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# The aqueous photochemistry of 2,6-dimethylphenol. Evidence for the fragmentation of the $\alpha$ C–C bond

Patrick Mazellier, Mohamed Sarakha, Annie Rossi, Michèle Bolte *

*Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Université Blaise Pascal, F-63177 Aubière Cedex, France*

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## Abstract

A study of the photochemical behaviour of 2,6-dimethylphenol in aerated aqueous solution upon excitation at 270 nm has been undertaken. High-performance liquid chromatography (HPLC) analyses indicated the primary formation of 2,6-dimethylbenzoquinone and the *para–para* coupling dimer as major products; two isomeric products resulting from $\alpha$ C–C scission were also observed. They account for about 20% of the conversion. Only the dimer was observed when the irradiation was carried out under deaerated conditions. The photoreaction has been shown to result from an electron ejection process leading to phenoxyl radical and solvated electron. The results indicate that $O_2^{\bullet -}$ and $HO_2^{\bullet}$ are among the species involved in the formation of the oxidized products and particularly those arising from the cleavage of the aromatic ring.

*Keywords:* 2,6-Dimethylphenol; Photooxidation; Photoscission reaction

## 1. Introduction

There has been a considerable interest in the photooxidation reactions of substituted phenols in aqueous as well as in organic solutions [1–5]. A great deal of effort has been put into both direct and induced phototransformation. It appears that the two processes lead to different photoproducts according to the phototransformation mode [6,7]. The substituted phenoxyl radical has been shown to be involved under most conditions [6,8,9]. Such a radical which has been generated by using different techniques and substrates, e.g., photoionization [6], pulse radiolysis [9,10], electron transfer [11–14], shows a behaviour that clearly depends on the surrounding medium, e.g., oxygen concentration, pH, etc. Upon direct excitation ($\lambda_{\mathrm{exc.}} < 300$ nm) of phenol derivatives in aerated aqueous solutions, quinones and dimers derivatives represent the major products whereas only dimers and oligomers are formed when the transformation is induced by excitation of cobalt azide complex, for example see Refs. [11–13]. Moreover, direct irradiation of *ortho*-phenylphenol in acidic solution leads to the cleavage of the aromatic ring [15]. This process has not been observed while investigating the photochemical behaviour of *meta*-phenylphenol and *para*-phenylphenol. Thus, only *ortho*-substituted phenols appear to undergo this type of reaction. Therefore, in order to have a better insight into the mechanism of this scission process, we have undertaken the aqueous photochemical study of 2,6-dimethylphenol which presents two methyl groups in the *ortho*-positions. The particular role of the photochemically generated oxidizing entities will be presented.

## 2. Experimental section

Solvent and chemicals were of purest grade commercially available and were used without further purification except for 2-6-dimethylphenol (Fluka), which was vacuum sublimed before use. Solutions were prepared with water purified by using a Millipore Milli-Q device and when necessary they were deaerated by bubbling with argon for 30 min at 22°C.

3,3′,5,5′-Tetramethyl-4,4′-dihydroxybiphenyl and the corresponding diphenoquinone were prepared according to Balogh et al. [16] and Finkbeiner et al. [17], respectively. The pH was adjusted using concentrated perchloric acid and concentrated sodium hydroxide or buffer composed of a mixture of $KH_2PO_4$ (M/15) and $Na_2HPO_4$ (M/15). All steady-state irradiations were carried out at 270 nm using a 1600 W xenon arc in conjunction with a high-intensity monochromator (Schoeffel). The half-width was about 10 nm. The reactor was a quartz cuvette of 1 cm path length. The incident light intensity was determined by chemical actinometry with ferrioxalate ($I_0 = 1.5 \times 10^{14}$ photons cm$^{-2}$ s$^{-1}$).

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* Corresponding author.

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Transient absorption experiments in the 20 ns to 500 $\mu$s region were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). The laser excitation at 266 nm from Quanta Ray GCR130-1 Nd:YAG (pulse width $\approx$9 ns) was used in a right-angle geometry with respect to the monitoring light beam. The transient absorbances at preselected wavelengths were monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and a 1P28 photomultiplier. A spectrometer control unit was used for synchronising the pulsed light source and programmable shutters with the laser output. It also housed the high voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32-bit RISC-processor kinetic spectrometer workstation was used to analyse the digitized signal.

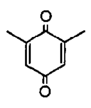
UV–visible absorption spectra were recorded on a Cary 3 double-beam spectrophotometer and electron spin resonance (ESR) spectra were obtained with a Brucker ER 200 D spectrometer operating at 9.30 GHz with 100 kHz modulation. 2,2-Diphenylpicrylhydrazyl was used as an internal standard for the determination of *g* values. Spin-trapping experiments were performed with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO). A Xe–Hg Hanovia lamp with appropriate cut-off filter was used for irradiation in the ESR spectrometer cavity. Since irradiation at $\lambda < 300$ nm generating radicals from the spin trap has been reported elsewhere [18], a solution of DMPO alone was used as blank and no ESR signal was observed under our experimental conditions.

The quantum yields of 2,6-dimethylphenol degradation and product formation were determined by high-performance liquid chromatography (HPLC) experiments, using a Waters 540 liquid chromatography system equipped with a Waters 996 diode array UV–visible detector and a reverse phase Merck column (LiChrospher 100 RP-18 5 $\mu$m–250 mm$\times$4 mm). Photoproducts were separated using a Gilson preparative HPLC apparatus equipped with a Waters model 490 detector and model 201 fraction collector.

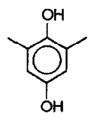
Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded at ambient temperature on a Brucker AC400 (Fourier transform) spectrometer in deuterated water (Aldrich).

Electrospray mass spectra were obtained from the analysis centre of the Centre National de la Recherche Scientifique (CNRS). The mass spectrum analyses were performed with the collaboration of Dr. Keravis from Université d'Orléans.

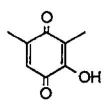
Throughout this paper, the following abbreviations referring to the corresponding structures will be used:



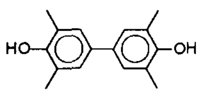
DMQ



$DMQH_2$



OHDMQ



dimer

## 3. Results

The steady state irradiation at $\lambda = 270$ nm of air saturated solutions of 2,6-dimethylphenol (0.5 mM) induced a continuous increase in the UV region (Fig. 1). The irradiated solutions appeared to be stable on standing in the dark at room temperature.

The HPLC analyses showed the presence of five major photoproducts (Fig. 2). Three of them were identified as 2,6-dimethylbenzoquinone (DMQ), 2-hydroxy-3,5-dimethylbenzoquinone (OHDMQ) and 3,3′,5,5′-tetramethyl-4,4′-dihydroxybiphenyl (dimer). They were identified by comparing their HPLC retention times and UV–visible spectra to those of reference samples. 2,6-Dimethylhydroquinone ($DMQH_2$) was only present in trace quantities.

A solution of the two unidentified products I and II which were observed at shorter retention times (3.8 min and 4.2 min), was obtained by using preparative HPLC. Evaporation of the eluent, i.e., methanol/water, from the mixture under reduced pressure with a rotatory evaporator favoured the disappearance of II or its conversion into I. Moreover when an aqueous solution of I was irradiated at 284 nm, the HPLC analysis showed the regeneration of II. These results suggest that these two products are isomers which can be photoequilibrated. The similarity of their absorption spectra strongly

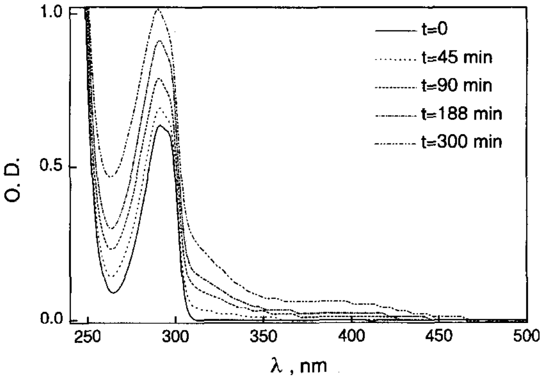


Fig. 1. Evolution of UV spectrum of an air-saturated aqueous solution of DMP (0.5 mM) at pH = 5.5 irradiated at 270 nm.

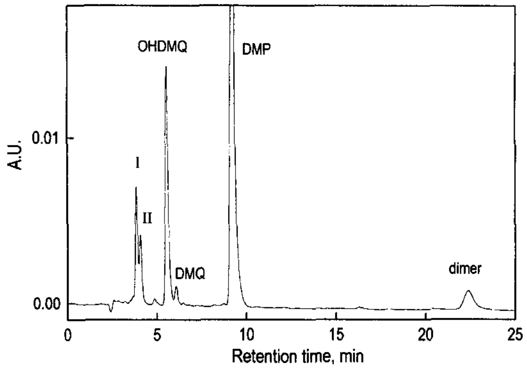


Fig. 2. HPLC chromatogram of an aerated aqueous solution of DMP (0.5 mM) irradiated at 270 nm. The percentage of conversion is 25%. $\lambda_{detection} = 270$ nm; 60% MeOH–40% $H_2O$ acidified.

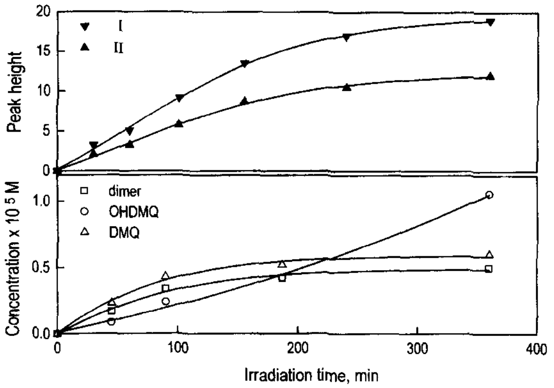
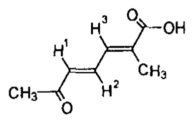


Fig. 3. Kinetics of formation of the photoproducts in an air-saturated solution of DMP (0.5 mM) irradiated at 270 nm.

favours this hypothesis ($\lambda_{max}$(I) = 284 nm, $\lambda_{max}$(II) = 280 nm). From the $^1$H NMR spectrum and the electrospray mass analysis, the following structure can be assigned to product I:



$^1$H NMR: 7.68 ppm, H$^1$ (d, $J$ = 15.8 Hz); 6.94 ppm, H$^2$ (dd, $J$ = 15.8 and 11.1 Hz); 6.43 ppm, H$^3$ (d, $J$ = 11.0 Hz); 2.44 ppm, $CH_3$ (s); 2.29 ppm, $CH_3$ (s).

The main peak on the negative ion electrospray mass spectrum corresponds to 153 (M-1). Chromatographic analysis showed that only two isomeric products among the four possible ones were present in the irradiated solution.

Besides these photoproducts, a solution that had been irradiated to more than 25% conversion revealed the presence of a large amount of trimer and tetramer, i.e., $m/e$ = 362 and 482. Their presence was demonstrated by the mass spectrum analysis (after the removal of unreacted DMP). Tetramethyldiphenoquinone has not been observed under our experimental conditions. The evolution of the products as a function of irradiation time (Fig. 3) showed that OHDMQ is a secondary product indicating that its formation is more likely owing to the direct photooxidation of DMQ at 270 nm [19].

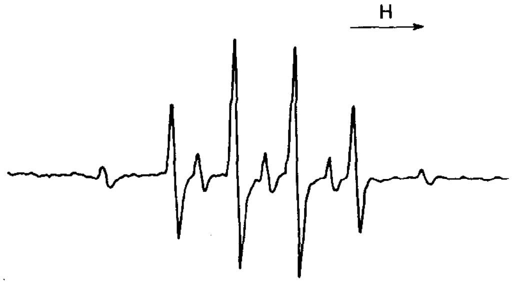


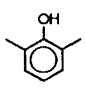
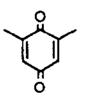
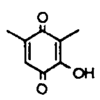
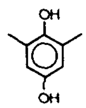
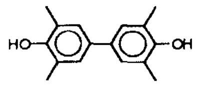
Fig. 4. ESR spectra of DMPO spin adducts generated on direct irradiation of an aerated aqueous solution of DMP (0.5 mM) at pH = 6.0. DMPO–hydrogen radical adduct ($a^H(2)$ = 22.2 G, $a^N(1)$ = 14.6 G) and DMPO–dimethylphenoxyl radical adduct ($a^H(1)$ = $a^N(1)$ = 14.1 G).

No pH effect was observed in the range 2–8, neither on the formation of the photoproducts nor on the disappearance of DMP.

The different quantum yields are gathered in Table 1. Different key findings can be deduced from Table 1: (1) The absence of oxygen made the quantum yield of DMP disappearance lower by a factor of 6. The C–C coupling dimer is the main detectable product formed under deoxygenated conditions and the residual concentration of oxygen is more likely responsible for the formation of DMQ in trace concentrations. (2) The initially formed products account for about 20% and 30% of the conversion in aerated and deaerated solutions, respectively. The formation of the oligomeric species evidenced by mass spectrometry could explain this large deficit in mass balance.

In order to detect free radical intermediates, the technique of spin trapping with ESR was used with DMPO as a trap. No adducts resulting from the spin trap itself were observed under our experimental conditions. As depicted in Fig. 4, the direct excitation of DMP (0.5 mM) with a Xe–Hg lamp in the presence of 10 mM of DMPO gave a spectrum resulting from a mixture of two spin adducts, $g$ = 2.0058 and 2.0061. They correspond to the adducts of DMPO with hydrogen atom and with dimethylphenoxyl radical respectively. It is worth noting that the adduct H-DMPO was not observed in system also generating 2,6-dimethylphenoxyl radical via photoinduced transformation of dimethylphenol [12,20]. The signal was not affected by the presence of isopropanol (2%) which leads us to the conclusion that no $^\bullet$OH radical is involved in the observed photoreactivity.

Table 1

| |  |  |  |  |  |
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| Aerated solution | $6.0 \times 10^{-2}$ | $4.7 \times 10^{-3}$ (7.8%)$^a$ | secondary product | traces | $3.4 \times 10^{-3}$ (11.4%)$^a$ |
| Deaerated solution | $1.0 \times 10^{-2}$ | traces | not formed | not formed | $1.4 \times 10^{-3}$ (29%)$^a$ |

[a] Percentage with regard to the conversion of DMP.

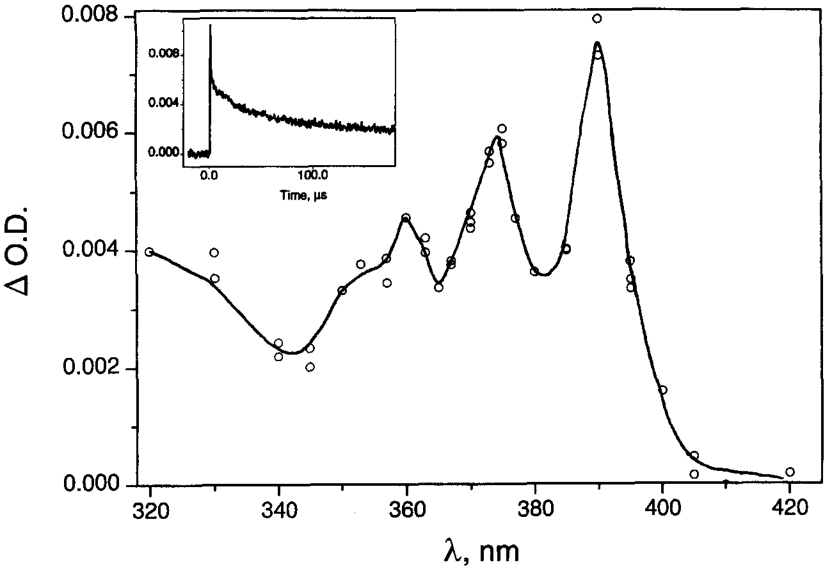


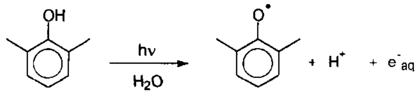
Fig. 5. Spectrum obtained on laser flash photolysis (266 nm) of an aqueous solution of DMP (0.5 mM). The insert shows a typical trace for the decay of the optical density at 375 nm.

Nanosecond laser photolysis at 266 nm of DMP in oxygen-free solution (0.5 mM, pH = 6.0) revealed, immediately after the pulse, an intense absorption assigned to the hydrated electron ($\lambda_{max}=720$ nm, $\varepsilon=18.5\times10^3$ M$^{-1}$ cm$^{-1}$ [21]). A transient absorption in the wavelength range 340–410 nm was also observed after 15 μs. The measurements were made at laser energies as low as possible to avoid biphotonic processes. The bands with maxima at 390, 375 and 360 nm mainly correspond to the characteristic spectrum of the dimethylphenoxyl radical (Fig. 5). This is in relatively good agreement with the reported spectrum observed in pulse radiolysis [10] and in induced oxidation of dimethylphenol by excitation of uranyl ion [14]. The dimethylphenoxyl radical and $e_{aq}^-$ concentrations were determined from the absorptions at 375 nm ($\varepsilon=2950$ M$^{-1}$ cm$^{-1}$ [9] and at 650 nm ($\varepsilon=13\times10^3$ M$^{-1}$ cm$^{-1}$), respectively. The quantum yield ratio $\Phi e_{aq}^- / \Phi_{radical}$ was found to be equal to unity. Therefore electron ejection from the singlet excited state is the only process involved in the photochemistry of dimethylphenol in aqueous solution. This is in good agreement with the results obtained in the studies undertaken in polar solvent with phenol [22]. The analysis of the trace observed at 375 nm showed that dimethylphenoxyl radical disappears via a second-order process with a rate constant of $6.0\times10^9$ M$^{-1}$ s$^{-1}$. The disappearance kinetics are not affected by oxygen which indicates that the coupling of the phenoxyl radical is the predominant reaction under laser flash photolysis experiments.

## 4. Discussion

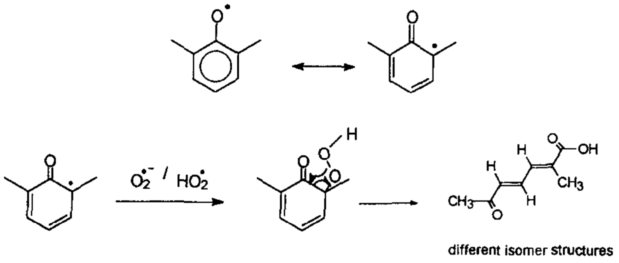
Upon excitation of 2,6-dimethylphenol in aqueous solution within the $S_1$ band, i.e., 270 nm, a variety of photoproducts have been identified, among them dimethylbenzoquinone, *para–para* coupling dimer and two isomers originating from the fragmentation of the α C–C bond. These isomers appear to be primary products. This scission is similar to the scission observed in the photochemical behaviour of *ortho*-phenylphenol in acidic solution [15]. In deaerated solution, only the dimer which accounted for 30% of the conversion was observed by HPLC analysis. The quantum yield of DMP disappearance and dimer formation strongly decreased in the absence of oxygen. Indeed, these results clearly show that oxygen plays a major role in the photochemical mechanism. In the present work, the formation of the products appeared to be pH-independent within the range 2–8.

The laser flash photolysis studies showed that dimethylphenoxyl radical and hydrated electron are formed in equimolar concentration, hence the photoionization is the only process involved in the mechanism and the sequence of the following reactions can be put forward.



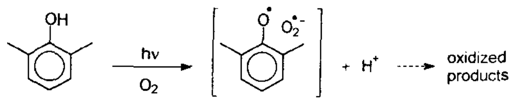
| | | |
|---|---|---|
| $e_{aq}^-+H^+\rightarrow H^+$ | $k=2.1\times10^{10}$ M$^{-1}$ s$^{-1}$ | [21] |
| $e_{aq}^-+O_2\rightarrow O_2^{\bullet-}$ | $k=2.0\times10^{10}$ M$^{-1}$ s$^{-1}$ | [21] |
| $O_2^{\bullet-}+H^+\rightleftharpoons HO_2^{\bullet}$ | p$K_a$=4.75 | |

Since the formation of isomers had not been observed in various systems also generating 2,6-dimethylphenoxyl radical upon irradiation of either iron(III) [20] or cobalt(III) [12] even in the presence of oxygen, the formation of the isomeric products I and II might arise from a radical reaction involving either $O_2^{\bullet -}$ or $HO_2^{\bullet}$. Due to the absence of any pH effect, these two species have to be efficient.

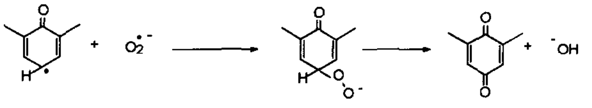


In the presence of isopropanol, no effect was observed neither on DMP disappearance nor on photoproducts formation. This indicates that hydroxyl radical did not take part in the observed photochemical reactions. Hence, the coupling of superoxide species, the only source of hydroxyl radicals in this system, is of very low importance.

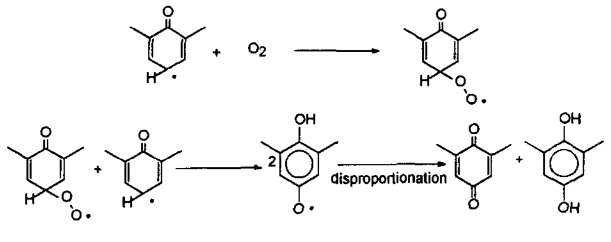
A plausible explanation for this behaviour is a cage phenomenon involving dimethylphenoxyl radical and superoxide anion which should be in favour of the formation of the desired products:



The formation of DMQ is suggested to arise from the reaction of the mesomeric form of the radical and $O_2^{\bullet -}$ according to the sequence [15]:

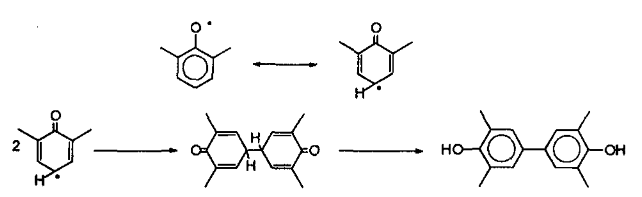


As already mentioned, 2,6-dimethylhydroquinone was shown to be formed in trace concentrations. Its formation can be the result of the reaction of molecular oxygen with 2,6-dimethylphenoxyl radical.



However, we can not exclude a direct excitation of 2,6-dimethylbenzoquinone at 270 nm giving rise to OHDMQ and $DMQH_2$ [19].

The formation of the dimer, observed in aerated as well as in deaerated solutions, is explained by the coupling of two phenoxyl radicals. In laser flash photolysis experiments this reaction represents the main pathway of radical disappearance.



## 5. Conclusion

The quite distinct products derived from the direct excitation of 2,6-dimethylphenol were shown to result from the reactivity of dimethylphenoxyl radical. In deaerated solution, the 3,3′,5,5′-tetramethyl-4,4′-dihydroxybiphenyl (dimer) together with oligomers were formed. In the presence of oxygen, reactions involving $O_2^{\bullet -}$ and $HO_2^{\bullet}$ species are occurring in competition with the *para–para* coupling process. These reactions were also shown to lead to isomeric products formed from the cleavage of the aromatic ring. So far, this reaction has only been observed for *ortho*-substituted phenols.

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