

# The photo-oxidation of 2,6-dimethylphenol and monophenylphenols by uranyl ion in aqueous solution

Mohamed Sarakha<sup>a</sup>, Michèle Bolte<sup>a</sup>, Hugh D. Burrows<sup>b,\*</sup>

<sup>a</sup> Laboratoire de Photochimie, URA CNRS 433, F-63177 Aubiere Cedex, France

<sup>b</sup> Departamento de Quimica, Universidade de Coimbra, P3049 Coimbra Codex, Portugal

Received 9 September 1996; accepted 28 January 1997

## Abstract

The photo-oxidation of 2,6-dimethylphenol and *o*-, *m*- and *p*-phenylphenols by uranyl ion was investigated in aqueous solution. Steady state and dynamic luminescence quenching studies at pH 0.8 show the rapid dynamic deactivation of excited uranyl ions by the phenols. At the natural pH of uranyl salt solutions (pH 2.3), differences are observed between the steady state and dynamic quenching behaviour, and it is suggested that these differences are due to uranyl hydrolysis. Flash photolysis studies with uranyl ion in the presence of 2,6-dimethylphenol and *m*- and *p*-phenylphenols show that the initial photoreaction leads to phenoxyl radical formation. The photolysis products were identified by high performance liquid chromatography (HPLC) and UV absorption spectroscopy. With 2,6-dimethylphenol in aerated solution, both quinone and dimer formation are observed. Kinetic studies show that these processes occur concurrently. In contrast, photolysis of degassed solutions leads to dimer formation only. The quantum yields for these processes are reported. The photo-oxidation of aerated solutions of *o*-phenylphenol in the presence of uranyl ions leads to the production of two dimers and the quinone, whereas with degassed solutions only the dimers are observed. The photo-oxidation of these substrates by uranyl ion is contrasted with the behaviour of  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$  as photo-oxidant of the same substrates. With *m*-phenylphenol, quinone and dimers are observed in aerated solution, whereas only the dimer is observed in deoxygenated solution. With *p*-phenylphenol, only dimer formation is observed. Possible mechanistic origins of the differences in the selectivity of oxidation by the different metal complexes are discussed. © 1997 Elsevier Science S.A.

**Keywords:** 2,6-Dimethylphenol; Electron transfer; Phenylphenols; Uranyl photo-oxidation

## 1. Introduction

The photochemical oxidation of phenols is of interest due to potential applications in synthesis and its relevance to the photochemical treatment of industrial effluents. In synthetic studies, on direct photolysis of aqueous solutions of substituted phenols, a variety of products have been reported, including dimers and quinones [1]. Many of these species are thought to be formed via intermediate phenoxyl radicals [2]. However, direct photolysis is limited to short-wavelength excitation, and it is of interest to find selective photo-oxidants of these compounds which absorb in the visible region. Transition metal complexes are good candidates for such photo-oxidations. However, differences between the oxidative behaviour of the various metal complexes in the ground and excited states may affect the nature of the final photoproducts. Various inorganic species, including chromium(III) [3], ruthenium(II) [3,4], cobalt(III) [5–7] and

uranium(VI) [8–11] complexes, have been shown to be capable of inducing such photo-oxidations at long wavelengths. In studies of the photo-oxidation of the three monophenylphenol isomers [5,6] and 2,6-dimethylphenol (DMP) [7] by cobalt(III) azide derivatives in aqueous solutions, it was found that the oxidation produced dimers as the major photoproducts, with no sign of the formation of quinones. The photolysis of degassed solutions of phenol in the presence of  $[\text{Ru}(\text{bpz})_3]^{2+}$  (bpz, 2,2'-bipyrazine) also leads to the formation of hydroxyphenyl dimers. In contrast, the photolysis of air-saturated aqueous solutions of phenol with  $[\text{Cr}(\text{bpy})_3]^{3+}$  or  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy, 2,2'-bipyridine) as sensitizer yielded 1,4-benzoquinone as the only organic photoproduct [3].

Excited uranyl ion,  $^*\text{UO}_2^{2+}$ , is a strongly oxidizing species ( $E^\circ = +2.6 \text{ V}$  [12,13]), and has been shown to react with phenols in a dynamic process [8] to produce phenoxyl radical–uranium(V) radical pairs [9,10], which may then decay to produce uranium(IV) species and organic products. However, although the fate of the uranium species has been rela-

\* Corresponding author. Fax: +351 39 27703.

tively well established, less has been reported about the nature of the organic photoproducts. In one study on the photocatalytic oxidation of phenol by uranyl ion in the presence of hydrogen peroxide, *p*-benzoquinone was identified as the major product, with a quantum yield of 0.005 [11]. In contrast with many of the other metal complexes studied, uranyl ion is weakly oxidizing in the ground state, but is a strong photo-oxidant. Because of the possibility of modifying the products of the photo-oxidation of phenols using such a photo-oxidant, we have studied the photo-oxidation by uranyl ion of DMP and *o*-, *m*- and *p*-phenylphenols (*o*PP, *m*PP and *p*PP), the same four derivatives as studied previously with  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$  as photo-oxidant [5–7]. The results are compared with those for the cobalt(III) azide complex and for direct photolysis.

## 2. Experimental section

All reagents were of the purest grade commercially available, and were used without further purification. Solutions were prepared in doubly distilled water, either in equilibrium with air or deaerated by bubbling with argon for 30 min at 22 °C. The ionic strength was not controlled. For luminescence quenching studies, the pH was controlled by the addition of dilute nitric acid.

3,3',5,5'-Tetramethyl-4,4'-dihydroxybiphenyl was prepared according to Ref. [14]. The diphenoquinone derivative, which is necessary for the synthesis, was prepared as described by Finkbeiner et al. [15].

### 2.1. Apparatus and procedure

Fluorescence spectra were run on a Spex Fluorolog model 111 spectrometer, and absorption spectral measurements were performed using Shimadzu UV-240 and Cary 3 spectrophotometers. The decay of the uranyl luminescence was studied using a nanosecond flash photolysis apparatus with a pulsed  $\text{N}_2$  laser ( $\lambda = 337$  nm) as the excitation source [16].

A high pressure mercury lamp (Osram HBO type 125 W) with a Bausch and Lomb grating monochromator or a medium pressure mercury lamp with appropriate filters was used for irradiation. General details have been given previously [5–7]. The quantum yields of degradation of the phenols were determined by high performance liquid chromatography (HPLC) using a Waters 540 liquid chromatography system equipped with a diode array UV-visible detector (Waters 990). A reverse phase Beckman column was employed, with a mixture of A (methanol–water, 80 : 20) and B (5 : 1 v/v sodium acetate (0.03 M) pH 5 and  $\text{CH}_3\text{CN}$ ) as eluent, using a gradient programme described elsewhere [5].

Flash photolysis studies were performed using a Nortech FPX-1 flash lamp emitting 130 J with a rise time of 10  $\mu\text{s}$ . Transient absorption spectra were registered using a standard lamp source–monochromator–photomultiplier set-up, and the photomultiplier signal was passed to a Tektronix 564 storage oscilloscope. Appropriate filters ( $\lambda > 320$  nm) were used in order to prevent direct excitation of the phenols.

## 3. Results

### 3.1. Fluorescence quenching and transient absorption studies

The quenching of the luminescence of aqueous solutions of uranyl nitrate (0.01 M) by the four phenols was studied by steady state measurements. Excitation of the above solutions with light of 428 nm leads to the well-characterized uranyl luminescence, which was found to be strongly quenched by all four phenols. The quenching was studied at the natural pH (pH 2.3) and at pH 0.8. Solutions were not degassed, as molecular oxygen does not affect excited uranyl ion [17,18]. Good Stern–Volmer plots were obtained in all cases, and typical results are shown in Fig. 1. From these, the Stern–Volmer constants and quenching rate constants were calculated, and are presented in Table 1. With *p*PP, the solubility was too low to study the quenching at pH 0.8. The quenching was also studied by following the decay of uranyl luminescence at 500 nm following excitation with a pulsed nitrogen laser. Again, good Stern–Volmer behaviour was observed, as shown in Fig. 1. The quenching rate constants at pH 0.8 are identical with those obtained in the steady state measurements (Table 1), confirming that we are looking at a dynamic quenching process involving a reaction between the phenols and excited uranyl ion. However, differences are observed in the rate constants calculated for the dynamic and steady state measurements at pH 2.3. This is probably associated with hydrolysis of the uranyl ion, either in the ground [19] or excited [20] state. Hydrolysis produces dimeric and oligomeric uranium(VI) species [19], which have different excited state lifetimes from the non-hydrolysed  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$  complex [20]. In addition, hydrolysed species may form complexes with the phenols, leading to static luminescence quenching.

The flash photolysis ( $\lambda > 320$  nm) of an aerated solution of DMP ( $2 \times 10^{-4}$  M) and uranyl nitrate ( $5 \times 10^{-3}$  M) produced a transient with a strong absorption in the 300–400 nm region, with well-defined maxima at 365 and 390 nm

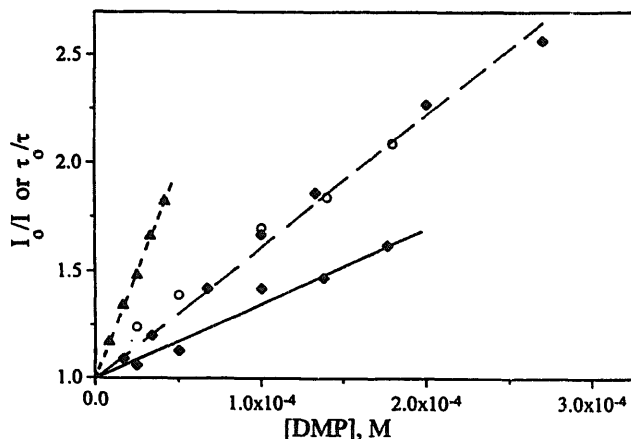


Fig. 1. Stern–Volmer plots for the quenching of uranyl excited state by DMP: data for the decay of uranyl luminescence at pH 0.8 (circles) and pH 2.3 (squares); steady state data for the quenching of uranyl luminescence at pH 0.8 (hexagons) and pH 2.3 (triangles).

Table 1  
Bimolecular rate constants and steady state Stern–Volmer constants for the quenching of  ${}^*UO_2^{2+}$  by phenols

Phenol	pH	$k_q$ ( $10^9 M^{-1} s^{-1}$ )	$K_{sv}$ ( $10^3 M^{-1}$ )	$(K_{sv}/\tau)^a$ ( $10^9 M^{-1} s^{-1}$ )
DMP	0.8	2.1	6.54	2.0
	2.3	1.4	18.9	7.7
oPP	0.8	2.3	6.55	2.0
	2.3	1.8	15.0	6.1
mPP	0.8	1.9	8.0	2.4
	2.3	<sup>b</sup>	13.4	5.5
pPP	2.3	<sup>b</sup>	18.3	7.5

<sup>a</sup> Calculated using  $\tau = 3.3 \mu s$  (pH 0.8) and  $\tau = 2.45 \mu s$  (pH 2.3) from luminescence decay measurements in the absence of phenols.

<sup>b</sup> Solubility of phenols too low to study quenching.

(Fig. 2(a)), assigned to the corresponding phenoxyl radical by comparison with a literature spectrum [21]. This decayed by a second-order process, with  $k/\epsilon_{360 nm} = 1.0 \times 10^4 cm s^{-1}$ . No transient absorptions were observed in this region on flash photolysis of solutions of uranyl ions in the absence of DMP. Transient species were also observed on flash photolysis of aerated aqueous solutions of uranyl nitrate in the presence of mPP or pPP. The transient absorption for pPP is shown in Fig. 2(b). These are assigned to the phenoxyl radicals, and show absorption maxima at 340 nm (mPP) and 355 nm (pPP). Both transients decay by second-order kinetics, with  $k/\epsilon_{375 nm} = 7 \times 10^4 cm s^{-1}$  (mPP) and  $k/\epsilon_{360 nm} = 13 \times 10^4 cm s^{-1}$  (pPP).

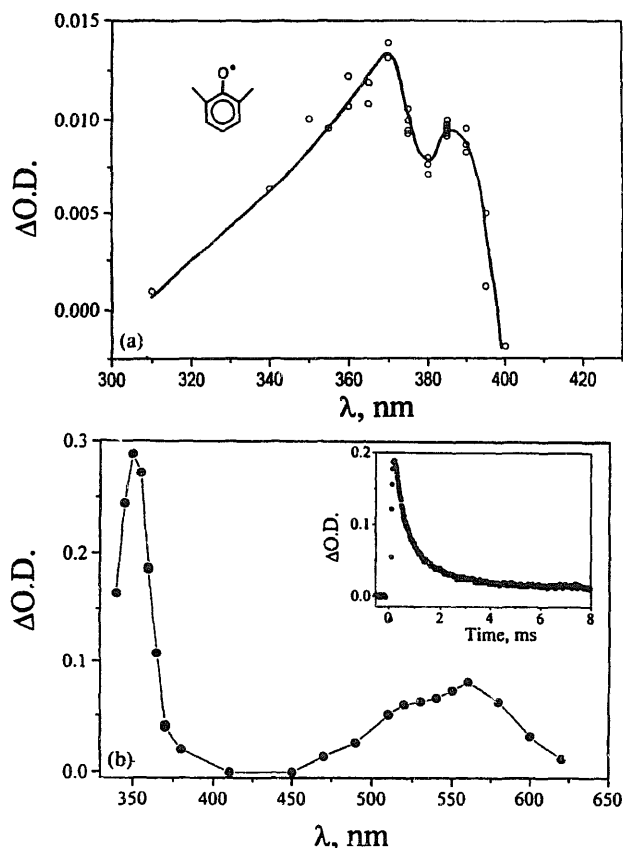


Fig. 2. Spectra obtained on flash photolysis ( $\lambda > 320 nm$ ) of aqueous solutions of uranyl nitrate ( $5 \times 10^{-3} M$ ) in the presence of: (a) DMP ( $2 \times 10^{-4} M$ ); (b) pPP ( $2 \times 10^{-4} M$ ). The inset shows a typical trace for the decay of the optical density,  $I_{obs} = 360 nm$ .

### 3.2. Continuous irradiation

Aerated aqueous solutions of uranyl nitrate ( $10^{-2} M$ ) and DMP ( $10^{-3} M$ ) were photolysed with 334 nm light, which selectively excites the uranyl ion. No indication of the formation of uranium(IV) was found when the progress of the reaction was followed by UV–visible spectroscopy. Analysis by HPLC shows the presence of two major products (Fig. 3). These were identified as 2,6-dimethylbenzoquinone (DMQ) and 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl by comparison of their HPLC retention times and UV absorption spectra with those of reference samples. Trace quantities of hydroxy-2,6-dimethylbenzoquinone, resulting from the direct photo-oxidation of DMQ, are observed following prolonged irradiation. It is worth noting that no formation of the diphenoquinone derivative is observed under our experimental conditions. The quantum yields of DMQ and dimer formation are given in Table 2. The kinetics of appearance of the quinone and dimer closely follow the disappearance of DMP (Fig. 4).

Somewhat different behaviour was observed on photolysis of degassed solutions of DMP and uranyl ion. Whilst 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl was still observed, no DMQ was formed. The quantum yields of DMP disappearance and dimer formation were much lower than those for aerated solutions (Table 2).

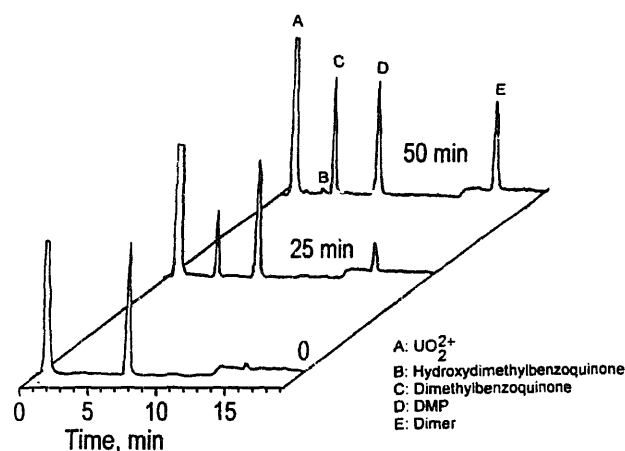


Fig. 3. High performance liquid chromatograms observed for the products of photolysis of aerated aqueous solutions of uranyl nitrate ( $10^{-2} M$ ) and DMP ( $10^{-3} M$ ) for  $t = 0, 25$  and  $50 min$ .  $\lambda_{detection} = 260 nm$ .

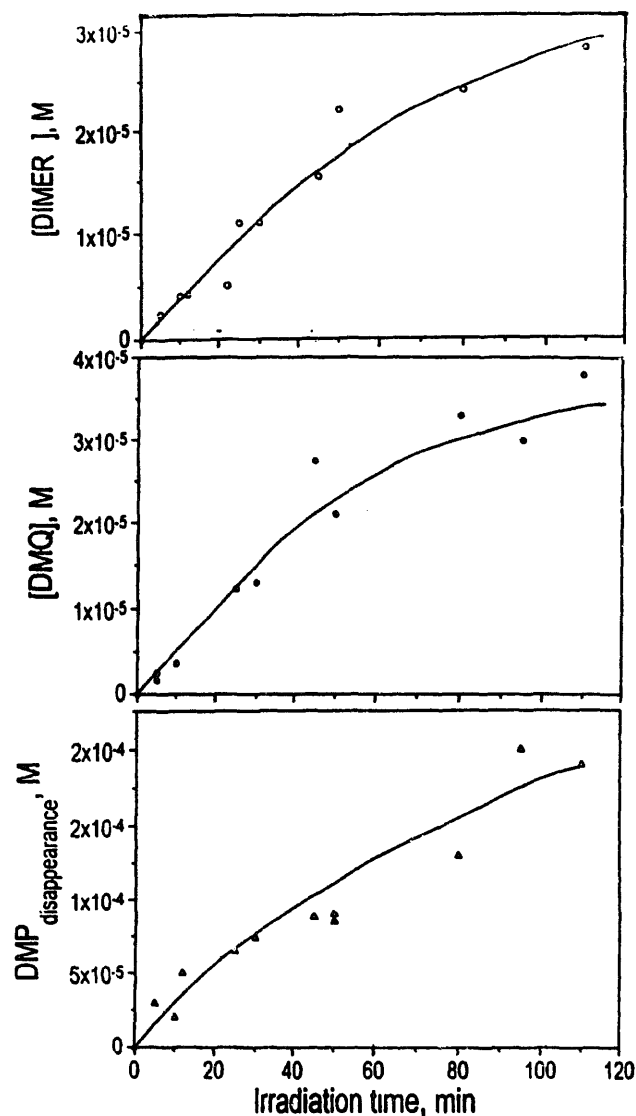


Fig. 4. Kinetics of disappearance of DMP (a) and formation of 2,6-dimethylbenzoquinone (b) and dimer (c) as a function of the irradiation time on photolysis of aerated aqueous solutions of uranyl nitrate ( $10^{-2}$  M) and DMP ( $10^{-3}$  M).

On photolysis of aerated solutions of uranyl nitrate ( $10^{-2}$  M) and *o*PP with 334 nm light, the main products identified by HPLC and UV spectroscopy were phenylbenzoquinone (I), 4,4'-dihydroxy-5,5'-diphenylbiphenyl (II) and 2,2'-dihydroxy-3,3'-diphenylbiphenyl (III).

Table 2  
Results from continuous photolysis experiments of uranyl nitrate with phenols

Compound	Experimental conditions	$\phi_{\text{phenol loss}}$	Product	$\phi^a$
DMP	Aerated solution	0.13	DMQ	0.026
	Deaerated solution	0.062	Dimer	0.021
<i>o</i> PP	Aerated solution	0.064	Dimer	0.006
			Phenylbenzoquinone	0.015

<sup>a</sup> For product formation.

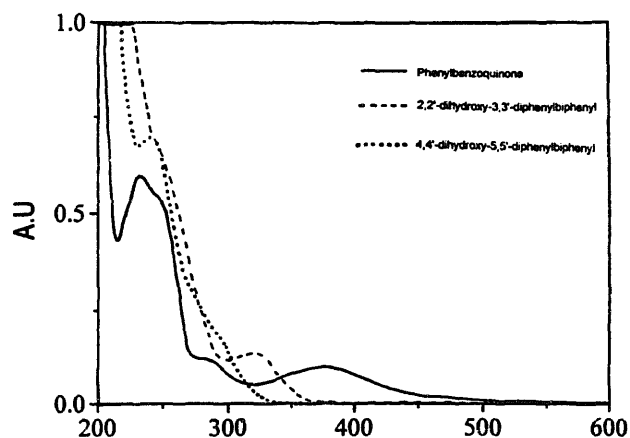
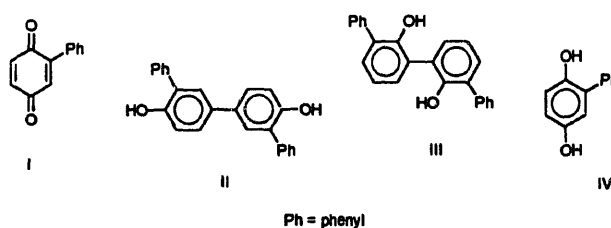
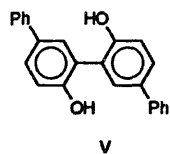


Fig. 5. UV absorption spectra and structures of main photolysis products obtained from aerated aqueous solutions of uranyl nitrate ( $10^{-2}$  M) and *o*PP ( $10^{-3}$  M).



The absorption spectra of these are shown in Fig. 5. The last two products were identified with reference to the products obtained during the photo-oxidation of *o*PP by  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$  [5]. Trace quantities of phenylhydroquinone (IV) were also observed. However, with both the cobalt(III) azide complex [5] and uranyl ion as photo-oxidants, there was no sign of the formation of 2,4'-dihydroxy-3,3'-diphenylbiphenyl (ortho-para dimer). It is clear that only the symmetric dimers are favoured under these experimental conditions. The quantum yields of *o*PP disappearance and phenylbenzoquinone formation are given in Table 2. In deoxygenated solution, the main photoproducts were the dimers II and III.

On irradiation of aerated solutions of uranyl nitrate and *m*PP under similar conditions, the main photoproducts were phenylbenzoquinone and dimers, whereas with deoxygenated solutions, only dimer formation was observed. With solutions of uranyl nitrate and *p*PP, the only organic photoproduct was the ortho-ortho dimer (V) in both aerated and deoxygenated solutions.



However, with *m*PP and *p*PP, accurate measurements of the quantum yields or kinetics were not attempted due to solubility problems.

#### 4. Discussion

The metal ion-induced photo-oxidation of phenols is, in general, thought to occur via the intermediate formation of phenoxyl radicals. Evidence for such species in the present studies using uranyl ion as photo-oxidant comes from flash photolysis experiments, and is in agreement with previous results using chemically induced dynamic nuclear polarization (CIDNP) [9] and magnetic field [10] effects. Both electron transfer and hydrogen atom abstraction mechanisms are possible [12,13]. However, if the latter were involved here, hydrogen atom abstraction from DMP would be expected to occur from the weaker C–H bond of the methyl groups rather than the O–H bond to produce the corresponding benzyl radicals. The lack of products from such species strongly suggests that the dominant oxidation process involves electron transfer. With the phenylphenols, both quinones and dimers were observed as stable organic products of photo-oxidation by uranyl ion. In contrast, on photolysis in the presence of  $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ , only dimers were observed [5,6]. The redox potentials of the  $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{3+/2+}$  (+0.33 V) and  $\text{UO}_2^{2+/+}$  (+0.16 V) pairs [22] are not very different, so that differences in behaviour between the cobalt azide and uranyl systems may well be associated with differences in the reactivities of the phenoxyl radical–metal ion pairs. Although the wavelengths for studying phenoxyl radical decay in these two cases were not the same, after correcting for differences in the extinction coefficient, the rate of decay of the transient produced by the reaction of excited uranyl ion with the phenols is about twice that observed for the cobalt(III) azide system [6]. Although this may be due to differences in pH, at the values used for these two studies it is unlikely that there is any protonation of the phenoxyl radical. A more probable explanation is that, in the latter case, we are observing the decay of the cobalt(II)–phenoxyl radical pair, which is slower than that of the “free” phenoxyl radical. Support for this comes from the presence of cobalt(II) in the final organic product and the lack of any quinone formation with this system.

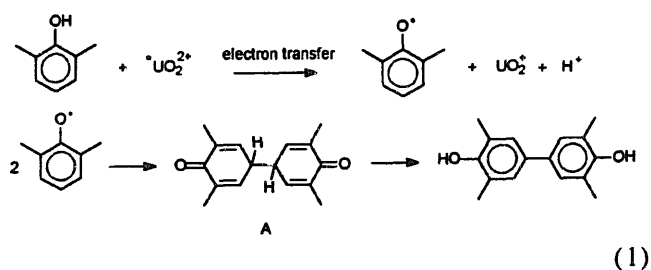
It is now necessary to explain the formation of quinone and the lack of significant overall reduction of uranium in the uranyl–phenol system. Phenoxyl radicals show little reactivity towards molecular oxygen [23]. It has been suggested that uranium(V) may react with oxygen to produce a uranium(VI) superoxide complex,  $[\text{U}^{\text{VI}}\text{O}_2(\text{O}_2^-)]^+$  [24],

which in acid solution is likely to protonate [24] to form the previously characterized uranyl–hydroperoxyl radical adduct [25]. We suggest that this may react with the phenoxyl radical to form quinones. The lack of quinone formation with the uranyl–*p*PP system is almost certainly due to steric blocking of the para position and to the instability of the *o*-quinone isomer.

Whilst the  $^*\text{UO}_2^{2+}$  quenching studies show that the deactivation by phenols occurs at rates close to diffusion-controlled rates, the quantum yields of phenol photo-oxidation are relatively modest. It has previously been suggested [8] that both chemical and physical processes are involved in the deactivation of excited uranyl ion by organic substrates. Matsushima [26] has suggested that aromatic hydrocarbons quench  $^*\text{UO}_2^{2+}$  via the formation of an exciplex. As suggested by Mao and Bakac [11], it is probable that exciplexes are also present here, and the low yields of phenol oxidation are a consequence of the preferential physical deactivation of these species.

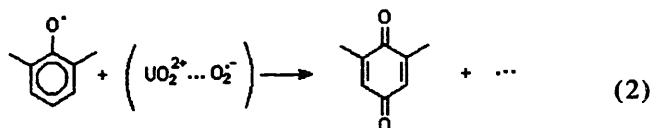
The major difference in the photo-oxidation of DMP by uranyl ion and the cobalt(III) azide complex is that, in the latter case, the predominant photoproduct is 3,3',5,5'-tetramethyldiphenylquinone (TMDQ) [7], whereas with uranyl ion, DMQ and dihydroxy dimers (or, in the absence of oxygen, just dihydroxy dimers) are formed. In both systems, dimeric species are formed by bimolecular reactions of metal ion–phenoxyl radical pairs. However, the formation of an oxidized product in the cobalt case and a reduced product with the uranium system, and the lack of the overall reduction of U(VI) in the total photoprocess, may be a consequence of the poor thermal oxidizing properties of uranium(VI). In contrast, it has been suggested that the cobalt(III) complex may be capable of oxidizing dimeric intermediates [7]. As indicated above for the phenylphenols, the formation of DMQ in the uranyl case may be associated with the reactions of hydroperoxyl radical adducts. However, it is also worth noting that dimethyl-*p*-benzoquinone and dimethylhydroquinone are observed on direct photolysis of DMP at 254 nm [7,27]. The mechanism of formation of these still remains obscure.

The overall mechanism for the oxidation of the phenols by uranyl ion, with DMP as an example, may be described as follows

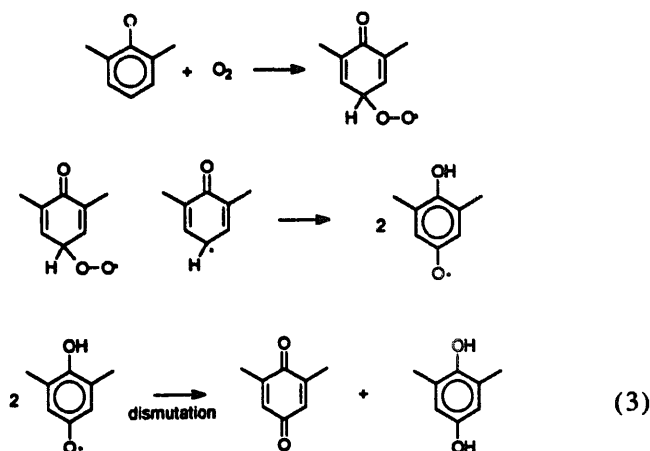


Flash photolysis experiments lead to a high concentration of organic radicals. Consequently, the coupling reaction is favoured and leads to the dimeric product.

The presence of oxygen is necessary for the formation of the quinone, and it is possible that this occurs via oxidation by a uranium(VI) superoxide (or hydroperoxyl) complex



Oxygen can also oxidize the dimethylphenoxyl radical



The presence of hydroquinone in trace concentrations provides evidence for a minor reactivity of oxygen towards the phenoxyl radical (reaction (3)). The photoinduced oxidation of DMP is dominated by reactions involving the primary formation of phenoxyl radical.

### Acknowledgements

Financial support for the collaboration between Clermont-Ferrand and Coimbra by JNICT and CNRS is gratefully acknowledged. One of us (H.D.B.) also thanks INTAS Project No. 93-1226 sponsored by the Commission of the European Community for support.

### References

- [1] L.-M. Coulangeon, G. Perbet, P. Boule, J. Lemaire, *Can. J. Chem.* 58 (1980) 2230, and references cited therein.
- [2] G. Dobson, L.I. Grossweiner, *Trans. Faraday Soc.* 61 (1965) 708.
- [3] C. Pizzocaro, M. Bolte, H. Sun, M.Z. Hoffman, *New J. Chem.* 18 (1994) 737.
- [4] M.I. Silva, H.D. Burrows, M.G. Miguel, S.J. Formosinho, *Ber. Bunsenges. Phys. Chem.* 100 (1996) 138.
- [5] M. Sarakha, A. Rossi, M. Bolte, *J. Photochem. Photobiol. A: Chem.* 85 (1995) 231.
- [6] M. Sarakha, H. Burrows, M. Bolte, *J. Photochem. Photobiol. A: Chem.* 97 (1996) 81.
- [7] M. Sarakha, M. Bolte, *J. Photochem. Photobiol. A: Chem.* 97 (1996) 87.
- [8] G. Sergeeva, A.K. Chibisov, L.V. Levshin, A.V. Karyakin, *J. Photochem.* 5 (1976) 253.
- [9] A.Z. Yankelevich, I.V. Khudyakov, A.L. Buchachenko, *Khim. Fiz.* 30 (1988) 46.
- [10] I.V. Khudyakov, A.L. Buchachenko, *Mendeleev Commun.* (1993) 135.
- [11] Y. Mao, A. Bakac, *Inorg. Chem.* 35 (1996) 3925.
- [12] H.D. Burrows, S.J. Formosinho, M. da G. Miguel, F. Pinto Coelho, *Mem. Acad. Ciências Lisboa (Classe de Ciências)* 19 (1976) 185.
- [13] V. Balzani, F. Bolletta, M.T. Gandolfi, M. Maestri, *Top. Curr. Chem.* 75 (1978) 1.
- [14] V. Balogh, M. Fetison, G. Golfier, *J. Org. Chem.* 36 (1971) 1339.
- [15] H. Finkbeiner, A.S. Hay, H.S. Blanchard, G.F. Endres, *J. Org. Chem.* 31 (1966) 549.
- [16] S.J. Formosinho, M.G.M. Miguel, H.D. Burrows, *J. Chem. Soc., Faraday Trans. 1* 80 (1984) 1717.
- [17] J.L. Kropp, *J. Chem. Phys.* 46 (1967) 843.
- [18] A.P. Darmanyan, I.V. Khudyakov, *Photochem. Photobiol.*, 52 (1990) 293.
- [19] R.N. Sylva, M.R. Davidson, *J. Chem. Soc., Dalton Trans.* (1979) 465.
- [20] M.E.D.G. Azenha, H.D. Burrows, S.J. Formosinho, M.G.M. Miguel, A.P. Darmanyan, I.V. Khudyakov, *J. Lumin.* 48/49 (1991) 522.
- [21] R. Terzian, N. Serpone, M.A. Fox, *J. Photochem. Photobiol. A: Chem.* 90 (1995) 125.
- [22] A.J. Bard, R. Parsons, J. Jordan (Eds.), *Standard Potentials in Aqueous Solutions*, Marcel Dekker, New York, 1985, p. 374, 650.
- [23] M. Simic, *Methods Enzymol.* 186 (1990) 89.
- [24] A. Bakac, J.H. Espenson, *Inorg. Chem.* 34 (1995) 1730.
- [25] D. Meisel, Y.A. Ilan, G. Czapski, *J. Phys. Chem.* 94 (1972) 2330.
- [26] R. Matsushima, *J. Am. Chem. Soc.* 94 (1972) 6010.
- [27] P. Mazellier, M. Sarakha, A. Rossi, M. Bolte, submitted to *J. Photochem. Photobiol. A: Chem.*