Mechanism of formation of phenoxyl radicals during the photo-oxidation of phenol in the presence of Fe^{III}

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The primary photochemical reactions of iron(III) either in the form of $Fe(ClO_4)_3$ or $FeCl_3$ with phenol in aqueous solution have been studied by nanosecond laser photolysis (λ = 347 nm). The mechanism leads to the formation of phenoxyl radical $PhO^{\bullet}$ and involves the photo-oxidation of phenol by $Cl^{\bullet}$ and $Cl_2^{\bullet -}$ radicals in the presence of added Cl^- anion.

Introduction

The photochemistry of iron(III) complexes in aqueous solution is important for understanding the redox processes of Fe^{II}–Fe^{III} in clouds, fresh and marine water.[1–3] The photochemistry of iron(III) complexes has recently been shown to play a key role in the photo-assisted Fenton catalysis of contaminated waters.[4–7] The equilibrium of iron(III) species coexisting in aqueous solutions complicates the behavior of these iron(III) complexes.[8–11] Steady-state photolysis of aqueous iron(III) solutions has been reported[12,13] but laser photolysis has not been reported in detail for iron(III) in the presence of a common industrial pollutant like phenol. The latter system is reported here in the presence and absence of Cl^- anion taking into account that the photo-assisted Fenton catalysis is capable of degrading PhOH contaminated waters.[4–7,14] The study of the Fenton photocatalyzed degradation mechanism of phenol in solutions of high ionic strength is of central importance for determining the mechanism of degradation of this common industrial pollutant. Industrial effluents containing Cl^- or SO_4^{2-} anions inhibit biological degradation. This is a major problem encountered during the degradation of this type of organic compound.

Materials and methods

$FeCl_3{\cdot}6H_2O$, $Fe(ClO_4)_3{\cdot}9H_2O$, $NaClO_4$ and NaCl were Fluka puriss. p.a. and used as received. The solution pH was adjusted with $HClO_4$ or HCl. The iron solutions were equilibrated and the stock solution prepared fresh before every experiment. Solutions were used only once to avoid accumulation of the irradiated products. All experiments were performed in 1 cm quartz cells in air at room temperature. Laser photolysis was carried out by using the second harmonic (λ = 347 nm) of a JK-2000 ruby laser operated in the Q-switched mode. The pulse width was ~15 ns and the energy per pulse was ~18 mJ. A detailed description of the laser system has been reported elsewhere.[14] Spectrophotometric measurements were carried out by means of a Hewlett-Packard 8452 diode array.

Results and discussion

The absorption spectra of iron(III) aqueous solutions in the presence or absence of PhOH and Cl^- anion are shown in Figs. 1(b), 2(a) and 3(b). The laser pulse induced transient spectra are shown in Figs. 1(a), 2(b) and 3(a).

The transient absorption spectrum and absorption spectra for iron(III) complexes in solution are shown in Fig. 1(a), (b). It is readily seen from Fig. 1(a), (b) that the absorption peak of $FeOH^{2+}$ at λ = 297 nm coincides with the maximum of the bleaching band (λ = 297 nm) after laser excitation.

Fig. 2(b) shows the laser induced transient absorption spectra of iron(III) species in the presence of [PhOH] = 0.45 M. The inset in Fig. 2(b) shows part of the transient spectrum near 400 nm with a higher resolution. The split band in the inset around 400 nm coincides with the spectrum reported for the phenoxyl radical $PhO^{\bullet}$ reported by pulse radiolysis.[15] A comparison of the spectra in Fig. 2(a) and (b) shows that the bleaching band around 550 nm [Fig. 2(b)] corresponds to the absorption at λ = 550 nm [Fig. 2(a)]. The growth of the bleaching band takes place within the laser pulse. It is so short that it cannot be resolved.

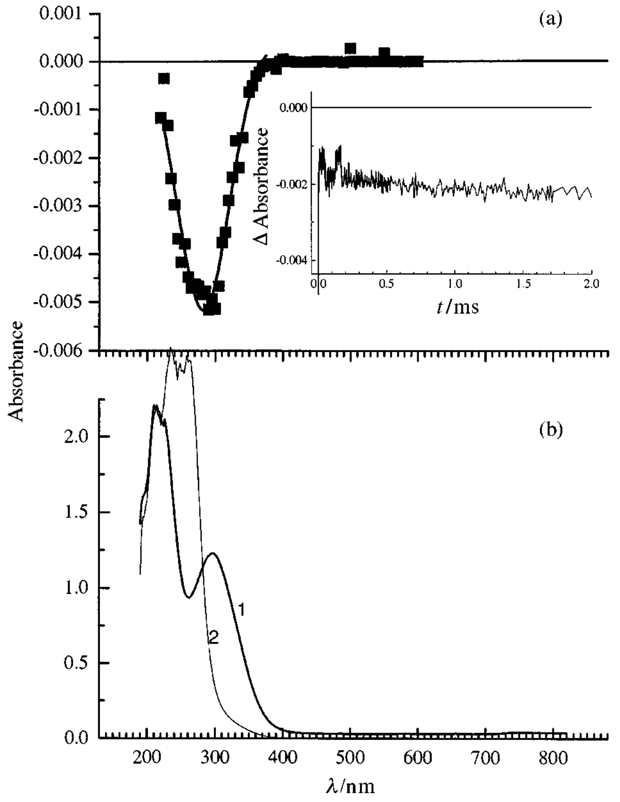

Fig. 1 (a) Transient absorption spectrum of the iron(III) aqueous solution, $[Fe(ClO_4)_3]$ = 0.72 mM, at pH 2.90. The inset shows the transient at λ = 300 nm. Cell d = 1 cm. (b) Absorption spectrum of the iron(III) aqueous solution, $[Fe(ClO_4)_3]$ = 0.72 mM. Trace 1, pH 2.90. Trace 2, pH 0.50.

Fig. 3(a) shows the transient absorption spectra for iron(III) solutions of PhOH in the presence of Cl^- anion. The split band of the $PhO^{\bullet}$ radical is observed around λ = 400 nm. The bleaching in Fig. 3(a) corresponds to the absorption band of the $FeCl^{2+}$ complex around λ = 345 nm shown in Fig. 3(b). In the absence of PhOH, the transient spectrum of the $FeCl^{2+}$ photolysis is different to that reported in Fig. 3(a). The spectrum has an absorption band extending from 250 to 450 nm with a maximum at λ = 340 nm corresponding to $Cl_2^{\bullet -}$ radical

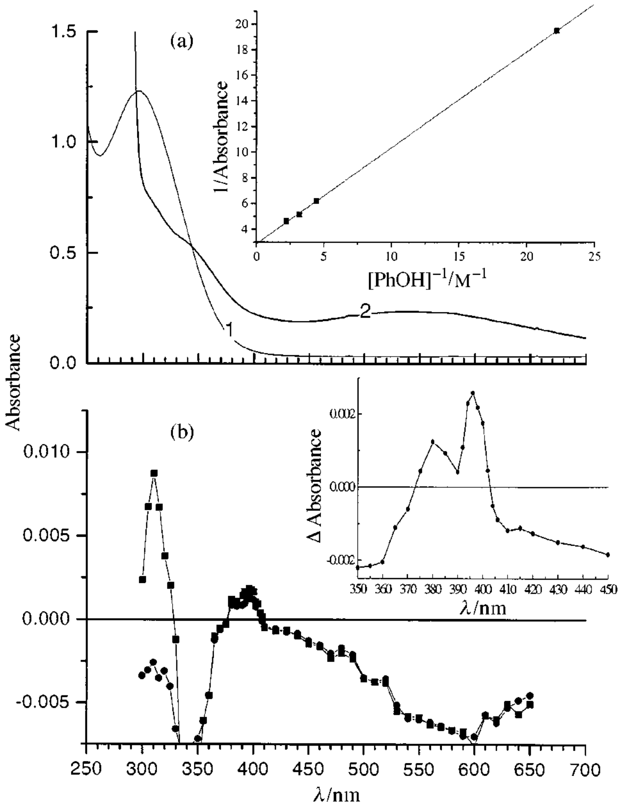

Fig. 2 (a) Spectrum of $[Fe(ClO_4)_3] = 0.76$ mM as shown in trace 1 and in the presence of $[PhOH] = 1$ M as shown in trace 2. Ionic strength $[NaClO_4] = 1$ M, pH 2.66. Inset shows the dependence of reciprocal absorbance at $\lambda = 550$ nm on the reciprocal phenol concentration. (b) Transient absorption spectra of $[Fe(ClO_4)_3] = 0.76$ mM, $[PhOH] = 0.45$ M. Ionic strength 1 M, at pH 2.66, ■ time delay 60 ns, ● time delay 5 μs. Inset shows transient absorption spectrum around 400 nm.

absorption.[16] The spectrum of $Cl_2^{\bullet-}$ has been reported elsewhere.[17]

Taking into account these spectral observations in Figs. 1–3 and the already known equilibria of iron(III) complexes in solution,[8,9,11] the presence of the iron(III) complexes is suggested to be as given in eqns. (1)–(3). Fe^{3+} is the aqua-complex of iron(III)

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_1 = 10^{-2.43}\ \text{M} \quad (1)$$

$$Fe^{3+} + PhOH \rightleftharpoons FeOPh^{2+} + H^+ \quad (2)$$

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \qquad K_3 = 5.34\ \text{M}^{-1} \quad (3)$$

(water molecules are omitted). The additional equilibria (4)–(6)

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^{+} + 2H^+ \qquad K_4 = 10^{-4.69}\ \text{M}^2 \quad (4)$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ K_5 = 0.8 \times 10^{-3}\ \text{M} \quad (5)$$

$$Fe^{3+} + 2Cl^- \rightleftharpoons FeCl_2^{+} \qquad K_6 = 1.82\ \text{M}^{-2} \quad (6)$$

are also taking place in solution.[8–11] The values of the K_2 constant were measured in the present work again, since the reaction medium used is different to the one cited in the literature.[18] As seen from Fig. 2(a) the addition of PhOH to a solution of iron(III) leads to the formation of an absorption band in the visible region at $\lambda = 550$ nm as well as the band between 300–400 nm. By maintaining constant the temperature, ionic strength, concentration of iron(III) and PhOH, a linear dependence is observed between 1/absorbance ($\lambda = 550$ nm) and $[PhOH]^{-1}$ (Benesi–Hildebrand relation) as shown in the inset in Fig. 1(a). The value of $K_2 = 0.021 \pm 0.008$ was obtained from this dependence. This value is about twice the value 0.0096 ± 0.0009 found for the dependence of the reciprocal absorbance *vs.* the $[H^+]$ concentration.[18]

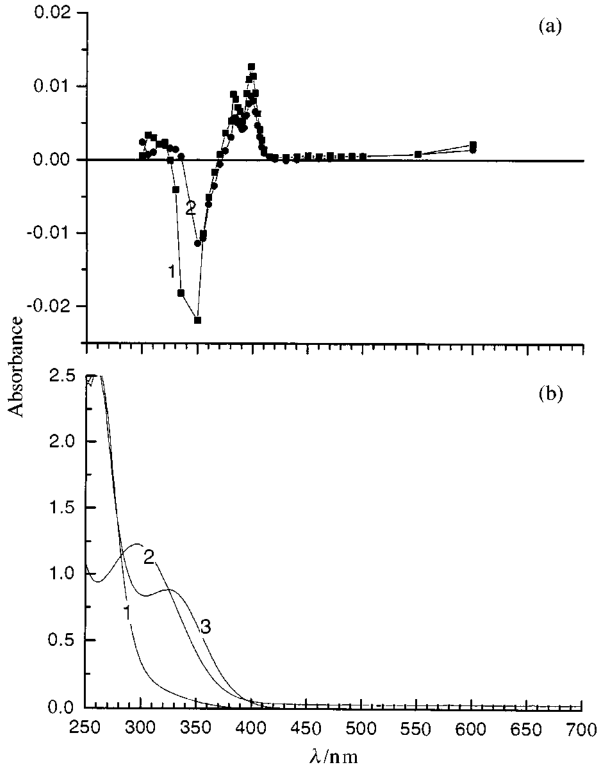

Fig. 3 (a) Transient absorption spectra of $Fe(ClO_4)_3$ solution at pH 0.6 in the presence of Cl^- anion ($[NaCl] = 1$ M) and $[PhOH] = 0.45$ M. ■ (Trace 1) time delay 60 ns; ● (trace 2) time delay 5 μs. (b) Absorption spectra of $Fe(ClO_4)_3$ solutions: trace 1, pH 0.60, $[NaCl] = 0$ M, $[PhOH] = 0.45$ M; trace 2, pH 2.66, $[NaCl] = 0$ M, $[PhOH] = 0$ M; and trace 3, pH 0.60, $[NaCl] = 1.0$ M, $[PhOH] = 0.45$ M.

Table 1 presents the calculated concentrations of iron(III) complexes in solution for the equilibria (1)–(6) taking into consideration the concentration of iron(III), pH, $[Cl^-]$ anion and [PhOH]. At relatively low pH, the hydrolysis shown in eqns. (1), (4), (5) and the phenolysis (2) shift to favor the formation of Fe^{3+} complexes. Due to this, in the presence of Cl^-, the concentration and absorption of the $FeCl^{2+}$ complex can be higher relative to $FeOH^{2+}$ and $FeOPh^{2+}$ complexes in acid media.

The data presented in Table 1 for the concentrations of iron(III) complexes indicate: (1) at pH 2.66 and in the absence of PhOH, the iron(III) exists in solution mainly as Fe^{3+} or $FeOH^{2+}$; (2) at pH 2.66 and $[PhOH] = 0.45$ M, the concentration of $FeOPh^{2+}$ is much higher than the concentration of $FeOH^{2+}$ complexes; (3) at pH 0.6 and in the presence of PhOH the composition of the iron(III) solution is determined by the concentration of Fe^{3+} and $FeCl^{2+}$ in solution. Absorbance of Fe^{3+} at $\lambda = 347$ nm in Figs. 1(b) and 3(b) is low, due to the low value of the molar absorption coefficient of the Fe^{3+} complex at <10 $\text{M}^{-1}\ \text{cm}^{-1}$.[9] Therefore, it can be concluded that the absorbance at $\lambda = 347$ nm of the iron(III) solution is due to: (1) $FeOH^{2+}$ at pH 2.66 in the absence of PhOH; (2) $FeOPh^{2+}$ and $FeOH^{2+}$ in the presence of [PhOH] 0.45 M at pH 2.66; and (3) the $FeCl^{2+}$ complex at pH 0.6. This is confirmed by the coincidence of the absorption peak in Fig. 1(b) (trace 1) at pH 2.66 in the absence of PhOH with the spectrum found in the literature for $FeOH^{2+}$ at $\lambda = 297$ nm.[8,11] Furthermore, the peak of trace 3 in Fig. 3(b), pH 0.6, $[Cl^-] = 1$ M with a maximum at $\lambda = 345$ nm[9] confirms that the spectrum reported previously by Byrne and Kester[9] at $\lambda = 345$ nm corresponds to $FeCl^{2+}$.

In the absence of PhOH at pH 2.66 the bleaching band in Fig. 1(a) should be ascribed to the photo-dissociation of $FeOH^{2+}$ [eqn. (7)],[12,13] because the $FeOH^{2+}$ complex acts as the

$$FeOH^{2+} \xrightarrow{h\nu = 347\ \text{nm}} Fe^{2+} + HO^{\bullet} \quad (7)$$

Table 1 Composition of iron(III) complexes ([iron(III)] = 1 mM) in aqueous solution at [PhOH] = 0.45 or 0.045 M in the presence or absence of Cl^- anions at pH 2.66 and 0.6

Conditions			Concentration of iron(III) complexes/M						
$[Cl^-]$/M	[PhOH]/M	pH	Fe^{3+}	$FeOH^{2+}$	$Fe(OH)_2^+$	$Fe_2(OH)_2^{2+}$	$FeOPh^{2+}$	$FeCl^{2+}$	$FeCl_2^+$
0	0.0	2.66	3.5×10^{-4}	6.0×10^{-4}	5.6×10^{-6}	2.1×10^{-6}	0.0×10^{-4}	0	0
0	0.45	2.66	1.4×10^{-4}	2.3×10^{-4}	2.2×10^{-6}	3.1×10^{-6}	6.2×10^{-4}	0	0
0	0.045	2.66	3.1×10^{-4}	5.2×10^{-4}	4.8×10^{-6}	1.6×10^{-5}	1.4×10^{-4}	0	0
1	0.45	2.66	6.5×10^{-5}	1.2×10^{-4}	1.1×10^{-6}	8.0×10^{-7}	3.1×10^{-4}	3.7×10^{-4}	1.3×10^{-4}
1	0.45	0.60	1.2×10^{-4}	1.8×10^{-6}	1.5×10^{-10}	1.9×10^{-10}	4.8×10^{-6}	6.5×10^{-4}	2.2×10^{-4}

chromophore in solution absorbing at $\lambda < 400$ nm. The maximum for the bleaching band in Fig. 1(a) coincides with the maximum of $FeOH^{2+}$ in Fig. 1(b). The bleaching is due to the build-up of non-absorbing Fe^{2+} species at $\lambda = 300$ nm at the expense of the $FeOH^{2+}$. The inset in Fig. 1(a) shows the transient at $\lambda = 300$ nm in the millisecond domain. The recovery of Fe^{2+} back to $FeOH^{2+}$ is seen to occur within a time interval longer than 2 ms, the maximum time domain available in the laser system.

Transient spectra observed in Fig. 2(b) suggest the photodissociation of the $FeOPh^{2+}$ complex, because: (a) $FeOPh^{2+}$ has a significant absorbance at $\lambda = 347$ nm and (b) during the laser pulse a bleaching growth band is observed with a maximum at $\lambda = 550$ nm. This corresponds to the absorption of the complex $FeOPh^{2+}$ in Fig. 2(a). The bleaching is due to the non-absorbing species Fe^{2+} and $PhO^{\bullet}$ in this region originating from $FeOPh^{2+}$ [eqn. (8)].

$$FeOPh^{2+} \xrightarrow{h\nu = 347\ \text{nm}} Fe^{2+} + PhO^{\bullet} \qquad (8)$$

Fig. 2(b) shows an absorption peak at $\lambda = 320$ nm. This absorption is attributed to the absorption of the dihydroxycyclohexadienyl radical[19] and coincides with the spectrum of the dihydroxycyclohexadienyl radical reported by pulse radiolysis.[19] Dihydroxycyclohexadienyl radical in this case can be formed due to the $OH^{\bullet}$ radical attachment to PhOH [eqn. (9)].

$$OH^{\bullet} + PhOH \rightarrow \rightarrow PhO^{\bullet} + H_2O \qquad (9)$$

The $OH^{\bullet}$ radicals necessary in eqn. (9) are formed in the reaction (7). As seen from Table 1 under these experimental conditions complexes $FeOPh^{2+}$ and $FeOH^{2+}$ coexist. The results presented in Fig. 3 suggest the photodissociation of $FeCl^{2+}$. Absorbance of $FeOPh^{2+}$ and $FeOH^{2+}$ complexes is small in acid media. The formation of $PhO^{\bullet}$ radicals is suggested in the sequence of reactions (10)–(13). These reactions

$$FeCl^{2+} \xrightarrow{\lambda = 347\ \text{nm}} Fe^{2+} + Cl^{\bullet} \qquad (10)$$

$$Cl^{\bullet} + PhOH \longrightarrow PhO^{\bullet} + H^+ + Cl^- \qquad (11)$$

$$Cl^{\bullet} + Cl^- \longrightarrow Cl_2^{\bullet -} \qquad (12)$$

$$Cl_2^{\bullet -} + PhOH \longrightarrow PhO^{\bullet} + 2Cl^- + H^+ \qquad (13)$$

(10)–(13) do not suggest the formation of dihydroxycyclohexadienyl radical. We observe a negligible weak peak at 320 nm in Fig. 3(a) but a strong peak at 320 nm is seen in Fig. 2(b). PhOH scavenges $Cl^{\bullet}$ and $Cl_2^{\bullet -}$ radicals. Therefore, no absorption of $Cl_2^{\bullet -}$ radical at $\lambda = 340$ nm is observed, but bleaching of $FeCl^{2+}$ at $\lambda = 345$ nm is readily seen. Comparison of Figs. 2 and 3 allows us to conclude that the amount of $PhO^{\bullet}$ produced in the system Fe^{III} + PhOH + Cl^- (pH 0.6) is about 3–4 times higher than in the system Fe^{III} + PhOH (pH 2.66) considering equal absorbance of the laser light at $\lambda = 347$ nm.

In conclusion, the formation of phenoxyl radicals has been observed during the photolysis of PhOH in aqueous solutions in the presence of iron(III). The route for phenoxyl radical formation has been shown to depend on the relative concentration of $FeOH^{2+}$, $FeOPh^{2+}$ and $FeCl^{2+}$ complexes generated in solution. The routes suggested for the formation of the phenoxyl radical are: (1) photolysis of $FeOH^{2+}$ complex with $OH^{\bullet}$ radical formation prior to the reaction of this radical with PhOH, (2) photolysis of $FeOPh^{2+}$ complex with formation of $PhO^{\bullet}$ radical and (3) photolysis of the $FeCl^{2+}$ complex and oxidation of PhOH by $Cl^{\bullet}$ and $Cl_2^{\bullet -}$ radicals.

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