The Photochemical Discolouration of Methoxy-*p*-benzoquinone in Solution

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Irradiation of a dimethoxyethane solution of methoxy-*p*-benzoquinone with sun-light lamps results in discolouration of the solution and the rapid disappearance of the starting material. A strongly coloured red dibenzofuran derivative, 8-hydroxy-3,7-dimethoxydibenzofuran-1,4-quinone, was isolated from the reaction mixture and identified by comparison with the synthesized compound. The photochemical reactions of the possible intermediates, the dimer quinones 5-methoxy-2-(2,5-dihydroxy-4-methoxyphenyl)1,4-benzoquinone and 4,4'-dimethoxybiphenyl-2,5,2',5'-bis-quinone, were also studied by visible light spectroscopy and significant changes in the spectra were observed. It is concluded that these dimer quinones and their rearrangement products play a significant role in the production of colour in old methoxy-*p*-benzoquinone solutions and other solutions in which this quinone participates as an intermediate. In alkaline aqueous solution the isolated dibenzofuran derivative rapidly disappears *via* radical reactions.

Methoxy-*p*-benzoquinone, *1*, has been suggested as a reactive intermediate in various chemical,[1–5] photochemical[6,7] and microbiological[8,9] transformations involving lignin and model lignin compounds. The further reactions of the unstable *p*-benzoquinone, *1*, are obscure and many different dissipation pathways have been proposed. In alkaline solution, the hydroxylation of *1* to coloured hydroxylated *p*-benzoquinone anions has been postulated,[7,10] and the ring cleavage reaction resulting in carboxylic acids, particularly under oxidative conditions, has been well established.[2,4] The oligomerization, polymerization and humification reactions of *1* and other *p*-benzoquinone under alkaline and acidic conditions, which yield complex dibenzofurans and other products, are also well documented.[11–14]

This prompted us to study the photochemically induced reaction of *1* in more detail in order to elucidate its possible contribution to the change in colour in the light-induced yellowing of lignin. We isolated a strongly coloured dibenzofuran-1,4-quinone (8-hydroxy-3,7-dimethoxydibenzofuran-1,4-quinone), *4*, from the direct photochemical reaction of *1* in dimethoxyethane (see Scheme 1). The same dibenzofuran derivative has previously been isolated from the thermal[15] and photochemical[16] reactions of 4,4'-dimethoxybiphenyl-2,5,2',5'-bis-quinone, *3*, which can be obtained from the acid-catalyzed reaction of *1* followed by chromic acid oxidation of the resulting dimer, *2*.[17,18] Other similar dibenzofurans have been reported as products of acid-catalyzed reactions of alkyl-*p*-benzoquinones with resorcinol.[19]

RESULTS AND DISCUSSION

*The photochemical reaction of methoxy-*p*-benzoquinone, 1.* After a 14.3×10^{-3} M solution of *1* in aerated dimethoxyethane had been irradiated for 6 h none of the starting *p*-quinone was detectable by TLC and GLC analysis (see Fig. 1, curve 1). The TLC plates revealed unidentified ascending spots in UV light, as well as substances which remained on the base line, possibly polymerization products. The original solution was yellow-green but darkened during the reaction to orange and red, after which the colour became weaker towards the end of the irradiation, as can be seen from the changes in the visible absorption spectra around 500 nm (Fig. 2). The most strongly coloured solution was obtained after irradiation for 1 h, with the greatest changes in absorbance around 500 nm. The absorbance of the solution then slowly decreased with prolonged
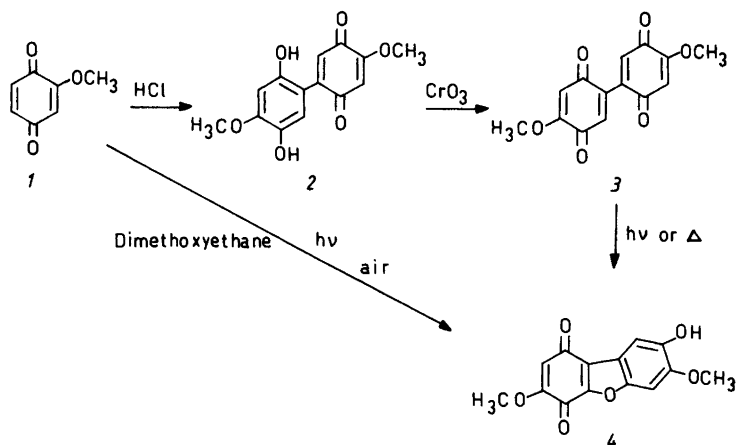
Scheme 1.

irradiation time. To test whether *1* is consumed under autoxidation conditions, air was bubbled through a solution of *1* in the dark and the result of the GLC analysis (Fig. 1, curve 2) shows that the autoxidation reaction is negligible. The colour of the solution did not change and the stability of *1* in the dark was further verified by the fact that no change was observed in the visible spectrum. After treatment of *1* for 6 h under autoxidation conditions the solution was irradiated for 1 h and the same rapid changes in absorbance were obtained as in Fig. 2.

4 was isolated at a yield of $1-2\%$ with the aid of column chromatography from the photochemical reaction of *1* in which the concentration of *1* was tripled. Although the reaction time was prolonged to 11 h, a small amount of *1* remained unchanged.
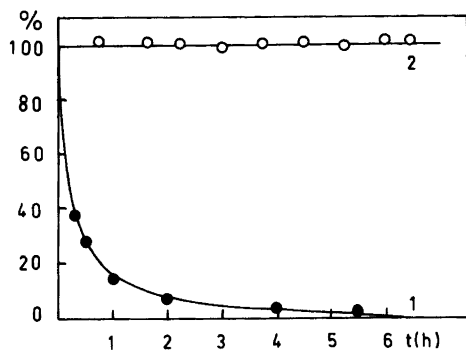
The identification of *4* was by direct comparison with the synthesized compound, which was made from *1* *via* the quinones *2* and *3* according to Scheme 1. Both compounds showed superposable IR spectra, identical melting points and similar chromatographic and spectral properties. The identification was further confirmed by comparison of their acetates after reductive acetylation.

No effort was made to optimize the yield of *4* in the irradiation reaction with respect to the concentration of *1* in the original solution.

Photochemical reactions of the dimer quinones 2, 3 and 4. The photochemical reactions of the dimer quinones *2* and *3*, in the presence of air, as well as

Fig. 1. Rate of disappearance of methoxy-*p*-benzoquinone, *1*, 14.5×10^{-3} M in aerated dimethoxyethane; curve 1 during irradiation at λ_{max} 350 nm and curve 2 in the dark.
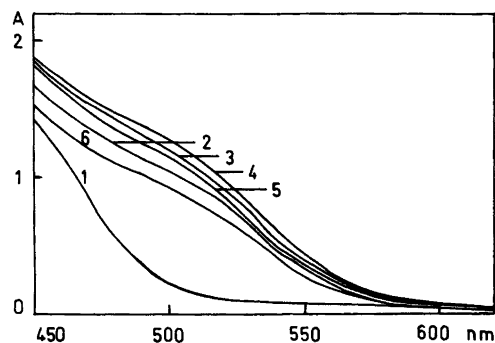
Fig. 2. VIS absorption spectra of the reaction mixture from the photochemical reaction of methoxy-*p*-benzoquinone, *1*, in aerated dimethoxyethane measured after different irradiation times at λ_{max} 350 nm; cell path length 1.65 cm; initial [*1*] 14.3×10^{-3} M. Irradiation times (h): 1(0); 2(0.25); 3(0.5); 4(1); 5(2); 6(4).
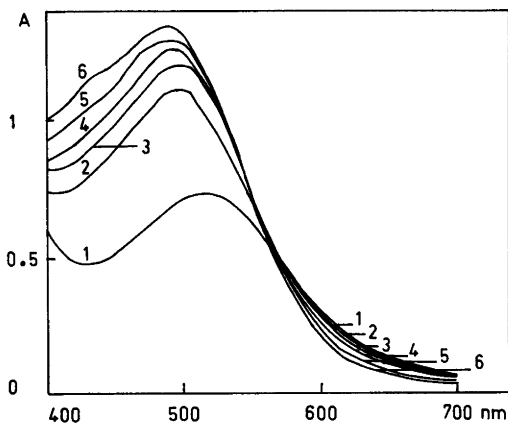
Photoreaction of Methoxybenzoquinone 391

Fig. 3. VIS absorption spectra of the solution from the photo-induced reaction of *2* in aerated dimethoxyethane measured after different irradiation times at λ_{max} 350 nm; cell path length 1.65 cm; initial [2] 0.31×10^{-3} M. Irradiation times (h): 1(0); 2(0.25); 3(0.5); 4(1); 5(2); 6(5).

the stability of the isolated product, *4*, were studied in dimethoxyethane in order to obtain more information about the progress of the reaction. The visible absorption spectra of the reaction mixture were measured at appropriate time intervals and significant changes were observed in the absorbance of the solution containing *2* (Fig. 3) and *3* (Fig. 4). For *2* the colour of the solution changed from red-violet to red and the λ_{max} shifted from 515 nm to 490 nm. For *3*, the colour shifted from yellow-green

to red and a λ_{max} of 490 nm developed during the reaction. After irradiation for 6 h the visible spectra of the two solutions were identical, if the concentration differences are taken into consideration.

The stability of *2* under identical conditions, but in the absence of light, was examined, and, according to the visible spectra, no reaction of *2* was observed during a reaction of 6 h.

When *4* was irradiated in the presence of air a slow decrease in the red colour, λ_{max} 490 nm, was observed, and, according to the visible spectra of the solution (Fig. 5), roughly half of the starting material remained after irradiation for 14 h.

TLC studies of the irradiated solutions of *2* and *3* revealed only one red spot which were attributable to *4*. The same result was obtained from a TLC study of the reductively acetylated reaction mixtures. On the other hand, if a solution of *2* was exposed to daylight, both *2* and *3* were detectable. It can thus be concluded that the dimer quinones *2* and *3* are very photosensitive and that both quinones very rapidly give the photochemically more stable dibenzofuran, *4*, when irradiated in air. This reaction has earlier been verified for *3*.[16] The yields of *4* from the above quinones, measured from the values of the absorbance at 490 nm, seem to be almost quantitative, taking into account the fact that the quinone, *4*, is itself photosensitive and slowly disappears from the solution during irradiation.

The photochemical reaction of methoxyhydroquinone, 5. The facile interconversion between *p*-
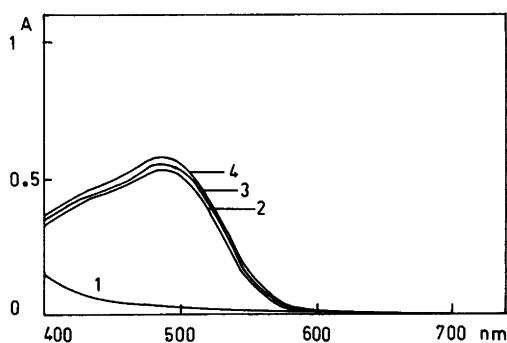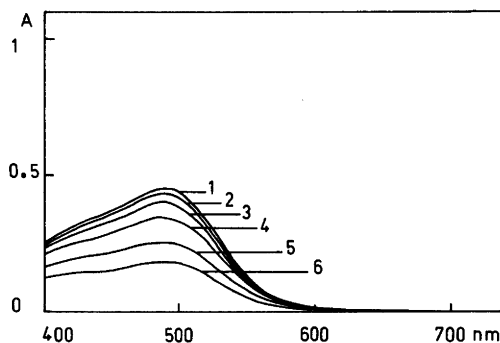

Fig. 4. VIS absorption spectra of *1*: 7 diluted solutions from the photo-induced reaction of *3* in aerated dimethoxyethane measured after different irradiation times at λ_{max} 350 nm; cell path length 1.65 cm; initial [3] 0.73×10^{-3} M. Irradiation times (h): 1(0); 2(0.5); 3(1.5); 4(2).

Fig. 5. VIS absorption spectra of the solution from the photo-induced reaction of *4* in aerated dimethoxyethane measured after different irradiation times at λ_{max} 350 nm; cell path length 1.65 cm; initial [4] 72.9×10^{-6} M (λ_{max} 490 nm, log ε 3.58). Irradiation times (h): 1(0); 2(1); 3(3); 4(6); 5(12); 6(18).
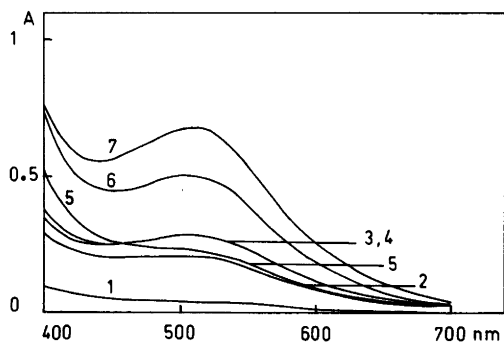
Acta Chem. Scand. B 35 (1981) No. 6

Fig. 6. VIS absorption spectra of the solution from the photo-induced reaction of 5 in aerated dimethoxyethane measured after different irradiation times at λ_{max} 350 nm; cell path length 1.65; initial [5] 14.3×10^{-3} M. Irradiation times (h): 1(0); 2(0.33); 3(0.67); 4(1); 5(2); 6(4); 7(6).

quinones and the corresponding hydroquinones is a common reaction under weakly oxidative and reductive conditions, and so the photochemical behaviour of methoxyhydroquinone, 5, in dimethoxyethane was investigated in air. The colourless solution became red-violet during irradiation for 6 h and a λ_{max} of 515 nm developed. The intensity of this peak steadily increased during the irradiation (see Fig. 6).

TLC of the irradiated solution revealed three spots, which were attributable to 2, to the starting material, 5, and to the corresponding p-benzoquinone, 1. Neither 3 nor 4 were observed. A c. 4 % yield of 2 was calculated from the values of the absorbance measured at 515 nm. The result of the GLC analysis of the silylated samples taken at different intervals showed a much lower consumption of 5 than in the experiments with the corresponding p-quinone 1; there was only a 6 % decrease in the concentration of 5 in 6 h compared with the total consumption of 1 during the same time (Fig. 2). Taking into account the error of 3 % in the GLC analyses, this 6 % decrease in 5 corresponds quite well to the calculated c. 4 % yield of 2.

This indicates that the photochemically induced oxidation of 2 to 3 is essential for the formation of 4, a reaction which, under the prevailing conditions, seems to be strongly inhibited by the presence of 5.

In the absence of light, the decrease in the concentration of 5 was negligible and no colour formation was observed during aeration for 6 h.

Reactions in water. The formation of dark precipitates ("humification") and the rapid discolouration of water solutions containing p-benzoquinones are well known, but not easily explained reactions.[11,12,20] Hydroxylated p-benzoquinones are considered to be intermediates in photochemical[21,22] and autoxidation reactions of p-benzoquinones in aqueous solutions and they have been shown to yield dihydroxyquinones, open-chained acids, cyclopentane derivatives by ring contraction and dimeric quinones.[23] Colour changes which are due to alterations in the spectrum at ~ 500 nm during oxidation of different methoxy-p-quinones, particularly in alkaline solutions, have been correlated to the formation of anions of hydroxylated quinones, but it has been difficult to isolate and identify these species.[7,10,24] The colour change has been found to be greatly dependent on the pH value, with a minimum at pH $5-6$.[10]

In the present work, irradiation of an aerated solution of 1 in distilled water also produced a very fast reaction according to the colour change and the formation of a dark precipitate which did not move on TLC plates. Visible spectra of the irradiated solution showed significant changes around 500 nm, which were much greater than in the experiments with dimethoxyethane as solvent. TLC analysis of the solution showed three spots which were attributable to the presence of 2, 4 and the starting material, 1.

The stability of 4 was tested in alkaline solution and it was observed that a very strong blue colour (λ_{max} 650 nm) developed immediately after the addition of a drop of dilute sodium hydroxide solution to either a water or dimethoxyethane solution of 4. The blue colour disappeared within a few minutes leaving a weakly coloured solution and a precipitate. The nature of the compound causing the blue colour (previously identified by Erdtman[15]) was studied by ESR and the presence of a radical in the solution was verified. The intensity of the ESR spectrum of the solution decreased gradually as the blue colour faded away.

Thus, it can be concluded that 4 is very unstable in alkaline solutions and that the chances of isolating 4 as an intermediate in alkaline reaction mixtures are extremely low. On the other hand, the formation of both 2 and 4 was demonstrated in neutral solutions.

Strong ESR signals, which decreased rapidly with time as the blue colour became weaker, were also obtained from irradiated dimethoxyethane

solutions of *2* and *3* immediately after sodium hydroxide addition. This indicated the presence of radical reactions, which ultimately resulted in dark brown solutions. ESR signals were also observed in irradiated dimethoxyethane solutions of *1*, but after alkali addition the instantly derived colour turned brown. Short-lived semiquinone radical anions derived from lignin models and from *p*-quinones have been observed by Clare and Steelink,[22] who explained the formation of red chromophores as the result of the reactions of these radicals.

The use of dimethoxyethane rather than water solutions as a solvent in photochemical reactions with *p*-quinones, has the advantage of slowing down the reaction so that possible intermediates, which are unstable in water solutions, can be isolated. Although the reactions in the two media are not necessarily directly comparable, the results from the dimethoxyethane experiments may be useful in explaining the reactions of *p*-quinones in water solutions.

A common procedure in the analysis of water solutions of photochemically treated mixtures is acidification before extraction with organic solvents. Because of the easy dimerization of *p*-quinones in acidic solutions there is always a possibility of the formation of secondary products during such treatment. Although the yields of dimers might be low under these conditions, these dimers can nevertheless cause a distinct change in the colour of the solution.

Adjusting the pH of the solution to the alkaline side may, on the other hand, cause even more profound changes in colour and reactivity in the solution, as was observed with *4*, which disappeared from an alkaline solution *via* a radical reaction. Therefore, in the analysis of photochemically treated mixtures containing intermediate *p*-quinones, care must be taken in order to correctly evaluate the actual role of the light in the colour reaction.

Conclusions. It can be concluded that methoxy-*p*-benzoquinone, *1*, is a highly reactive compound, and if formed as an intermediate in different chemical and photochemical reactions, it is both chemically reactive and photochemically unstable, giving strongly coloured dimers and other products. These dimers undergo further light-induced reactions yielding a moderately stable dibenzofuran-1,4-quinone, *4*. This quinone is very reactive in alkaline aqueous solutions and probably disappears

via radical reactions. These will be the subject of further studies.

EXPERIMENTAL

General methods

Reagents and solvents were of analytical grade if not otherwise stated. Melting points are uncorrected. Dimethoxyethane was distilled and dried over 4 Å Molecular Sieves (Merck), kept in the dark and distilled once more just before use. IR spectra were recorded on a Pye Unicam SP 1100 spectrometer, VIS absorption spectra were measured on a Perkin Elmer Coleman 259 spectrometer and ESR spectra on a Varian E 3 ESR spectrometer.

The irradiation experiments were performed using a 100 ml Pyrex test tube containing a cold finger and a reflux condenser in a Rayonet Photochemical Reactor RPR-208 fitted with 8 UV lamps (RUL 350 nm) yielding light of wavelengths 305 – 420 nm with one maximum centering around 350 nm. The reaction mixture was stirred by purging with dried air and 5 – 8 ml samples were withdrawn at different time intervals. Although the air-bubbling through the solution during the irradiation was not quite uniform, it can nevertheless be assumed that the solution was continually saturated with oxygen. In spite of the cooling, there was always a loss of solvent during irradiation. Corrections to the concentrations due to solvent losses before measuring the absorbance of the solution were made either by determining the volume after irradiation and by assuming a constant evaporation rate, as in the reactions of *1, 2, 3* and *5*, or by filling up to the initial mark before measuring each absorbance, as in the reaction of *4*.

The autoxidation experiments were performed in the dark at 20 °C with the same apparatus as in the irradiation experiments. TLC experiments were performed on silica gel plates containing a fluorescence indicator and ethyl acetate – cyclohexane 2:1 as eluent 1, or toluene – ethyl acetate 1:1 as eluent 2. Column chromatography was performed on silica gel (70 – 325 mesh, Merck) with eluent 1.

GLC analyses were performed with a Perkin Elmer 990 gas chromatograph and recorder 159 equipped with flame ionization detectors and two 2 m(Ø 3 mm) packed columns (5 % SE – 30 on Varaport 90, 80 – 100 mesh) and a Hewlett Packard 3373 B integrator. Dodecane was used as internal standard. The quantitative GLC analyses of *1* were performed both directly from the reaction mixture and from the reduced and silylated samples. One ml of the reaction mixture was reduced with sodium dithionite in water and the products were extracted

with diethyl ether, dried with sodium sulfate and the solution concentrated and silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) for 2 h at 40 °C. The quantitative analyses of the reduced and silylated test solutions gave essentially the same result as that obtained from the unreduced solutions, but the accuracy was inferior due to the extraction procedure, although the peak shape of the reduced and silylated *1* was much better than from *1* directly.

The acetates were prepared from the phenols by refluxing for ten minutes in acetic anhydride containing a little pyridine, and from the quinones by reductive acetylation in acetic anhydride containing sodium acetate and zinc dust at reflux temperature for ten minutes. The reaction products were poured into water and the acetyl derivatives were recrystallized from ethanol.

Syntheses

Compound *1* was prepared by chromic acid oxidation of *5* and the sublimed product was kept under nitrogen in a refrigerator before use. Compounds *2 — 5* were synthesized according to Refs. 18 (*2* and *3*), 16 and 25, and the diacetate of *5* according to Ref. 11.

Acetylation of *2* gave the *diacetate:* orange crystals, m.p. 183 — 185 °C. IR (KBr): 1770, 1665, 1615, 1595 cm^{-1}. TLC (eluent 2) R_f 0.30.

The *tetraacetate* was prepared from *2* by reductive acetylation, white crystals, m.p. 186 — 187 °C. IR (KBr): 1760, 1615, 1495 cm^{-1}. The tetraacetate[26] was also obtained from the diacetate of *2* and from *3* by reductive acetylation and was identical with the tetraacetate made from *2* in all respects (m.p., mixed m.p., IR and TLC data).

The *triacetate* of *4* was prepared by reductive acetylation, white crystals m.p. 234 — 235 °C (lit.[15] 232 — 233 °C). IR (KBr): 1785, 1770, 1635, 1495 cm^{-1}. TLC (eluent 2) R_f 0.60. TLC data for compounds *2 — 4* and the diacetate of *5*, R_f values (eluent 2): 0.20 (tailing), 0.50, 0.40 and 0.65.

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