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# Photochemical behaviour of 2,6-dimethylbenzoquinone in the absence and in the presence of iron(III)

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**Abstract**

The photochemical behaviour of 2,6-dimethylbenzoquinone (DMBQ) in aqueous solution was investigated in the absence and in the presence of iron(III). Upon excitation at 365 nm, the photodegradation of DMBQ leads to the formation of 2,6-dimethylhydroquinone (DMHQ) and of 3-hydroxy-2,6-dimethylbenzoquinone (OHDMBQ) with a quantum yield of 0.47. When irradiated in the presence of iron(III), even in a large excess, the major route of DMBQ degradation remains the direct photolysis but subsequent thermal oxidation of DMHQ by iron(III) occurs which gives back the starting DMBQ. In this case, OHDMBQ appears to be the only photoproduct. However, traces of a second photoproduct are detected. Its formation results from the attack of OHDMBQ by $^{\bullet}$OH radicals arising from $Fe(OH)^{2+*}$.

*Keywords:* Photochemical behaviour; 2,6-Dimethylbenzoquinone; Iron(III); Photodegradation

## 1. Introduction

Our interest in the degradation of organic pollutants photosensitized by iron(III) in aqueous solution led us to investigate the photochemical behaviour of iron(III)–phenol derivative systems in dilute solution. A study was undertaken on 2,6-dimethylphenol (DMP) chosen as a model molecule, the substitution of hydrogen atoms by methyl groups in the two *ortho* positions being expected to make the overall mechanism simpler; the only available possibility of the mesomeric form of the phenoxyl radical was the *para* position. From the experimental results related to the photochemical behaviour of the DMP–iron(III) system, it appeared that 2,6-dimethylbenzoquinone (DMBQ) was the real primary photoproduct upon irradiation at 365 nm but its phototransformation into 3-hydroxy-2,6-dimethylbenzoquinone (OHDMBQ) was too fast to make DMBQ observable upon continuous excitation. It was only detectable by flash photolysis–high performance liquid chromatography (HPLC) experiments [1]. The question arises of what the process of DMBQ photodegradation was in the presence of iron(III); was it a direct photolysis with a very high quantum yield to compensate the very low absorption of DMBQ at 365 nm or a degradation pl[illegible]sitized by iron(III)? Both were possible; iron(III) in a [illegible]ous dilute solution absorbs up to 400 nm and we can expect a very high quantum yield of DMBQ degradation by analogy with benzoquinone (BQ) photoreactivity ($\phi = 0.5$ [2]).

So we decided to investigate the photochemical behaviour of DMBQ in the presence and in the absence of iron(III) upon irradiation at 365 nm, that wavelength being representative of solar emission.

## 2. Experimental details

### 2.1. Materials

$Fe(ClO_4)_3 \cdot 9H_2O$ was purchased from Fluka and used without further purification. DMBQ was purchased from Aldrich. When necessary, the pH was adjusted with $HClO_4$ (Merck) and measured with an ORION pH meter to ±0.01 pH units. The ionic strength was not controlled. Deaerated solutions were obtained by bubbling with argon for 40 min at room temperature. 2,6-Dimethylhydroquinone (DMHQ) was prepared as described by Balogh et al. [3].

### 2.2. Apparatus

A high pressure Hg lamp with a Bausch and Lomb monochromator was used for irradiations at 365 nm. The beam was parallel and the reactor was a square quartz cuvette with a 1

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cm path length. The incident light intensity measured by ferrioxalate actinometry was about $1.6 \times 10^{15}$ photons $s^{-1}$ $cm^{-2}$. UV–visible spectra were recorded on a Cary 3 double-beam spectrophotometer. HPLC experiments were carried out using a Beckman 420 chromatograph equipped with a Beckman 163 UV detector. The eluent was a 60:40 methanol:water mixture acidified by $H_3PO_4$ (0.1%). The flow rate was 1 ml $min^{-1}$ and the column was a Merck Lichrospher 100 RP18 (5 μm) of 25 cm length.

### 2.3. Analysis

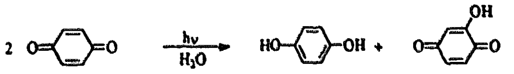
The iron(II) concentration was determined by complexometry with *ortho*-phenanthroline. DMBQ degradation and photoproducts formation were measured by HPLC using UV detection at 270 nm.

## 3. Results

A dilute aqueous solution of DMBQ ($1.9 \times 10^{-5}$ M at pH 5.50 or pH 2.90) reacted slowly in the dark to give a very small amount of DMHQ. When iron(III) was added at a concentration of $5.0 \times 10^{-4}$ M, no dark reaction was observed.

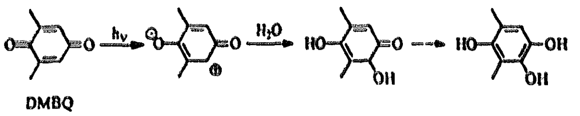
### 3.1. Direct photolysis of 2,6-dimethylbenzoquinone in aqueous solution

The spectral evolution of a $1.9 \times 10^{-5}$ M solution of DMBQ (pH 5.50) irradiated at $\lambda_{exc}$ = 365 nm is presented in Fig. 1; two isosbestic points are observed at 232 nm and 271 nm. The quantum yield of DMBQ disappearance measured by HPLC is equal to 0.47. Two photoproducts were detected. Photoproduct A was identified as DMHQ by comparison with an authentic sample prepared at the laboratory by reduction of DMBQ with $Na_2S_2O_4$ as described by Balogh et al. [3]. Photoproduct B was assumed to be OHDMBQ by analogy with the photolysis of benzoquinone where hydroquinone and 3-hydroxybenzoquinone were formed [2,4] according to the reaction

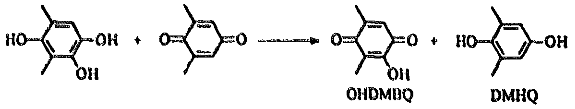


(1)

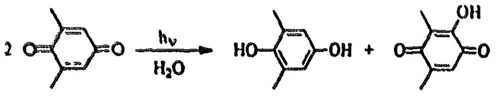
So we can put forward a similar mechanism for DMBQ direct photolysis:



Then 1,3,4-trihydroxy-2,6-dimethylbenzene reacts with a second molecule of DMBQ:



The overall reaction becomes



(2)

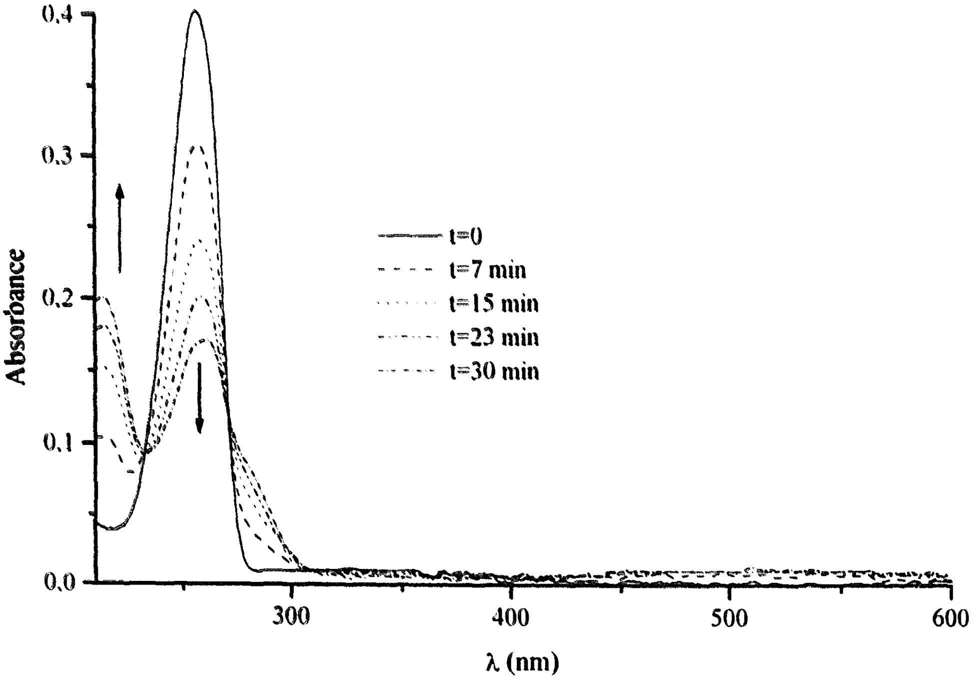


Fig. 1. Spectral evolution of a DMBQ solution ($c = 1.9 \times 10^{-5}$ M; pH 5.50) upon irradiation at 365 nm.

The quantum yield of DMHQ formation was measured; it is equal to 0.22. The quantum yield of OHDMBQ formation was estimated by HPLC measurements from the values of $\epsilon_{max}$ and $\lambda_{max}$ given in the literature [2,5]: $\lambda_{max} = 265$ nm and $\epsilon_{max} = 13\,600 \pm 10\%$ (pH $< 3.5$) and by using DMBQ as an internal standard.

The quantum yield for OHDMBQ formation appears to be equal to 0.27. The difference between these two values of quantum yield can be assigned to some uncertainty in the calculation for OHDMBQ.

Similar experiments performed at pH 2.90, the natural pH of a solution containing $5.0 \times 10^{-4}$ of iron(III), led to identical results. There is no significant effect of the pH on the direct photodegradation of DMBQ (in the pH domain 2.90–6.00).

### *3.2. Phototransformation of 2,6-dimethylbenzoquinone in the presence of iron(III)*

The irradiated mixtures contained a large excess of iron(III) to be representative of what happened with DMP with which it was impossible to detect DMBQ [1]: [iron(III)] $= 5.0 \times 10^{-4}$ M; [DMBQ] $= 1.9 \times 10^{-5}$ M; pH 2.92, the natural pH of the mixture (Fig. 2).

When mixed with such a large excess of iron(III), DMBQ did not undergo any transformation in the dark; no complexation was observed in the ground state. In fact, the UV–visible spectrum of the mixture was the sum of the UV–visible spectra of the components.

The number of photons absorbed by each component upon irradiation at 365 nm was calculated and under these conditions; only 1% ($I_a/I_0 = 0.009$) of the light was absorbed by DMBQ.

Table 1
$\lambda_{max}$ and $\phi$ for $Fe(OH)^{2+}$ and $Fe_2(OH)_2^{4+}$

| | References | $\lambda_{max}$ (nm) | $\phi$ |
|---|---|---|---|
| $Fe(OH)^{2+}$ | [6] | 297 | 0.017 at $\lambda_{exc} = 360$ nm |
| $Fe_2(OH)_2^{4+}$ | [6,7] | 335 | 0.007 at $\lambda_{exc} = 350$ nm |

Iron(III), the main absorbing species, was present under our experimental conditions (pH, concentration) as a monomeric species ($Fe(OH)^{2+}$) and a dimeric species ($Fe_2(OH)_2^{4+}$) whose spectra and photochemical features have been described in the literature [6] (Table 1). Whatever the iron(III) species present in solution, a redox photoprocess is observed upon irradiation giving rise to the reduced metal and ·OH radicals according to

$$Fe^{3+} \xrightarrow[\lambda > 300\ nm,\ H_2O]{h\nu} Fe^{2+} + {}^{\bullet}OH + H^+ \qquad (3)$$

The spectral evolution of the DMBQ–iron(III) mixture upon irradiation at 365 nm is given in Fig. 3. The analysis by HPLC gave evidence for the disappearance of DMBQ together with the formation of OHDMBQ and an apparently very minor photoproduct P2, OHDMBQ formation roughly accounted for DMBQ disappearance (Fig. 4).

No DMHQ was formed, contrary to what was observed by direct photolysis. In addition, the rate of DMBQ disappearance in the presence of iron(III) was lower than that in the absence of iron(III) by a factor of approximately 2.

We calculated the quantum yield of DMBQ disappearance with the assumption that iron(III) was not involved in the process. The following values are obtained:

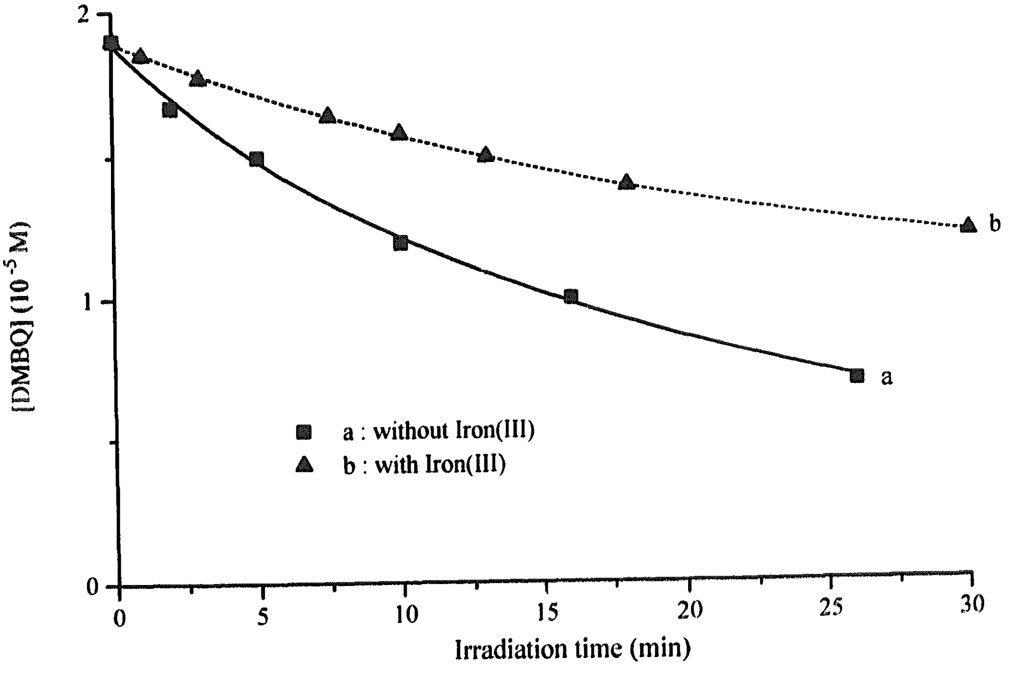


Fig. 2. Kinetics of DMBQ disappearance $\lambda = 365$ nm; [DMBQ= $1.9 \times 10^{-5}$ M): (a) without iron(III), pH 5.50 or pH 2.92; (b) with iron(III), pH 2.90.

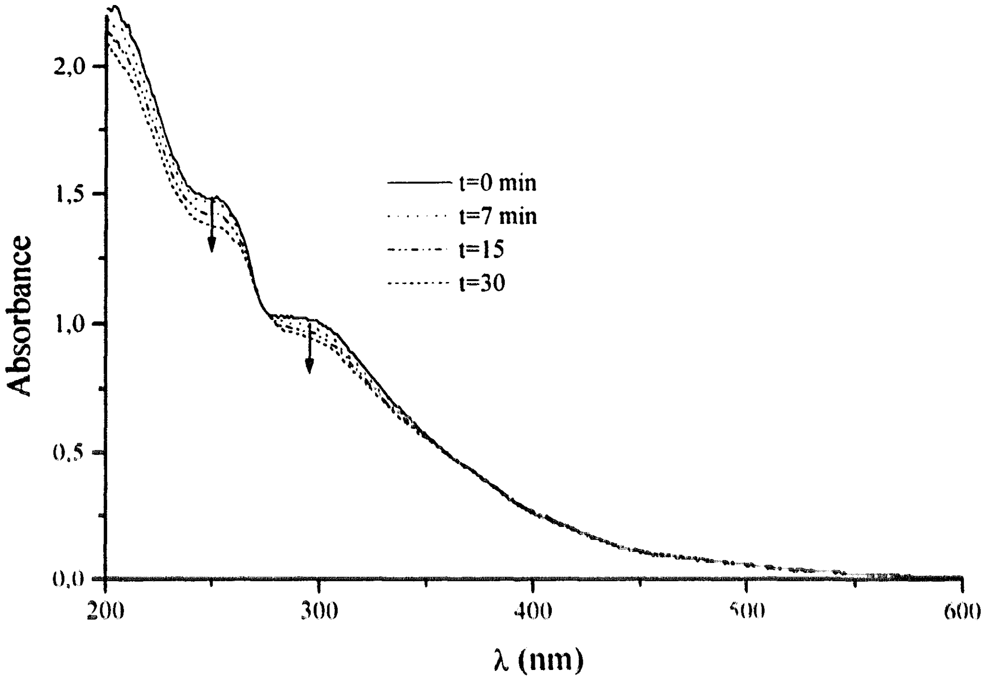


Fig. 3. Spectral evolution of a solution with [DMBQ] = $1.9 \times 10^{-5}$ M and [iron(III)] = $5.0 \times 10^{-4}$ M upon irradiation at 365 nm (pH 2.90).

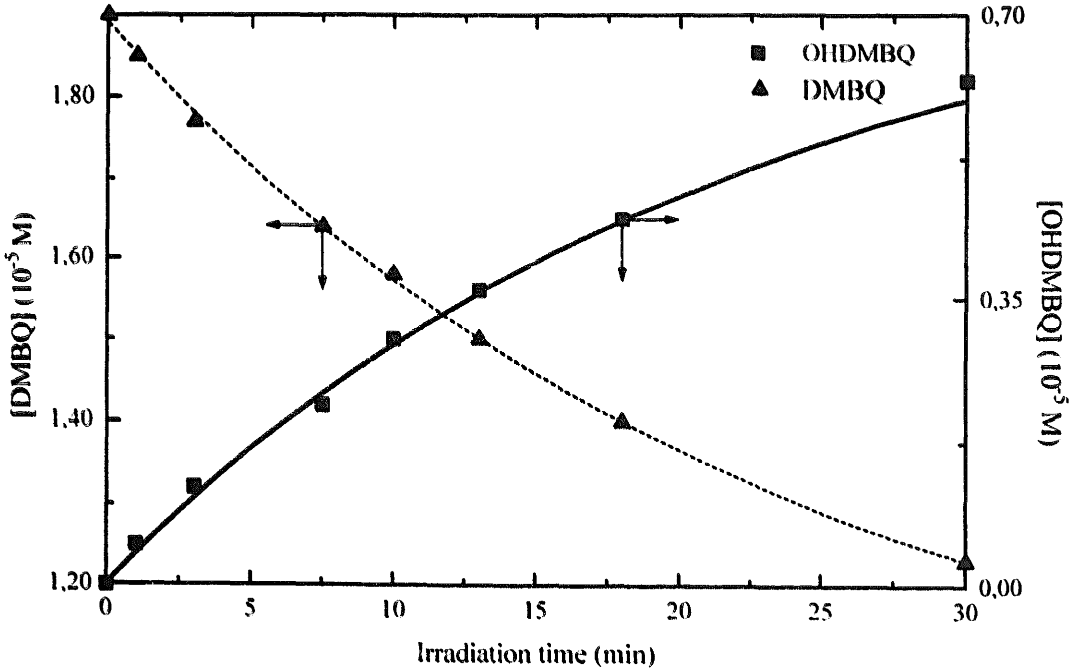


Fig. 4. DMBQ disappearance and OHDMBQ formation upon irradiation at 365 nm with [DMBQ] = $1.9 \times 10^{-5}$ M and [iron(III)] = $5.0 \times 10^{-4}$ M

$$\mathrm{DMBQ}\begin{cases}\phi_{\mathrm{disp}} = 0.47 \text{ without iron(III)}\\ \phi_{\mathrm{disp}} = 0.27 \text{ with iron(III)}\end{cases}$$

This assumption was confirmed by the experiments performed in the presence of isopropanol used as an ˙OH radical scavenger in which no inhibition was observed (see later).

Simultaneously, iron(II) formation was monitored at 510 nm by complexometry with *ortho*-phenanthroline. The experiments were carried out in the presence and in the absence of DMBQ. The initial formation of iron(II) was faster in the presence of DMBQ. As already observed in a similar system [1], the concentration in iron(II) reached a plateau between $4.5 \times 10^{-5}$ M and $5.0 \times 10^{-5}$ M owing to the reoxidation of iron(II) to iron(III). This plateau of iron(II) concentration was reached more rapidly in the presence of DMBQ than in the absence of DMBQ.

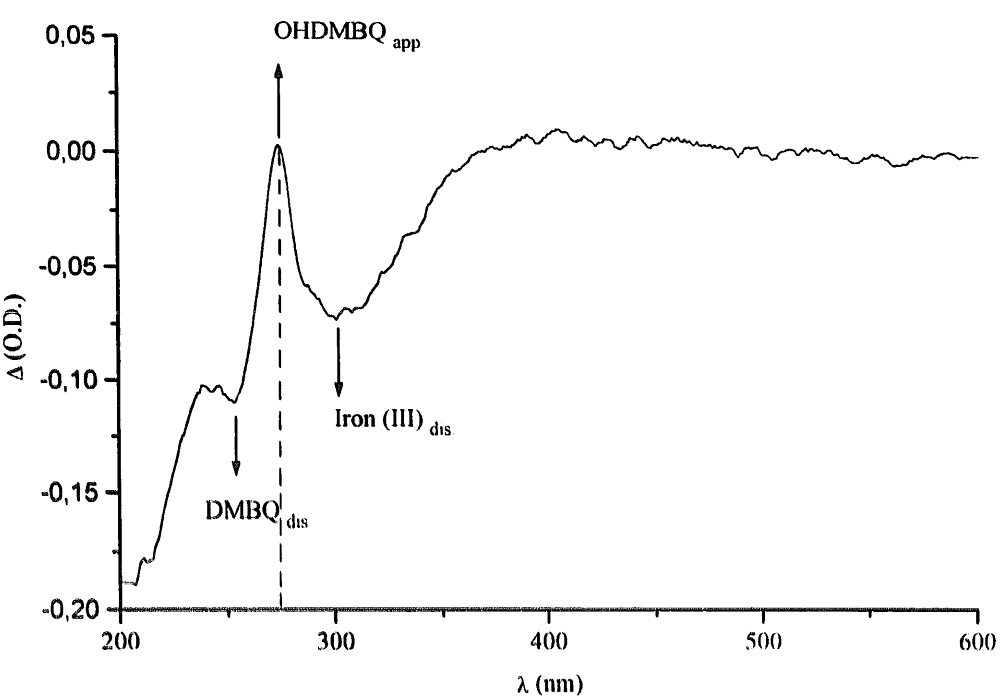


Fig. 5. Δ (O.D.) as a function of λ with an irradiation time of 30 min and a solution with [DMBQ] = $1.9\times10^{-5}$ M and [iron(III)] = $5.0\times10^{-4}$ M.

The quantum yields of iron(II) formation were measured:

$\phi_{\rm form} = 0.022$ iron(III) alone (iron(III) = $5.0\times10^{-4}$ M)

$\phi_{\rm form} = 0.046$ iron(III) + DMBQ

(iron(III) = $5.0\times10^{-4}$ M; [DMBQ] = $1.9\times10^{-5}$ M)

The disappearance of iron(III) and DMBQ together with the formation of OHDMBQ are very well revealed by the plot giving the optical density change Δ(O.D.) as a function of λ (Fig. 5). We can observe near 300 nm the disappearance of iron(III) present as $\mathrm{Fe(OH)^{2+}}$, a species which absorbs with a maximum at 297 nm [6]. The DMBQ disappearance is also observed at 255 nm together with OHDMBQ formation with an absorption maximum at 265 nm as seen in Fig. 5.

When the mixture was irradiated in the absence of oxygen, the quantum yield of DMBQ disappearance remained unchanged. The kinetics of OHDMBQ formation were also unchanged. Oxygen has no significant effect on DMBQ degradation.

When a solution of $1.9\times10^{-5}$ M DMBQ + $5.0\times10^{-4}$ M iron(III) was irradiated in the presence of isopropanol used as scavenger of ˙OH radicals, the quantum yield of DMBQ disappearance and OHDMBQ formation remained unchanged. The rate of OHDMBQ formation was also not affected; the process did not involve ˙OH radicals. The only difference observed with isopropanol was the absence of P2.

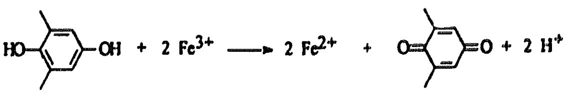
## 4. Discussion

Upon irradiation at 365 nm of DMBQ in the presence of iron(III), two phenomena can be present separately or simultaneously; DMBQ degradation was photosensitized by iron(III) and/or DMBQ underwent a direct photolysis. The fact that ˙OH radicals are not involved in the reaction, the rates of degradation being identical in the presence and in the absence of a scavenger of ˙OH radicals, argues against the significant involvement of ˙OH radicals arising from excited iron(III).

The experimental results allow us to assess the fact that DMBQ disappears by direct photolysis owing to the 1% incident light that it absorbs. The differences between the photochemical behaviours of the systems with and without iron(III) are (1) that no DMHQ formed in the presence of iron(III) and (2) the quantum yield for DMBQ disappearance is lower in the presence of iron(III).

First we checked that DMHQ resulting from direct photolysis of DMBQ was not stable under our experimental conditions.

In fact, we observed immediate oxidation of DMHQ to DMBQ in the presence of iron(III):



(4)

As the redox potentials of the two couples $\mathrm{Fe^{3+}/Fe^{2+}}$ and $\mathrm{DMHQ_{ox}}$/DMHQ are 0.77 V and 0.59 V respectively [8] at pH 3.00, this makes the redox reaction between iron(III) and DMHQ quite efficient. This is in agreement with the absence of DMHQ formation during the slow dark reaction of DMBQ in aqueous solution in the presence of iron(III).

Reaction (4) accounts for all the observed differences.

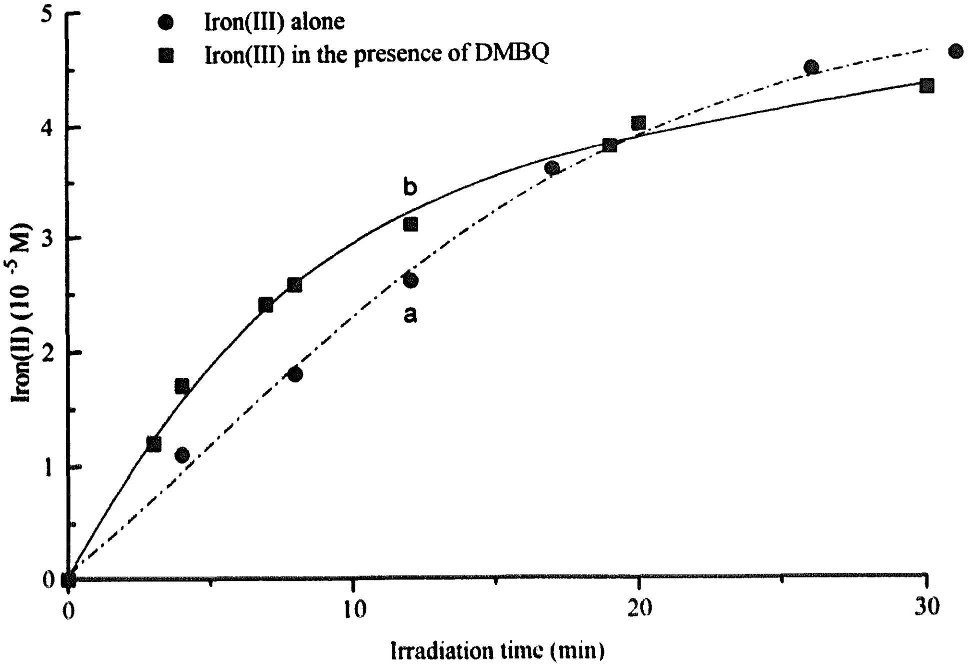


Fig. 6. Concentration of iron(II) as a function of irradiation time λ = 365 nm; iron(III) = 5.0 × $10^{-4}$ M): (a) without DMBQ; (b) with DMBQ.

(1) DMBQ was regenerated in the presence of iron(III), leading to an overall quantum yield of degradation lower than that measured in the absence of iron(III).

(2) Iron(II) was formed, making the quantum yield of iron(II) formation higher when DMBQ is added to the solution (Fig. 6).

This was further confirmed by considering the curves giving the concentration of DMHQ formed in the absence of iron(III) and the disappearance of DMBQ in the presence and in the absence of iron(III).

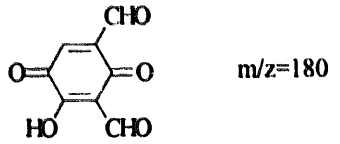
The curve obtained by subtraction of [DMHQ] from the concentration of DMBQ measured in the absence of iron(III) for different irradiation times fits very well with that giving the concentration of DMBQ in the presence of iron(III) (Fig. 7).

According to all the experimental results, the degradation of DMBQ in the presence of iron(III) and upon irradiation at 365 nm can be adequately described by Scheme 1.

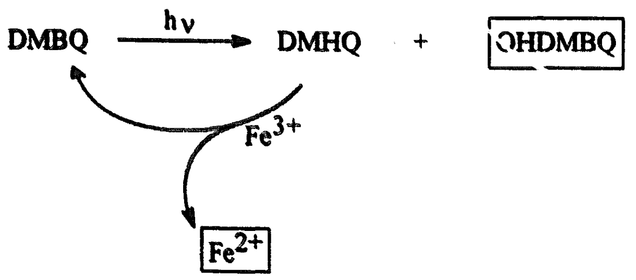
The photoreaction

$$Fe^{3+} \xrightarrow[\lambda > 300\ nm\ H_2O]{h\nu} Fe^{2+} + HO^{\bullet}$$

accounts for the formation of P2, its formation being totally inhibited by isopropanol. According to its mass spectrum, a possible structure for P2 could be the following:



This results from the attack of $^{\bullet}$OH radicals on OHDMBQ. The formation of P2 appears to be very minor; the formation of OHDMBQ roughly accounts for the disappearance of DMBQ.



Scheme 1.

## 5. Conclusion

The presence of iron(III), even in a large excess, does not significantly affect the photochemical behaviour of DMBQ in aqueous solution. With only 1% of the light absorbed by DMBQ, the direct photolysis remains the major phenomenon. The involvement of iron(III) is only in terms of the subsequent thermal reaction with the photoproduct of the reaction, regenerating the starting DMBQ. As a result, the overall quantum yield of DMBQ is divided by approximately 2 and the only photoproduct is OHDMBQ. The attack of $^{\bullet}$OH radicals arising from $Fe(OH)^{2+*}$ leads to very minor formation of P2. All these results account for the experimental observation that was the starting point of this work; for example DMBQ was not observed upon continuous excitation at 365 nm of an iron(III)–2,6-dimethylphenol mixture in aqueous solution. DMBQ is the real primary photoproduct but it dis-

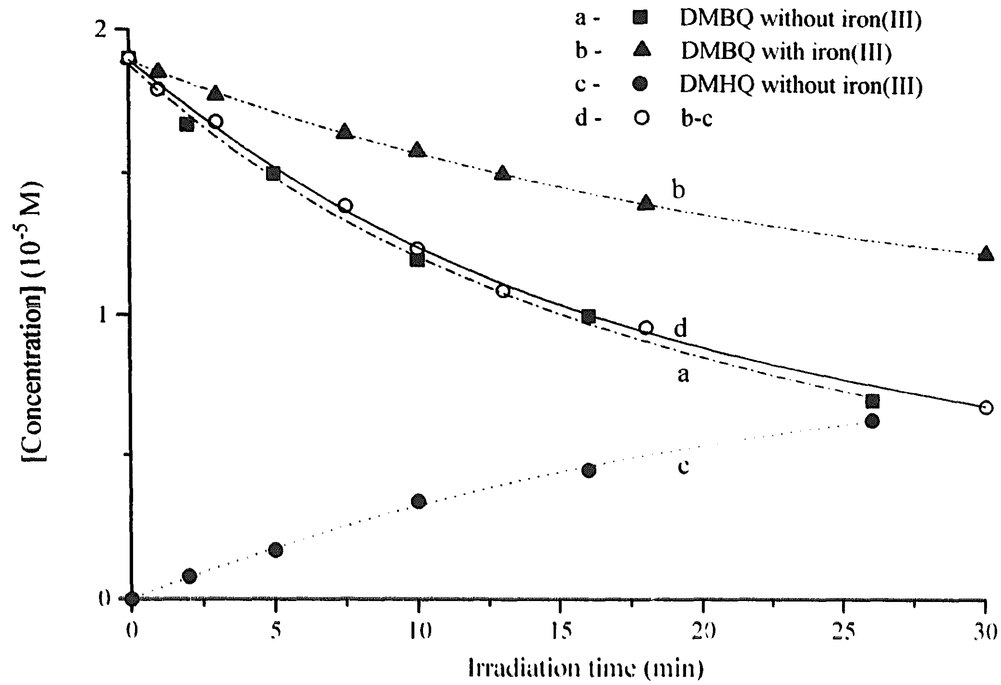


Fig. 7. Concentration as a function of irradiation time: curve a, ■, DMBQ in the absence of iron(III); curve b, ▲, DMBQ in the presence of iron(III); curve c, ●, DMHQ in the absence of iron(III); curve d, ○, curve b minus curve c.

appears by a very efficient photoprocess that prevents it from being detected.

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