Unexpected 2,4,6-trimethylphenol oxidation in the presence of Fe(III) aquacomplexes

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Received (in Montpellier, France) 17th October 2005, Accepted 25th November 2005
First published as an Advance Article on the web 14th December 2005
DOI: 10.1039/b514691g

2,4,6-Trimethylphenol (TMP) was efficiently oxidised by Fe(III) aquacomplexes. HPLC analysis was used to follow the kinetics of the redox process. Two degradation products were detected and identified: 2,6-dimethyl-4-(hydroxymethyl)phenol (P1) and 3,5-dimethyl-4-hydroxybenzaldehyde (P2) accounting for 100% of TMP degradation in the early stages of the reaction. The formation of the products was concomitant with the reduction of Fe(III) into Fe(II). The direct relation between TMP oxidation and the concentration of the monomeric species $\{Fe(H_2O)_5(OH)\}^{2+}$ gives evidence for the initial reaction to take place between TMP and this particular species. Moreover, the correlation between P2 formation and P1 disappearance during the reaction implies the sequence of reactions: TMP → P1 → P2. A mechanism leading to the two degradation products is proposed.

Introduction

Probe molecules are often used to evaluate the photodegradation processes in aqueous systems. For this purpose, 2,4,6-trimethylphenol (TMP) was chosen to test the photoinductive properties of humic substances.[1,2] The extension of its use to other systems, especially systems used in heterogeneous photocatalysis, was then considered. Iron being very often proposed to modify the properties of photocatalysts, more particularly TiO_2, it was necessary to investigate TMP behaviour in the presence of iron.

In addition, industrial processes used to prepare 2,6-dimethylphenol (DMP), a starting compound for various syntheses, led to the formation of 2,4,6-trimethylphenol (TMP) as a major by-product of little practical use. Methods involving metal catalysts to transform TMP into DMP were investigated in which iron complexes were used to catalyse the reaction.[3,4]

Actually, Fe(III) aquacomplexes were proved to be able to promote oxidation of organic compounds in aqueous solution. Wong-Wah-Chung *et al.*[5] observed a very fast reaction between 4,4′-diaminostilbene-2,2′-disulfonic acid (DSD) and Fe(III). Two oxidation products corresponding to the oxidation of the stilbene double bound were identified: the DSD epoxide derivative and 5-amino-2-formylbenzenesulfonic acid. In the investigated system, the redox process essentially depends on the concentration of monomeric species $\{Fe(H_2O)_5(OH)\}^{2+}$ which appears to be the major oxidative agent in the reaction. Under the same conditions, Mazellier and Bolte[6] observed a redox process between 2,6-dimethylphenol (DMP) and Fe(III): the reaction requires an excess of $\{Fe(H_2O)_5(OH)\}^{2+}$. The major product is the 3,3′,5,5′-tetramethyldiphenoquinone together with DMP dimer and 2,6-dimethylbenzoquinone. From a mechanistic point of view, the schemes of degradation are completely different. DMP degradation involves the intermediate formation of the 2,6-dimethylphenoxyl radical detected by EPR spectroscopy. From this radical, the dimer can be formed, together with 3,3′,5,5′-tetramethyldiphenoquinone obtained by further oxidation of the dimer by Fe(III). 2,6-Dimethylbenzoquinone is also formed by subsequent oxidation of the radical. In the case of DSD, Wong-Wah-Chung *et al.*[5] proposed an intermediate radical with one Fe(III) linked to the ethylenic carbon of DSD through an oxygen atom. Then, from this radical, two pathways are possible: formation of the epoxide derivative or reaction with another Fe(III) leading to the 5-amino-2-formylbenzenesulfonic acid.

So work on TMP oxidation induced by Fe(III) aquacomplexes was undertaken and is reported in this paper.

Experimental

Reagents

2,4,6-Trimethylphenol was an Aldrich product (99%) used without further purification. Ferric perchlorate nonahydrate [$Fe(ClO_4)_3 \cdot 9H_2O$; purity 97%] was a Fluka product kept in a dessicator. 3,5-Dimethyl-4-hydroxybenzaldehyde was an Aldrich product (95%). The Fe(III) solutions were prepared by diluting a stock solution [2.0×10^{-3} mol L^{-1} $Fe(ClO_4)_3 \cdot 9H_2O$] to the appropriate Fe(III) concentration. All the solutions were prepared with ultrapure aerated water (Millipore αQ, resistivity = 18.2 MΩ cm). Deoxygenated solutions were obtained by bubbling with argon for 30 min at room temperature.

Apparatus

UV-visible spectra were recorded on a Cary 3 double beam spectrophotometer. HPLC were carried out using a Merck L6200 chromatograph equipped with a Hewlett Packard 1050

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detector and using a Waters chromatograph equipped with a Waters 996 photodiode array detector. The eluent was a mixture of methanol–water (60 : 40) acidified by H_3PO_4 (0.1%). The flow rate was 1 mL min^{-1} and the column was a ZORBAX Rx C8 (5 μm) of 25 cm length. Liquid chromatography-mass spectra analyses were obtained on a Thermo Ion Trap DECA XP Ion Max apparatus by using APCI negative mode. NMR spectra were recorded with a Bruker Advance 400 MHz, using solutions in deuterated water. Electron paramagnetic resonance (EPR) spectra were obtained using a Brucker ER-200D spectrometer at 9.30 GHz with a modulation field of 100 KHz. An Xe–Hg Hanovia Lamp was used for irradiation in the EPR spectrometer cavity (λ > 345 nm).

Analysis

Fe(II) concentration was determined by complexometry with 2,2′-bipyridine at 520 nm [ε (L mol^{-1} cm^{-1}) 8600].[7] The monomeric concentration of Fe(III) species was determined by using the modified[8] Kuenzi procedure with 8-hydroxyquinoline-5-sulfonic acid (HQSA).[9]

The kinetics of TMP disappearance and of the formation of oxidation products were determined by HPLC experiments ($\lambda_{detection}$ = 278 nm).

Results

Characterisation of the Fe(III)–TMP mixture

TMP is soluble in water (1.01 × 10^3 mg L^{-1})[10] and its UV-visible spectrum presents an absorption band at λ_{max} (H_2O) (nm) 278 [ε (L mol^{-1} cm^{-1}) 1250].

The UV-visible spectrum of Fe(III) in aqueous solution continuously evolved. Under our starting experimental conditions of concentration ([Fe(III)] between 5 × 10^{-5} and 1.0 × 10^{-3} mol L^{-1} and pH (4.2 > pH > 3.0) according to Fe(III) concentration), the species present just after dissolving $Fe(ClO_4)_3 \cdot 9H_2O$ was the monomeric form $\{Fe(H_2O)_5(OH)\}^{2+}$, simply noted as $Fe(OH)^{2+}$. The concentration of monomeric species rapidly decreased after the dissolution of ferric perchlorate in water. As a result it is almost impossible at such low concentrations (5 × 10^{-5} to 3 × 10^{-4} mol L^{-1}) to get 100% of $Fe(OH)^{2+}$. The disappearance was attributed to the possible formation of soluble aggregates.[11] Using the 8-hydroxyquinoline-5-sulfonic acid (HQSA) method, we were able to measure the percentage of monomeric species in the starting Fe(III) solution:

$$\%\ Fe(OH)^{2+} = 100 \times \{[Fe(OH)^{2+}]/[Fe(III)_{tot}]\}$$

where $Fe(III)_{tot}$ is the concentration of Fe(III) added in the solution. The different percentages of monomeric species were obtained by the use of Fe(III) stock solutions with different ageing.

Two maxima at 280 nm and 298 nm, corresponding, respectively, to TMP and $Fe(OH)^{2+}$, were observed in the UV-visible spectrum of a freshly prepared mixture of TMP (1.0 × 10^{-4} mol L^{-1}) and $Fe(OH)^{2+}$ (3.0 × 10^{-4} mol L^{-1}). There was no detectable complexation between $Fe(OH)^{2+}$ and TMP in our experimental conditions. At t = 0, the UV-visible spectrum of the mixture was roughly the sum of the two spectra of the components (Fig. 1). The difference between the sum and the spectrum of the mixture was assigned to the very fast reaction between Fe(III) and TMP (*cf.* Fig. 2). The spectral evolution of the mixture was monitored as a function of time. A typical evolution is represented in Fig. 2. HPLC analysis gave evidence for TMP disappearance and the formation of two products, together with Fe(II) formation detected by complexometry.

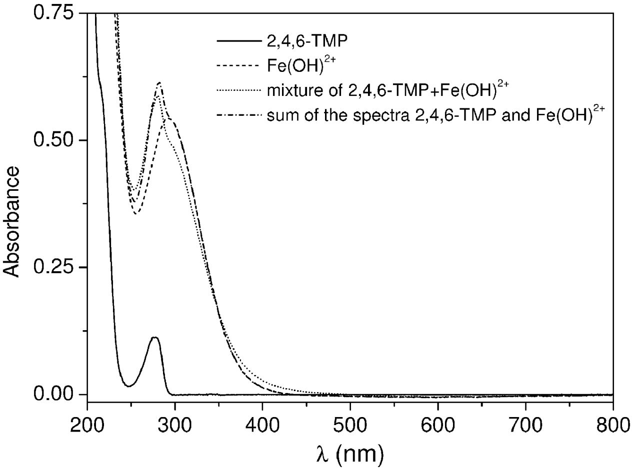


Fig. 1 UV-visible spectra of TMP (1.0 × 10^{-4} mol L^{-1}), $Fe(OH)^{2+}$ (3.0 × 10^{-4} mol L^{-1}), the mixture TMP–$Fe(OH)^{2+}$ and the sum of the spectrum of TMP and the spectrum of $Fe(OH)^{2+}$.

TMP degradation

The observed "thermal" (in the dark and at room temperature) degradation of TMP was directly related to the presence of Fe(III) since TMP alone was stable in aqueous solution. In order to estimate the influence of Fe(III) and of its speciation on the process, two sets of experiments were carried out. Firstly the concentration of Fe(III) was varied and taken as 0.5 × 10^{-4}, 1.0 × 10^{-4}, 1.5 × 10^{-4}, 2.0 × 10^{-4}, 2.5 × 10^{-4} and 3.0 × 10^{-4} mol L^{-1}; in all cases the percentage of $Fe(OH)^{2+}$

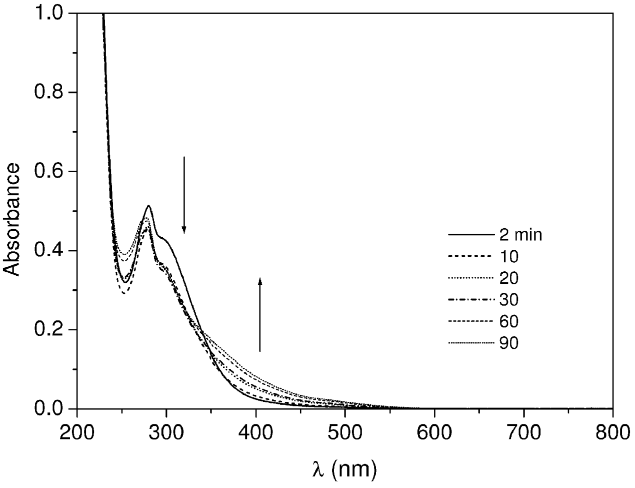


Fig. 2 UV-visible spectra of the mixture TMP (1.0 × 10^{-4} mol L^{-1})–$Fe(OH)^{2+}$ (3.0 × 10^{-4} mol L^{-1}) as a function of time.

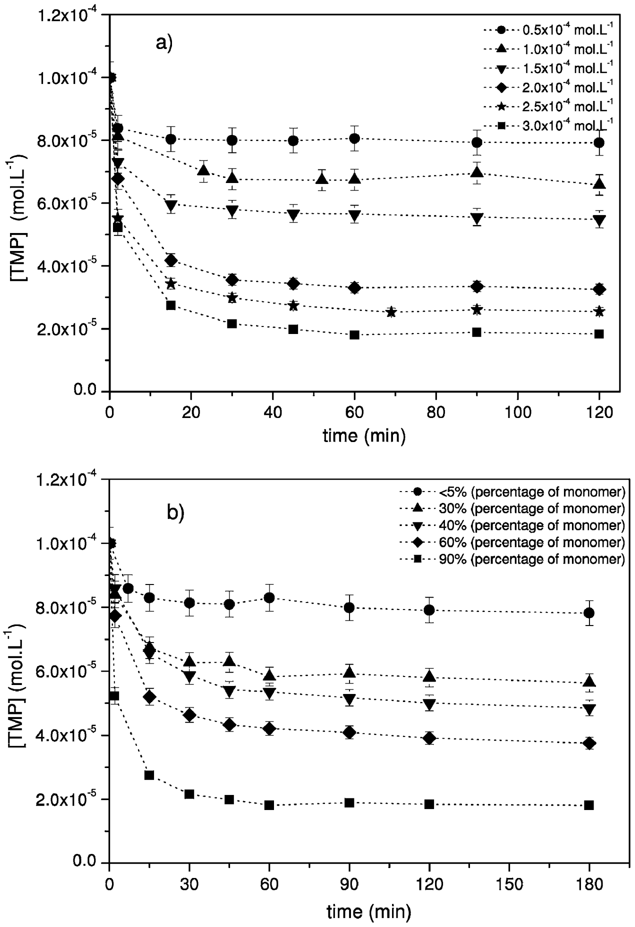


Fig. 3 TMP disappearance as a function of time under different conditions, $[TMP]_0 = 1.0 \times 10^{-4}$ mol L^{-1}. (a) ● [Fe(III)] = 0.5×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). ▲ [Fe(III)] = 1.0×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). ▼ [Fe(III)] = 1.5×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). ◆ [Fe(III)] = 2.0×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). ★ [Fe(III)] = 2.5×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). ■ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). (b) ● [Fe(III)] = 3.0×10^{-4} mol L^{-1} (<5% of $Fe(OH)^{2+}$). ▲ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (30% of $Fe(OH)^{2+}$). ▼ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (40% of $Fe(OH)^{2+}$). ◆ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (60% of $Fe(OH)^{2+}$). ■ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$).

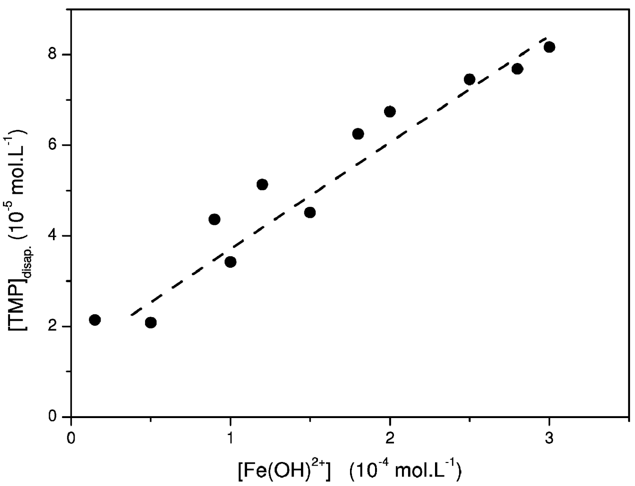


Fig. 4 Degraded TMP as a function of initial $Fe(OH)^{2+}$ concentration.

species was equal to 90 ± 5% and the initial concentration of TMP was equal to 1.0×10^{-4} mol L^{-1}. Secondly, to confirm the involvement of $Fe(OH)^{2+}$ in the reaction, the effect of the percentage of $Fe(OH)^{2+}$ species was investigated at constant Fe(III) total concentration (3.0×10^{-4} mol L^{-1}) and with the same initial concentration of TMP (1.0×10^{-4} mol L^{-1}). The starting percentage values were determined using the HQSA method; the results are presented in Fig. 3a and 3b, respectively. The disappearance of TMP was fast at the beginning, slowed down and reached a pseudo plateau-value. The concentration of TMP at the pseudo plateau depends on both the concentration of Fe(III) and the $Fe(OH)^{2+}$ percentage. It clearly appeared that the higher the $Fe(OH)^{2+}$ percentage or $Fe(III)_{tot}$ concentration, the higher the abatement in TMP was. In addition, there was a roughly linear relationship between initial $[Fe(OH)^{2+}]$ and degraded [TMP] (Fig. 4). The order of the reaction with respect to $Fe(OH)^{2+}$ was then determined. The initial rate can be expressed as followed:

$$V_0 = k([Fe(OH)^{2+}]_0)^{\alpha} \times [TMP]_0 \qquad (1)$$

where V_0 is the initial rate, k is the rate constant, $[Fe(OH)^{2+}]_0$ and $[TMP]_0$ are the initial concentrations of both products, $[TMP]_0$ being kept constant. The value of α was evaluated to 0.73 by plotting $\ln(V_0)$ as a function of $\ln[Fe(OH)^{2+}]_0$.

Fe(II) formation

The formation of Fe(II) was followed by complexometry, giving evidence for the involvement of Fe(III) in a redox reaction with TMP at room temperature in the dark (Fig. 5). The plateau value of the Fe(II) concentration increased with increasing the $Fe(OH)^{2+}$ percentage. Moreover, the ratio $[Fe^{2+}]_{form.}/[TMP]_{disap.}$ was calculated all along the process at two percentages of $Fe(OH)^{2+}$ species, 40 and 90%. It reached a common value of around 2 for the two percentages.

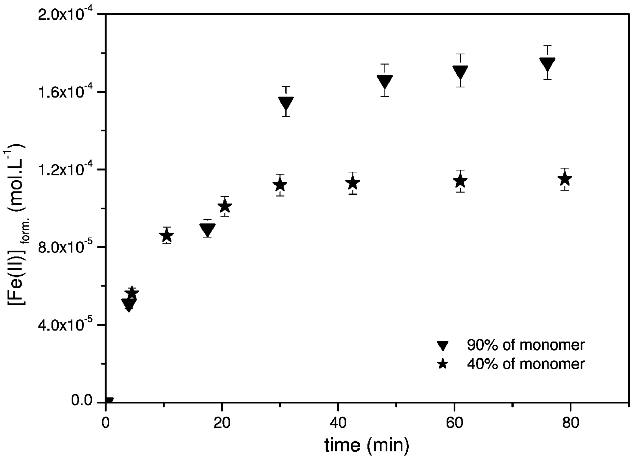


Fig. 5 Fe(II) formation during the reaction under different conditions, $[TMP]_0 = 1.0 \times 10^{-4}$ mol L^{-1}. ▼ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (90% of $Fe(OH)^{2+}$). ★ [Fe(III)] = 3.0×10^{-4} mol L^{-1} (40% of $Fe(OH)^{2+}$).

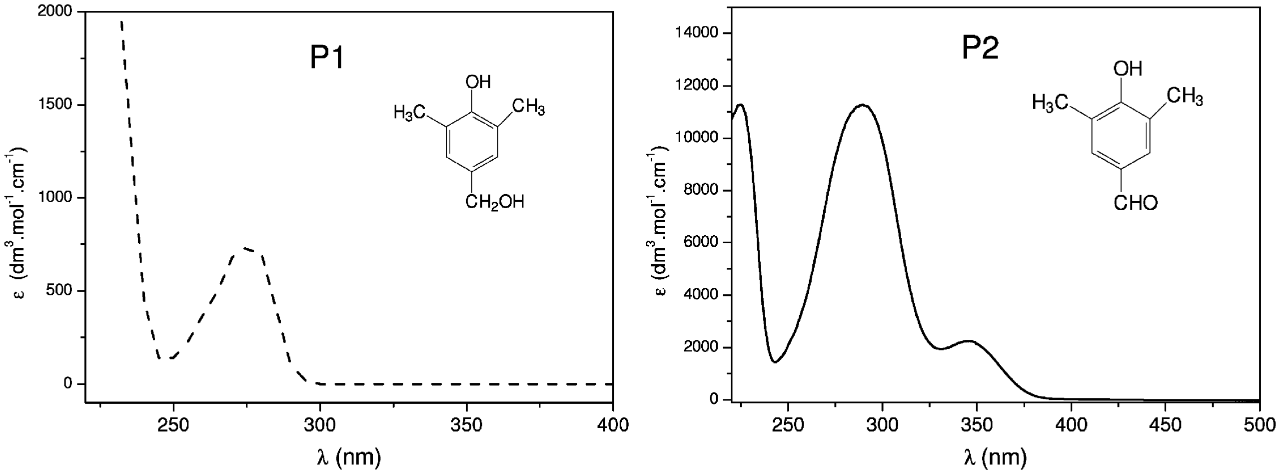


Fig. 6 Chemical structures and UV-visible spectra of P1 and P2.

Transformation products

The formation of two products P1 and P2 was detected by HPLC when mixing Fe(III) with TMP. Both were more polar than TMP; the retention time was 3.7, 5.8 and 8.6 min for P1, P2 and TMP, respectively. The peaks were observed whatever the percentage of monomeric species and the Fe(III) concentration ($0.5 \times 10^{-4} \le$ [Fe(III)] $\le 3.0 \times 10^{-4}$ mol L^{-1}). Product 1 was identified by classical analytical techniques: ^{1}H NMR spectroscopy and mass spectrometry. The results of ^{1}H NMR in D_2O are gathered below:

δ_H(400 MHz; D_2O; Me_4Si): 2.32 (6H, s, Me), 4.58 (2H, s, CH_2), 7.13 (2H, s, Ph).

The analysis by LC-MS gave two major peaks at *m*/*z*: 151.2 (M$^-$, 100%) and 149.2 (20%). From these results, product 1 (P1) was assigned as 2,6-dimethyl-4-(hydroxymethyl)phenol. Product 2 (P2) was identified as 3,5-dimethyl-4-hydroxybenzaldehyde by comparison with a commercially available authentic sample. The chemical structures and the UV spectra of these products are given in Fig. 6. In the mixtures, P2 concentration was determined by a calibration procedure. Taking into account that only two products were detected by HPLC, the quantitative conversion of TMP to P1 and P2 was admitted. With this hypothesis, P1 concentration was calculated by subtracting P2 formation from TMP disappearance:

$$[\mathrm{P1}]_{\mathrm{formed}} = [\mathrm{TMP}]_{\mathrm{disap.}} - [\mathrm{P2}]_{\mathrm{formed}}$$

The ratio [P2]/([P1] + [P2]) for different concentrations of monomeric species was determined at constant concentration in TMP (1.0×10^{-4} mol L^{-1}). As shown in Fig. 7, the ratio [P2]/([P1] + [P2]) appears to be favoured when the concentration of monomeric species increases. In order to confirm this tendency, TMP disappearance and P1 and P2 formation were investigated in a mixture of TMP (1.0×10^{-4} mol L^{-1}) and freshly prepared Fe(III) (90% of Fe(OH)$^{2+}$) at a higher concentration $c = 1.0 \times 10^{-3}$ mol L^{-1}. With the increase of the reaction time, P1 concentration decreased whereas P2 continuously accumulated in the solution, implying that P2 results from the oxidation of P1 by Fe(III). This hypothesis was corroborated by plotting P2 concentration as a function of P1 concentration (Fig. 8). A linear correlation was found

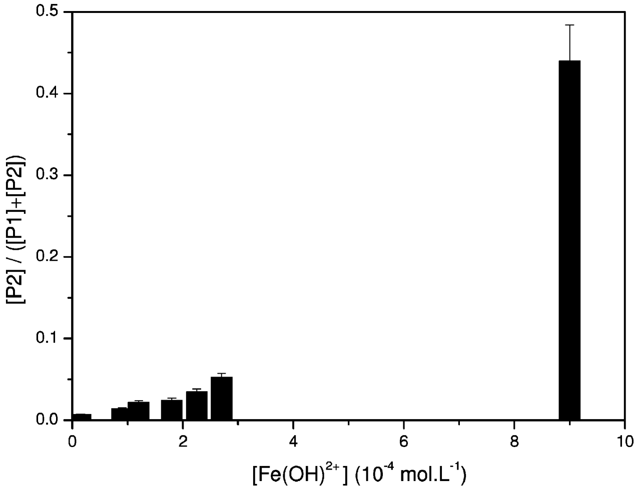


Fig. 7 Influence of Fe(OH)$^{2+}$ concentration on the ratio [P2]/([P1] + [P2].

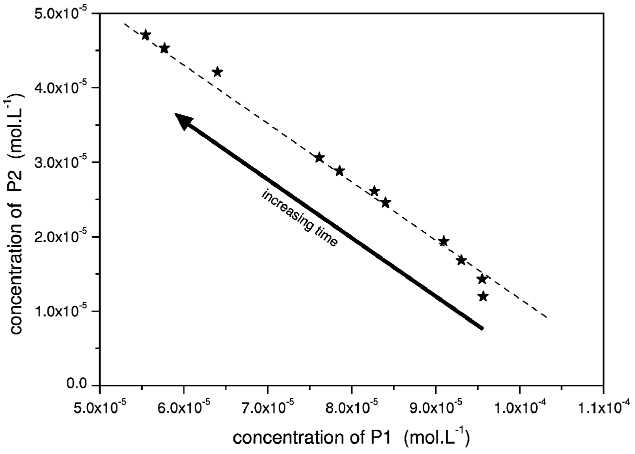


Fig. 8 Plot of P2 concentration as a function of P1 concentration.

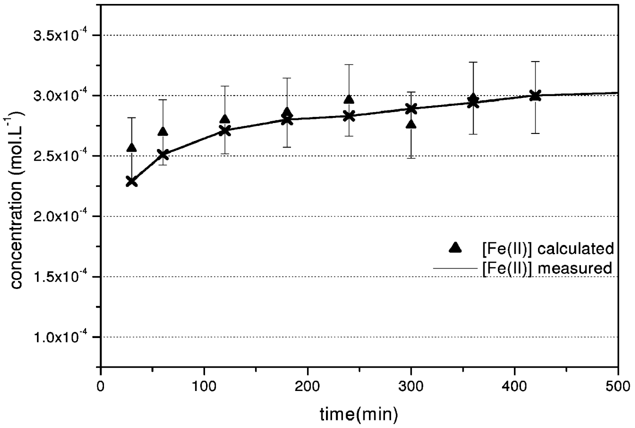


Fig. 9 Evolution of Fe(II) concentration formed as a function of the reaction time, $[TMP]_0 = 1.0 \times 10^{-4}$ mol L^{-1}, $[Fe(III)]_0 = 1.0 \times 10^{-3}$ mol L^{-1} (90% of $Fe(OH)^{2+}$). ▲ [Fe(II)] calculated. × [Fe(II)] measured.

between the two concentrations, supporting the following sequence of reaction:

TMP → P1 (alcohol derivative) → P2 (aldehyde derivative)

The ratio $[Fe^{2+}]_{form}/([P1]_{form.} + [P2]_{form.})$ was calculated throughout the reaction for the concentration of Fe(III) equal to 1.0×10^{-3} mol L^{-1}. At the beginning of the reaction, corresponding to the higher concentration of P1, the ratio took a value of around 2 (see Fe(II) formation). In addition, throughout the reaction, Fe(II) concentration, calculated on the basis of two Fe(II) formed for one molecule of P1 detected and two additional Fe(II) to transform P1 into P2, fits the measured Fe(II) concentration very well (Fig. 9).

Effects of oxygen and isopropanol

The effect of oxygen was investigated on a mixture of freshly prepared Fe(III) (3.0×10^{-4} mol^{-1} L) and TMP (1.0×10^{-4} mol^{-1} L). TMP degradation was not affected by the absence of oxygen. Isopropanol used as a hydroxyl radical scavenger was also added: no effect was observed on the reaction indicating that hydroxyl radicals were not involved in TMP transformation.

EPR spectroscopy

Because the phenoxyl radical was established as the first intermediate in the oxidation of 2,6-dimethylphenol in presence of Fe(III) aquacomplexes,[6] spin-trapping experiments in EPR spectroscopy were undertaken. 5,5′-Dimethylpyrroline-*N*-oxide (DMPO, 1 g L^{-1}) was added to the aqueous solution of Fe(III) (3.0×10^{-3} mol L^{-1} with 90% of monomeric species) and TMP (1.0×10^{-3} mol L^{-1}). A 1 : 2 : 2 : 1 quartet (with coupling constant a = 15.0 Gauss) was observed (Fig. 10). The existence of a quartet instead of the triplet of doublets usually observed with DMPO is due to the identical value of the coupling constants of the electron with nitrogen a_N and with hydrogen a_H. In the presence of 1% of isopropanol the signal detected by EPR spectroscopy was unchanged, in agreement with the involvement of the phenoxyl radical.

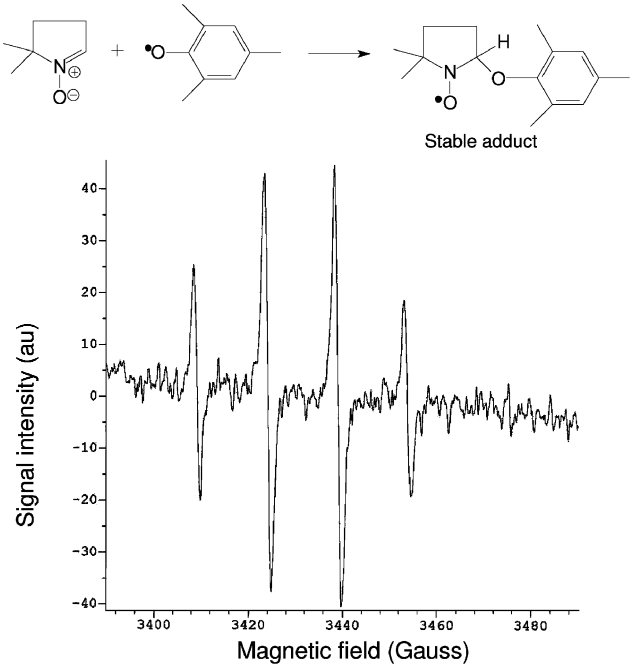
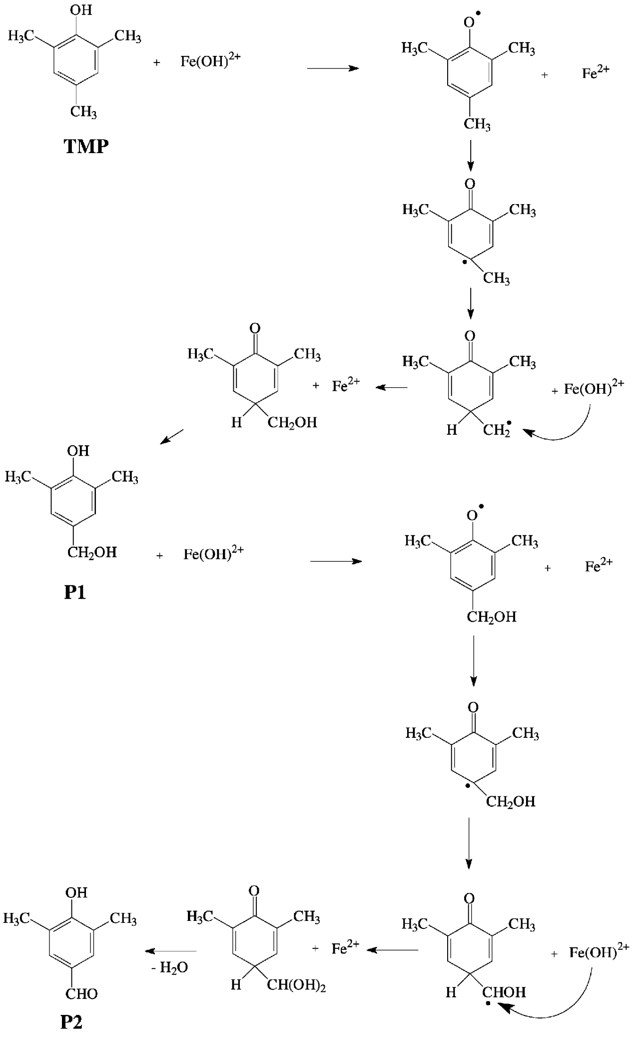


Fig. 10 Spin trapping experiments with DMPO (1 g L^{-1}) by EPR spectroscopy on irradiation ($\lambda > 345$ nm): $[TMP]_0 = 1.0 \times 10^{-3}$ mol L^{-1} , $[Fe(III)]_0 = 3.0 \times 10^{-3}$ mol L^{-1} (90% of $Fe(OH)^{2+}$).

Discussion

Reaction of TMP in the presence of Fe(III) was studied in aqueous solution. Formation of two main products was observed. The first one was identified as 2,6-dimethyl-4-(hydroxymethyl)phenol and the second one as 3,5-dimethyl-4-hydroxybenzaldehyde.

Such products were also mentioned in the study of Li and Liu[4] in the case of experiments performed with TMP in the presence of iron salts in alcoholic solvent. If the products were well described, the mechanism was unclear and did not fit our observations very well. The authors proposed the radical cation formed *via* electron transfer from 2,4,6-TMP to Fe(III) as the first intermediate of the reaction. Loss of a proton gives rise to the benzyl radical which reacts with oxygen to form a peroxy species. This last species is reduced in the presence of the Fe(II) formed in the first step of the reaction. In this process, the Fe(III) species are totally regenerated. Our observations, showing the accumulation of Fe(II) and the lack of oxygen effect, did not agree with such a mechanism. In our case, and according to the set of results provided by the EPR experiments, the redox reaction between TMP and Fe(III) involves the phenoxyl radical in a primary step. As demonstrated by the linear correlation between the concentration of $Fe(OH)^{2+}$ species and the degraded [TMP] (Fig. 4), $Fe(OH)^{2+}$ appears to be the most active species in terms of oxidative properties. The formation of two Fe(II) for one degraded TMP argues for the P1 formation resulting from a two electron



Scheme 1

oxidation. The nature of the product requires the addition of an oxygen atom. Because of the lack of a molecular oxygen effect on the rate of TMP disappearance, the redox process has to be associated with a concerted mechanism of addition of an hydroxide ion leading to P1. Taking into account that two Fe(III) were once again necessary to form P2, the formation of the aldehyde should be explained by a similar sequence of reactions. The final step corresponds to a dehydration of the resulting diol leading to the aldehyde. The overall mechanism is presented in Scheme 1.

Conclusion

Fast oxidation of 2,4,6-trimethylphenol is observed in the presence of Fe(III) aquacomplexes. The efficient redox process leads to the formation of two products: 2,6-dimethyl-4-(hydroxymethyl)phenol (P1) followed by 3,5-dimethyl-4-hydroxybenzaldehyde (P2), together with the formation of Fe(II). This process essentially depends on the concentration of monomeric species $Fe(OH)^{2+}$, which appears to be the major oxidative agent in the reaction. The correlation between the decrease of P1 and the increase of P2 concentrations indicates that P1 is primarily formed and then by a further oxidation process gives rise to P2. An oxidation mechanism involving a two electron transfer from TMP to $Fe(OH)^{2+}$ and then from P1 to $Fe(OH)^{2+}$ was proposed. This redox reaction between TMP and Fe(III) aquacomplexes raises the question of TMP use as a probe molecule when iron is present in the tested systems. Our results prove that iron traces could produce an oxidative transformation of TMP and alter the final conclusion.

Acknowledgements

We wish to thank Dr Patrick Mazellier (Université de Poitiers) for his help in performing LC-MS experiments and Anne-Sophie Martin (Université Blaise Pascal, SEESIB Laboratory) for the NMR spectra.

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