New insights into the mechanisms of the thermal Fenton reactions occurring using different iron(II)-complexes

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Abstract Although the Fenton reagent (a mixture of hydrogen peroxide and an iron(II) salt) has been known for more than a century, the manifold mechanisms occurring during the thermal Fenton reaction are still under discussion. Indeed, this discussion served as a powerful driving force for the steadily increasing insight into the field of inorganic radical and electron transfer chemistry. In this work, an experimental approach towards the elucidation of the first steps taking place in the reaction between several iron(II)-complexes and hydrogen peroxide (H$_2$O$_2$) in water at pH = 3.0 is presented. 2,4-xylidine (2,4-dimethylaniline) reacts differently with reactive intermediates via the addition or hydrogen abstraction by the hydroxyl radical (HO·) or electron transfer reactions to higher valent iron-species, such as a hydrated ferryl-complex (Fe(IV)). The chemical reactivity of the employed iron(II)-complexes with H$_2$O$_2$ differed strongly depending on their ground-state one-electron oxidation potentials. The results are interpreted in accordance with the paradigm originally developed by Goldstein et al. which is based on the evidence obtained from the Marcus theory that outer-sphere electron transfer reactions between metal complexes are not likely to occur because they are too slow. Therefore, most of the “Fenton-reagents” form transient metal complexes, which can be described as [Ln–Fe–H$_2$O$_2$]$^{m+}$. They form, depending on the reaction conditions, either the hydroxyl radical or higher-valent iron complex species.

Keywords Ferryl species; homogeneous photocatalysis; hydroxyl radical; mechanistic elucidation; thermal Fenton reaction

Introduction

Although the Fenton reagent (a mixture of hydrogen peroxide and an iron(II) salt) has been known for more than a century and has long been proven to be a powerful oxidant, the mechanism of the Fenton reaction is still under intense discussion. According to the classic interpretation of the Fenton reaction, the reaction of iron(II) with hydrogen peroxide (H$_2$O$_2$) in aqueous solution leads to the formation of an hydroxyl radical (HO·) (see Walling, 1998 for a detailed account).

$$\text{Fe}^{2+}_{\text{aq}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+}_{\text{aq}} + \text{HO}^+ + \text{HO}^- \quad (1)$$

However, an alternative to the classic interpretation of the Fenton reaction consists in the formation of a ferryl complex (Fe(IV), denoted as Fe$^{4+}_{\text{aq}}$ in the equation below) or a ferrate (Fe(V) or Fe(VI)) as intermediate iron-species. Several research groups found experimental evidence for the prevailing of an intermediate of the Fenton reaction, which differs from the hydroxyl radical. Various very different methods led to this conclusion (Koppenol, 1985; Rush et al., 1990; Wink et al., 1994; Bossmann et al., 1998; Pignatello et al., 1999).

$$\text{Fe}^{2+}_{\text{aq}} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{4+}_{\text{aq}} + 2\text{HO}^- \quad (2)$$
In contrast to the hydroxyl radical, which is very short lived, the ferryl species is a rather long-lived intermediate (Rush and Bielski, 1986), which is able to react with organic substrates via a diffusion controlled electron transfer mechanism. 2,4-xylidine can serve as an ideal model substrate, because the reaction products formed during the thermal Fenton reaction are indicative of the nature of the prevailing redox intermediate: if the hydroxyl radical is formed, hydroxylated amines can be detected using GC/MS analysis. However, if the ferryl species prevails, 2,4-dimethylphenol is generated (Bossmann et al., 1998). It must be noted that the detection of radicals during the thermal Fenton reaction (Walling, 1998; Ingold et al., 1998) is not necessarily indicative of a reaction pathway according to Eq. (1). A manifold of thermal reactions takes place, which is able to generate radical intermediates without the participation of HO· or RO· radicals (Goldstein and Meyerstein, 1999).

This work presents the mechanistic elucidation of the oxidation of 2,4-xylidine by H$_2$O$_2$ employing various iron(II)-complexes as homogeneous Fenton catalysts possessing different ground state redox potentials of the redox couple Fe(II)/(III). Evidence for the participation of hydroxyl radicals as well as higher-valent iron-species (most likely a ferryl species), depending on the chemical nature of the homogeneous iron(II)-catalyst, was obtained.

**Methods**

**General, reactor and analysis procedures**

All reagents and solvents used were of the highest purity available and were purchased from Aldrich and Fluka. H$_2$O was of tridest. quality (UHQ-II). The Fenton experiments were carried out in a pilot reactor (V$_{\text{total}}$ = 3.50 L; V$_{\text{experimental}}$ = 2.0 L). The experimental setup is described in detail in the literature (Bossmann et al., 1998). The concentrations of 2,4-xylidine and of iron(II) were 0.052 mol L$^{-1}$ and 1.0 $\times$ 10$^{-3}$ mol L$^{-1}$, respectively. When iron(II)-complexes were used, the concentration of complexed iron(II) was 1.0 $\times$ 10$^{-3}$ mol L$^{-1}$ also. A 2,4-xylidine stock solution of pH = 2.0 was prepared using conc. sulfuric acid and diluted by a factor of 10 prior to use. All experiments were performed at 40 $\pm$ 1°C. H$_2$O$_2$ (0.09 mol L$^{-1}$) was added at once at the beginning of the reaction and was allowed to proceed for 30 min. The reaction system was purged with compressed air. The analysis was performed immediately after taking the samples (at 0, 1, 2, 5, 10, 20 and 30 min.), which were filtered using Nylon Luer-Lock-membrane filters (Roth, 0.22 $\times$ 10$^{-6}$ m). For quantitative HPLC-analysis an HP series II 1090 liquid chromatograph, equipped with a diode-array-detector (DAD) and a LiChrospher-100 RP 18 column and precolumn, were used (mobile phase: (0.10 mol L$^{-1}$ (C$_2$H$_5$)$_3$N/H$_3$PO$_4$ (pH = 7.0)/acetonitrile, 75:25 v/v)) for the determination of 2,4-xylidine and reaction intermediates.

**Synthesis of iron(II)-complexes.** K$_4$[Fe(CN)$_6$], Na[Fe(EDTA)], Na$_4$[Fe(oxalate)$_3$] and FeSO$_4$ $\times$ 7 H$_2$O were purchased. All other iron(II)-complexes were synthesized in situ by adding stoichiometric amounts of solid 2,2$'$-bipyridine, 1,10-phenanthroline, 4,4-dimethyl-2,2$'$-bipyridine and 4,7-dimethyl-1,10-phenanthroline to FeSO$_4$ $\times$ 7H$_2$O in H$_2$O, pH = 2.74.

**DP voltammograms.** All electrochemical experiments were performed with a computer interfaced potentiostat/galvanostat (Princeton Applied Research, model 263A and software 270) using a conventional one-compartment cell and three-electrode configuration. The redox potentials were determined from differential pulse voltammetric (DPV) data. The setting of the pulse amplitude was 50 mV, the scan rate 5 mV s$^{-1}$ and a platinum disc (diameter: 3 mm) was used as the working electrode. A saturated sodium calomel electrode...
(SSCE) was used as reference. Before each experiment, the electrolyte solutions were purged with argon.

**GC-MS/FTIR-analysis.** For the qualitative and quantitative analysis of the reaction products generated during the \( \text{H}_2\text{O}_2 \)-photolysis and both the thermal and the photochemically enhanced Fenton-reaction, the samples (2 ml) were injected into a GC [HP 5971A MSD] (mass selective detector), coupled with a HP 5965B ID (infrared detector). An HP-INNOWAX capillary column (cross-linked polyethylene glycol) was employed. All reaction products were identified by a combination of MS- and FTIR-spectroscopy in comparison with analytical data available from databases (MS: Wiley, Reference Mass-Spectra, 1990; FTIR: EPA, Reference FTIR-spectra, 1992). For the structural determination of the reaction products formed, samples of 2,4-xylidine, 2,4-dimethylphenol, 1-amino-2,4-dimethyl-3-phenol and oxalic acid were coinjected (dissolved in CHCl₃) and in all cases, a superposition of the corresponding peaks in the chromatograms was observed. Furthermore, calibration curves were recorded for the compounds listed above. In all cases, linear dependences of both the MS- and FTIR-peak areas were obtained.

**DOC.** The dissolved organic carbon was measured by means of a Dohrmann DC-190 analyzer.

**Calculation of the ionization potentials.** The calculations were performed employing the AM1 and Gaussian 98 software package (Gaussian, 1998). The optimizations were obtained using the UB3LP/6-31++g* method. The optimization of the geometry was followed by a frequency calculation, in order to exclude any imaginary frequencies.

**Results and discussion**

**The 2,4-xylidine method revisited**

The method of the chemical intermediate analysis formed in the reaction of 2,4-xylidine with either hydroxyl radicals or electron transfer intermediates was developed in 1998 (Bossmann et al., 1998). From the comparison of the reaction products of 2,4-xylidine formed during \( \text{H}_2\text{O}_2 \)-photolysis and the thermal, as well as the photochemically enhanced Fenton reactions, it was concluded that the redox intermediates differ remarkably. In Scheme 1, both principal pathways are summarized. Whereas in the presence of hydroxyl...
radicals (from H₂O₂-photolysis or any other chemical source of hydroxyl radicals) a mixture of hydroxylated amines is formed among other reaction products. 2,4-dimethylphenol is the first stable product occurring from electron transfer oxidation of 2,4-xylidine. Neither the photolysis of the starting material in the absence of the H₂O₂ nor the thermal reaction of 2,4-xylidine and H₂O₂ yielded comparable reaction products or reaction yields. In Figure 1 the typical product distribution resulting from both reaction pathways is shown. It becomes immediately clear that hydroxylated amines are only formed when the hydroxyl radical is generated as the reactive intermediate.

A new insight into the mechanisms of the interaction of hydroxyl radicals with aromatic hydrocarbons in water was obtained by time resolved resonance Raman spectroscopy (Tripathi, 1998). Depending on the ionisation potential (IP) of the molecule in water, two principally different reaction pathways for the hydroxyl radical exist. The first concludes that below the threshold of an IP of 7.0 eV, the hydroxyl radical reacts via electron transfer, which proceeds according to an addition/elimination mechanism (HO· adds to the aromatic ring system, immediately followed by the elimination of HO–). The second concludes that above an IP > 8, the addition of the hydroxyl radical to the aromatic ring system is the only observed reaction mechanism. Inbetween these thresholds, addition and electron transfer occur simultaneously. This rule was originally established for neutral molecules. The ionisation potential of aromatic hydrocarbons can be calculated employing the AM1/Gaussian 98 approach (Vedernikova et al., 1999; Feng et al., 2002). In Figure 1, a comparison between the ionisation potentials calculated for 6 aromatic hydrocarbons (1: diamino-benzene; 2: anisidine; 3: 2,4-xylidine; 4: phenol; 5: dimethoxy-benzene, 6: 2,4-xylidinium) and data from the literature is shown. It becomes clear that the majority of water-soluble benzene-derivatives reacts with the hydroxyl radical according to both principal mechanisms. At pH = 3.0, where the optimal reaction rates of the Fenton reaction are usually found, 2,4-xylidine is protonated to approximately 60 ± 5%, as was shown by electrochemical methods (Bossmann et al., 1998). Therefore, we have to take into account that both the protonated and the unprotonated form of 2,4-xylidine react with hydroxyl radicals, if they are present in the reaction system. The protonated form (2,4-xylidinium) possessing an IP > 8.0 eV, seems to be “out of reach” for electron transfer reactions to HO·; however, the corresponding base (2,4-xylidine) definitely lies within the region of coexistence of both mechanisms. In accordance with this theory, a mixture of 3 amino-dimethyl-phenols as

![Figure 1](https://iwaponline.com/wst/article-pdf/49/4/75/420792/75.pdf)
well as small amounts of 2,4-dimethylphenol were detected during the photolysis of H₂O₂ (production of hydroxyl radicals) in the presence of 2,4-xylidine in aqueous solution at pH = 3.0. Under such conditions, the small amount of 2,4-dimethylphenol found is most probably formed by electron transfer from the unprotonated 2,4-xylidine to H₂O₂. The mixture of amino-dimethyl-phenols arises from HO· addition to 2,4-xylidine as well as to 2,4-xylidinium. This result leads to the conclusion that the detection of a mixture of amino-dimethyl-phenols can be regarded as definite proof for the presence of the free hydroxyl radical. On the other hand, if 2,4-dimethylphenol is the only oxidation intermediate detected, then electron transfer can definitely be verified.

The thermal Fenton reaction in dependence on the redox potential of iron(II) complexes

In order to study the nature of the redox intermediates generated in the thermal Fenton reaction employing 2,4-xylidine as model pollutant, a series of 10 iron(II)-complexes possessing very different ground state redox potentials of the oxidation from iron(II) to iron(III) was investigated. Under the experimental conditions chosen here, pseudo-first-order decays of 2,4-xylidine were observed in each conducted experiment. From these disappearances of the starting material, apparent rate constants for the removal of 2,4-xylidine (−k₂₄ₓyl [s⁻¹]) were calculated. Furthermore, the chemical nature of the intermediates allowed the elucidation of the prevailing redox intermediate.

The experimental series summarized in Figure 2 reveals that the formation of both intermediates, the hydroxyl radical and the ferryl species (or other high-valent iron redox intermediates) depends on the formal oxidation potential of Fe(II/III). All iron(II)-polypyridyl complexes (as well as iron(II) aquo-complex) dissolved in H₂O react with 2,4-xylidine according to an electron transfer mechanism. All these complexes are found at the “positive branch” of Figure 3. Note that the dependence of the apparent rates of 2,4-xylidine removal are linearly dependent on the formal oxidation potential of Fe(II/III). In contrast, iron(II)-tris-oxalate, iron(II)-EDTA and iron-hexa-thiocyanate generate hydroxyl radicals as redox intermediates in the thermal Fenton reaction. Note that the efficiency of the thermal Fenton

![Figure 2](https://iwaponline.com/wst/article-pdf/49/4/75/420792/75.pdf)
reaction does not depend on the formal redox potential of the iron(II)-complexes in a straightforward manner. The highest efficiencies were found at the highest and the lowest redox potential investigated, belonging to \([\text{Fe(SCN)}_6]^{3–}\) and \([\text{Fe(phen)}_3]^{2+}\). Interestingly, those iron(II)-complexes react differently with \(\text{H}_2\text{O}_2\).

**Conclusions**

These experimental results strongly support the mechanistic paradigm originally developed by Goldstein *et al.* (1993). We interpret our findings as follows: all iron(II)-complexes investigated form transient metal complexes with \(\text{H}_2\text{O}_2\), which can be described as \([L_n\text{Fe–H}_2\text{O}_2]^{m+}\). The Markus theory predicts that inner-sphere electron transfer reactions are much more likely to occur because they are significantly faster than outer-sphere reactions. Therefore, electron transfer reactions from iron(II) to \(\text{H}_2\text{O}_2\) always proceed after coordination. In the first electron transfer step, iron(III) and a complex-coordinated hydroxyl radical is found. Depending on the reaction condition, it will either escape or perform a second oxidation step, in which the ferryl species and a complex-coordinated hydroxide anion will be generated. In this case, the substrate will react with the ferryl species.

**References**


