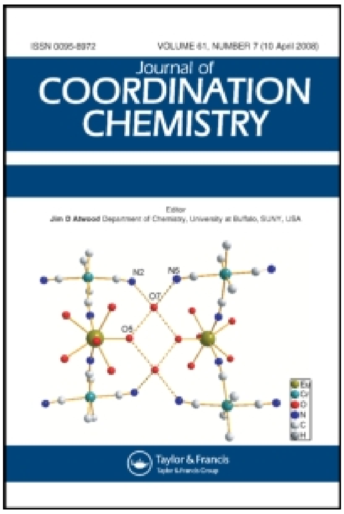

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Photoproduction and determination of hydroxyl radicals in aqueous solutions of Fe(III)-tartrate complexes: a quantitative assessment

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Photoproduction and determination of hydroxyl radicals in aqueous solutions of Fe(III)–tartrate complexes: a quantitative assessment

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Benzene has been used as a probe to determine the photogeneration of $^{\cdot}$OH radicals in aqueous solutions containing Fe(III) and tartrate (Tar) when they are irradiated ($\lambda \geq 313$ nm, 250 W). Products were determined by HPLC. Results show that tartrate has a positive effect on the photogeneration of $^{\cdot}$OH. The influence of pH, temperature, and concentrations of Fe(III) and Tar were systematically investigated. Production of $^{\cdot}$OH radicals was greatest at pH 3.0. Concentrations of $^{\cdot}$OH increased with increasing Fe(III) and tartrate concentrations, but at a certain ratio they decreased. The quantum yield of $^{\cdot}$OH radicals at 328 K was nearly twice that at 298 K.

Keywords: Iron(III); Tartrate; Photolysis; Hydroxyl radicals

1. Introduction

Reports of the occurrence of transition metal in rain and in cloud and fog water show a wide variation of concentrations, with higher concentrations occurring near industrial sites. The most abundant transition metal is iron, typically found in concentrations of several μM. Thus the photochemistry of iron complexes in natural aquatic environments has received considerable attention over the past fifty years. Graedal *et al*. [1, 2] first attempted to explain the complicated redox chemistry of transition metals in atmospheric waters through the development of a detailed kinetic model. They predicted the photolysis of Fe(III) complexes as being important in cloud sources of $^{\cdot}$OH radicals, and they also predicted transition metals as the most important sinks for $O_2^{\cdot-}/HO_2^{\cdot}$ radicals in clouds.

Free Fe(III) cations absorb weakly in the solar UV region (290–400 nm), but the absorption spectra of hydrated or otherwise complexed iron species (iron pairs) are

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shifted toward the visible, which might make their reaction in sunlight possible [3]. It is known that photolysis of Fe(III)–hydroxy complexes can produce hydroxyl radicals at acidic pH values [4]. This system has been widely explored for the degradation of organic contaminants in aqueous media. The most predominant photoactive monomeric Fe(III)–hydroxy complex in the pH range $2.5 \sim 5.0$ is $Fe(OH)^{2+}$. An advantage of this system is that its charge transfer band strongly overlaps the solar UV spectrum and therefore can be easily photolyzed using sunlight [1, 5]. Photolysis can yield $^{\bullet}OH$ radicals, believed to be formed as a result of electron transfer from the ligand (OH^-) to Fe(III) in the excited state (1).

$$Fe(OH)^{2+} + h\nu \rightarrow [Fe(OH)^{2+}]^* \rightarrow Fe^{2+} + {}^{\bullet}OH \tag{1}$$

However, there could be another photochemical mechanism for the generation of $^{\bullet}OH$ radicals in the presence of Fe(III) ions and a carboxylate. The presence of chelating ligands such as oxalate, citrate and so on, has a significant effect on the speciation and photoactivity of Fe(III) irons in acidic conditions, because they form stable complexes with Fe(III) ions. In natural waters, photochemically induced electron transfer from the complexing organic ligand to Fe(III) in the excited Fe(III)–org complexes can take place, and electron deficient Fe(III)–org complexes further reduce O_2 to $O_2^{\bullet-} \cdot O_2^{\bullet-}$ ultimately reacts to yield the hydroxyl radical [6–8], as represented in the following reactions:

$$\begin{aligned} &\text{Fe(III)}-\text{org complex} + h\nu \\ &\quad \rightarrow [\text{Fe(III)}-\text{org complex}]^* \rightarrow \text{Fe(II)} + \text{org radical} \end{aligned} \tag{2}$$

$$\text{org radical} + O_2 \rightarrow O_2^{\bullet-} + \text{oxidized org} \tag{3}$$

$$\text{Fe(III)} + O_2^{\bullet-} \rightarrow \text{Fe(II)} + O_2 \tag{4}$$

$$2H^+ + 2O_2^{\bullet-} \leftrightarrow H_2O_2 + O_2 \tag{5}$$

$$H_2O_2 + \text{Fe(II)} \rightarrow \text{Fe(III)} + {}^{\bullet}OH + OH^- \tag{6}$$

Zuo and Hoigné [9] have shown that Fe(III)–oxalate complexes can be predominant Fe(III) species in many atmospheric waters. They point out that Fe(III)–oxalate complexes can photolyze to produce hydrogen peroxide and hydroxyl radicals. Many researchers have shown that photochemical dissociation of Fe(III)–citrate complexes in aqueous solution involves reduction of Fe(III) to Fe(II) and concomitant oxidation of the carboxylic acid, resulting in the formation of acetone and carbon dioxide as final products [10, 11]. Deng and Wu [12–14] studied Fe(III)–carboxylate complexes used to promote the degradation and decolourization of dyes in aqueous solution under UV and sunlight. Carboxylic acids can promote photodegradation efficiency.

Tartaric acids in aqueous solution are of considerable significance in many biochemical and chemical processes. Neutral and acid salts of tartaric acid (H2Tar) are produced in large quantities and used in the food, cosmetic, pharmaceutical and chemical industries. Tartrate ions are ubiquitous in environmental samples and are found in the concentration range from low ppb to ppm. The formation of Fe(III)–Tar complexes has been reported many times, but there has been no study of its photochemical reactivity. If Fe(III)–Tar complexes have high photochemical reactivity, it may produce some kinds of active species, such as $^{\bullet}OH$ radicals, $O_2^{\bullet -}$, H_2O_2 and organic radicals. Thus it could play an important role in the oxidation of organic compounds in natural waters and in the remediation of wastewaters. The aim of the study reported below was the photo-generation of $^{\bullet}OH$ radicals in the aqueous solutions of tartrate containing Fe(III) ions.

2. Experimental

2.1. *Chemicals and preparation of solutions*

All reagents were of analytical grade and used without further purification. Ferric chloride was used as the iron source and potassium sodium tartrate as the tartrate source. Water was doubly distilled. The pH of the aqueous solutions was adjusted with HCl or NaOH. Benzene and phenol standards were used for HPLC analyses. Care was taken in the preparation of solutions of Fe(III) to prevent precipitation. An appropriate amount of ferric chloride was diluted in a few cm^3 of hydrochloric acid (0.1 M) and added to an appropriate volume of doubly distilled water to give the desired concentration of Fe(III) at pH 3.0.

2.2. *Photoreaction system*

Irradiation experiments were performed under a metal halide light ($\lambda \geq 313$ nm, 250 W). The light intensity was 1.2×10^5 Lux, as was detected by a digital lux meter (TES 1332). The photochemical reactions were carried out in pyrex tubes (diameter 1.5 cm, length 11.5 cm, wall thickness 1 mm). The reaction system consisted of a plate with a central hole and eight smaller holes placed symmetrically around it. The metal halide lamp was positioned in the centre of the plate and a water jacket was used to maintain constant temperature (298 ± 1 K). Eight identical pyrex tubes were placed vertically in the remaining holes such that the lamp and the tubes were kept parallel at a fixed distance of 7 cm. The plate was rotated at 50 rpm to ensure equal irradiation of samples.

2.3. *General methods*

Electronic spectra of aqueous solutions containing Fe(III)–Tar complexes were recorded using a Shimadzu UV-1601 spectrophotometer. Benzene (0.007 M) was added to aqueous solution containing Fe(III)–Tar complexes and photochemically oxidized to phenol. It is thought that the $^{\bullet}OH$-mediated oxidation of benzene forms phenol with nearly 100% yield [15–17] and the phenol concentration was regarded as the concentration of hydroxyl radicals produced during photolysis. The formation of phenol from benzene was monitored at 270 nm using a Shimadzu LC-10AT HPLC fitted with a Shimadzu SPD–10A detector. The eluent was 40% acetonitrile at a flow rate of $0.8\,cm^3\,min^{-1}$ through a Kromasil KR100-5C18 column.

Scavenging of $^{\bullet}OH$ by benzene has been used to determine the $^{\bullet}OH$ quantum yield. Aromatic hydroxylation is a typical reaction of $^{\bullet}OH$ and has been used for detection

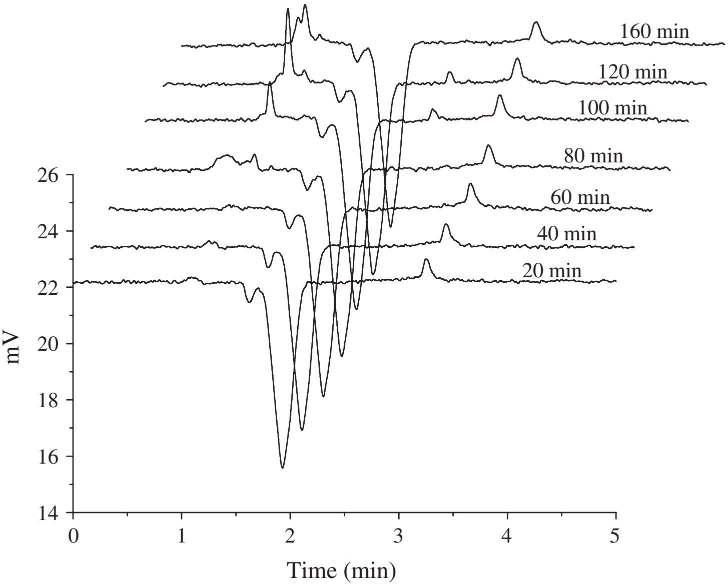

Figure 1. HPLC chromatograms measuring the photogeneration of phenol as a function of photochemical reaction time. Retention time of phenol is 4.2 min.

of $^{\bullet}OH$ in the Fenton reaction and during the photolysis of aqueous of HNO_2, NO_3^- and $NO_2^{\bullet}$ [18]. Benzene is very unreactive toward O_2 ($^1\Delta_g$) [8] and hydroxylation of benzene is a fairly selective process. Given the high reactivity of benzene with $^{\bullet}OH$ [19, 20], under the conditions of these experiments virtually all of the $^{\bullet}OH$ should have been scavenged. As shown in figure 1, direct photolysis of 0.007 M benzene in doubly distilled water showed no detectable loss of benzene or formation of phenol after 2.5 h of irradiation (the retention time of phenol was 4.2 min in these experiments). Destruction of phenol by direct photolysis and by peroxyl radicals, O_2 ($^1\Delta_g$) and other oxidents is expected to be slow by comparision to rate of formation of phenol [21].

3. Results and discussion

3.1. *Photogeneration of $^{\bullet}OH$ radicals under different conditions*

Photogeneration of hydroxyl radicals by photolysis of Fe(III)–Tar complexes has been quantitatively determined using benzene as a probe. Since Fe(III)–OH complexes can photolyze to produce $^{\bullet}OH$ radicals, we carried out control experiments on aqueous solution without Tar. As shown in figure 2, under the same irradiation and pH, $^{\bullet}OH$ concentrations generated in systems containing Fe(III)–Tar complexes is higher than in those containing only Fe(III). Dark reactions were also carried out in parallel, and in which no $^{\bullet}OH$ was produced. The availability of oxygen in the aqueous solution is an important factor. Aqueous solutions containing Fe(III)–Tar complexes were all in contact with air. Control experiments were carried out under anaerobic solution

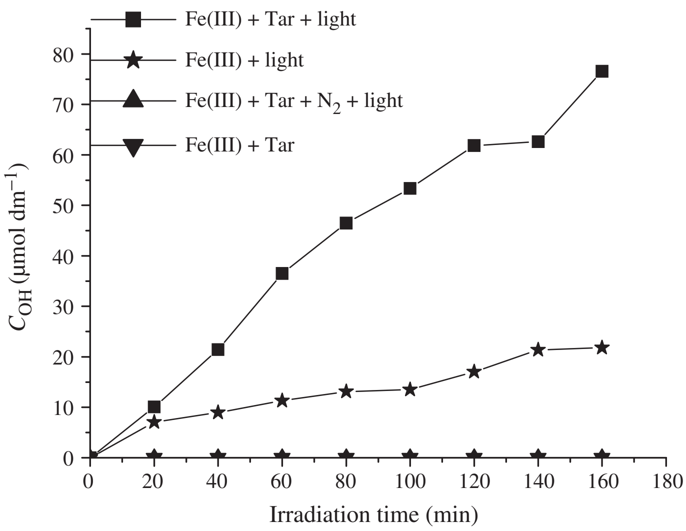

Figure 2. Comparison of $^{\bullet}$OH quantum yield under different conditions for an aqueous solution with $C_{\mathrm{Fe(III)}} = 10.0\,\mu\mathrm{mol\,dm^{-1}}$, $C_{\mathrm{Tar}} = 150.0\,\mu\mathrm{mol\,dm^{-1}}$. The initial pH of the aqueous solutions was 3.0 ± 0.1.

by purging the solution with N_2 for ten minutes. Results showed that no $^{\bullet}$OH radicals were generated in these cases, in line with equations (3) to (6).

3.2. *Quantum yields*

Figure 3 shows chromatograms as a function of photochemical reaction time. Peak 1 is a low molecular weight carboxylic acid. Peak 2 is phenol produced during irradiation. The concentration of phenol increased with longer reaction time, and there are no side products. For the reaction between benzene and $^{\bullet}$OH, the quantum yield of phenol was reported to be nearly 100% [17] so photochemically formed $^{\bullet}$OH is directly related to phenol concentration. It should be noted that $^{\bullet}$OH concentrations reported are total concentrations generated during the given irradiation time and not the steady-state concentrations. In aqueous solution, the photogeneration of $^{\bullet}$OH can occur through the different pathways shown in figure 4. An important step is the photolysis of the Fe(III)–Tar complexes. Light absorption results in an electronically excited state. Electron transfer *via* this electronically excited state leads to a reduced iron centre and oxidized Tar. At the same time, organic radicals further reduce O_2 to $O_2^{\bullet-}$ and $O_2^{\bullet-}$ is rapidly protonated to its conjugate acid, the hydroxyl radical.

3.3. *Effect of the initial pH*

Experiments were carried out to investigate the effect of the initial pH value on the photogeneration of $^{\bullet}$OH. Reactions were carried out in aqueous solutions that had been adjusted to pH values of 1.5, 2.0, 3.0, 4.0 and 5.0 with hydrochloric acid (0.1 M). The results indicate that the pH value affects the quantum yield of $^{\bullet}$OH;

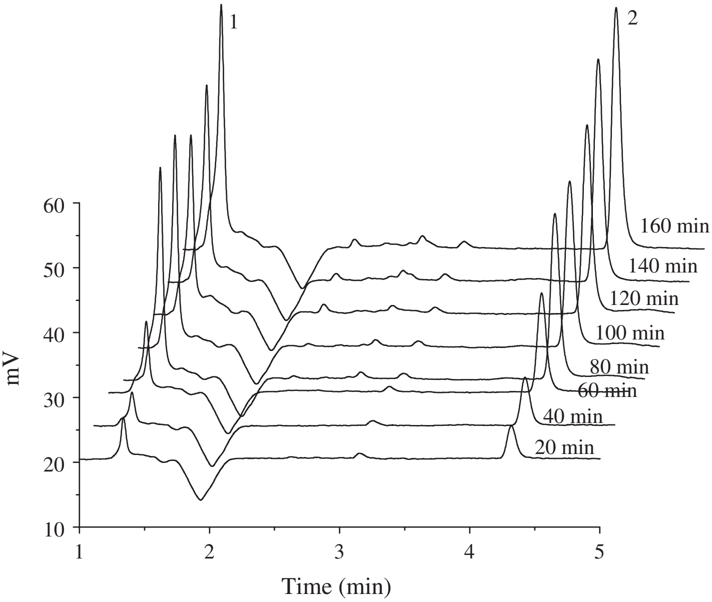

Figure 3. HPLC chromatograms showing photogeneration of phenol with time for an aqueous solution with $C_{\mathrm{Fe(III)}} = 10.0\,\mu\mathrm{mol\,dm^{-1}}$, $C_{\mathrm{Tar}} = 150.0\,\mu\mathrm{mol\,dm^{-1}}$ and 7 mM benzene. The initial pH value of the aqueous solutions was 3.0 ± 0.1.

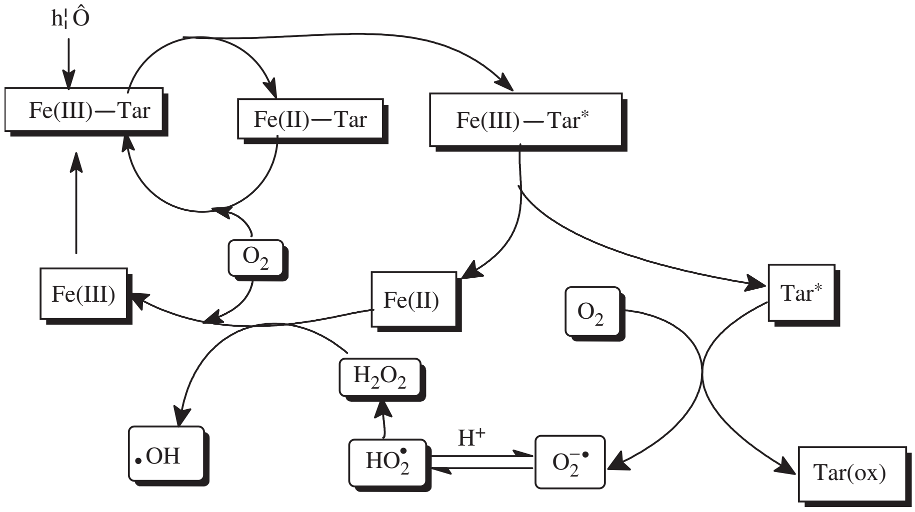

Figure 4. Possible pathways for the reaction suite.

the quantum yield increases with increasing pH, is optimal at pH 3.0, and thereafter decreases (figure 5).

Many studies have shown that pH value has a great effect on the photolysis of Fe(III)–carboxylate complexes in producing H_2O_2 and degrading organic compounds. The pH may influence the competition between the reaction of Fe(III)/Fe(II) and active intermediate $HO_2^{\bullet}/O_2^{-\bullet}$ (as in reactions (5) and (7)). It also influences the

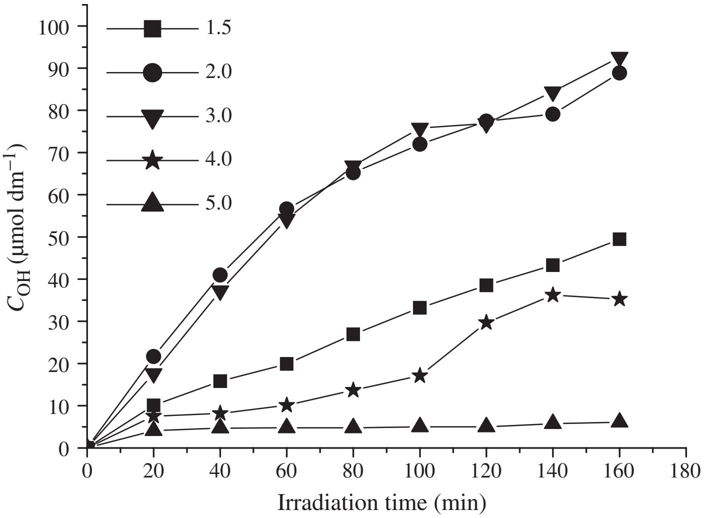

Figure 5. Effect of initial pH on $^{\bullet}$OH quantum yield for an aqueous solution with $C_{Fe(III)} = 30.0\,\mu mol\,dm^{-1}$, and $C_{Tar} = 60.0\,\mu mol\,dm^{-1}$.

decomposition of H_2O_2; the rate of decomposition of H_2O_2 increases in the pH range 0.0 to 3–3.2 [22]. Moreover, the Fenton reaction is believed to be favoured by acid and more $^{\bullet}$OH radicals are generated in the system at acidic pH values.

$$HO_2^{\bullet}/O_2^{-\bullet} + Fe(II) + H^+ \rightarrow Fe(III) + H_2O_2 \tag{7}$$

On the other hand, pH can affect the distribution of Fe(III) species in solution. We computed the speciation of Fe(III) using the Visual MINTEQ computer program. Results showed that Fe(III)–Tar$^+$ was the predominant species when pH value ranged from 2.5 to 4.0 (see figure 6). $Fe(OH)^{2+}$ is another photoactive species in the system. Pozdnyakov *et al.* [23] investigated the mechanism of $^{\bullet}$OH formation upon excitation of $[Fe(OH)^{2+}]$. When pH is below 2.0, Fe^{3+}(aq) is the major species and from pH 4.5 to 6.0 it is $Fe(OH)_2^+$. However, no reports on the photochemical properties of $Fe(OH)_2^+$ are available. It is likely that $Fe(OH)_2^+$ photolyzes to generate $^{\bullet}$OH radicals, but we assume that the quantum yield is low as generation of $^{\bullet}$OH was less than at other pH values (see figure 5). Thus we consider that Fe(III)–Tar$^+$ is the major photoactive species in the system.

3.4. *Effect of the Tar concentration*

For comparison, we chose pH 3.0 as the initial pH for these experiments. The concentration ratio Fe(III) : Tar was another important factor. Further experiments to study its effects were all carried out at pH 3.0 with Fe(III) : Tar from about 1 : 3 to 1 : 12. Results are shown in figure 7. The $^{\bullet}$OH concentrations generated in the system increased with increasing Tar concentration but at a certain ratio decreased with increasing Tar concentration. When Tar concentration was much higher than

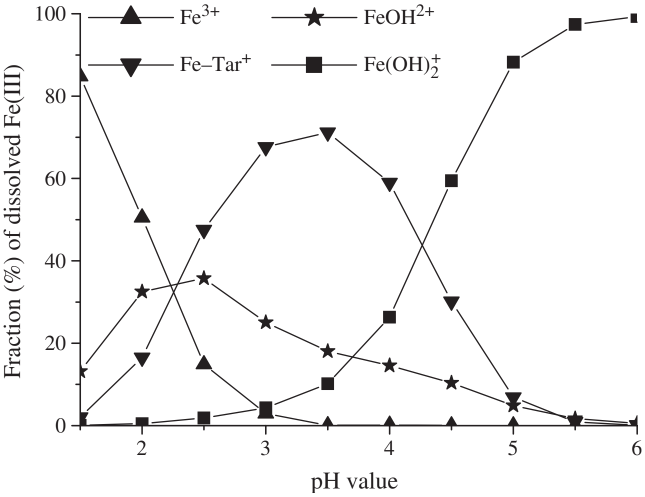

Figure 6. Distribution of iron and tartrate species as a function of pH in a system with $C_{\mathrm{Fe(III)}} = 10.0\,\mu\mathrm{mol\,dm^{-1}}$, and $C_{\mathrm{Tar}} = 30.0\,\mu\mathrm{mol\,dm^{-1}}$.

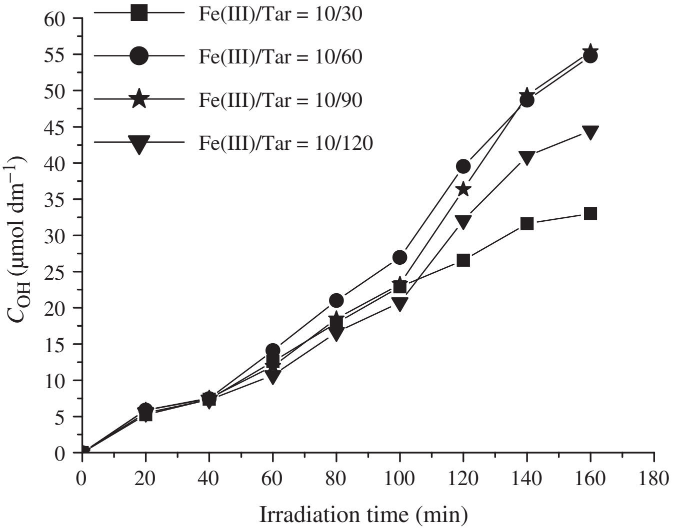

Figure 7. Effect of Tar concentration on $^{\bullet}$OH quantum yield. The initial pH of the aqueous solutions was 3.0 ± 0.1.

that of Fe(III), Visual MINTEQ calculations showed that H_2Tar and $HTar^-$ were the major species present. We suggest that these species may consume $^{\bullet}$OH radicals so that competition exists in the system, and only a proportion of the total $^{\bullet}$OH produced is trapped by benzene.

3.5. *Effect of the Fe(III) concentration*

Fe(III) species in solution promote the photogeneration of $^{\bullet}$OH in a continuous Fe(III)/Fe(II)/Fe(III) cycle. The quantum yield of $^{\bullet}$OH increased with increasing

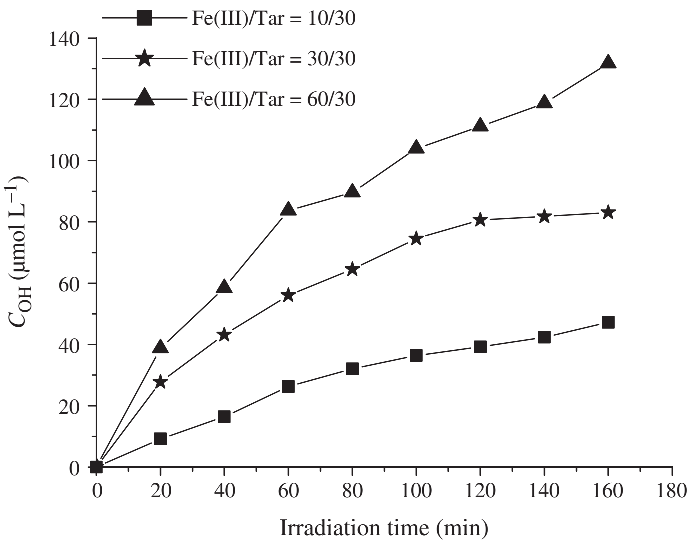

Figure 8. Effect of the Fe(III) concentration on the $^{\bullet}$OH quantum yield. The initial pH value of the aqueous solutions was 3.0 ± 0.1.

initial Fe(III) concentration. Data in figure 8 show that Fe(III) plays an important role in the photochemical reaction. At pH 2–5, Fe(III)–Tar^{+} forms in the conventional manner. When Fe(III) concentration is relative higher than that of Tar, it will participate in the so-called photo-Fenton reaction. Fe(OH)$^{2+}$ is considered to be the predominant photoactive monomeric Fe(III)–hydroxy complex in the pH range 2.5–5.0.

$$\mathrm{Fe(III)} + \mathrm{H_2O} + h\nu \rightarrow \mathrm{Fe(II)} + {}^{\bullet}\mathrm{OH} + \mathrm{H^+} \tag{8}$$

3.6. *Effect of temperature*

Finally, we carried out control experiments without the water jacket; results are shown in figure 9, when the reaction temperature was about 328 K. The quantum yield of $^{\bullet}$OH at 328 K was nearly twice than at 298 K. Although higher temperatures will hasten the main reactions, they can also enhance side reactions.

Formation of phenol from benzene has been used to determine the quantum yield of $^{\bullet}$OH radicals produced by the photolysis of Fe(III)–Tar complexes. The study confirms that pH has a great effect on the photolysis of Fe(III)–Tar complexes. The quantum yield of $^{\bullet}$OH radicals at pH 3.0 was greatest (pH ranged from 1.5 to 5.0) and $^{\bullet}$OH concentrations increased, then decreased, with increasing Tar concentration. The quantum yield of $^{\bullet}$OH radicals at 328 K was nearly twice that at 298 K. Since $^{\bullet}$OH concentrations generated in the systems containing Fe(III)–Tar complexes were higher than in systems only containing Fe(III), it is concluded that Tar has positive effects on the photogeneration of $^{\bullet}$OH. Thus Fe(III)–carboxylate complexes can potentially use sunlight as an irradiation source. Especially in natural waters, which contain Fe(III)/Fe(II) and many kinds of organic acids, these processes may play an important

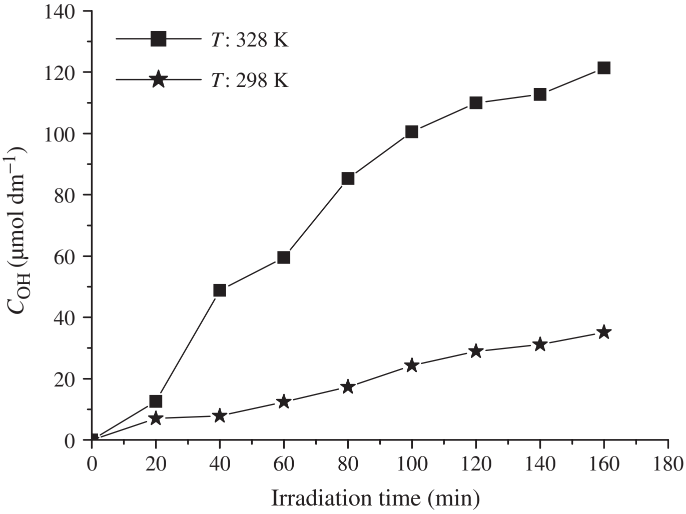

Figure 9. Effect of temperature on $^{\bullet}$OH quantum yield for an aqueous solution with $C_{Fe(III)} = 10.0\,\mu mol\,dm^{-1}$, and $C_{Tar} = 30.0\,\mu mol\,dm^{-1}$. The initial pH value of the aqueous solutions was 3.0 ± 0.1.

role in the oxidation of organic materials. However, further experimental and theoretical work is needed to fully understand system and its application in natural aquatic or atmospheric environments.

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