aromatic rings.

In flash photolysis experiments, oscillographic traces of a very poor quality were recorded in the respective 351 and 532 nm flash irradiations of O_2 -saturated solutions containing various concentrations of lignin and $[\text{Al}(\text{tspc})]^{3-}$. The poor quality of the traces resulted from the very large absorbance at the monitoring wavelengths in solutions where the concentrations of lignin and $[\text{Al}(\text{tspc})]^{3-}$ were appropriate for the absorption of the laser light. While transient spectra could not be collected and oscillographic traces for kinetics were devoid of the necessary quality, the absorbance changes were consistent with the formation of the lignin radical seen when $\text{O}_2^{\cdot -}$ was the oxidant in pulse radiolysis.

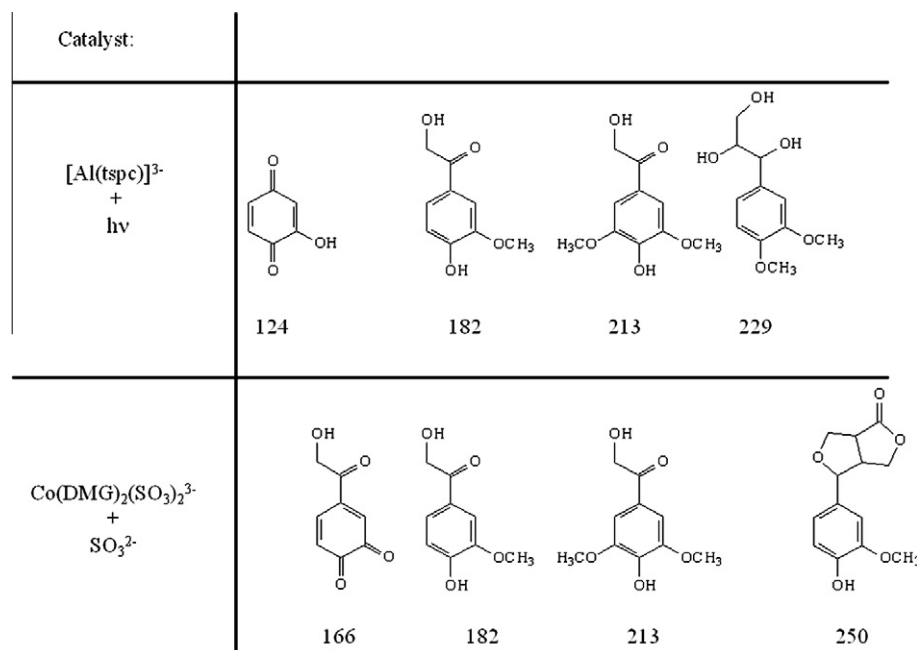


Fig. 4. Tentative assignment of structures to some of the light fw products generated in the $[\text{Al}(\text{tspc})]^{3-}$ photocatalyzed and $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ thermally catalyzed degradations of lignin. The fw masses, derived from the MS spectra, are indicated under each structure. The analytical methods are described elsewhere in the text.

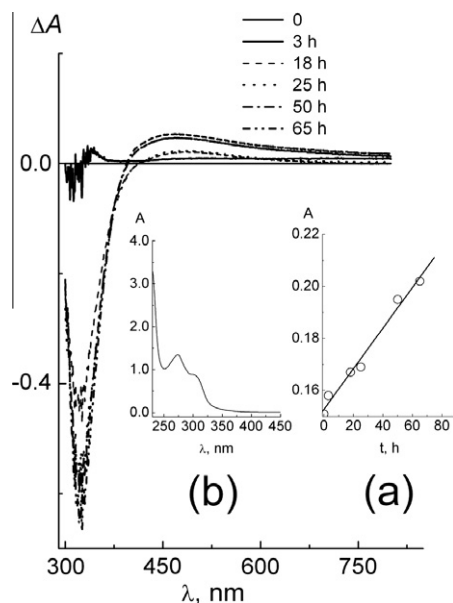


Fig. 5. Difference spectrum of the products extracted with CH_2Cl_2 from the reaction mixture. The inset (a) shows the 485 nm absorbance growth with time. The optical spectrum of the products in CH_2Cl_2 is shown in the inset (b).

3.4. Homogeneous catalysis by $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ of the lignin degrading process

Another catalysts of the lignin degrading process investigated in this work were the complexes $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ and $[\text{Co}(\text{DMG})_2\text{Cl}_2]^-$. Although the lignin degrading process is photocatalyzed by these Co complexes, it also proceeded in the absence of light. The dark processes were investigated with O_2 -saturated solutions containing 23 mg of lignin and the catalyst in 30 cc of H_2O buffered at pH 10. Because $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ catalyzes the O_2 oxidation of SO_3^{2-} [11], different concentrations of Na_2SO_3 were

used with the $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ catalyst so as to test the effect of excess sulfite on the reaction rate and on the products formed by the lignin degrading process. In these experiments, 78 mg of $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ and 375, 125 or 0 mg of Na_2SO_3 were added to the lignin solution. The difference spectrum of samples taken from these solutions at different periods of the reaction demonstrated that the lignin was been transformed in all of them, Fig. 5. Absorption bands between 250 and 350 nm are characteristic of the reaction products, inset (b) to Fig. 5. Indeed, no absorption bands above 250 nm were observed in the spectrum of the CH_2Cl_2 solutions prepared with blanks. It is worth to note that the optical spectra of compounds with quinonic structures have features consistent with the spectroscopic changes in Fig. 5 and are those features who give a light yellow color to the extracts. The rate of lignin degradation, determined from changes in the absorption spectrum of the aqueous solutions, increased with the presence of Na_2SO_3 . A linear dependence of the absorbance change with time was maintained over a long period of time, Fig. 5 insert b. Using the slope of the line as measure of the reaction rate, a threefold increase in the rate was observed when the Na_2SO_3 concentration was increased from 3.0×10^{-2} M to 1.0×10^{-1} M. This is consistent with a mechanism where the oxidation of SO_3^{2-} determines the rate of the lignin degrading process.

Periods of three or four days from the mixing of the lignin and the catalysts were allowed before the products in the reaction mixture were investigated. Numerous products of the lignin degrading process were extracted from the reaction mixture and detected with the LC-MS and GC techniques. In the MS analyses of the products, peaks corresponding to masses below the 350 range were observed, Fig. 4. Although the masses of these products were in the same range of those obtained in the $[\text{Al}(\text{tspc})]^{3-}$ photocatalyzed lignin degradation, differences on the peak masses, i.e., different products, were observed. It is possible to reconcile the dissimilar distribution of products with the different mechanisms of the photochemical and thermal processes.

The reaction of the lignin with O_2 was also catalyzed by $[\text{Co}(\text{DMG})_2\text{Cl}_2]^-$. The lignin degrading process was investigated with a O_2 -saturated solutions containing 0.12 g of lignin ($\sim 1.8 \times 10^{-2}$ M

repeating units), 78 mg of $[\text{Co}(\text{DMG})_2\text{Cl}_2]^-$ and 375, 125 or 0 mg of Na_2SO_3 in 30 cc of H_2O buffered at pH 10. Therefore the degradation process proceeds in the absence of Na_2SO_3 but the latter accelerates the degradation of the lignin in the same proportion described for the degrading process catalyzed by $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$. If S(V) radicals, e.g., $\text{SO}_3^{\cdot-}$, are formed when Na_2SO_3 is present, superoxo intermediates, e.g., $\text{O}_2^{\cdot-}$, must be the active species in its absence.

3.5. Spectroscopic observation of the lignin attack by $\text{O}_2^{\cdot-}$ and N_3^{\cdot} radicals

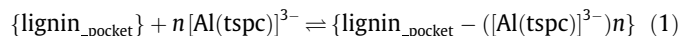
The respective attacks of the lignin by the oxidizing radicals $\text{O}_2^{\cdot-}$ and N_3^{\cdot} were investigated following changes of the absorption spectrum of lignin solutions. The aim was to observe the lignin radicals produced by the N_3^{\cdot} oxidant and to establish if $\text{O}_2^{\cdot-}$ radicals were able to attack the lignin. A solution containing 0.2 M NaN_3 and 3.3×10^{-4} M repeating units of lignin (0.164 g of lignin in 200 cc) was deaerated and saturated with N_2O . With these concentrations, the N_3^{\cdot} radicals are fully prepared in less than 5 μs after the radiolysis pulse and a broad spectrum ($\lambda_{\text{max}} \sim 420$ nm) grows next, over a 400 μs period, Fig. 6. The spectrum has some features that can be ascribed to the formation of phenoxyl radicals in the lignin frame. In contrast to the species produced in the N_3^{\cdot} attack of the lignin, only a progressive bleach of the solution's spectrum was observed when $\text{O}_2^{\cdot-}$ radicals react with lignin, Fig. 6. $\text{O}_2^{\cdot-}$ radicals were radiolytically generated in much less than 10 μs after the radiolysis pulse in a O_2 -saturated solution, $[\text{O}_2] \sim 2.6 \times 10^{-4}$ M, containing 0.2 M NaHCO_2 and 3.3×10^{-4} M repeating units of lignin (0.164 g of lignin in 200 cc). The attack of the $\text{O}_2^{\cdot-}$ radical bleached the lignin's spectrum in a 400 μs time period after the formation of the peroxy radical anions. A marked disparity can be seen between the spectra in Fig. 6 and a literature spectrum of a lignin radical produced by the radiolytic oxidation of black liquor of sulfate cellulose with radiolytically generated H^{\cdot} and OH^{\cdot} radicals [18]. Although lignin is the main component of the latter material, its absorption spectrum and the

absorption spectrum of the polymer used in this work are different. One reason for the dissimilarities between the difference spectra can be differences between the absorption spectrum of the polymers. In addition, the lignin radicals formed by the addition reactions of the H^{\cdot} and OH^{\cdot} radicals can be expected to be different of those generated with $\text{O}_2^{\cdot-}$ and N_3^{\cdot} .

4. Discussion

The experimental observations show that $[\text{Al}(\text{tspc})]^{3-}$ and $\text{Co}^{\text{III/II}}$ dimethylglyoximate complexes respectively catalyze the photo and thermal O_2 oxidative lignin degrading process in aqueous homogeneous solutions. While $(^1\Delta_g)\text{O}_2$ and $\text{O}_2^{\cdot-}$ radicals are the active species in the $[\text{Al}(\text{tspc})]^{3-}$ catalyzed process, radicals derived of the reaction of $\text{SO}_3^{\cdot-}$ with O_2 are the active species in the $\text{Co}^{\text{III/II}}$ dimethylglyoximate catalyzed process. The product diversity, Fig. 4, is therefore explained by the different mechanisms of the photo and thermal catalyses and the formation of specific adducts. Aspects of these mechanisms are discussed in the following paragraphs.

The formation of lignin adducts with these complexes is in agreement with literature reports where the adducts have been assigned as inclusion complexes [19]. The adduct with $[\text{Al}(\text{tspc})]^{3-}$ is remarkably stable and dissociates slowly. Furthermore, there is a strong resemblance between the spectrum of the Al(III) phthalocyanine chromophore in the inclusion complex, Fig. 2, and the spectrum of the oligomers, $([\text{Al}(\text{tspc})]^{3-})_n$ where $n \geq 2$ [20]. The marked difference between the spectra of the inclusion complex and the free $[\text{Al}(\text{tspc})]^{3-}$ can be seen in Fig. 2. One possible reason for the spectrum of $[\text{Al}(\text{tspc})]^{3-}$ in the adduct is that incorporation of the complex in pockets of the lignin displaces the oligomer formation equilibrium, Eq. (1). Either or both specific interaction of the $[\text{Al}(\text{tspc})]^{3-}$ with lignin groups and medium conditions can produce larger concentrations in the pockets than in the bulk and a consequent displacement of Eq. (1) towards the oligomers.



Differences in the mass spectra of the products obtained from the lignin when O_2 is respectively photochemically activated with $[\text{Al}(\text{tspc})]^{3-}$ or thermally activated with $\text{Co}(\text{III})$ complexes makes necessary to invoke different mechanisms for each of these processes. A baseline for comparison is provided by the $[\text{Al}(\text{tspc})]^{3-}$ photocatalyzed lignin degrading process. It has been shown previously that irradiation of oxygenated solutions of $[\text{Al}(\text{tspc})]^{3-}$ at $\lambda_{\text{exc}} \geq 470$ nm, i.e., principally in the Q-band, sensitizes the conversion of $(^3\Sigma_g^-)\text{O}_2$ to the powerful oxidant $(^1\Delta_g)\text{O}_2$ [10,20–23]. The flash photolysis experiments show that $(^1\Delta_g)\text{O}_2$ produced in this manner attack the model compound and must do the same with phenolic groups in the lignin. Reactions of $(^1\Delta_g)\text{O}_2$ with the different phenolic groups in the lignin structure are expected to form phenoxyl and $\text{O}_2^{\cdot-}$ radicals via electron transfer or hydrogen abstraction [23]. $(^1\Delta_g)\text{O}_2$ can also form endoperoxides by adding to aromatic groups [24]. The resulting radicals in the lignin structure must undergo structural reorganizations and subsequent oxidations by oxidants present in the medium, e.g., $(^3\Sigma_g^-)\text{O}_2$, to form the more stable products. The participation of the $\text{O}_2^{\cdot-}$ radicals in the lignin degrading process will be discussed in connection with the $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ and $([\text{Co}(\text{DMG})_2\text{Cl}_2]^- + \text{SO}_3^{2-})$ catalyzed O_2 degrading of the lignin.

No $(^1\Delta_g)\text{O}_2$ is produced with $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ and $([\text{Co}(\text{DMG})_2\text{Cl}_2]^- + \text{SO}_3^{2-})$ catalysts. The catalysis must be related to the ability of the cobalt complexes to shuttle between the $\text{Co}(\text{III})$ and $\text{Co}(\text{II})$ oxidation states in the presence of O_2 and a reducing substrate [11]. This cyclic process was applied, for example, to the $[\text{Co}(\text{DMG})_2(\text{SO}_3)_2]^{3-}$ -catalyzed aerobic oxidation of SO_3^{2-} shown in Eq. (2). The cycle produces sulfur radicals, i.e.,

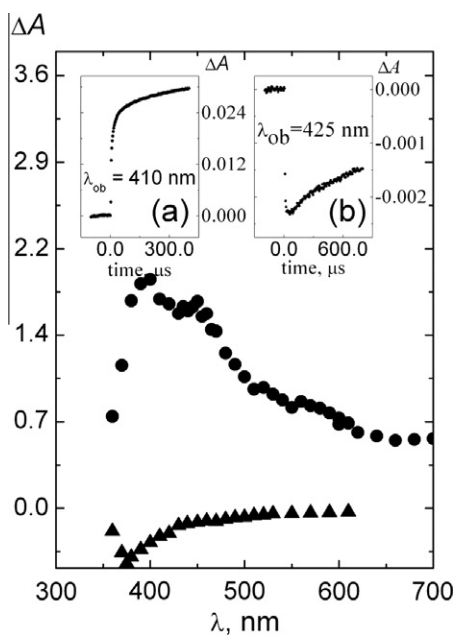


Fig. 6. Transient spectra recorded 350 μs after the attack of lignin (5.4×10^{-3} M repeating units) by pulse radiolytically generated N_3^{\cdot} radicals (●) and $\text{O}_2^{\cdot-}$ (▲) radicals. Oscillographic traces (top of the figure) correspond respectively to the time-resolved growth of the 410 nm absorbance in the reaction of the lignin with N_3^{\cdot} radicals (a) and the bleach of the 425 nm lignin's absorbance in the reaction with $\text{O}_2^{\cdot-}$ radicals (b).

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