Letter

Primary mechanism for the iron(III) photoinduced degradation of 4-chlorophenol in aqueous solution

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The photoinduced degradation of 4-chlorophenol by iron(III) has been investigated by continuous irradiation at 365 nm as well as by nanosecond laser flash photolysis at 355 nm. The process involves the most photoreactive species of iron(III), namely $Fe(OH)^{2+}$. Upon irradiation, an intramolecular redox process leads to the formation of hydroxyl radicals and iron(II). The continuous formation of $^{\bullet}OH$ radicals causes the complete mineralization of 4-chlorophenol. Laser flash photolysis experiments clearly showed that two different pathways are initially present in the degradation of 4-chlorophenol: formation of the $^{\bullet}OH$ adduct, 4-chlorodihydroxycyclohexadienyl radical, and of the chlorophenoxyl radical. The quantum yields of these processes have been determined to be 0.056 and 0.015, respectively.

Chlorophenols are widely distributed in soils and the aquatic environment, arising mostly from their use as biocides and preservatives. These compounds are highly toxic and most of them have been listed as toxic or priority pollutants by the United States Environmental Protection Agency.[1] Accordingly, research into ways and methods for the chemical detoxification of aqueous solutions of hazardous organic compounds appears to be of great interest. Photochemical processes have been shown to play an important role in the elimination of such pollutants from aquatic media. Since they weakly absorb solar emissions, only photoinduced transformations may represent an important role in their elimination from natural waters. Among these processes, hydroxyl radicals formed upon excitation of iron(III) alone[2] or in the presence of H_2O_2 [3] can provide an efficient method for the photoinduced degradation of pollutants.

The photoredox process taking place upon excitation of iron(III) in aqueous solution is well-known:[2,4–7]

$$Fe^{3+} \xrightarrow[H_2O]{h\nu} Fe^{2+} + HO^{\bullet} + H^{+}$$

The simultaneous reoxidation of iron(II) into iron(III) by oxygen as well as by appropriate products present in the solution confers an interesting catalytic aspect to the process.[8]

In a previous work, we reported the degradation of 2,6-dimethylphenol (DMP) photoinduced by iron(III).[2] The results clearly showed that two processes were involved. The first one consists of a reaction between DMP and $HO^{\bullet}$ radicals while the second one involves a charge transfer process between iron(III) excited species and DMP. As a continuation of our work, we have undertaken the study, by continuous irradiation and laser flash photolysis in aqueous solution, of the 4-chlorophenol transformation photoinduced by iron(III) species, in order to determine the nature of the primary transients generated during the process and the quantum yields of their formation. The results reported herein show that iron interferes in the process not only as a photoinductor but also as an oxidant and/or a reductant of the resulting intermediates. The complete mineralization of 4-chlorophenol photoinduced by iron(III) species, leading to carbon dioxide, chloride ions and water, has also been carried out at a high $Fe(OH)^{2+}$ percentage.

Unless otherwise noted the concentration used in this work was 1.0×10^{-4} mol L^{-1}. No significant absorption was observed at $\lambda > 320$ nm. The natural pH of the mixture varied between 2.6 and 3.4, depending on the iron(III) concentration.

As already described[4], $Fe(OH)^{2+}$ is the predominant monomeric iron(III) aqua-complex under our experimental conditions $\{[\text{iron(III)}]_0 > 1.0 \times 10^{-4}$ mol L^{-1} and $2.6 < pH < 3.4)$. Its concentration decreased after the dissolution of ferric perchlorate in water, leading to the formation of oligomeric species (the formation of dimeric species has never been observed under our experimental conditions).

It has been extensively demonstrated that $Fe(OH)^{2+}$ is the most active species in terms of $HO^{\bullet}$ radical formation when the excitation takes place at $\lambda > 300$ nm.[4,5] The experiments were performed with different percentages of $Fe(OH)^{2+}$ defined as $[Fe(OH)^{2+}] \times 10^2/[\text{iron(III)}]_{\text{total}}$.

The mixture of 4CP–iron(III) was thermally stable. There was neither perceptible precipitation nor redox reaction in the dark at room temperature. No evidence for ground state complexation was observed when the UV-vis spectrum of the mixture was compared to the individual spectra of the components.

When a mixture of iron(III)–4CP was irradiated at 365 nm, we observed the formation of iron(II) and the degradation of 4CP. The formation of iron(II) and the disappearance of 4CP were fast at the beginning of the irradiation, then they slowed down and the concentration of iron(II) reached an upper limiting value corresponding, within the experimental errors, to the starting value of the $Fe(OH)^{2+}$ concentration (Table 1).

Since the experimental results showed that the most photoreactive iron(III) species was $Fe(OH)^{2+}$, we calculated the quantum yield of 4CP disappearance by taking into account the fraction of light absorbed by $Fe(OH)^{2+}$ in the mixture iron(III)–4CP. This quantum yield, Φ^{m}_{4CP}, was determined by

Table 1 Comparison between the limiting value of the iron(II) concentration and the initial concentration of $Fe(OH)^{2+}$. $[\text{iron(III)}]_0 = 6.0 \times 10^{-4}$ mol L^{-1}, $[4CP]_0 = 1.0 \times 10^{-4}$ mol L^{-1}, $\lambda_{exc} = 365$ nm

Percentage of $Fe(OH)^{2+}$	$10^4 \times [Fe(OH)^{2+}]_0$/ mol L^{-1}	$10^4 \times [\text{iron(II)}]_{\text{limit value}}$/ mol L^{-1}
26	1.6	1.8
52	3.0	3.0
75	4.5	5.0
≈100	6.0	5.8

the following relation:

$$\Phi^{\mathrm{m}}_{4\mathrm{CP}} = \Phi \times \frac{\mathrm{O.D.}_{\cdot\mathrm{total}}}{\mathrm{O.D.}_{\cdot\mathrm{Fe(OH)}^{2+}}}$$

where Φ is the uncorrected value of the quatum yield, $\mathrm{O.D.}_{\cdot\mathrm{total}}$ is the absorbance of the mixture at 365 nm and $\mathrm{O.D.}_{\cdot\mathrm{Fe(OH)}^{2+}}$ is the absorbance of $\mathrm{Fe(OH)}^{2+}$ in the mixture calculated according to $\mathrm{O.D.}_{\cdot\mathrm{Fe(OH)}^{2+}} = \varepsilon_{\mathrm{Fe(OH)}^{2+}} \times [\mathrm{Fe(OH)}^{2+}] \times l$ with $\varepsilon_{\mathrm{Fe(OH)}^{2+}} = 270$ L mol^{-1} cm^{-1}.[4] The results are presented in Table 2.

Whereas $\Phi_{\mathrm{iron(II)}}$ increased when either the initial iron(III) concentration or the initial concentration of $\mathrm{Fe(OH)}^{2+}$ increased, $\Phi^{\mathrm{m}}_{4\mathrm{CP}}$ was roughly constant. This is in agreement with the fact that $\mathrm{Fe(OH)}^{2+}$ is the main species that induces the degradation of 4CP.

An apparent first-order reaction was observed for the disappearance of 4CP under the following conditions: $[\mathrm{iron(III)}]_0 = 6.0 \times 10^{-4}$ mol L^{-1}, ≈100 or 75% of $\mathrm{Fe(OH)}^{2+}$. The two apparent rate constants were 3.7×10^{-4} and 1.2×10^{-4} s^{-1}, respectively. This reflects a photostationary concentration of HO$^{\cdot}$ radicals, provided the percentage in $\mathrm{Fe(OH)}^{2+}$ is high enough. The inhibition of 4CP degradation was almost complete (>99%) when the mixture iron(III)–4CP (6.0×10^{-4}mol L^{-1}, 75% $\mathrm{Fe(OH)}^{2+} = 1.0 \times 10^{-4}$ mol L^{-1}) was irradiated at 365 nm in the presence of 2-propanol (0.20 mol L^{-1}), used as an HO$^{\cdot}$ radical scavenger. The degradation of 4CP was owing to the HO$^{\cdot}$ radicals: these species are the only oxidizing species generated upon excitation of $\mathrm{Fe(OH)}^{2+}$, as reported by Benkelberg and Warneck.[5]

As already mentioned, the concentration of iron(II) reached a plateau value that exactly corresponded to the initial concentration of $\mathrm{Fe(OH)}^{2+}$. The degradation of 4CP continued after the concentration of iron(II) had reached the plateau value. This phenomenon could be due to a reoxidation of iron(II) to iron(III) by different oxidizing species. The formation of chloride ions, detected by capillary electrophoresis analysis, could be explained by the reaction of Cl$^{\cdot}$ radicals arising from the HO$^{\cdot}$–4CP adduct (*cf.* below). The redox potential of the couples $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ and $\mathrm{Cl}^{\cdot}/\mathrm{Cl}^{-}$ being 0.77 V (NHE) and 2.5 V (NHE),[9] respectively, the following set of reactions may occur:

$$\mathrm{HO}^{\cdot}\text{–4CP} \rightarrow \text{hyroquinone} + \mathrm{Cl}^{\cdot}$$

$$\mathrm{Fe}^{2+} + \mathrm{Cl}^{\cdot} \rightarrow \mathrm{Fe}^{3+} + \mathrm{Cl}^{-}$$

In laser flash photolysis experiments, with excitation at 355 nm and analysis at $\lambda < 400$ nm of air-saturated solutions of iron(III), an important bleaching corresponding to the disappearance of iron(III) in the ground state was observed. No return to the original baseline was seen within 400 μs, reflecting the photoreduction of iron(III) into iron(II).

Laser excitation of an air-saturated mixture of iron(III) (1.0×10^{-3} mol L^{-1}) and 4CP (2.0×10^{-3} mol L^{-1}) gave the absorption spectra shown in Fig. 1. It is worth noting that on the time scale of the experiments the percentage of $\mathrm{Fe(OH)}^{2+}$ in the mixture was maintained roughly constant at 100%. The resolved absorption spectra recorded 1 and 18 μs after the laser pulse show that two distinct transients are initially formed: one absorbs at 350 nm while the other absorbs at 415 nm. After 18 μs, the intermediate absorbing at 350 nm had disappeared leaving the transient absorbing at 415 nm. The latter disappeared as well but on a much longer time scale (200 μs). By comparison with the studies carried out by pulse radiolysis,[10] the short-lived transient is associated with the HO$^{\cdot}$–4CP adduct, that is, the 4-chlorodihydroxycyclohexadienyl radical, and the long-lived one with the 4-chlorophenoxyl radical. Both absorption intensities corresponding to the generated intermediates were investigated *via* variation of the laser energy. In every case, they were linearly dependent on the energy *per* pulse leading to the conclusion that they were formed *via* monophotonic processes.

Table 2 Quantum yields of iron(II) formation and quantum yields of 4CP disappearance. $[\mathrm{iron(III)}]_0 = 6.0 \times 10^{-4}$ mol L^{-1}, $[\mathrm{4CP}]_0 = 1.0 \times 10^{-4}$ mol L^{-1}, $\lambda_{\mathrm{exc}} = 365$ nm

Percentage of $\mathrm{Fe(OH)}^{2+}$	$\Phi_{\mathrm{iron(II)}}$	$\Phi^{\mathrm{m}}_{4\mathrm{CP}}$
26	0.006	0.018
38	0.009	0.019
52	0.015	0.018
75	0.05	0.013
≈100	0.20	0.016

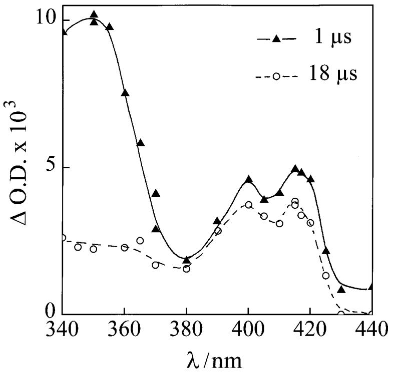


Fig. 1 Time-resolved spectra recorded after the 355 nm flash irradiation of an aqueous mixture of iron(III) [1.0 mM, ≈100% of $\mathrm{Fe(OH)}^{2+}$] and 4CP (2.0 mM).

The growths of the absorbances was followed at 350 and 415 nm [Fig. 2(a) and (b)]. They clearly showed that the two transients were initially formed (Scheme 1). Both growth curves showed a pseudo first-order dependence on 4CP concentration. A similar second-order rate constant of 1.0×10^{10} mol^{-1} L s^{-1} was found for both processes.

Since the transients did not disappear appreciably within 100 ns after the pulse, we were able to determine the effective quantum yields for the formation of the two intermediates by using $[\mathrm{Co(NH_3)_5Br}]^{2+}$ as an actinometer.[11] The absorbance at 350 nm was corrected for the bleaching and for the absorption of the 4-chlorophenoxyl radical. The quantum yield for $^{\cdot}$OH–4CP adduct formation was determined to be 0.056 and the one for formation of the 4-chlorophenoxyl radical to be 0.015. Assuming that reactions 1 and 2 are the only processes involved in $^{\cdot}$OH scavenging reactions, the overall quantum yield for $^{\cdot}$OH formation by excitation of iron(III) at 355 nm can then be estimated as 0.071. This result is in good agreement with the effective quantum yield of $^{\cdot}$OH radical formation upon excitation at 360 nm of $\mathrm{Fe(OH)}^{2+}$ obtained by Benkelberg and Warneck by using 2-propanol as a HO$^{\cdot}$ radical scavenger,[5] that is $\Phi = 0.075$. This confirms the involvement of $^{\cdot}$OH radicals only in the degradation process.

Both transients showed a second-order decay [Fig. 2(c) and (d)]. The rate constant for the disappearance of 4-chlorophenoxyl radical was calculated to be 1.2×10^{10} L mol^{-1} s^{-1}, in agreement with the values reported in the literature.[10] In the case of the adduct, $^{\cdot}$OH–4CP, the rate constant was evaluated to be 3.5×10^{10} L mol^{-1} s^{-1}, which is two orders of magnitude higher than the one reported by Getoff and Solar.[12] This may be owing to the presence in the medium of different oxidizing and reducing species. The reactions shown in Scheme 2 can be put forward as a conceivable explanation for the fast disappearance of $^{\cdot}$OH–4CP.

Because our starting motivation was related to the fate of phenolic derivatives in the environment, we tested the efficiency of the degradation of 4-chlorophenol photoinduced by

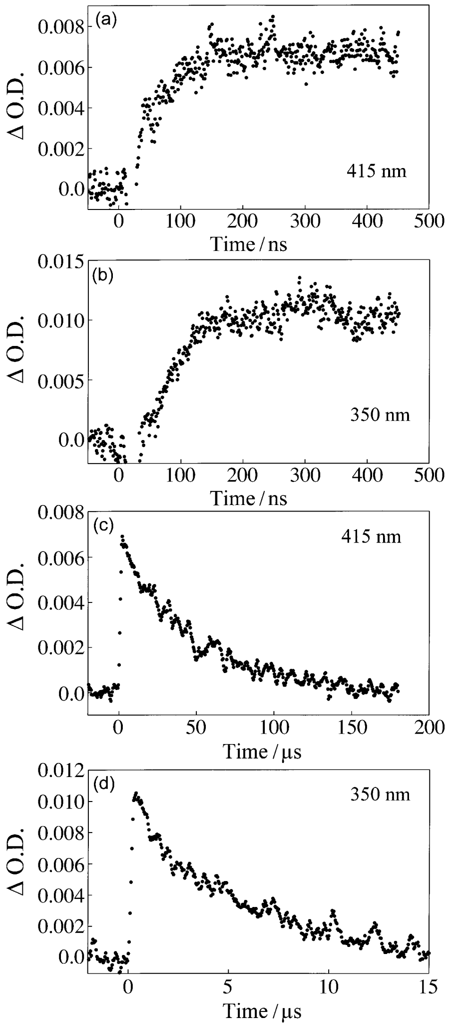
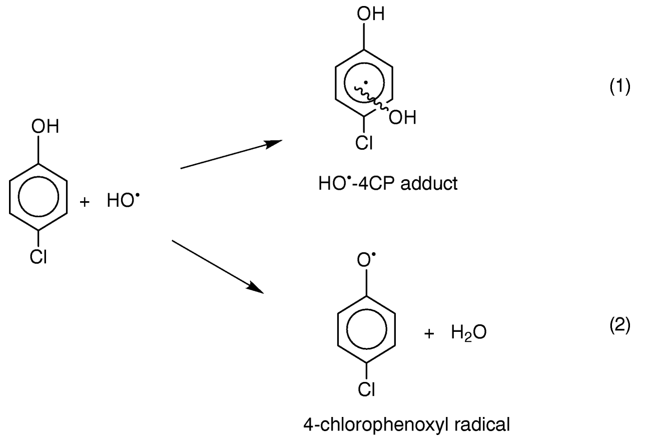
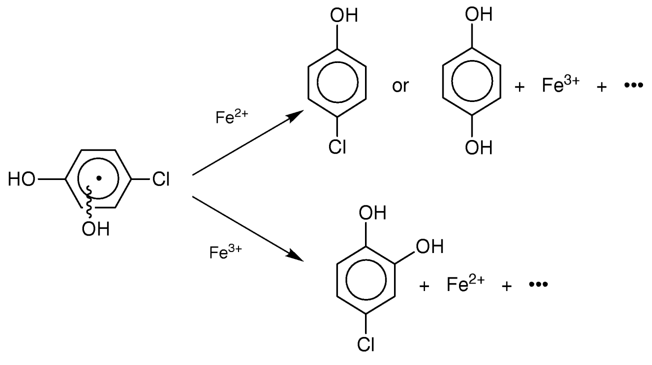


Fig. 2 Absorbance growth and decay traces after laser flash excitation at 355 nm of an iron(III)–4CP mixture. (*a*) and (*c*) 4-Chlorophenoxyl radical (415 nm); (*b*) and (*d*) 4-chlorodihydroxycyclohexadienyl radical (350 nm).



Scheme 1



Scheme 2

iron(III) species. This was obtained by following the CO_2 evolution during the irradiation of an iron(III)–4CP solution. The concentrations used for these experiments were $[\text{iron(III)}]_0 = 4.0 \times 10^4$ mol L^{-1} and $[4CP]_0 = 4.0 \times 10^{-4}$ mol L^{-1}. The reaction was carried out with a freshly prepared solution of iron(III) [80% of $Fe(OH)^{2+}$]. The formation of CO_2 started only after 15 h of irradiation and total mineralization into CO_2, Cl^- and H_2O could be obtained after 150 h.

In the case of prolonged irradiation, we can not rule out any participation of a photo-Fenton reaction.[13] With a solution containing $<5\%$ of $Fe(OH)^{2+}$ the degradation was slower and the evolution of CO_2 reached a limiting value corresponding to 50–55% of 4CP disappearance.

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