Electron-Transfer Oxidation of Chlorophenols by Uranyl Ion Excited State in Aqueous Solution. Steady-State and Nanosecond Flash Photolysis Studies

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The oxidation of chlorophenols by photoexcited uranyl ion was studied in aqueous solution at concentrations where the ground-state interactions were negligible. Nanosecond flash photolysis showed that a clean electron-transfer process from the chlorophenols to the excited uranyl ion is involved. This is suggested to lead to the formation of a U(V)/chlorophenoxyl radical pair complex. The efficiency of this charge-transfer process is unity for the three chlorophenols. However, low product yields suggest that in the absence of oxygen, back electron transfer, both within the radical pair and from separated uranium(V) to phenoxyl radicals, appears to be the major reaction pathway. In the presence of oxygen the quantum yields of disappearance of chlorophenol and of photoproduct formation increased. This leads to the conclusion that oxygen favors reaction with uranium(V) and/or the uranium(V)−phenoxyl radical pair, leading to the formation of the superoxide anion and its conjugate acid, $HO_2{}^{\bullet}$, which then regenerate $UO_2{}^{2+}$. Based on this, a catalytic cycle for chlorophenol photooxidation involving uranyl ion and molecular oxygen is proposed.

Introduction

Chlorophenols are widely used as fungicides, herbicides, etc.[1] They have applications in wood protection[2] and are produced in the Kraft bleaching of paper pulp.[3] However, the increasing awareness of the possible environmental effects of these compounds has led to the demand for limiting their usage and for the development of new methods of treating contaminated waters in which they are present. Particular emphasis has been given to advanced oxidation processes (AOPs)[4] using photochemical methods with either direct or sensitized photolysis. The general aspects of photooxidative degradation of chlorophenols have recently been extensively reviewed.[5]

Excited uranyl ion, $*UO_2{}^{2+}$, is a strongly oxidizing species ($E^\circ = +2.6 \pm 0.1$ V),[6−8] and has been shown to be capable of oxidizing a variety of substrates. The electronic structure[9] and photochemistry[10−12] of uranyl ion have recently been reviewed. Photooxidation of substrates by $*UO_2{}^{2+}$ is thought to occur by both atom[13−22] and electron-transfer[18,20,23−38] processes. With phenols, reaction has been shown to occur by a dynamic process[25] involving intermediate phenoxyl radical−uranium(V) radical pairs.[30,35] Although many of the early studies on photooxidation of phenols by uranyl ion concentrated on the kinetics of these processes,[25] we have recently reported results of a combined study of the kinetics and product characterization on the uranyl-ion-sensitized photolysis of 2,6-dimethylphenol and monophenylphenols in aqueous solution.[38] In this paper we extend these studies to the photooxidation of selected chlorophenols by uranyl ion.
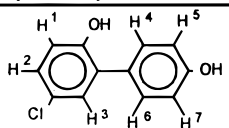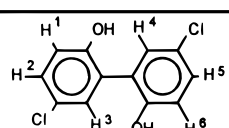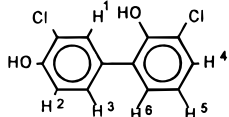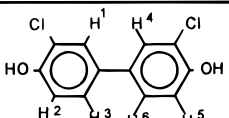
Experimental Section

Time-Resolved Transient Absorption and Emission Measurements. Transient absorption experiments in the 20 ns to

400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitation (355 nm) was from the third harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width $\approx$ 5 ns), and was used in a right-angle geometry with respect to the monitoring light beam. A 3 cm^3 volume of solution was used in a quartz cuvette, and was stirred after each flash irradiation. Individual cuvette samples were used for a maximum of 5 consecutive experiments. 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 synchronizing the pulsed light source and programmable shutters with the laser output. This 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 analyze the digitized signal. Emission decay measurements used the same system without the analyzing light source. Some steady-state luminescence quenching measurements were also carried out on a Spex Fluorolog model 111 spectrometer, as described in a previous publication.[38]

Steady-State Photolysis and Analytical Procedures. For steady-state irradiations either 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.[38−41] The quantum yields of degradation of the chlorophenols 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), and a reverse phase Merck column (Lichrospher 100RP-18 5 μm-250 mm × 4 mm). Photoproducts were separated using a Gilson preparative HPLC apparatus equipped with Waters model 490 detector and model 201 fraction collector.

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CHART 1

Studied system	photoproducts	^{1}H NMR features
4-chlorophenol/UO$_2^{2+}$	m/e = 220	In MeOD : 6.91 ppm H^1 (d, J = 9.4 Hz); 7.28 ppm H^2 (dd, J = 9.6 and 2.5 Hz); 7.19 ppm H^3 (d, J = 2.5 Hz); 6.97 ppm H^4 and H^6 (d, J = 9.0 Hz); 7.33 ppm H^5 and H^7 (d, J = 8.9 Hz);
	m/e = 254	In MeOD : 6.98 ppm H^1 and H^6 (d, J = 8.7 Hz); 7.30 ppm H^2 and H^5 (dd, J = 8.6 and 2.6 Hz); 7.26 ppm H^3 and H^4 (d, J = 2.6 Hz);
2-chlorophenol/UO$_2^{2+}$	m/e = 254	In CD$_3$OD : 7.07 ppm, H^5 (t, 8.0 Hz); 7.14 ppm, H^2 (d, J = 8.4 Hz); 7.34 ppm, H^4 (dd, J = 8.4 and 1.8 Hz); 7.46 ppm H^6 (dd, J = 8.4 and 1.7 Hz); 7.48 ppm H^3 (dd, J = 8.3 and 2.0 Hz); 7.69 H^1 (d, J = 1.9 Hz)
	m/e = 254	In CD$_3$OD : 7.14 ppm, H^2 and H^5 (d, J = 8.4 Hz); 7.50 ppm, H^3 and H^6 (dd, J = 8.4 and 2.3 Hz); 7.66 ppm, H^1 and H^4 (d, J = 2.2 Hz)

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on a Bruker AC400 (Fourier Transform) spectrometer in deuterated methanol or chloroform (Aldrich). Chart I shows the ^{1}H NMR features of the isolated photoproducts.

GC mass spectral analyses were performed on a Hewlett-Packard 5985 model apparatus equipped with a capillary column Supelco (30 m length, i.d. 0.25 mm, and a film thickness of 25 μm). The injection and detector temperatures were 250 and 200 °C, respectively. A high grade helium was used as a carrier gas.

Materials

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

Results

At room temperature, the absorption spectra of mixtures of UO$_2^{2+}$ ([UO$_2^{2+}$] $\geq$ 1.0 × 10^{-2} M) with the three chlorophenols used in the present work ([chlorophenol] < 5.0 × 10^{-3} M) were shown to be equal to the sum of the component spectra, showing that under the conditions of our experiments no significant ground-state interaction between uranyl ion and chlorophenols was present. Luminescence quenching and flash photolysis data, which will be presented later, support this. However, it should be noted that under conditions where the concentration of chlorophenol was higher than that of uranyl ion (i.e., [chlorophenol]/[UO$_2^{2+}$] >1), an increase in absorbance over the whole absorption spectrum was observed (Figure 1). This phenomenon can be related to that previously reported for complexing of the phenolic hydroxyl group with UO$_2^{2+}$.[42]
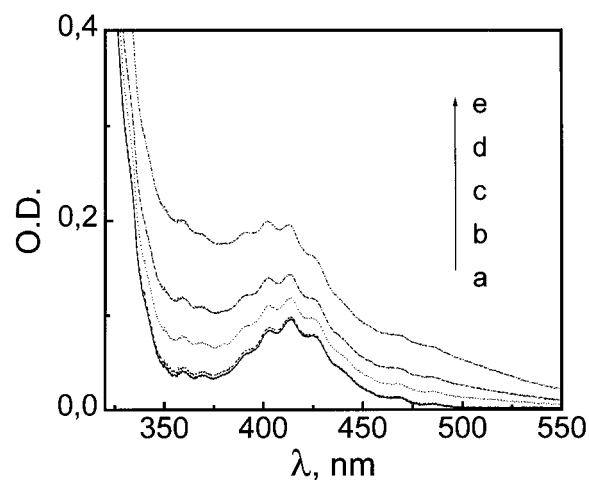
Figure 1. UV−visible absorption spectra of uranyl alone and uranyl/4-chlorophenol. (a) UO$_2^{2+}$, 1.0 × 10^{-2} M; (b) UO$_2^{2+}$, 1.0 × 10^{-2} M/4-chlorophenol, 5.0 × 10^{-3} M; (c) UO$_2^{2+}$, 1.0 × 10^{-2} M/4-chlorophenol, 1.0 × 10^{-2} M; (d) UO$_2^{2+}$, 1.0 × 10^{-2} M/4-chlorophenol, 2.0 × 10^{-2} M; (e) UO$_2^{2+}$, 1.0 × 10^{-2} M/4-chlorophenol, 5.0 × 10^{-2} M.

Steady-State Studies. The photolysis at 334 nm of aqueous solutions of 4-chlorophenol (1.0 × 10^{-3} M) in the presence of UO$_2^{2+}$ (5.0 × 10^{-2} M) led to a continuous increase of the absorbance over the whole UV−visible absorption spectrum. The HPLC analysis of the irradiated solution gave evidence for the formation of three main photoproducts (Figure 2c). The first, benzoquinone (E), was easily identified by comparison of its retention time and UV−visible spectrum with a reference sample. The photoproducts F and G were isolated from the irradiated solution and identified by ^{1}H NMR as 2,4′-dihydroxy-5-chlorobiphenyl (λ_{max} = 257 and 295 nm), and 2,2′-dihyrodoxy-5,5′-dichlorobiphenyl (λ_{max} = 280 nm) respectively (see Experimental Section for NMR spectral features). The evolution of these products as a function of irradiation time clearly showed
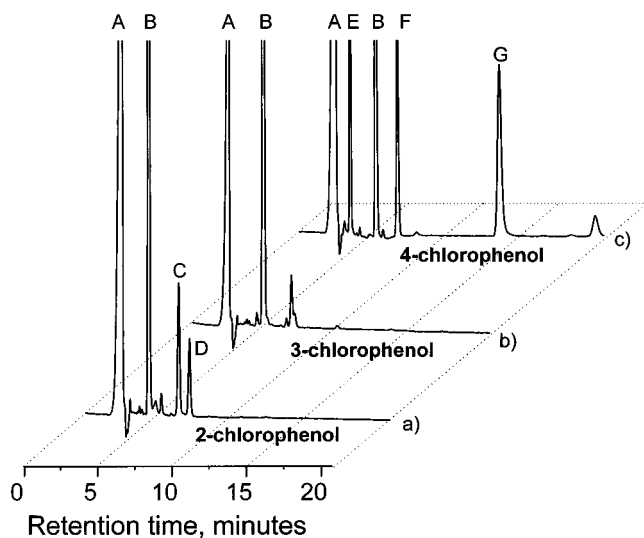
Figure 2. High-performance liquid chromatograms observed for the products of photolysis of aerated aqueous solutions of UO_2^{2+} (5.0×10^{-2} M) and monochlorophenol (1.0×10^{-3} M): 2-chlorophenol (a); 3-chlorophenol (b); 4-chlorophenol (c). Detection wavelength = 280 nm. A: UO_2^{2+}; B: starting material; C: 2,4′-dihydroxy-3,3′-dichlorobiphenyl; D: 4,4′-dihydroxy-3,3′-dichlorobiphenyl; E: benzoquinone; F: 2,2′-dihyrodoxy-5,5′-dichlorobiphenyl; G: 2,4′-dihydroxy-5-chlorobiphenyl.

that they are primary photoproducts. However, upon prolonged irradiation a secondary photoproduct with longer retention time was also formed, although it has not yet proved possible to accurately assign it. In the case of 2-chlorophenol, the irradiation at 334 nm in the presence of UO_2^{2+} led to the formation of chlorobenzoquinone, the *ortho-para* and *para-para* coupling dimers (2,4′-dihydroxy 3,3′-dichlorobiphenyl and 4,4′-dihydroxy 3,3′-dichlorobiphenyl) as the main detectable photoproducts. In the case of 3-chlorophenol, although disappearance of the phenol was observed, the amounts of the generated photoproducts were too small to enable their separation and identification from the irradiated mixture, even on prolonged irradiation. HPLC data on the products of photolysis of all three chlorophenols in the presence of uranyl ion are illustrated in Figure 2.

Quantum yields were determined for photolysis of 4-chlorophenol in the presence of uranyl ion in aerated, deaerated, and oxygenated solutions, and are presented in Table 1.
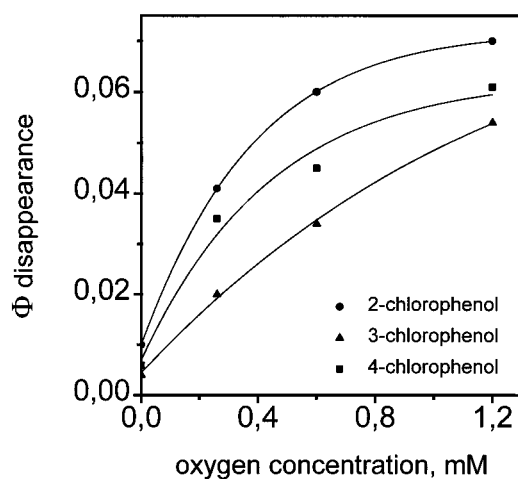
These results clearly show that the disappearance of 4-chlorophenol is favored by the presence of oxygen. Benzoquinone accounts for roughly 15% and 25% of the conversion in aerated and oxygenated solutions, respectively. Similar effects were observed for the formation of 2,4′-dihydroxy-5-chlorobiphenyl and 2,2′-dihydroxy-5,5′-dichlorobiphenyl. No formation of U(V) was detected by UV−visible absorption spectroscopy under our experimental conditions.

Similar behavior was observed for the disappearance of 2-chlorophenol and 3-chlorophenol photoinduced by UO_2^{2+} (Table 1).

Figure 3. Effect of the oxygen concentration on the quantum yield of monochlorophenol disappearance.

Although only three oxygen concentrations were studied, the quantum yield for disappearance is clearly not a linear function of oxygen concentration for the three compounds (Figure 3).

Transient Absorption and Fluorescence Quenching Studies. To establish the mechanism and kinetic details of the chlorophenol degradation photoinduced by uranyl ions, we employed a nanosecond laser flash photolysis technique. When UO_2^{2+} (0.05 M) in argon-purged aqueous solutions at pH 2.3 is flash photolyzed, a transient absorption appears with absorption maximum at approximately 580 nm (Figure 4a). The spectrum is identical to that reported in the literature and assigned to the excited UO_2^{2+}*.[17,25,44] The amount of formation of uranyl ion excited state, as monitored by its initial absorption at 580 nm, was linearly dependent upon the initial light intensity within the $1-10$ mJ laser energy range, clearly showing that we are dealing only with a monophotonic process. Under our experimental conditions the decay of UO_2^{2+}* followed good first-order kinetics at all wavelengths of the absorption spectrum, with $k_0 = 7.0 \times 10^5$ s^{-1}. This is close to what has previously been reported for the decay of unhydrolyzed excited uranyl ion, *$[UO_2(H_2O)_5]^{2+}$, in acidic media.[17,32,45] The decay of the uranyl luminescence at 520 nm following excitation with the Nd:YAG laser was similar to that of the 580 nm absorption, although under certain conditions a better fit was obtained to a biexponential decay for the luminescence data. Biexponential decay of uranyl luminescence has previously been reported for aqueous solutions at the natural pH,[26,46−52] and the current consensus is that this is due to emission from various hydrolyzed species, produced in both ground and excited states.[46,50,52] The fact that we observe only a single component in the decay of the excited-state absorption may reflect a higher molar absorption coefficient for *$[UO_2(H_2O)_5]^{2+}$ than for any hydrolyzed uranium species at the analyzing wavelength. As previously reported,[46,53] k_0 is unaffected by the presence of oxygen.

TABLE 1: Effect of Oxygen Concentration on the Quantum Yield of 4-Chlorophenol Disappearance and Benzoquinone Formation, and of 2-Chlorophenol and 3-Chlorophenol Disappearance ($[UO_2^{2+}] = 5.0 \times 10^{-2}$ M and [Chlorophenol] $= 1.0 \times 10^{-3}$ M, $\lambda_{excitation} = 334$ nm)

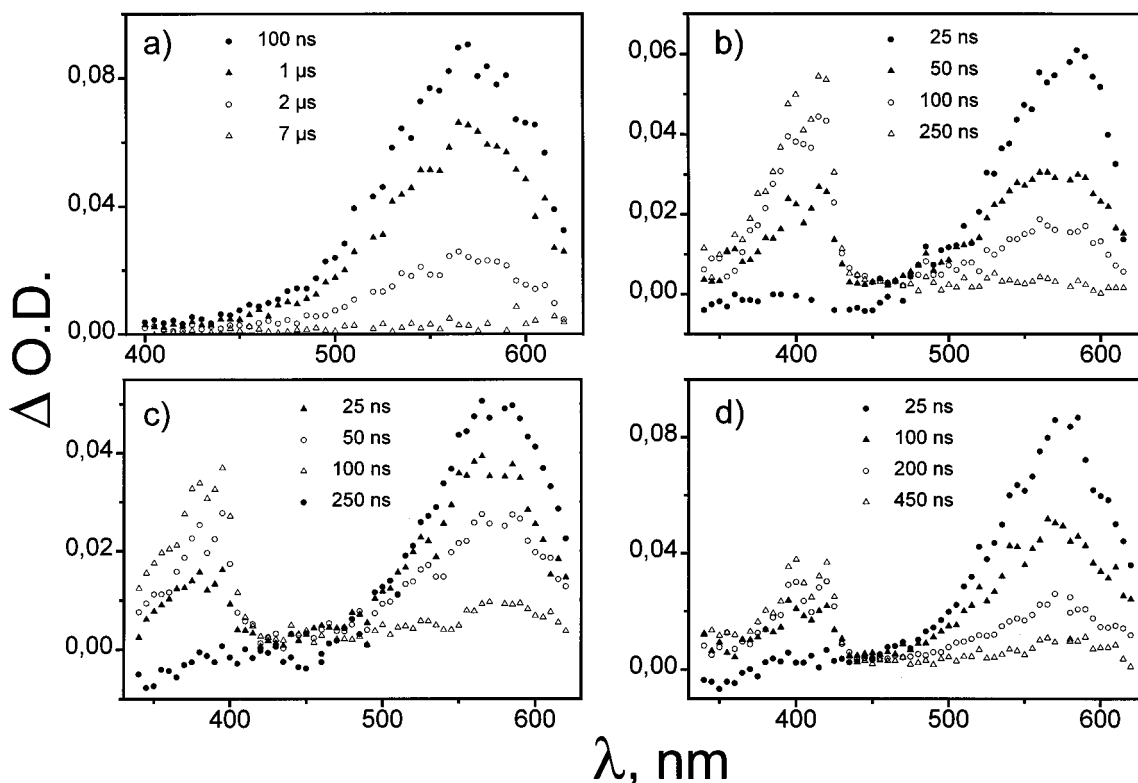| oxygen concentration, M	4-chlorophenol		2-chlorophenol	3-chlorophenol
	$\Phi_{disappearance}$	$\Phi_{benzoquinone}$	$\Phi_{disappearance}$	$\Phi_{disappearance}$
$<5 \times 10^{-6}$	5.9×10^{-3}	traces	1.0×10^{-2}	4.0×10^{-3}
2.6×10^{-4} (ref 43)	3.5×10^{-2}	5.0×10^{-3}	4.1×10^{-2}	2.0×10^{-2}
6.0×10^{-4} M^a	4.5×10^{-2}	9.6×10^{-3}	6.0×10^{-2}	3.4×10^{-2}
1.2×10^{-3}	6.1×10^{-2}	1.5×10^{-2}	7.0×10^{-2}	5.4×10^{-2}

^{a} Obtained by bubbling a 1:1 mixture O_2/N_2.

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Figure 4. Transient absorption spectra for uranyl ion alone (1.0×10^{-2} M) (a) and uranyl (1.0×10^{-2} M) plus 4-chlorophenol (2.0×10^{-3}) (b); 3-chlorophenol (2.0×10^{-3}) (c) and 2-chlorophenol (2.0×10^{-3}) (d).

When the monochlorophenols were present in the solutions at concentrations up to 2.3×10^{-3} M, the initial $*UO_2^{2+}$ absorbance decays more rapidly, following the overall rate law:

$$-\frac{d[*UO_2^{2+}]}{dt} = (k_o + k_q[\text{chlorophenol}])[*UO_2^{2+}]$$

where k_o and k_q represent the rate constant for $*UO_2^{2+}$ decay in the absence of the quencher and the second-order rate constant for the quenching process, respectively.

For all three monochlorophenols, the buildup of a new absorbance was observed in the region 350–420 nm on time scales identical to the decay of the excited uranyl ion decay. Typical transient absorption spectra for the three chlorophenols are illustrated in Figure 4, while kinetic traces for decay of $*UO_2^{2+}$ absorption and grow-in of transient absorption at 400 nm for the case of 4-chlorophenol are shown in Figure 5a, b. Comparison of these new spectra with those observed upon pulse radiolysis of aqueous solutions of chlorophenols in the presence of the one-electron oxidant azide radical[54–56] indicates that they are due to the monochlorophenoxyl radicals species. These results, and the observation of reasonable isosbestic points, indicate a clean oxidation, which we suggest involve an electron-transfer process from the monochlorophenol to excited uranyl ion. The growth of the monochlorophenoxyl radical obeyed a pseudo-first-order rate law, similar to that obtained for $*UO_2^{2+}$ decay in the presence of the monochlorophenols. In Table 2 we report average values, with standard deviations, for k_o and k_q obtained from the linear dependence of the pseudo-first-order rate constant for decay of the $*UO_2^{2+}$ species or grow-in of the monochlorophenoxyl radical upon monochlorophenol concentration. The values of k_o are in all cases identical to that observed in the absence of chlorophenol. The values of k_q are close to but slightly lower than those for a diffusion-controlled process.

TABLE 2: Bimolecular Rate Constants and Steady-State Stern−Volmer Constants for the Quenching of $*UO_2^{2+}$ by Monochlorophenols in Aqueous Solutions

	$k_0{}^a/10^5$ s^{-1}	$k_q{}^a/10^9$ $M^{-1}\,s^{-1}$	$K_{SV}{}^b/10^3$ M^{-1}	$K_{SV}/\tau/10^9$ $M^{-1}\,s^{-1}$
2-chlorophenol	6.5	1.4	5.61^c 10.05^d	1.7^c 4.1^d
3-chlorophenol	7.2	1.1	4.95^c 10.78^d	1.5^c 4.4^d
4-chlorophenol	7.5	1.7	5.94^c 10.05^d	1.8^c 4.1^d

[a] Values obtained by using linear regression of pseudo-first-order rate constants for decay of $*UO_2 2*$ absorption at 580 nm or uranyl fluorescence at 520 nm as functions of monochlorophenol concentration; see text for meaning of symbols. [b] Determined with $\lambda_{\text{excitation}} = 350$ nm. [c] For pH 0.8, using $\tau = 3.3$ μs. [d] For pH 2.3 using $\tau = 2.45$ μs.

Both steady-state and dynamic quenching of uranyl luminescence by the monochlorophenols was also studied. The uranyl luminescence decays were linear functions of substrate concentration for all three chlorophenols, and followed kinetic similar behavior to the decay of the uranyl excited-state absorption at 580 nm. In steady-state measurements, the luminescence between 480 and 650 nm was quenched by all three chlorophenols, and Stern−Volmer plots were found to be linear up to millimolar concentrations. From the slopes of these and the excited uranyl ion lifetime, values of k_q were calculated at pH 1 and 2.3, and are also given in Table 2. The excellent agreement between the steady-state values for k_q at pH 1 and those obtained from flash photolysis supports the earlier suggestion that quenching of uranyl excited-state involves a dynamic process with the chlorophenols leading to charge transfer.

Taking the values of the molar absorption coefficients reported in the literature:[55] $\epsilon_{395\text{ nm}} = 1800$ M^{-1} cm^{-1} for the 2-chlorophenoxyl radical, $\epsilon_{415\text{ nm}} = 2220$ M^{-1} cm^{-1} for the 3-chlorophenoxyl radical, $\epsilon_{420\text{ nm}} = 5100$ M^{-1} cm^{-1} for the 4-chlorophenoxyl radical,[43,44] and $\epsilon_{580\text{ nm}} = 5800$ M^{-1} cm^{-1} for the excited $*UO_2^{2+}$ species,[44] the efficiency, ξ, of the electron-transfer process was calculated according to
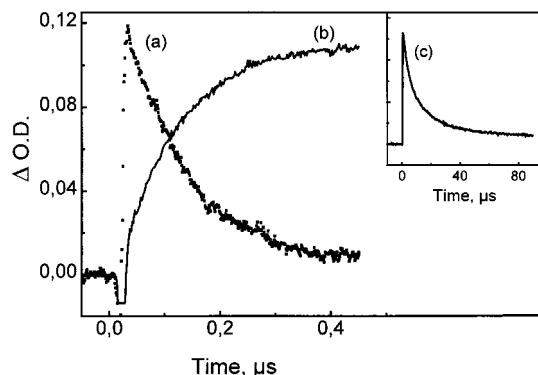
Figure 5. Kinetic traces for uranyl/4-chlorophenol (1.0×10^{-2} M/ 2.0×10^{-3}) mixture. (a) Decay of excited uranyl ion absorption at 580 nm; (b) grow-in of 4-chlorophenoxyl radical absorption at 400 nm; (c) decay of 4-chlorophenoxyl radical absorption at 400 nm.

$$\xi = \frac{A_o(*UO_2^{2+})}{A_\infty(\text{radical})} \frac{\epsilon_{\text{max radical}}}{\epsilon_{580}}$$

where $A_o(*UO_2^{2+})$ is the absorbance at 580 nm of the excited $*UO_2^{2+}$ species observed immediately after the flash, and A_∞ (radical) is the absorbance of the monochlorophenoxyl radical determined after completion of its grow-in at the maximum of its absorption spectrum.

The values of the efficiency associated with the electron-transfer process ($\xi_{2-\text{chlorophenol}} = 0.97$; $\xi_{3-\text{chlorophenol}} = 1.0$; $\xi_{4-\text{chlorophenol}} = 0.99$) are within the experimental errors, equal to unity. These appear to be unaffected by the presence of oxygen. These results can be contrasted with the quenching of excited uranyl ion by alkylbenzenes, which is suggested to proceed purely by a physical process involving exciplex formation, with no overall electron transfer.[14] Electron transfer has, however, been demonstrated in the quenching of $*UO_2^{2+}$ by naphthalene[37] and in the reaction of photoexcited [Ru-(bpy)₃]²⁺ with chlorophenolate anions.[57-59]

The decays of the chlorophenoxyl radical absorbances were examined in the presence and in the absence of oxygen. In both cases the absorbance disappeared to the baseline via a second-order process (Figure 5 c). Using values for the molar extinction coefficients from ref 56, second-order rate constants (k) for decay of chlorophenoxyl radicals at 400 nm of 4.5 (± 0.3) $\times$ 10^9 M⁻¹ s⁻¹ (2-chloro-), 9.6 (± 0.7) $\times 10^9$ M⁻¹ s⁻¹ (3-chloro-), and 6.1 (± 0.2) $\times 10^9$ M⁻¹ s⁻¹ (4-chloro-) were determined. The nature of this decay process will be considered in the Discussion section.

Discussion

The transient absorption and fluorescence quenching observations in this study clearly show that excited uranyl ion is capable of rapidly oxidizing monochlorophenols. Although both electron and hydrogen atom transfer are possible, the high bond dissociation energy for the phenolic hydrogen (≈ 90 kcal mol⁻¹)[5,60] makes atom transfer unlikely, and we suggest that the mechanism is similar to that previously proposed for oxidation of phenols by $*UO_2^{2+}$.[30,38] The initial step in this mechanism is an electron transfer from $*UO_2^{2+}$ species to the chlorophenol derivative leading to the formation of a uranium-(V)−chlorophenol radical cation complex. The highly acidic phenol radical cation (pK_a −10 to −13)[60] is then expected to rapidly deprotonate within the radical pair to give the phenoxyl radical. The efficiency of this overall electron transfer between chlorophenols and excited uranyl ion was found to be close to 100%. For quenching of excited uranyl ion by naphthalene, about 30% of the reaction proceeds by electron transfer while

the rest is suggested to involve physical deactivation via an exciplex.[37] With alkylbenzenes, quenching of uranyl excited state has been suggested to occur purely through the physical process.[14] However, it should be noticed that a small fraction (ca. 1%) of quenching of excited uranyl ion by toluene involves hydrogen atom abstraction.[61] Despite the high oxidation potential of excited uranyl ion, some additional factor is necessary to favor electron transfer over physical quenching. In studies on electron transfer from polychlorophenolate anions to excited [Ru(bpy)₃]²⁺ in various water−methanol mixtures a marked dependence of the yield of cage escape on the percentage of methanol was observed.[58,59] For the studies of both quenching of uranyl ion luminescence by substituted benzenes[14] and oxidation of naphthalene by excited uranyl ion,[37] it was necessary to use mixtures of water and organic solvents to dissolve the aromatic compound, and it is possible that a similar dependence of the yield of electron transfer on solvent polarity occurs. However, as with uranium(V)−halogen atom radical pairs, energetic factors are also expected to be important.[32]

In the absence of oxygen, two different pathways can be suggested for the disappearance of the uranium(V)−phenoxyl radical pair:
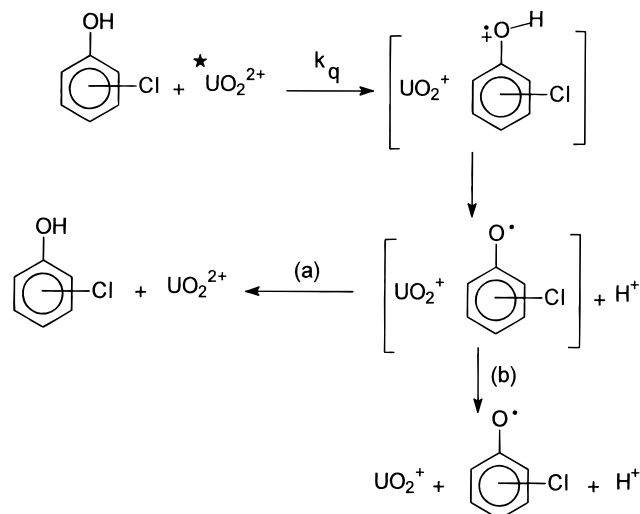
(a) back electron transfer leading to the formation of uranyl ion in its ground state and monochlorophenol, and (b) cage escape leading to the formation of phenoxyl radical and U(V).

Good evidence for back electron transfer within uranium-(V)-radical pairs has been presented for a system with halogen atoms,[32] and the fact that the quantum yield of disappearance of chlorophenol in deaerated solutions was very low (<6 $\times$ 10^{-3}), even though the efficiency of electron transfer was roughly equal to unity, may suggest that this is an important process here. However, such a decay should follow first-order kinetics, while the observed decay of phenoxyl radicals is second-order. We feel therefore, in agreement with the suggestion of Mao and Bakac for the uranyl−naphthalene system,[37] that much of the uranium(V)−chlorophenoxyl radical pair decays by cage escape followed by oxidation of uranium(V) by the phenoxyl radical.

$$UO_2^+ + ClPhO^\bullet \rightarrow UO_2^{2+} + ClPhO^-$$
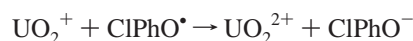
This reaction is thermodynamically favorable ($E° UO_2^{2+/+}$ + 0.16V,[62] 4-ClPhO⁻/⁻ + 0.80 V [54]), and expected to be fast.

In the presence of oxygen, a third pathway must be involved since the quantum yields of monochlorophenol disappearance and of photoproduct formation increase, and show a dependence

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upon the concentration of oxygen. Neither excited uranyl ion[46,53] nor phenoxyl radicals[5,63,64] react with oxygen. In addition, while uranium(V) is oxidized to UO_2^{2+} by molecular oxygen, the reaction is relatively slow.[65,66] However, autoxidation of uranium(V) probably involves the formation of the superoxouranium(VI).[65] This can protonate to produce the previously characterized uranyl−hydroperoxyl radical adduct,[67] which can dissociate to yield free hydroperoxyl radical. Although our results do not allow us to distinguish between formation of such a species by reaction of the uranium(V)−chlorophenoxyl radical pair with oxygen and autoxidation of free uranium(V), we feel it likely from the observed oxygen dependence of the quantum yield of chlorophenol disappearance that at least some of the oxidation occurs in the radical pair. The hydroperoxyl radical, $HO_2^•$, has been shown to oxidize a variety of organic substrates[68] and may also disproportionate to produce hydrogen peroxide and oxygen either directly,[68] or catalyzed by uranyl ion.[67,69] Hydrogen peroxide may then react with substrates, or dissociate to give the hydroxyl radical, •OH. The involvement of hydroxyl radical in the photooxidation of various aromatic substrates by uranyl ion has been reported.[37,61,70] In addition, the reactions of hydroxyl radicals with chlorophenols have been reviewed.[5] However, the products are rather different from those observed in the present study. For example, the reaction of hydroxyl radical with 4-chlorophenol yields mainly 4-chlorocatechol,[71,72] while the present studies indicate that the principal products of uranyl photooxidation are benzoquinone and dimers. We, therefore, feel that in our system reactions of hydroperoxyl radicals or other transient species are more important than those of hydroxyl radicals.

The evidence for the involvement of oxygen in the process of chlorophenol disappearance highlights the fact that uranyl ion acts as a photocatalyst in the process. As the solution is continuously irradiated, the uranyl ion regenerated may be excited again, reduced by chlorophenol, and again oxidized by oxygen leading to a catalytic cycle. Similar catalytic cycles have previously been reported for the photooxidation by uranyl ion of toluene,[61] naphthalene,[37] and various other hydrocarbons.[36] Following formation of the uranium(V)−chlorophenoxyl radical pair, the subsequent steps of the catalytic cycle is suggested to involve the formation of hydroperoxyl radicals.
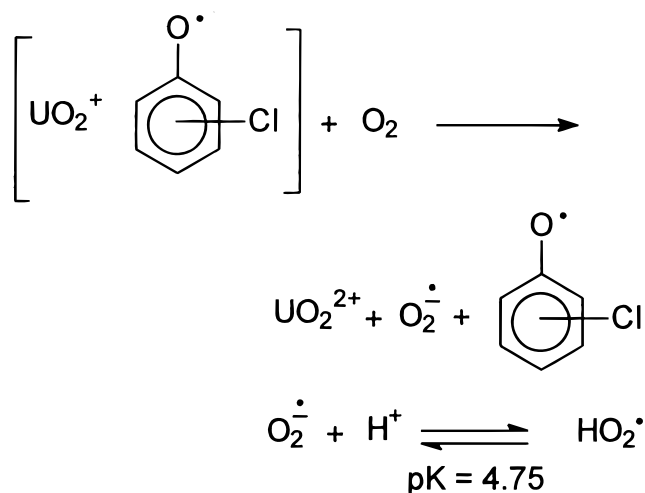

The formation of the different photoproducts can be explained through the reactivity of the phenoxyl radical, in its different mesomeric structures, with the different species present in the solution.

The formation of benzoquinone in the case of 4-chlorophenol may involve reaction involving the hydroperoxyl radical, $HO_2^•$ as follows:
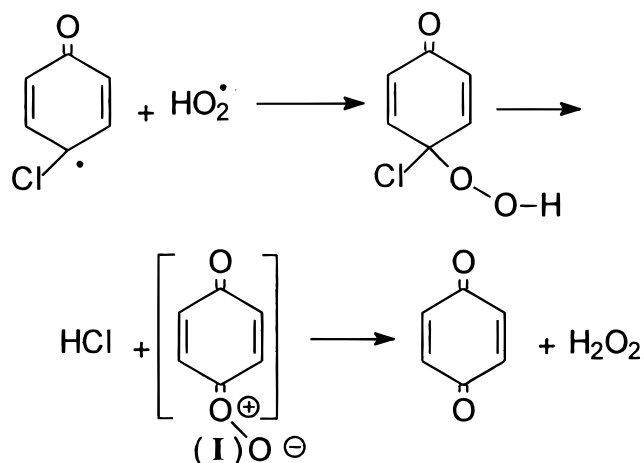

with the intermediacy of the benzoquinone oxide, (**I**). This species has been proposed by Grabner et al. in their flash photolysis study of the phototransformation of 4-chlorophenol.[73] This species was suggested to be formed by reaction of oxygen with the carbene 4-oxocyclohexa-2,5-dienylidene (**II**). The transient (**II**) is also suggested to react with 4-chlorophenol to give 2,4′-dihydroxy 5- chloro biphenyl,[73] one of the products of uranyl-sensitized photooxidation of 4-chlorophenol, by the reaction
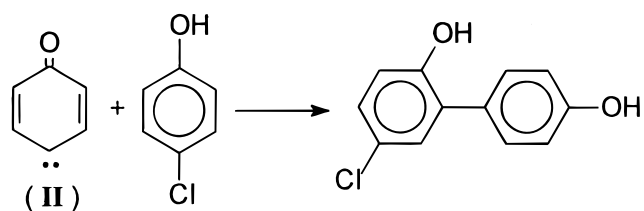
However, the carbene (**II**), which absorbs at 370 and 384 nm, was not detected in our study, and although it may be formed and present at low concentrations, an alternative rout to form (**I**) involves addition of hydroperoxyl radical to the 4-chlorophenoxyl radical followed by elimination of HCl.

The formation of 2,4′-dihydroxy 5-chlorobiphenyl may be explained by a reaction of the phenoxyl radical with the starting 4-chlorophenol.
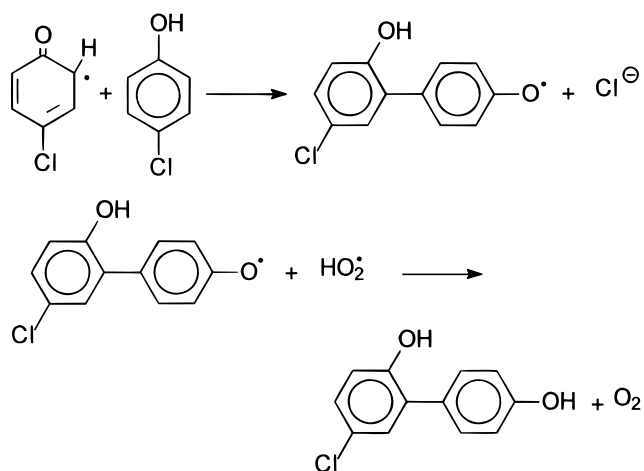
The formation of the dimeric photoproducts in the case of 4-chlorophenol and 2-chlorophenol correspond to reaction involving the phenoxyl radical in its different mesomeric forms:
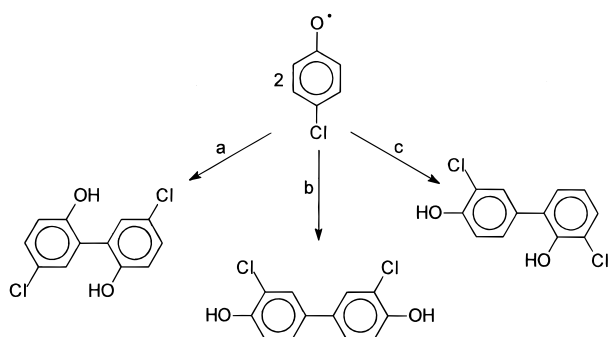
a : *ortho-ortho* coupling of the 4-phenoxyl radical
b : *para-para* coupling of the 2-phenoxyl radical
c : *ortho-para* coupling of the 2-phenoxyl radical

Conclusion

The uranyl ion is shown to be an effective photocatalyst for the oxidative degradation of chlorophenols. The process involves the primary formation of a radical pair complex. In all cases, the decay of the generated chlorophenoxyl radical follows good second-order kinetics indicating an efficient back electron transfer. However, in the presence of molecular oxygen an overall photoreaction is observed, leading to a catalytic cycle:
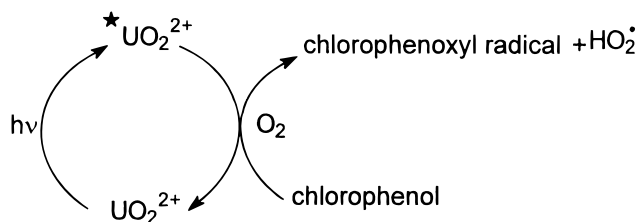
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