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Are quinone methides responsible for yellowing of paper in light?

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Abstract—Irradiation of tetrahydrofuran solutions of quinone methide **1** at 350 nm resulted in the formation of yellow oligomeric products and guaiacol. The rate constants determined for the disappearance of the starting compound and those of guaiacol formation show that the primary reaction involves homolysis of the C–O bond between the allylic carbon atom and the oxygen of the phenolic group. © 2002 Elsevier Science Ltd. All rights reserved.

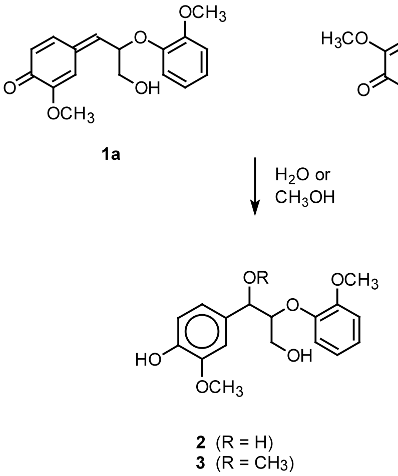
The yellowing of paper is initiated by lignin-chromophores that absorb near UV light (300–400 nm).[1] The range of possible chromophores includes carbonyl compounds, stilbenes, phenyl coumarins, coumaryl alcohols, biphenyls and quinone methides. Previous studies on lignin and model compounds[2–4] have underlined the key role of phenols and α-carbonyl groups in the photoyellowing process. Three mechanistic routes by which the yellowing proceeds were proposed.

1. Direct excitation or free radical scavenging by phenolic groups to give phenoxyl radicals (the 'free phenoxyl radical' pathway).
2. Direct excitation of carbonyl groups (the 'phenacyl' pathway).[5]
3. Via formation of ketyl radicals (the 'ketyl' pathway).[6]

It is also important to take into account that the solid-state chemistry of chromophores in lignin may be slightly different from that of model compounds in solution. Paper always contains some water, so hydrolysis[7] and photolysis of quinone methides as competitive reactions can take place.

The results of our study on the possible influence of the quinone methide chromophore group on the yellowing of paper are presented herein.

In order to carry out the study, the quinone methide **1** was synthesized by modification of the literature procedure[8] and a mixture of the two isomers was obtained (**1a**,**b**) in the ratio of 1:2. The UV–vis absorption maxima of **1** appear at 280, 300 and 350 nm. Irradiation of a tetrahydrofuran solution of **1** was carried out at 350 nm in a photochemical reactor equipped with a 12 W lamp. During the course of irradiation, the initially colourless solution turned yellow. Several attempts to analyze directly, as well as to separate the reaction mixture by HPLC failed, due to the presence of unreacted quinone methide, which is highly reactive[9] and reacts with water and methanol[10] present in the mobile phase. In order to obtain consistent results, methanol was added to the reaction mixture prior to HPLC analysis, resulting in conversion of the residual quinone methide to a stable addition product (Scheme 1).



Scheme 1. Addition products of **1** with methanol and water.

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The presence of yellow oligomeric products and guaiacol in the reaction mixture was established by the use of GPC (using polystyrene as reference), UV–vis spectrophotometry, ^{1}H and ^{13}C NMR spectroscopy and FAB mass spectrometry. GPC analyses (Fig. 1) of the oligomeric materials showed a broad peak extending from a retention time of 17 min (corresponding to oligomers with 16 units) to 21 min (corresponding to trimeric product).

The UV–vis spectra of the oligomers show, beside the absorption in the UV region, an absorption at about 420 nm, which confers the colour of these materials. To gain an understanding of the mechanism of photolysis, the rate of disappearance of quinone methide and the rate of the formation of guaiacol **5** were determined and the effect of the quinone methide concentration on the rate of the reaction was studied. As evident from Table 1, an increase in quinone methide concentration results in a higher rate constant for its disappearance.

In light of the fact that all of the preceding reactions are first order, the above observations suggest that the initially formed intermediates act as photoinitiators. The rate constants measured for the disappearance of the starting compound are slightly higher than those of the guaiacol formation, which can be explained by a further oxidation of guaiacol. On the basis of the results presented, the mechanism shown in Scheme 2 is suggested.

Primarily, the homolytic C–O bond cleavage between the allylic carbon atom and the oxygen atom of the aromatic ether moiety in the excited state of the molecule of the quinone methide occurs. This is supported by the fact, that the energy of excitation is 330 kJ/mol, while the bond dissociation energy is 320 kJ/mol. Upon homolytic bond cleavage, a highly delocalized allylic radical and a phenoxyl radical are formed. Whereas subsequent reactions of the allylic radicals lead to the formation of oligomeric products, the phenoxyl radical can be further transformed to guaiacol by the abstraction of a hydrogen atom from the solvent (Scheme 2). In the presence of oxygen, the reaction of the allylic radical with oxygen can also proceed, leading to peroxyl radicals. In solutions of tetrahydrofuran, which is a good hydrogen atom donor, abstraction of hydrogen atoms occurs, leading to formation of hydroperoxide **6**, the presence of which was shown by an iodide test. Under photochemical conditions, the hydroperoxides are transformed by O–O bond cleavage into alkoxyl and hydroxyl radicals. The latter have a high oxidation potential and can oxidize guaiacol or the phenoxyl radical to a mixture of oxidation products.

These suggestions were further confirmed by a series of observations. Comparative irradiation experiments were performed in air (Table 1, entry 4) and in solutions saturated with oxygen (Table 1, entry 5). Although the rate constants for quinone methide disappearance are comparable in both series of experiments, the rate constant for guaiacol formation was much lower in the case of irradiation of the solution saturated with oxygen. This can be explained by a much faster oxidation of the initially formed guaiacol, when the concentrations of oxygen in solution are higher.

Furthermore, in the latter case, the iodide tests showed a much higher concentration of peroxides than was observed in experiments run in air (Table 1, entry 4).

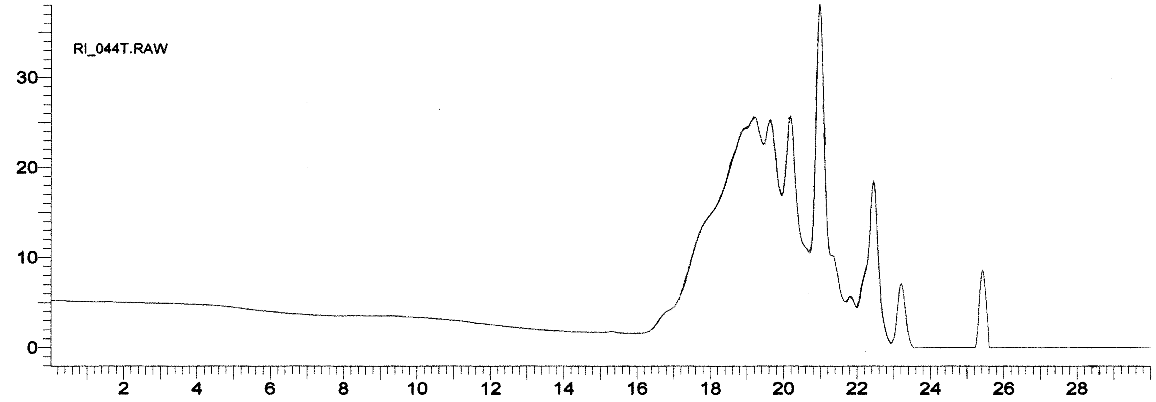
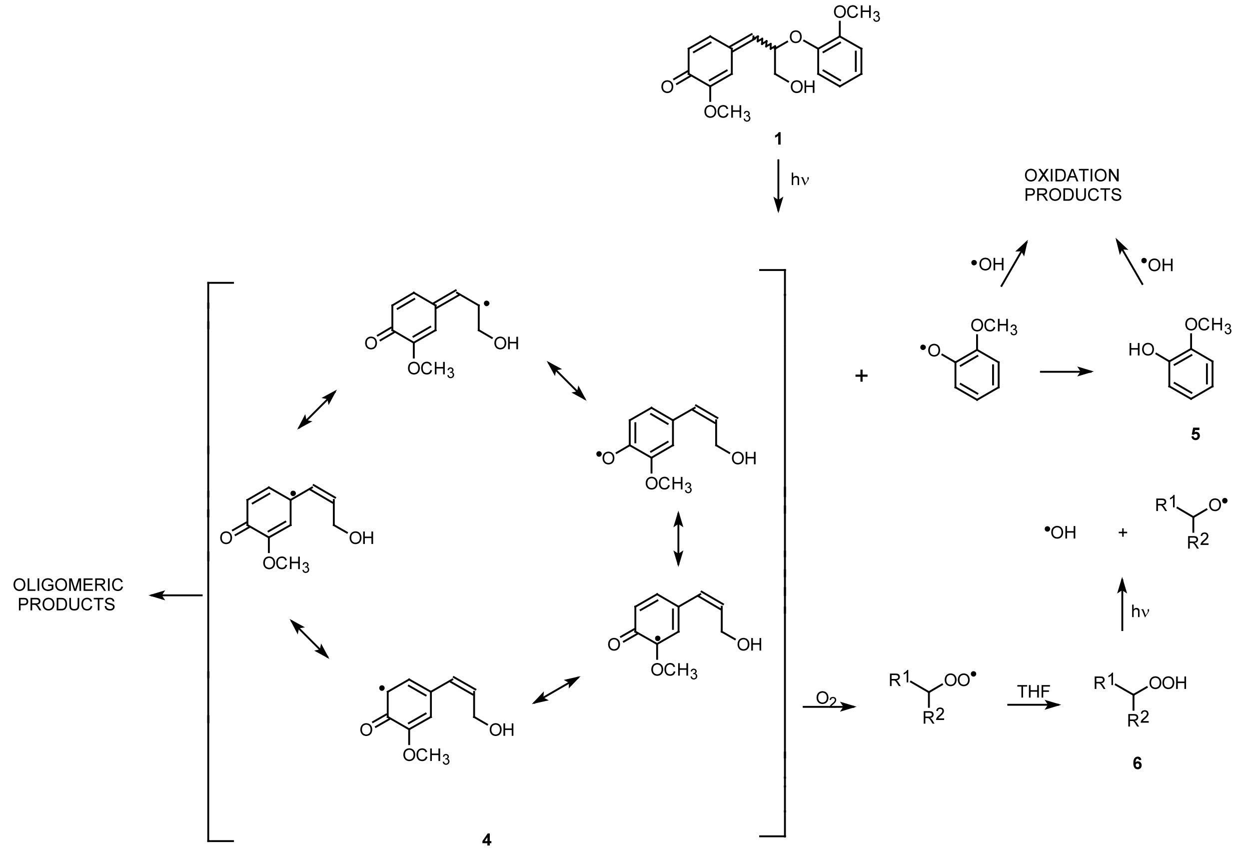


Figure 1. GPC chromatogram of an irradiated solution of **1**. Polystyrene as reference. t_R 20 min represents 1000 g/mol; t_R 17 min represents 3000 g/mol.

Table 1. Rate constants for the disappearance of quinone methide and formation of guaiacol as a function of initial concentration (c_0) of the quinone methide

Entry	c_0 (mmol/L)	k (quinone methide) 10^{-7} mol/Ls	k (quiacol) 10^{-7} mol/Ls
1	1.2	1.82	1.45
2	2.5	2.67	2.13
3	6.8	2.93	2.30
4	18.3	7.66	3.97
5	18.3 under oxygen	8.23	0.85



Scheme 2. Photoproducts obtained after irradiation of **1**.

In summary, the results obtained in the present study show that beside the phenolic and carbonyl groups, compounds possessing a quinone methide chromophore can also play an important role in the process of the yellowing of paper during irradiation with visible light.

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