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High-intensity laser generation of *ortho*-quinones from 2-methoxyphenols; relevance to the question of color reversion in pulp and paper

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Abstract

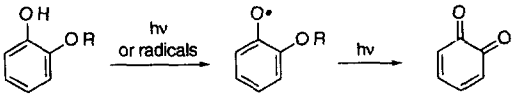
High-intensity photodecomposition of 2-methoxyphenols using 248 nm laser excitation leads to the formation of small yields of *ortho*-quinones through the intermediacy of phenoxyl radicals, which undergo photocleavage of the O–C bond. This process was studied using the laser-drop technique and the products were characterized by fluorescence spectroscopy following derivatization with 1,2-phenylenediamine. It is suggested that, given the long lifetime (several days) of related lignin-derived phenoxyl radicals in paper, similar processes may be partially responsible for quinone-mediated color development in papers manufactured from high-yield pulps.

Keywords: Color reversion; High-intensity laser generation; 2-Methoxyphenols; *ortho*-Quinones

1. Introduction

A considerable amount of research has been conducted recently in an attempt to understand the mechanism of photodegradation of lignin-containing high-yield papers such as newsprint [1,2]. It is generally accepted that the understanding of the chemical processes responsible for yellowing may help prevent this undesired phenomenon.

Most of the results reported have not been obtained in the solid matrix of the paper itself, but rather by studying model compounds in solution [3–17], since paper is a very complex system in which it is difficult to control the conditions sufficiently to be able to draw reliable conclusions. Models have generally been designed to incorporate some of the key chromophores in lignin. However, it is well known that the chemical behavior can be very different in solid matrices and in solution. For example, phenoxyl radicals have lifetimes of several days in solid matrices as opposed to values in the microsecond domain in solution [18]. The absorption of photons by phenoxyl radicals is improbable in solution, given their short lifetime and low steady state concentration; however, in a solid matrix, such as paper, phenoxyl radicals are probably sufficiently long lived to undergo photoinduced processes. Furthermore, the final outcome of these multiphoton processes may be the formation of substituted 1,2- and 1,4-benzoquinones, which are known to be highly colored products. It is thus of interest to examine whether the two-photon process given in Eq. (1) is possible. Some of the laser techniques developed in our laboratory offer a unique opportunity to explore this question [19–22].



(1)

On the surface of the paper, direct spectroscopic characterization of quinones is almost impossible due to either the interference of other similar chromophores (IR, NMR) or the lack of fluorescence of quinones (fluorescence techniques). Recently, several research groups have shown that quinones are present in high-yield pulp [23,24]. In our laboratory, we have also shown that quinones are present and that their amount increases on irradiation up to a certain time, and then decreases [25].

We wished to determine whether quinones could be formed directly from phenols or phenoxyl radicals. In solution, the short lifetime of phenoxyl radicals limits the probability of their participation in further photochemical processes. Therefore we employed the technique of laser-drop photolysis (LDP) developed in our laboratory [21,22] which favors multiphotonic rather than monophotonic processes.

We chose fluorescence spectroscopy to study quinone formation, because of its high sensitivity, since in our system we expected only a small amount of product formation due

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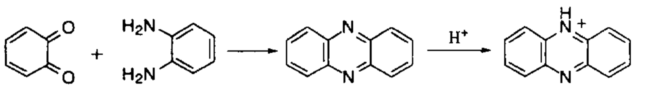
to the low efficiency (see below) of Eq. (1) and the photodegradation of quinones. Quinones are generally non-fluorescent, and therefore in order to detect them they need to be derivatized. Recently, Zhu et al. [24] have shown that *ortho*-quinone and 1,2-phenylenediamine react readily to form phenazine on the surface of paper (Eq. (2)); furthermore, the characteristic fluorescence of the protonated phenazine can be easily detected. In addition, since phenazines are more stable than quinones, it should be possible to characterize the products in the reaction mixture using gas chromatography–mass spectrometry (GC–MS) techniques.



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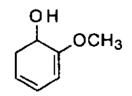
In this paper, we report our results on the solution multiphoton photochemistry of several substituted 2-methoxyphenoxyl radicals derived from the phenols shown below.



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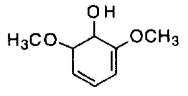

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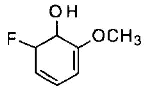

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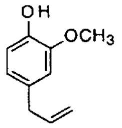

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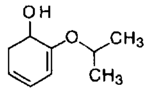

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2. Experimental section

2.1. *Laser flash photolysis (two-laser two-color)*

These experiments were carried out using for excitation a Lumonics EX-510 excimer laser filled with a Kr–F_2–He mixture (248 nm, approximately 70 mJ per pulse), a Lumonics EX-530 filled with an Xe–HCl–Ne mixture (308 nm, approximately 80 mJ per pulse) or the third harmonic from a Surelite Nd:YAG laser (355 nm, approximately 30 mJ per pulse). All pulse durations were less than 10 ns. The system was controlled by a Power Macintosh computer with software developed in the LabVIEW 3.1.1 environment from National Instruments. The full description of a similar system, including the modifications for the adaptation of the system for two-laser two-color experiments, has been reported elsewhere [9,26].

2.2. *Laser-drop photolysis (LDP)*

Deaerated solutions of the starting material with an absorbance of unity (at the laser wavelength; for an optical path length of 7 mm) were exposed to 248 nm irradiation (60 mJ per pulse). Some experiments were conducted in the presence of tert-butylperoxide using 308 nm irradiation. In this case, the absorbance of the solution at the laser wavelength was 0.3. Photodecomposition of the peroxide yields tert-butoxyl radicals that readily abstract hydrogen atoms from phenols [27]. Further details of the LDP technique have been published elsewhere [22].

2.3. *Low-intensity irradiation*

The same solutions were irradiated in a photochemical reactor equipped with six RPR-254 lamps. The temperature of the reactor was typically between 32 and 35 °C. Once the samples had been irradiated, 1 ml of a phenylenediamine solution in methanol (2 mg ml^{-1}) was added, and the solvent volume was reduced under vacuum to 0.5 ml. The mixture was kept at 80 °C for 5 min.

2.4. *Fluorescence spectroscopy*

The fluorescence spectra were recorded with a Perkin–Elmer LS-50 spectrofluorometer.

2.5. *Synthesis of quinone model compounds*

Several quinones had to be prepared in order to provide suitable reference materials for the fluorescence work; these included 1,2-benzoquinone (**6**), 3-methoxy-1,2-benzoquinone (**7**), 3-fluoro-1,2-benzoquinone (**8**) and 4-allyl-1,2-benzoquinone (**9**). In all the syntheses, we used the corresponding methoxyphenols (0.02 mol in 50 ml of solution), which were stirred in cold water with one equivalent of $NaIO_4$ dissolved in cold water [28]. After a short period of mixing, the solution was extracted with CH_2Cl_2, dried over Na_2SO_4 and filtered. After concentrating the solution to 20 ml, hexane was added and the precipitate was filtered. In the case of eugenol and 6-fluoro-2-methoxyphenol, the solvent was totally evaporated and the oil obtained was used for the experiments. The compounds obtained were not pure, but all attempts to improve the purification failed. The major contaminants were the starting material and the corresponding *ortho*-diphenol, and since these compounds do not interfere in the fluorescence experiments, we used the mixtures as obtained.

2.6. *Fluorescence quantum yield measurements*

Given the problems in purifying these unstable *ortho*-quinones, we were only able to determine the relative quantum yields of emission. 1,2-Benzoquinones were reacted with 1,2-phenylenediamine (see Eq. (2)). Acetic acid (20 μl) was added, the sample absorbances were matched at the excitation wavelength and the fluorescence was recorded and integrated.

3. Results

1,2-Benzoquinones can participate in cycloaddition reactions with several compounds (e.g. trialkyl phosphite [23], 1,2-phenylenediamine [24] and diphenyl ethylene [29,30]); the resulting compounds are frequently stable and can be well characterized. The reaction of *ortho*-benzoquinone with 1,2-phenylenediamine readily leads to the formation of phenazine [30]. The protonated form of phenazine has a characteristic fluorescence band with a maximum at 520 nm. Another advantage of using phenazine is that it absorbs at relatively long wavelengths at which the starting material and other products present do not; hence selective phenazine fluorescence excitation is possible.

3.1. *Low-intensity irradiation*

Fig. 1 shows the results of low-intensity irradiation of 2-methoxyphenol compared with an unirradiated solution subjected to the same treatment with 1,2-phenylenediamine. The small emission enhancement observed is probably due to either slight decomposition of 1,2-phenylenediamine during the attempted quinone derivatization or to traces of quinone present in the starting phenol. The latter possibility may be due to the decomposition of the starting material, which in the presence of oxygen can form quinones [31]. Pure 1,2-phenylenediamine does not absorb in this wavelength region (above 375 nm); hence it should not luminesce, although it is light and heat sensitive and the oxidation products are fluorescent in the same region. *ortho*-Quinone formation was not observed using any of the starting materials (**1**–**5**) under conditions of low-light intensity excitation.

3.2. *High-intensity experiments*

We studied the multiphoton chemistry of 2-methoxyphenol (**1**), 2,6-dimethoxyphenol (**2**), 2-methoxy-6-fluorophenol (**3**), 2-methoxy-4-allylphenol (**4**) and 2-isopropoxyphenol (**5**) (see Section 1). Through the study of these compounds, we were able to explore the importance of electron-donating groups in the ortho or para position on the formation of phenoxyl radicals (**2** and **4** respectively), the influence of electron-withdrawing groups (**3**) and the role of different leaving groups (**5** vs. **1**) in the photochemical second step in the pathway to 1,2-benzoquinone formation.

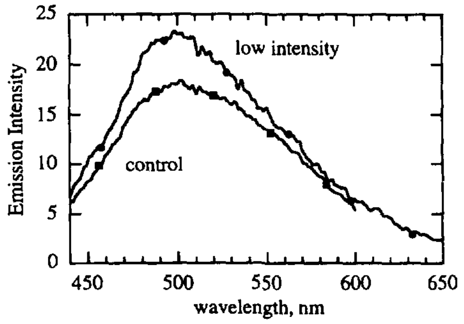

Fig. 1. Comparison of the fluorescence from a control sample with that of a sample irradiated with low-intensity 254 nm light (sample of 2-methoxyphenol in hexane) following treatment with 1,2-phenylenediamine. Excitation wavelength, 420 nm.

We also attempted to evaluate the occurrence of multiphotonic processes of phenoxyl radicals using two-laser two-color laser flash photolysis [20]. In this technique, the first laser (synthesis laser) is used to generate the phenoxyl radicals, and the second laser (photolysis laser) is used to supply the second photon which is necessary for quinone formation [20]. Using a 308 nm laser as synthesis laser and α-guaiacoxyacetoveratrone as an efficient phenoxyl radical source, we did not observe any bleaching of the guaiacoxy radical using 355 nm excitation for the photolysis laser. The same result was obtained when the phenoxyl radicals were generated from 2-methoxyphenol in the presence of tert-butylperoxide. This suggests that the quantum yield of reaction must be low (see below), although it should be noted that this wavelength is not ideal and may lead to some signal compensation due to weak absorption by the precursors in this region.

In LDP, the laser is focused on a stream of solution droplets and, in this way, a relatively large photon dose is concentrated on a small volume of solution. This technique is very efficient in promoting multiphotonic processes [22]. We also used the LDP technique (308 nm) with solutions of 2-methoxyphenol and tert-butylperoxide. These solutions did not lead to any detectable formation of *ortho*-benzoquinone from 2-methoxyphenol after irradiation. The 308 nm LDP of α-guaiacoxyacetoveratrone (a frequent choice as a lignin model [4,5,10,12,13,32]) produced a very complex mixture of products, and it was not possible to characterize unambiguously the fluorescence of the derivatized *ortho*-quinones. However, there was some indication that the process was more efficient in non-polar solvents. When a 248 nm laser was used as synthesis laser in the presence of 2-methoxyphenol, the yield of phenoxyl radicals was very small. However, in LDP using the same laser we were able to detect *ortho*-quinone formation. It is possible that under these conditions absorption of a second photon by the radical itself is favored.

Fig. 2 shows the emission and excitation fluorescence spectra of irradiated and unirradiated samples of 2,6-dimethoxyphenol in hexane. Clearly, phenazine is not the only product of irradiation and subsequent derivatization of the products. One of the other products, according to GC–MS, is 9-fluorenone, which also fluoresces at slightly longer wavelengths, although the origin of this compound remains unclear. Unreacted 1,2-phenylenediamine is also present as well as the other radical products of the reaction. To achieve better discrimination, we changed the excitation wavelength (see Fig. 3). Increasing the excitation wavelength helps to separate the signals, since at longer wavelengths the other products and the starting material are transparent. The experiment was also repeated using acetonitrile (see Fig. 4). No product formation was observed under these conditions.

Fig. 5 (bottom) shows the fluorescence spectra of the different substituted 2-methoxyphenols after LDP and 1,2-phenylenediamine derivatization. In each case, we observed the formation of the corresponding 1,2-benzoquinone. The exci-

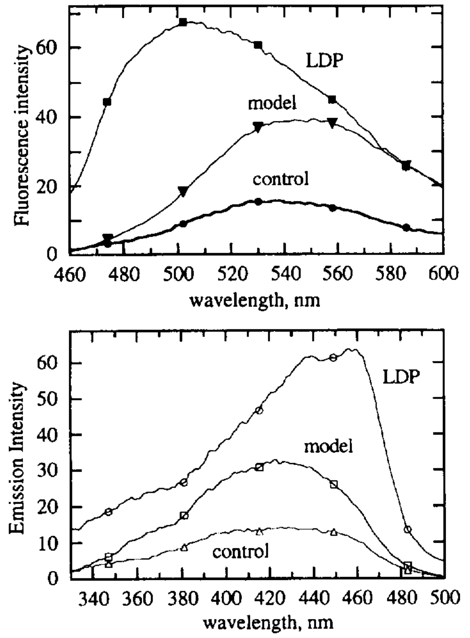

Fig. 2. Fluorescence spectra (top) of LDP sample (248 nm) and control 2,6-dimethoxyphenol after treatment with 1,2-phenylenediamine. The spectrum labeled "model" corresponds to the *ortho*-quinone. Excitation, 440 nm. Bottom: excitation spectra with the emission monitored at 520 nm.

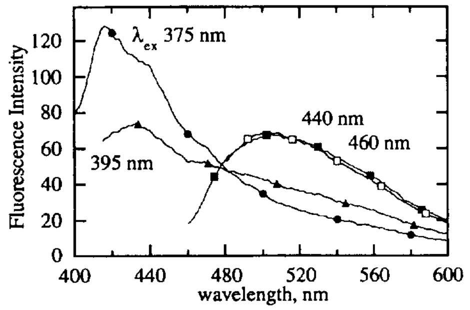

Fig. 3. Effect of the excitation wavelength on the fluorescence spectrum of the reaction mixture following laser-drop excitation of 2,6-dimethoxyphenol in hexane at 248 nm and treatment with 1,2-phenylenediamine.

tation spectra (Fig. 5, top) show that electron-donating substituents lead to a decrease in the yield of the two-photon product, and this effect is especially pronounced in the allyl-substituted case. Electron-withdrawing groups lead to a small increase in the yield. An explanation may be that the electron-withdrawing groups weaken the C–O bond, which aids product formation, but destabilizes the final products. The electron-donating groups have the opposite effect.

To gain information about the relative amounts of substituted *ortho*-quinones formed, we measured the relative quantum yields, taking the unsubstituted compound as reference (see Table 1). The quantum yield is especially high in the case of the allyl compound. When 2-isopropoxyphenol (**5**) was used instead of 2-methoxyphenol (**1**), we observed some increase in product formation (see Fig. 6).

In two cases (**1** and **2**), we monitored the formation of the corresponding phenazine by GC–MS analysis. The mass spectra confirm the formation of the fluorescent sensor; however, the yields are very small. The relatively high 1,2-phenylenediamine to *ortho*-quinone ratio used during derivatization caused serious problems in GC–MS analysis, since the amine itself can decompose, thereby making the obser-

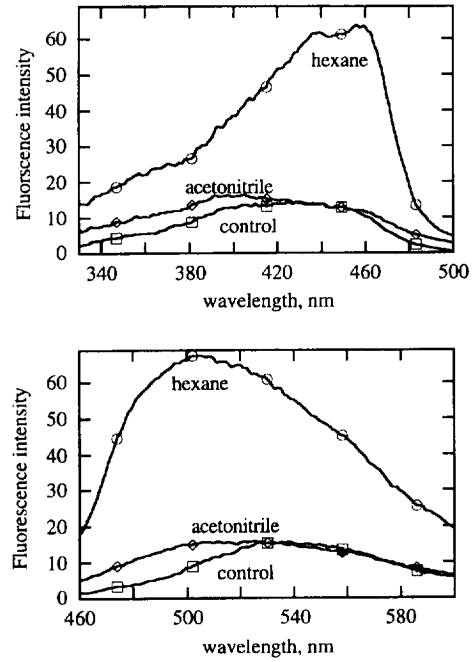

Fig. 4. Top: fluorescence excitation spectra (excitation wavelength, 520 nm) of 2,6-dimethoxyphenol LDP samples in hexane and acetonitrile after treatment with 1,2-phenylenediamine, and of an unirradiated sample (control in hexane) after treatment with 1,2-phenylenediamine. Bottom: fluorescence excitation spectra (emission wavelength, 440 nm) of the same samples.

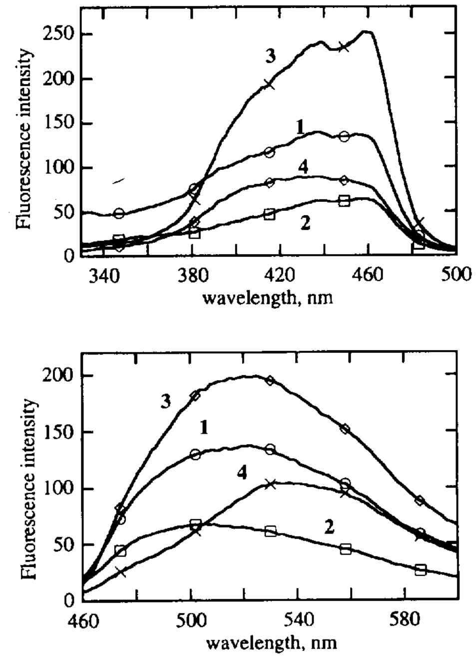

Fig. 5. Top: fluorescence excitation spectra of different substituted 2-methoxyphenols (emission wavelength, 520 nm) after LDP in hexane and treatment with 1,2-phenylenediamine. Bottom: fluorescence emission spectra of the same samples (excitation wavelength, 440 nm).

Table 1
Room temperature relative quantum yields of fluorescence for substituted phenazines formed by reaction of 1,2-phenylenediamine with various quinones

Compound	Relative quantum yield of fluorescence
1,2-Benzoquinone (**6**)	1
3-Methoxy-1,2-benzoquinone (**7**)	2.52
3-Fluoro-1,2-benzoquinone (**8**)	2.03
4-Allyl-1,2-benzoquinone (**9**)	47.0

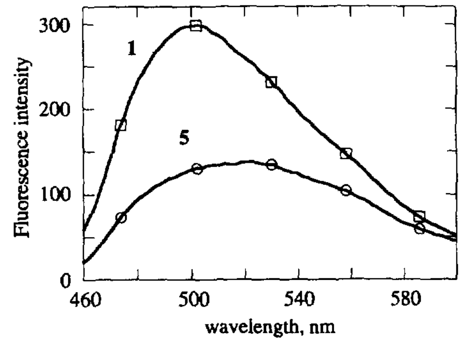

Fig. 6. Fluorescence emission spectra (excitation at 420 nm) of 2-methoxyphenol (1) and 2-isopropoxyphenol (5) in hexane after LDP and derivatization with 1,2-phenylenediamine.

vation of phenazine difficult. Some attempts using the different basicity of the amine and phenazine were made to remove the amine by selective protonation. Although this procedure worked well with the model experiments, it failed when it was used with the reaction mixture, probably because of the large difference in the amount and ratio of compounds present. Thus it was not possible to remove the amine using this technique.

4. Discussion

In all our experiments, the extreme instability of the 1,2-benzoquinones represented a major problem. The parent compound decomposes at 40 °C [28]. In addition, *ortho*-quinones are light sensitive. Most probably, this problem will effectively reduce the apparent yields of quinone due to in situ photodecomposition. Methoxy substituents increase the stability of the quinone, and this may be the manner in which quinones achieve additional stabilization within the lignin structure.

The results of our work show that *ortho*-methoxyphenols can lead to *ortho*-quinones via a two-photon process. The first step in this sequence is the formation of the corresponding phenoxyl radical, which can occur by the absorption of the first photon or by hydrogen abstraction from the corresponding phenol [27]. This is followed by the absorption of a second photon by the phenoxyl radical, breaking the methoxy carbon–oxygen bond and forming the corresponding 1,2-benzoquinone with a low quantum yield. In solution, this process occurs only under high-intensity irradiation, although we can anticipate that the same result will be obtained at low intensities if the phenoxyl radical lifetime is extremely long [18].

In a solid matrix, such as pulp or paper, phenoxyl radicals may indeed be sufficiently long lived to absorb other photons [18], even if the irradiation is not of high intensity, such as ambient light or sunlight. This process is possible since the absorption spectra of many phenoxyl radicals have a band in the 370–410 nm region, well within the spectral region to which papers are exposed under normal use. Clearly, this is not expected to be the only source of *ortho*-quinones; most of the *ortho*-quinones are probably formed from the reaction of phenoxyl radicals and other radicals present in the oxidative environment of the pulp.

It is interesting to note that the current work links several complementary pieces of information to add another pathway (Eq. (1)) to the known routes for quinone formation in pulp and paper. Specifically, Wan and Depew [18] have shown that phenoxyl radicals are very long lived on paper, thus making them excellent candidates for further photolysis. Weir [33] has shown that deep-UV photolysis of lignin leads to the formation of methane, consistent with the formation of methyl radicals in Eq. (1) ($R \equiv CH_3$). Zhu et al. [24] have shown that 1,2-phenylenediamine reacts with *ortho*-quinones to yield phenazines as excellent fluorescent reporters for quinone formation. Combined, these tools provided the basis of the analysis of Eq. (1).

Acknowledgements

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