

# Photoinduced Mineralization of Xylidine by the Fenton Reagent. 2. Implications of the Precursors Formed in the Dark

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Xylidine (2,4-dimethylaniline, XYL) mineralization via photoassisted Fenton reactions was studied as a function of the solution parameters and the irradiation conditions. Complete mineralization was observed under medium Hg lamp, with a significant UV, component within few minutes but this was not the case when a solar simulator was used. A less efficient photodegradation of XYL in the presence of  $\text{Cl}^-$  anion was observed as compared to sulfate or perchlorate ions. The competition for the  $\text{Cl}^-$  ions occurring in XYL solutions upon addition of  $\text{Cl}^-$  ions is reported. During the XYL degradation, the photoactive iron complex intermediates that formed in the dark, but not the organic intermediates, are responsible for XYL degradation after the initial induction period.

## Introduction

Photoinduced reactions used in environmental detoxification have attracted considerable interest in recent years (1–3). The photoassisted Fenton reaction as a source of  $\text{OH}^\bullet$  radicals has shown to be effective in the photodegradation of nonbiodegradable contaminants (3–6). The photoassisted Fenton reaction accelerates the degradation rates of many organic pollutants, e.g., herbicides (7) compared with dark Fenton processes. Other more traditional methods for the elimination of amino aromatics, phenols, halocarbons, and PAHs have recently been reported in the literature (1–3). But these methods are nondestructive and involving adsorption, air stripping, chlorination, and flocculation/filtration. In this study we investigate the photodegradation of XYL, a toxic nonbiodegradable intermediate found in the chemical, pharmaceutical, and pigment industries (8). The optimal conditions for the accelerated photodegradation of XYL by photoassisted Fenton reactions, the role of the intermediates formed in the dark, and the effect of the  $\text{Cl}^-$  ion during photodegradation is explored complementing Part 1 of this study (3).

## Experimental Section

**Reagents.** XYL,  $\text{H}_2\text{O}_2$ ,  $\text{FeCl}_3$ , iron sulfate, and iron perchlorate were Fluka p.a. and used without further purification. The consumption of  $\text{H}_2\text{O}_2$  in solution was monitored by with a Merck peroxide test (Merkoquant) in the range 0.2–25 mg/L.

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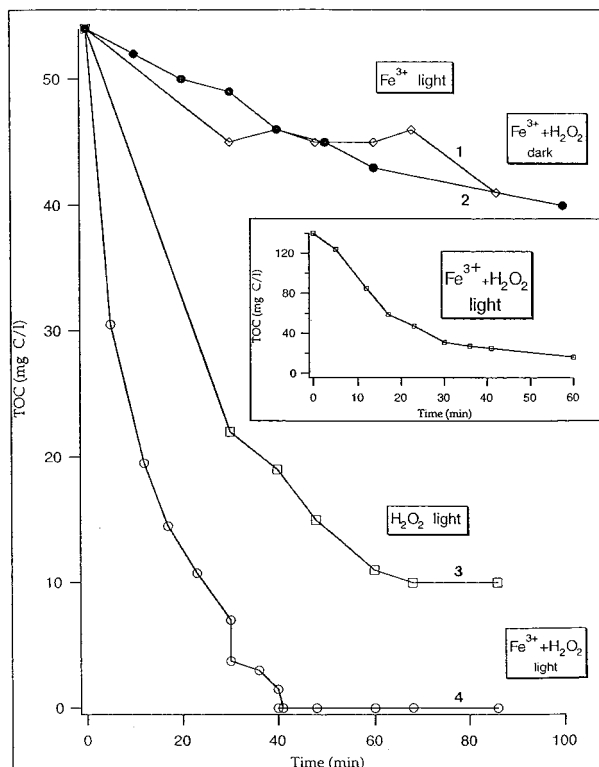


FIGURE 1. TOC degradation and photodegradation of XYL (0.58 mM) by medium-pressure Hg lamp. Solutions were  $\text{Fe}^{3+}$  (3 mM) and  $\text{H}_2\text{O}_2$  (40 mM). See text for other experimental details.

**Analyses and Methods.** Spectrophotometric analysis was carried out by means of a Hewlett-Packard 8452A diode array. The total organic carbon (TOC) during the reaction was monitored via a Shimadzu 500 instrument equipped with an ASI 502 automatic sample injector. High-pressure liquid chromatography (HPLC) was carried out via a Varian 5500 unit provided for with a Spherisorb ODS-2 column. Signals for XYL were detected at  $\lambda = 260\text{--}2\text{ nm}$  with a retention time of 20.1 min, using a gradient of acetonitrile/water. When  $\text{Fe}$ –XYL complexes were analyzed in solution, the peaks in the HPLC spectrogram could not be separated and identified due to the absorption of  $\text{Fe}^{3+}$ /XYL– $\text{Fe}^{3+}$  occurring in the same spectral region as XYL. Detection of  $\text{CO}_2$  was performed via a Gow-Mac instrument, using Ar as carrier gas and a Poropak Q column.

**Irradiation Procedures.** The irradiation of the solutions was carried out in Pyrex cylindrical flasks (60 mL volume) transmitting light at  $\lambda > 290\text{ nm}$ . Two types of lamps were used (a) a Hanau Suntest solar simulator with  $90\text{ mW/cm}^2$ , having  $\sim 8\%$  of the total light flux below  $400\text{ nm}$ , and (b) a Hg medium-pressure lamp ( $250\text{ mW/cm}^2$ ). The radiation of these lamps was filtered through a circulating water cuvette ( $d = 6\text{ cm}$ ) which helped to maintain the solution's temperature by avoiding warming (over  $\sim 2^\circ\text{C}$ ) caused by the infrared component of the incident light. The radiant flux was measured with a power meter of Yellow Springs, CO.

## Results and Discussion

**i. Accelerated XYL Photodegradation in Oxidative Media.** Figure 1 presents the features of the dark- and light-induced

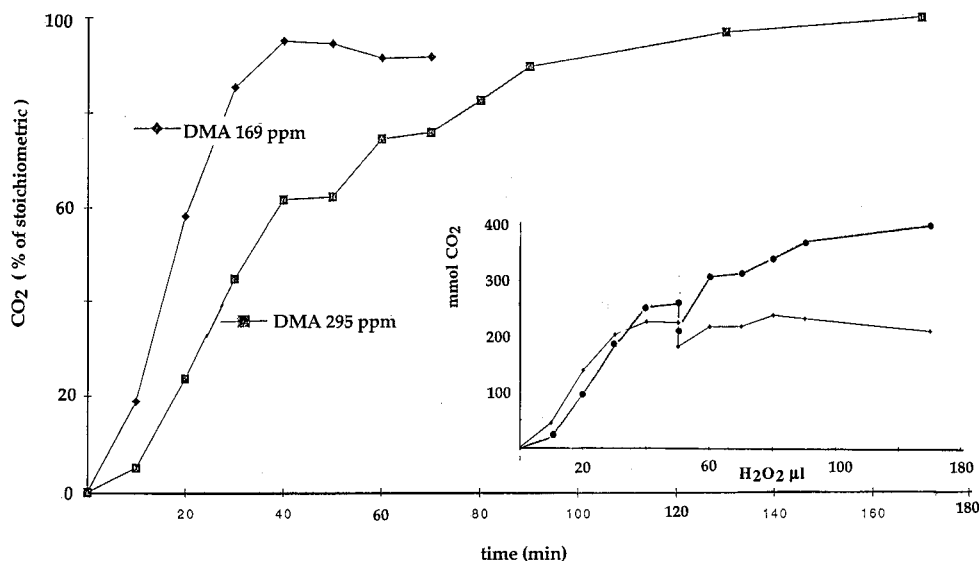


FIGURE 2. CO<sub>2</sub> formation for XYL solutions as a function of light with a medium-pressure Hg lamp using the same solution as in Figure 1. The inset shows CO<sub>2</sub> formation as a function of H<sub>2</sub>O<sub>2</sub> consumed.

(medium-pressure Hg lamp) degradation of a solution of XYL (0.58 mM) at pH 2.5 under a variety of experimental conditions. Figure 1 (trace 1) shows that only a small reduction in the TOC is observed for XYL solutions adding Fe<sup>3+</sup> ion (3 mM) under light irradiation. Trace 2 shows the TOC reduction when the Fenton reagent (Fe<sup>3+</sup> + H<sub>2</sub>O<sub>2</sub>) was added in the dark. A significant acceleration in the degradation rate was observed when H<sub>2</sub>O<sub>2</sub> was added alone under light irradiation. Approximately 85% of the initial XYL was seen to photodegrade (trace 3). Fenton photoassisted reactions led to XYL mineralization within ~40 min (trace 4). H<sub>2</sub>O<sub>2</sub> aliquots were seen to be consumed in ~5 min after being added, and the detection was carried out by the Merckoquant test (see Experimental Section). The Fenton photoassisted reaction involves complexes between the Fe<sup>3+</sup> ion and the organic substrate (9–11) and 'OH/HO<sub>2</sub>' radicals (12–14). The inset in Figure 1 shows a longer XYL photodegradation time at higher XYL concentration. The observed kinetics did not follow pseudo-first-order kinetics, revealing a more complex photodegradation pattern.

Figure 2 shows the mineralization of XYL/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> under Hg lamp irradiation and the same experimental conditions as in Figure 1 (trace 4). The CO<sub>2</sub> generation occurs within the time reported for TOC reduction (Figure 1), excluding the formation of long-lived transients in solution. As expected the reaction time is seen to be longer as the initial XYL concentration is increased. The inset in Figure 2 shows the CO<sub>2</sub> evolution vs the total H<sub>2</sub>O<sub>2</sub> added during irradiation. A stoichiometric ratio [H<sub>2</sub>O<sub>2</sub>]/[XYL] ≈ 26–30 was observed during the mineralization for the two concentrations of XYL in Figure 2.

**ii. Photoactive Intermediates Formed during Reactions in the Dark.** Figure 3a shows the TOC decrease in the dark for a solution of XYL/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> with the same composition as in Figure 1. The reduction of TOC values is significant up to ~70 min. The dark oxidation only leads to 40–45% reduction in the TOC values within ~8 h. The dark, initial degradation seems to produce an intermediate in solution that precludes further degradation. In Figure 3b, light irradiation is applied for 10 min after ~1200 min dark reaction (see arrow). Complete mineralization is observed under these conditions after only a few minutes irradiation with a medium-pressure Hg lamp. But only partial mineralization was observed with a Suntest solar simulator with 40% of the residual TOC remaining in solution since the UV component

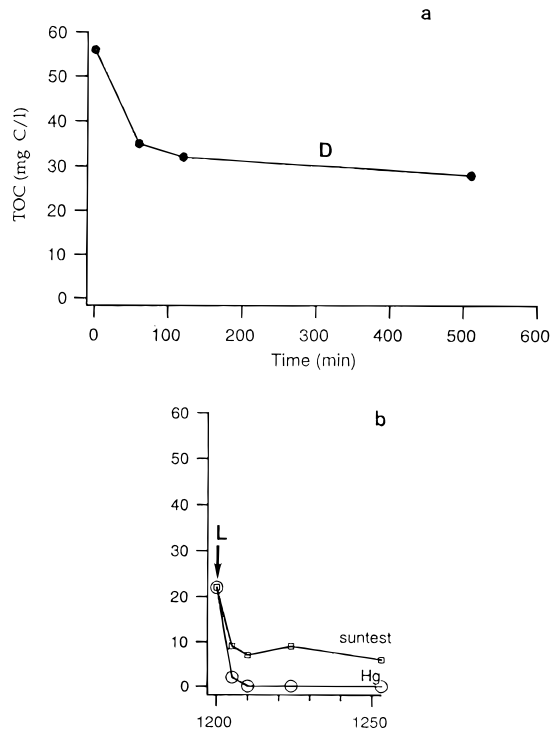


FIGURE 3. (a) TOC decrease vs time observed during XYL degradation in the dark, for the same solution as used in Figure 1. (b) TOC decrease vs time for the intermediate(s) after 20 h dark reaction. At times (L, see arrow), the Suntest lamp or medium-pressure Hg lamp was applied for 10 min.

of the applied light was absent. The nature of the dark intermediates for subsequent light-induced decomposition (Figure 3b) was tested in the following way: Iron is removed from suspension by adding 0.1 N NaOH until the solution becomes basic. The solution was then separated from the precipitate by filtering. The iron-free solution was then acidified to pH < 3 and reused but no degradation was observed as shown before in Figure 3b. This suggests the formation of dark intermediates involving Fe–XYL, and not purely organic intermediates of XYL, is necessary for further photodegradation. Oxalic acid formation was also detected by HPLC during photodegradation. This acid would at latter

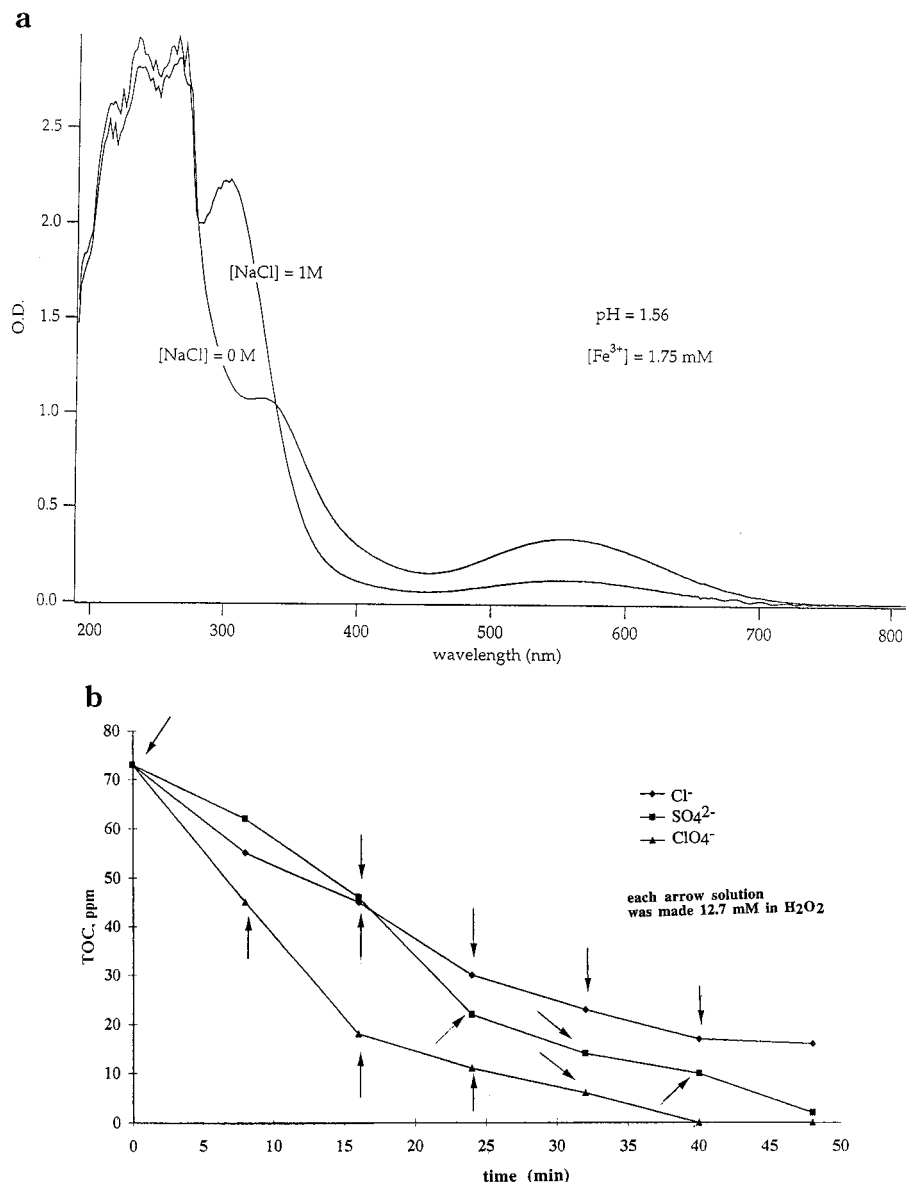


FIGURE 4. (a) Effect of NaCl on the spectra of XYL (24 mM, saturated) and FeCl<sub>3</sub> (0.90 mM) solutions at pH 1.56. (b) Effect of different counterions during the photodegradation of a XYL solution as used in Figure 1.

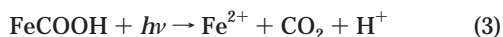
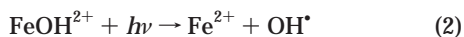
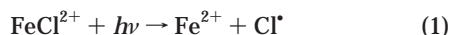
stages compete with H<sub>2</sub>O<sub>2</sub>, OH<sup>•</sup>, or Cl<sup>-</sup> in solution during XYL degradation.

**iii. Effect of the Counterion during XYL Photodegradation.** Figure 4a shows that in the presence of ferric chloride, the XYL forms a visible absorption band having a maximum around  $\lambda = 550$  nm. This visible band is attributed either to the initial complexation of Fe<sup>3+</sup> ions by XYL or to the XYL oxidation products generated during the photodegradation. This band has a half time of formation of  $\sim 3$  h and is seen to increase at  $\lambda = 315$  nm upon Cl<sup>-</sup> ion addition with a concomitant decrease at  $\lambda \approx 550$  nm. To explore the nature of the band at  $\lambda = 550$  nm, identifying experiments were carried out and the results are as follows: (a) Bands having a pronounced absorption in the presence ferric ions disappeared completely upon addition of oxalate, a strong ferric ion complexing agent. (b) Ferrous salt addition did not induce any absorption bands added to XYL. (c) Oxygen did not have any effect on the rate of formation of this band. (d) An isomer of XYL like 3,5-dimethylaniline did not induce this band in the presence of ferric ions. Assuming that a complex between ferric ion and aniline is formed, a spectra similar to the one reported in Figure 4a for 2,4-dimethylaniline

and 3,5-dimethylaniline should have been formed. But only significant differences in the spectra were observed for the ferric ion spectra with respect to the last two anilines. (e) Addition of ferric-ions to a phenol solution showed an absorption band around  $\lambda = 550$  nm immediately after mixing. The colored complex of phenols and ferric ions is known to be a qualitative test for phenol compounds (15). And finally, (f) the spectra of solutions of XYL (20 mM) and FeCl<sub>3</sub> (1 mM) did not show any changes up to 15 days. The oxidation of the XYL to phenol and the subsequent complex formation seems therefore to be a slow process. This agrees with the slow growth kinetics observed for the band at  $\lambda = 550$  nm.

Figure 4b shows the effect of the counterion anion of the Fe<sup>3+</sup> salt used on the photodegradation of XYL with a medium-pressure Hg lamp. The photo-Fenton degradation in the presence of FeCl<sub>3</sub> shows a residual TOC after  $\sim 50$  min (Figure 4b). Laser photolysis in part 1 (3) showed that the degradation of XYL involves the Cl<sup>-</sup> anions in solution. The perchlorate ion was selected in Figure 4b since it is non-complexing toward iron ions (2-4) and the sulfate ion was tested since sulfate salts are usually used in Fenton-type

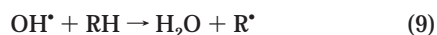
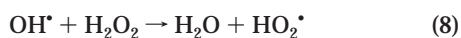
processes (1, 5). The presence of  $\text{Cl}^-$  ions during the photolysis of  $\text{XYL}/\text{Fe}^{3+}$  suggest the reactions



and the main reactions of  $\text{Cl}^{\bullet}$  atoms (3)



Similar reactions occur involving the  $\text{OH}^{\bullet}$  radical:



The rate constant  $k_6$  and  $k_9$  are close to the limit of diffusion-controlled reactions (1, 3). In reactions 5 and 8, the  $\text{HO}_2^{\bullet}$  radical is formed but its reactivity toward the oxidation of organic compounds is low (1, 2, 17). At the same time  $k_5$  is  $1.8 \times 10^{10} \text{ (M s)}^{-1}$ , whereas  $k_8$  is  $(1.7-3.7) \times 10^7 \text{ (M s)}^{-1}$ . Since the value of  $k_8$  is low relative to  $k_9$ , the  $\text{OH}^{\bullet}$  radical reacts mainly with RH as indicated above in eq 9. The  $\text{Cl}^{\bullet}$  reaction with  $\text{H}_2\text{O}_2$  (eq 5) has been found to be fast (3). Consequently the  $\text{H}_2\text{O}_2$  consumption during XYL degradation is due to radical attack and  $\text{Cl}_2^{\bullet-}$  reacting with  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^{\bullet}$ . The latter species does not play a significant role during XYL degradation since  $\text{HO}_2^{\bullet}$  is a slow oxidant in solution (1-5). Equation 9 involves  $\text{OH}^{\bullet}$  addition to the benzene ring. The rate constants of hydroxyl radicals  $\text{OH}^{\bullet}$  with aromatics (RH) are known to be close to the diffusion-controlled limit. Therefore, reaction 9 will not be the rate-determining step during XYL mineralization. This observation suggests that iron complexes are the main precursors leading to  $\text{OH}^{\bullet}$  radical production during XYL degradation and provides some rational for the less efficient photodegradation of XYL in the presence of ferric chloride.

In conclusion XYL was mineralized rapidly under the experimental conditions by photoassisted Fenton reactions using a medium-pressure Hg lamp. Suntest solar simulated radiation was not efficient for total XYL abatement due to the lack of the UV light component. The dark oxidation of XYL is slower relative to other aromatic ring containing substances like Orange II, coumaric acid, or nitrophenols as observed recently in our laboratory (3, 6, 11). This indicates a higher stability of the intermediates produced during the dark induction period in the case of XYL as compared to the latter three substances. Dark oxidation of XYL produced photoactive intermediates which underwent full decomposition only under UV irradiation.

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