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## DETERMINATION OF HYDROXYL RADICALS FROM PHOTOLYSIS OF Fe(III)-PYRUVATE COMPLEXES IN HOMOGENEOUS AQUEOUS SOLUTION

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### Abstract

Benzene was used as a probe to detect  $\cdot\text{OH}$  produced by photolysis of Fe(III)-pyruvate complexes in a homogeneous system. The Fe(III)-Pyr system was found to be not catalytic. Influence of pH, temperature, as well as the concentration of Fe(III) and pyruvate (Pyr) on the  $\cdot\text{OH}$  yield was investigated.

*Keywords:* Pyruvate, iron(III), hydroxyl radicals, photolysis

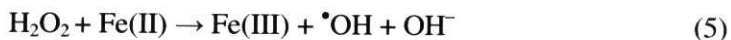
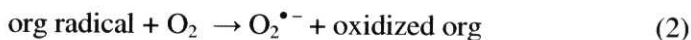
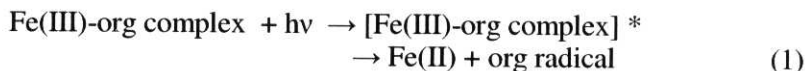
## INTRODUCTION

Iron is the most abundant transition metal in the environment, typically found in concentrations of several  $\mu\text{M}$ . Therefore, 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. They predicted the photolysis of Fe(III) complexes as important in cloud sources of

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$\cdot\text{OH}$ , and they also predicted transition metals as the most important sink for  $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$  radicals in clouds.

Carboxylic acids constitute one of the dominant classes of organic compounds found in the atmosphere in a variety of phases [3-5]. They have been found in rainwater, snow and ice, on aerosol particles and in the gas phase. Organic acids with a low molecular weight have been identified and measured in a wide variety of environments, such as marine and continental air, urban, rural and remote atmospheres of tropical and temperate zones. The presence of carboxylic acids, in the forms of oxalate, citrate and so on, has a significant effect on the speciation and photoactivity of Fe(III) ions in acidic conditions, because they may form stable complexes with Fe(III) ions. Free Fe(III) ions absorb weakly in the solar UV region (290–400 nm), but the absorption spectra of hydrated or otherwise complexed iron species (iron pairs) are shifted toward the visible region, which might make their use in sunlight possible [6]. In natural waters, photoinduced electron transfer from the complexing organic ligand to Fe(III) in the excited Fe(III)-org complexes can take place, and the resulting Fe(II)-org $^{\cdot+}$  radical complexes can further reduce  $\text{O}_2$  to  $\text{O}_2^{\cdot-}$ .  $\text{O}_2^{\cdot-}$  rapidly reacts to yield hydroxyl radical [7-9], as represented in the following reactions:



Deng and Wu [10-12] studied Fe(III)-carboxylate complexes which are used to promote the degradation and decolorization of dyes in aqueous solutions under UV light and sunlight. They found that carboxylic acids can increase the photodegradation efficiency.

Pyruvic acid  $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{OH}$  is one of the most abundant ketoacids found in the Earth's atmosphere. Its presence has been reported in aerosols, rainwater and in the gas phase of the urban atmosphere as well as in remote continental and marine areas. This acid is a product of photochemical oxidation of natural organic compounds such as isoprene and cresols [13]. It is expected to play an important role in the precipitation acidity [14]. The available data indicate that pyruvic acid is lost in the gas phase mainly through photolysis. Mellouki and Mu [15] have detected  $\cdot\text{OH}$  radicals upon the photolysis of pyruvic acid in the gas phase with the relative quantum yield of  $(5 \pm 3)\%$ . The rate constant of the gas-phase reaction between the  $\cdot\text{OH}$  radical and pyruvic acid was found to be  $k_{\text{PA}} = (1.2 \pm$

$0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K [15]. Pyruvic acid is known to form complexes with Fe(III) of the form Fe(III)(Pyr)<sub>x</sub> ( $x = 1, 2$ ), however, corresponding equilibrium constants are unavailable from the literature. Until now, there are no published studies on the photochemical reactivity of Fe(III)-Pyr complexes and their photolysis in the aqueous solution. If the Fe(III)-Pyr complex has high photochemical reactivity, it may produce some kinds of active species, such as  $\cdot\text{OH}$ ,  $\text{O}_2^{\cdot-}$ ,  $\text{H}_2\text{O}_2$  and organic radicals. The aim of this work was to investigate the effect of Pyr on the photogeneration of  $\cdot\text{OH}$  in homogeneous aqueous solutions containing Fe(III) ions.

## EXPERIMENTAL

The homogeneous reaction solutions were prepared in doubly distilled water with Fe(III) and Pyr ions. Benzene (7.0 mM) was added to the aqueous solution prior to illumination in order to scavenge efficiently all of the  $\cdot\text{OH}$  produced. The formation of phenol from benzene was monitored at 270 nm using HPLC (Shimadzu LC-10AT) with a Shimadzu SPD-10A UV-Vis detector.

After the components were completely mixed, pH of the aqueous solution was adjusted to the desired value. The aqueous solutions prepared above were irradiated under the light ( $\lambda \geq 350 \text{ nm}$ , 250 W) of a metal halide lamp in a rotating photochemical reactor. The reactor consisted of quartz tubes 1.5 cm in diameter, 1 mm wall in thickness, and 10 cm in length [11]. The light intensity was  $34 \mu\text{W cm}^{-2}$ , which was detected by an irradiance meter of the FS type (Peixian Photoelectric Instruments Co. Jiangsu, PRC). The sampling was performed with the 20 min intervals. In a HPLC analysis, 20  $\mu\text{L}$  of the reaction solution was injected into a Kromasil KR100-5C18 column. The eluent used for HPLC was 40% aqueous solution of acetonitrile at the flow rate of  $0.8 \text{ mL min}^{-1}$ . The formation of the  $\cdot\text{OH}$  radicals was monitored via the appearance of phenol from the  $\cdot\text{OH}$ -mediated oxidation of benzene. The measurements for each sample were made in triplicate, the error for the peak area was less than 5%.

In this study, the concentration of benzene was much higher than that of the other substances, such as Fe(III) or Pyr. 7 mM of benzene was enough to capture all of the hydroxyl radicals generated in the reaction. It was thought that the  $\cdot\text{OH}$ -mediated oxidation of benzene forms phenol with a nearly 100% yield [8,16], and thus the concentrations of photochemically formed hydroxyl radicals were determined as

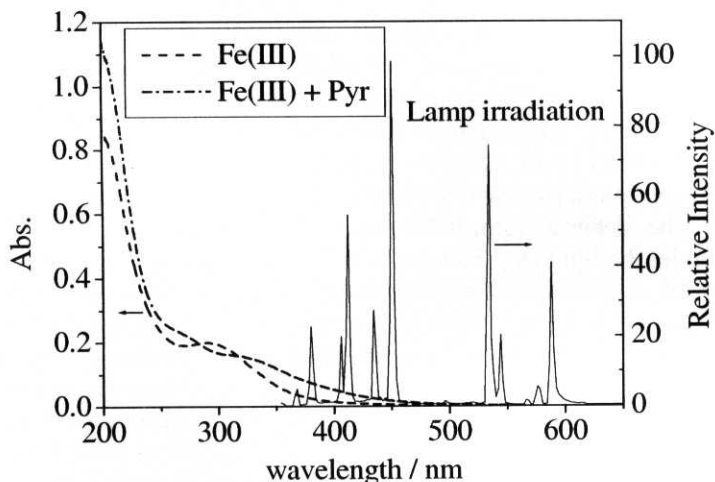
$$C_{OH} = C_{phenol} \quad (6)$$

where  $C_{phenol}$  is the concentration of phenol at time  $t$ . The experimental photokinetic curves were fitted using a one-exponential model.

## RESULTS AND DISCUSSION

### Wavelength-averaged quantum yield of the $\cdot\text{OH}$ production

Figure 1 presents the UV-Vis spectra of both the solutions containing only Fe(III) ions (pH = 3) and the solutions containing Fe(III) ions with additions of Pyr. In the case of solution without Pyr, the spectrum belongs to the  $\text{Fe}(\text{OH})^{2+}$  complex. The change in the spectrum after addition of Pyr indicates the formation of the Fe(III)-Pyr complex (Fig. 1). The absorption of Fe(III)-Pyr complex in the region of 320–500 nm is sufficiently higher than that of  $\text{Fe}(\text{OH})^{2+}$ . This allows one to assume that the Fe(III)-Pyr complex can be used in the processes of photodegradation of organic impurities in natural water systems.



**Fig. 1.** UV-Vis spectrum of solutions with  $C_{\text{Fe(III)}} = 100 \mu\text{M}$  or with  $C_{\text{Fe(III)}} = 100 \mu\text{M}$  and  $C_{\text{Pyr}} = 300 \mu\text{M}$ . The light path was 1 cm. Initial pH of the aqueous solution  $3.0 \pm 0.1$ . The spectrum of the metal halide light used in this work is also shown

Figure 1 also demonstrates the emission spectrum of the metal halide lamp. The spectrum consists of several narrow bands. The light of the narrow bands with the maxima at 380, 406, 412, 438, and 452 nm could be absorbed by the Fe(III)-Pyr complex. These bands were used to calculate the quantum yield of the  $\cdot\text{OH}$  produced in the system. The fraction of the light absorbed at the major irradiation wavelengths and the light intensities incident into the reaction volume are shown in Table 1. The total fraction of the light absorbed in the sample containing  $10 \mu\text{M}$  of Fe(III) and  $60 \mu\text{M}$  of Pyr (pH = 3.0) was about 12%. The light intensity incident into the reaction mixture was  $8.9 \times 10^{15} \text{ photon s}^{-1}$ .

**Table 1**  
Light intensity distribution of the lamp

Spectrum energy			
$\lambda$ (nm)	Energy fraction (%)	$W \cdot \text{cm}^{-2}$	photon $\cdot \text{s}^{-1}$
380	0.7	$2.6 \times 10^{-4}$	$4.9 \times 10^{14}$
406	0.7	$2.3 \times 10^{-4}$	$4.7 \times 10^{14}$
412	3.0	$1.0 \times 10^{-3}$	$2.1 \times 10^{15}$
438	1.3	$4.3 \times 10^{-4}$	$9.4 \times 10^{14}$
452	6.2	$2.1 \times 10^{-3}$	$4.8 \times 10^{15}$

By detecting phenol formed *via* the reaction of benzene with  $\cdot\text{OH}$ , we quantified  $\cdot\text{OH}$  generated during the photolysis of the Fe(III)–Pyr complexes in the homogeneous aqueous solution. In the solution containing 10.0  $\mu\text{M}$  of Fe(III) and 60.0  $\mu\text{M}$  of Pyr at pH = 3.0, a 160-min irradiation resulted in the formation of 34  $\mu\text{M}$  of  $\cdot\text{OH}$ . This corresponds to the generation of  $\cdot\text{OH}$  with the rate constant  $k_{\text{OH}} = 0.21 \mu\text{M L}^{-1} \text{min}^{-1}$ . Using this value, the quantum yield of  $\cdot\text{OH}$  can be calculated by the following formula:

$$\Phi = \frac{k_{\text{OH}} \cdot V \cdot N_{\text{A}}}{f \cdot I_{\text{abs}}} \quad (7)$$

where  $f$  is the fraction of light that is absorbed by the reaction mixture,  $V = 10 \text{ mL}$  is the photoreactor volume,  $N_{\text{A}}$  is the Avogadro number, and  $I_{\text{abs}} = 8.9 \times 10^{15} \text{ photon s}^{-1}$  is the intensity of the incident light. In our experiments,  $\Phi_{\text{OH}}$  was found to be  $2 \times 10^{-2}$ . The value obtained for  $\Phi_{\text{OH}}$  gives an estimation of the quantum yield in the region of 370–460 nm (corresponding to the red wing of the less energetic absorption band of the Fe(III)-Pyr complex).

The possible dependence of the  $\cdot\text{OH}$  quantum yield on the irradiation wavelength will be studied in future experiments. In this work, the dependence of the average quantum yield on the experimental conditions (concentrations of the reagents, pH and temperature) is presented.

The  $\cdot\text{OH}$  photoproduction mechanism in aqueous solutions with Fe(III)-Pyr complexes can presumably be interpreted as the reaction scheme shown in Fig. 2.

The relative quantum yields of the  $\cdot\text{OH}$  radical production upon the photolysis of the Fe(III)-Pyr complex and the Fe(OH) $^{2+}$  complex (Fe(OH) $^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{OH}^- + \cdot\text{OH}$ ) [17]) were compared. As shown in Fig. 3, under the same pH and irradiation time, the concentration of  $\cdot\text{OH}$  generated in the system containing the

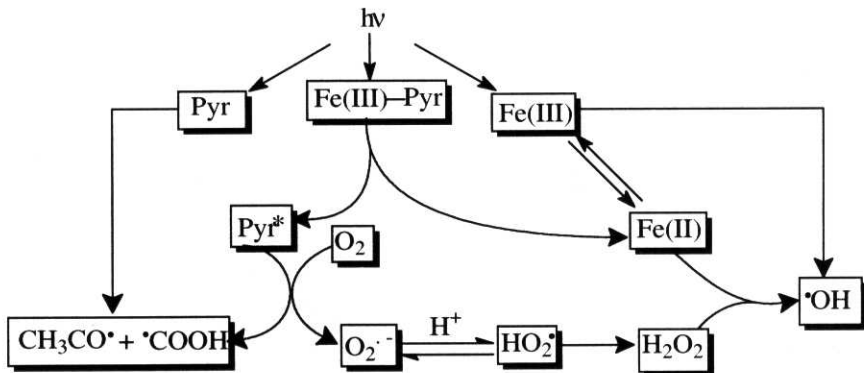


Fig. 2. Possible photoreaction mechanism

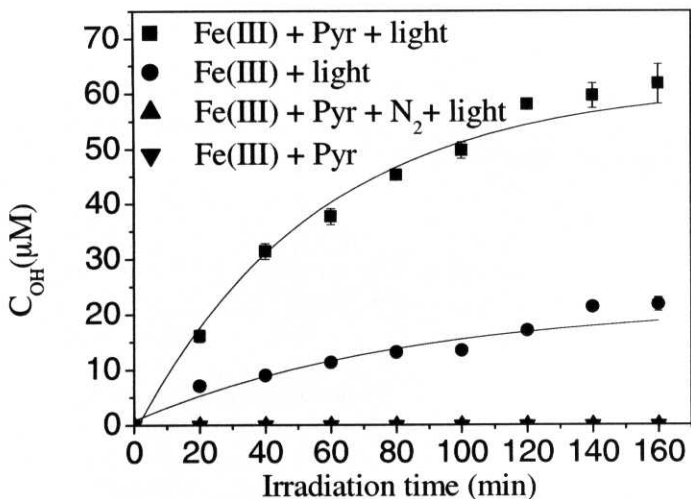
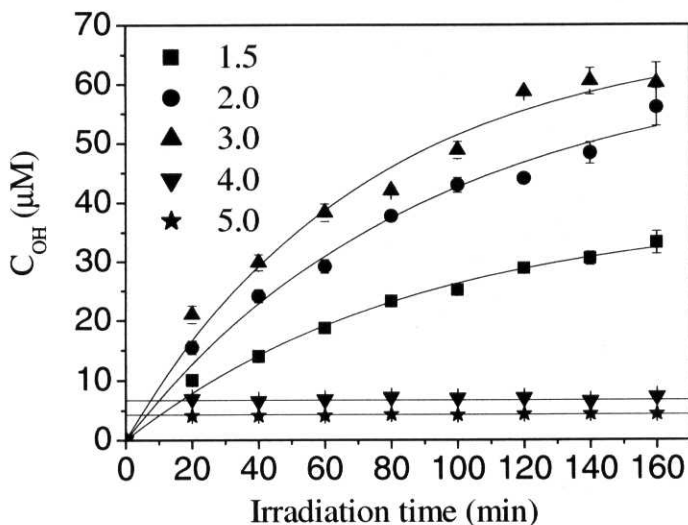


Fig. 3. Comparison of total  $\cdot\text{OH}$  yields under different conditions for an aqueous solution with  $C_{\text{Fe(III)}} = 10 \mu\text{M}$ ,  $C_{\text{Pyr}} = 90 \mu\text{M}$ . Initial pH of the aqueous solution  $3.0 \pm 0.1$ . Solid lines are 1-exponential fits

Fe(III)-Pyr complex is higher than that in the system with  $\text{Fe}(\text{OH})^{2+}$ . The possible production of the hydroxyl radical in the thermal reaction was experimentally checked and ruled out (Fig. 3). The availability of oxygen in the aqueous solution was found to be an important factor for the  $\cdot\text{OH}$  production, because in anaerobic conditions, the experiments showed that no  $\cdot\text{OH}$  was generated (Fig. 3).

### Effect of initial pH on the $\cdot\text{OH}$ yield

The experiments were performed in the homogeneous aqueous solutions at pH values of 1.5, 2.0, 3.0, 4.0 and 5.0, which were provided by an addition of hydrochloric acid. A significant effect of pH on the  $\cdot\text{OH}$  yield was observed (Fig. 4). The  $\cdot\text{OH}$  concentration at pH = 3.0 appeared to be higher than that at all other pH values in the range studied (Fig. 4). The great effect of pH on the production of  $\text{H}_2\text{O}_2$  upon the photolysis of different Fe(III)-carboxylate complexes was reported previously [10, 18, 19].

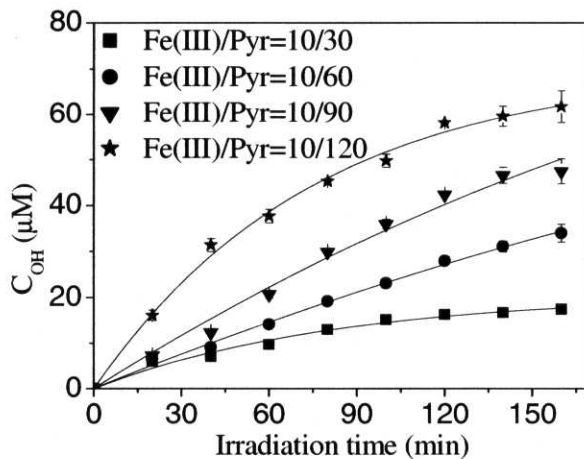


**Fig. 4.** Effect of the initial pH value on the total  $\cdot\text{OH}$  yield for an aqueous solution with  $C_{\text{Fe(III)}} = 30 \mu\text{M}$ ,  $C_{\text{Pyr}} = 60 \mu\text{M}$ . Solid lines are 1-exponential fits for curves with pH = 1.5, 2.0, 3.0 and average values for pH = 4.0 and 5.0

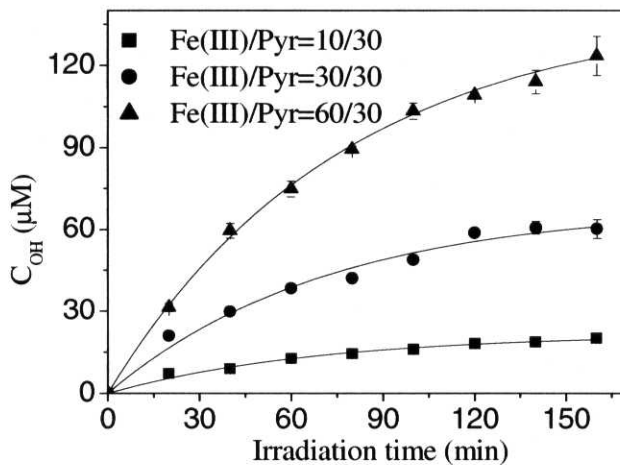
We believe that the influence of pH on the photolysis of the Fe(III)-Pyr complex could be explained by two reasons. First, pH can affect the distribution of different species (Fe(III) complexes and pure pyruvic acid) present in the solution. These species [(Fe(III)-Pyr,  $\text{Fe}(\text{OH})^{2+}$ ,  $\text{Fe}(\text{OH})_2^+$ ,  $\text{Fe}^{3+}_{\text{aq}}$ , pyruvic acid] possess different photochemical reactivity, and it would affect the  $\cdot\text{OH}$  yield. Secondly, pH can influence the rates of reactions 4 and 5, which control the  $\cdot\text{OH}$  formation rate.

### Effect of Fe(III) and Pyr concentrations on the $\cdot\text{OH}$ yield

The concentration ratio Fe(III) / Pyr is another important factor. To evaluate this factor, the experiments in solutions with pH = 3.0 were performed. Results



**Fig. 5.** Effect of the Pyr concentration on the  $^{\bullet}\text{OH}$  total yield for aqueous solutions with  $C_{\text{Fe(III)}} = 10 \mu\text{M}$ . Initial pH of the aqueous solution  $3.0 \pm 0.1$ . Solid lines are 1-exponential fits



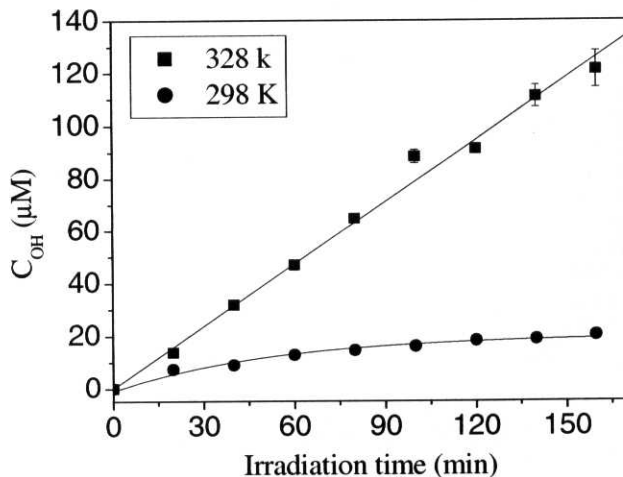
**Fig. 6.** Effect of Fe(III) concentration on the  $^{\bullet}\text{OH}$  total yield for aqueous solutions with  $C_{\text{Pyr}} = 30 \mu\text{M}$ . Initial pH of the aqueous solution  $3.0 \pm 0.1$ . Solid lines are 1-exponential fits



are shown in Figs 5 and 6. It can be concluded that both the Fe(III) and Pyr concentrations affect the  $\cdot\text{OH}$  yield. The  $\cdot\text{OH}$  concentration increased with an increase in the Pyr concentration in the range from 30.0 to 120.0  $\mu\text{M}$ , or with an increase in the Fe(III) concentration in the range from 10.0 to 60.0  $\mu\text{M}$ . At a given pH value, a change in the Fe(III) / Pyr ratio can lead to a change in the relative content of different Fe(III)(Pyr)<sub>x</sub> ( $x = 1, 2$ ) complexes in the solution. When the Pyr concentration was much higher than that of Fe(III), the direct photolysis of Pyr could affect the  $\cdot\text{OH}$  yield. In turn, when the Fe(III) concentration is relatively higher than that of Pyr, Fe(III) species in the solution can promote the  $\cdot\text{OH}$  yield in a continuous Fe(III)/ Fe(II)/ Fe(III) cycle. At pH = 2.0–5.0, Fe(III) will participate in the so-called photo-Fenton reaction. Fe(OH)<sup>2+</sup> is thought to be the predominant photoactive species in the pH range 2.5–5.0.

### Effect of temperature on the $\cdot\text{OH}$ yield

To examine the effect of temperature on the quantum yield, experiments were performed at 298 and 328 K. Results are shown in Fig. 7. The  $\cdot\text{OH}$  yield at 328 K was much higher than that at 298 K. Although higher temperatures will hasten the main reactions, they can also enhance side reactions.



**Fig. 7.** Effect of temperature on the  $\cdot\text{OH}$  total yield for an aqueous solution with  $C_{\text{Fe(III)}} = 10 \mu\text{M}$ , and  $C_{\text{Pyr}} = 30 \mu\text{M}$ . Initial pH of the aqueous solution  $3.0 \pm 0.1$ . Solid curves are the linear fit for 328 K and the 1-exponential fit for 298 K

## CONCLUSIONS

In this study, we investigated the photochemical reactivity of Fe(III)-Pyr complexes and determined the amount of  $\cdot\text{OH}$  produced by the photolysis of the Fe(III)-Pyr complexes in the aqueous solution. It was found that the Fe(III)-Pyr system is not catalytic. In the aqueous solution containing 10.0  $\mu\text{M}$  of Fe(III) and 60.0  $\mu\text{M}$  of Pyr at pH = 3.0,  $\cdot\text{OH}$  was produced after 160-min irradiation in amount of 34  $\mu\text{M}$ . The generation rate constant of  $\cdot\text{OH}$  was 0.21  $\mu\text{M L}^{-1} \text{min}^{-1}$  and the quantum yield of  $\cdot\text{OH}$  was  $2 \times 10^{-2}$ . The study confirms that pH, temperature, concentration of the Fe(III) and Pyr, all have a great effect on the  $\cdot\text{OH}$  yield. Pyr and many other carboxylates can form complexes with Fe(III) and other metal ions in aqueous solutions. Especially in natural waters, these complexes can potentially use sunlight as the irradiation source to produce reactive species, such as  $\cdot\text{OH}$ , which would play an important role in the oxidation of organic materials.

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