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Photoaccelerated oxidation of chlorinated phenols†

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Exposure to visible light increases the rate of oxidation of chlorinated phenols by hydrogen peroxide in aqueous solution in either the presence or the absence of iron-based catalysts, which may be explained by the aqueous photoreactions of chloroquinone intermediates.

Chlorinated phenols are used as wood preservatives, pesticides, or disinfectants, and they are also present in the waste of paper mills. Because of their toxicity and high persistency, these compounds are regarded as priority pollutants for which efficient chemical treatment processes are needed. Oxidative degradation is probably the most advantageous reaction type for this purpose and several different methods have been reported.[1–6] These methods usually use H_2O_2 or $KHSO_5$ as an oxidant and iron(II) or iron(III) complex catalysts with ligands such as TAML,[5] tetrasulfophthalocyanine,[2] or water soluble porphyrins,[1] although TiO_2-based systems for photodegradation[4,6] and ozonization[3] are also employed. 2,4,6-Trichlorophenol (TCP) is one of the most significant chlorinated phenols and is often used to test the efficiency of oxidative degradation methods.[2,5] In this paper, we report our findings about the effect of light on a broad class of oxidation reactions of TCP and other chlorinated phenols.

The uncatalyzed, very slow oxidation of TCP by H_2O_2 was monitored by UV-vis spectrophotometry (λ_{max} = 293 nm, ε = 2200 M^{-1} cm^{-1} for TCP) using the oxidant in large excess. In a sample kept in the dark, a 4% decrease in the concentration of TCP was observed over the course of 18 days. In contrast, an identical sample exposed to fluorescent room light showed a 23% decrease in TCP concentration under the same conditions.

The catalytic oxidation of TCP was monitored using a chloride ion selective electrode. Earlier work showed that Cl^- is produced from TCP during destructive oxidation almost quantitatively.[2,5] The iron catalysts used in this study were hexaaquairon(III), iron(III) *meso*-tetra(4-sulfonatophenyl)porphine ($Fe(TPPS)^+$), iron tetrasulfophthalocyanine,[2] the iron(II) complex of tris(2-pyridylmethyl)amine,[7] and the *cis*-cyclam complex of iron(III).[8] The use of these catalysts results in destructive oxidation of the chlorophenols, which is evidenced by the fact that total organic carbon measurements (depending on the particular system studied) showed that 35–60% of the original organic carbon content was converted to CO_2 after the completion of the reaction. In all of these systems, the rate of Cl^- formation during catalytic oxidation is faster in room light than in the dark, and it is much faster if the sample is illuminated with a lamp (500 W, halogen). Fig. 1 shows one experiment as an example where $Fe(TPPS)^+$ was used as a catalyst. The experiment was started in the dark. Exposure to room light after about 14 h resulted in a sudden 25% increase in the rate of Cl^- buildup (inset in Fig. 1). Direct illumination gave a 10-fold rate increase, which levelled off because a quantitative yield of Cl^- was obtained within 5 h after the illumination began. Similar light effects were observed when $KHSO_5$ was used as an oxidant instead of H_2O_2. All experiments were carried out without the addition of buffers in order to avoid possible interference from the oxidation of organic buffers or complexation of the catalysts with inorganic buffers. The pH decreased from 4.6 to 2.7 in the experiment shown in Fig. 1. However, the acid produced in the reaction is not an important factor. In fact, experiments showed that the rate of the reaction was pH-independent in this pH range in the most intensely studied $Fe(TPPS)^+/H_2O_2$ system. It should also be noted that the light effect was caused primarily by visible light, as the lamp was shown to have very little emission in the UV (the emission spectrum of the lamp is given in Fig. S2 of ESI†), and all experiments were done in pyrex glassware.

Efforts were made to identify the source of light sensitivity in these systems. Stock solutions of TCP, H_2O_2 and the catalysts were stable in room light for months as evidenced by UV-vis spectroscopy. Photo-Fenton effects reported in recent literature[4] do not explain our observations for several reasons. The complexes used here, except hexaaquairon(III), do not catalyze decomposition of H_2O_2 and they usually activate H_2O_2 toward selective oxidations.[1,7,9,10] The catalysts, except $Fe(TPPS)^+$, do not have absorption in the visible region at the low concentration levels used in this study. Indeed, the samples were initially colorless, but they turned pink as the oxidation proceeded. The light effect was also observed in the uncatalyzed oxidation of TCP by H_2O_2 and in the $Fe(TPPS)^+/HSO_5^-$ system, where Fenton chemistry is not expected. These facts strongly suggest that the origin of the light sensitivity is a colored intermediate in all of the studied systems.

The major product of the chemical oxidation of TCP in non-aqueous solvents with oxidizing agents such as PbO_2, or CrO_3 is 2,6-dichloro-1,4-benzoquinone (DCQ).[11] DCQ is usually

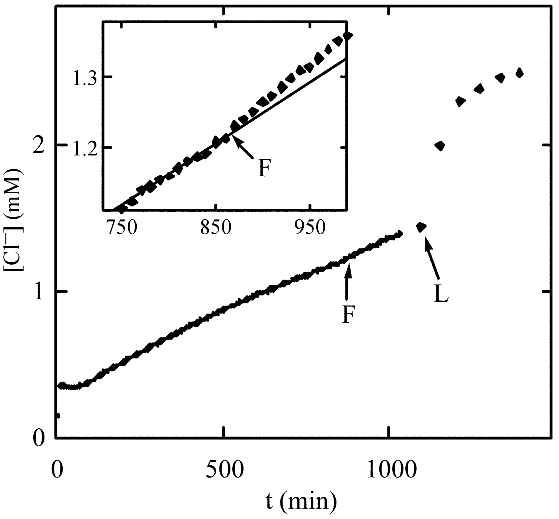

Fig. 1 Effect of light on Cl^- formation during the oxidation of TCP by $H_2O_2/Fe(TPPS)^+$. $[TCP]_0$ = 0.83 mM, $[H_2O_2]_0$ = 50 mM, $[Fe(TPPS)^+]_0$ = 5.0 μM, T = 25.0 °C, μ = 0.1 M ($NaNO_3$); F = fluorescent room light turned on; L = halogen lamp turned on. Inset: part of the curve between 700 and 1000 min showing the accelerating effect of room light.

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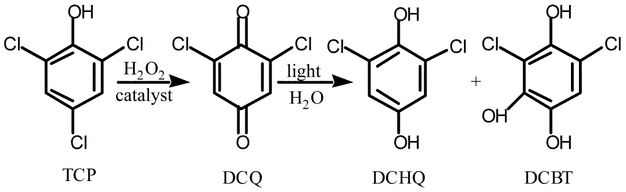
also implicated as a major intermediate of the destructive oxidation of TCP.[2] In citrate buffer and CH_3CN solvent, DCQ was a final product of TCP oxidation with $KHSO_5$ or H_2O_2 using $Fe(TPPS)^+$ catalyst.[1] Our data showed that the same catalytic system in unbuffered aqueous solution gives destructive oxidation and an almost quantitative yield (> 95%) of Cl^- from TCP. Quinones are usually colored (the absorption spectrum of DCQ is given in Fig. S14 of ESI†) and known to undergo a variety of photoinduced reactions,[12] and we hypothesized that the formation of DCQ as an intermediate may explain the photoacceleration.

Indeed, DCQ was shown to undergo light-induced reactions in water, the major final product of which is 2,6-dichlorohydroquinone (DCHQ), but a small amount of 3,5-dichloro-1,2,4-benzenetriol (DCBT) is also formed. Thus, the early phase of the oxidation can be summarized as:



To study the photoreaction, an aqueous solution of DCQ (2 mM) was illuminated with the lamp, and changes in this sample were monitored by different on-line methods. Considerable spectral changes were seen within 5 minutes as the yellow color of the solution darkened and new resonances appeared in the NMR spectrum. No Cl^- was produced in any detectable amounts (> 10 μM) during the photoreaction. Small amounts of an intermediate, identified as 3,5-dichloro-2-hydroxy-1,4-benzoquinone (DCHB), were detected by both ^1H NMR and UV-vis spectroscopy. This intermediate is not surprising as a reaction between DCQ and DCBT is expected to form DCHB and DCHQ based on redox potentials.[13] DCHB is also expected to give DCBT in a photoreaction similar to that of DCQ. A sample exposed to room light showed quite similar but slower changes. A sample kept in the dark did not change for several hours. After spectral changes were no longer seen in the illuminated sample (10–12 h), water was evaporated and ^1H NMR, ^{13}C NMR and MS were used to identify the remaining solid as DCHQ along with a small amount (~ 5–10%) of DCBT and even smaller amounts of unidentified byproducts. A standard sample of DCHQ was also prepared independently[14] and used to confirm the identity of the photoreaction product. No significant amount of H_2O_2 was found in the final aqueous solution. However, a 60% increase in the concentration of dissolved O_2 was detected in the sample after 10 minutes of illumination strongly suggesting that water is oxidized to molecular oxygen by DCQ in the photoreaction.

Similar photoreactions with quinones have been reported in the literature. The photoreaction of 1,4-benzoquinone in water gives 1,2,4-benzenetriol (63%) and hydroquinone (37%).[15] A recent study on the photochemical oxidation of water by 2-methyl-1,4-benzoquinone provided evidence against the involvement of free hydroxyl radical.[16] It is reasonable to assume that other quinones will show similar reactions and light sensitivity can be expected whenever quinones are intermediates in aqueous processes.

To extend our experimental observations for chlorinated phenols other than TCP, it was shown that the oxidations of 2,6-dichlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, and 2,3,4,6-tetrachlorophenol by $H_2O_2/Fe(TPPS)^+$ are also subject to light effects similar to that observed for TCP. The source of the light sensitivity may be very similar in these cases. To test the internal consistency of our interpretation, we oxidized DCQ and DCHQ with $H_2O_2/Fe(TPPS)^+$. These reactions were also accelerated by illumination. The rate of Cl^- formation was very similar for DCQ and DCHQ oxidation. This is not surprising as DCHQ is likely to be oxidized to DCQ rapidly under catalytic conditions. Because the photoreaction of DCQ does not produce Cl^- either in the presence or in the absence of TCP, the photochemical effect during the oxidation of TCP may be that DCBT is oxidized by $H_2O_2/Fe(TPPS)^+$ much faster than DCQ. Thus light helps the oxidation to proceed from DCQ to form further oxidized products. Oxidation of DCQ seems to be a slow step in the catalytic system, and it is quite possibly the overall rate controlling step.

In conclusion, we have shown that the rate of oxidation of chlorinated phenols in water is enhanced by visible light most probably because of the light sensitive quinone intermediates. Any mechanistic study of these reactions should take this fact into account and experimental procedures should be designed accordingly. Without adequate precaution, a photochemical reaction could be easily mistaken for a thermal reaction. In addition, it can also be postulated that exposure to light (even sunlight) in possible industrial waste treatment methods may considerably help the oxidation of chlorinated phenols.

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