A Novel Catalyst Iron(II) Tetra(1,4-dithin)porphyrazine for Oxygenating Degradation of Organic Pollutants in Aqueous Solutions

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(Received August 11, 2003; CL-030742)

An efficient catalyst of the title complex (abbreviated as FePz(dtn)$_4$) is a porphyrin-like complex, which is able to activate molecular oxygen for oxidative degradation of organic compounds in an extensive pH region without light excitation. The experiments indicated that the FePz(dtn)$_4$/O$_2$ system showed an excellent oxygenation capability, in which the Rhodamine B(RhB) was degraded nearly 52% in alkaline aqueous solution in the seven hours and the *p*-nitrobenzoic acid(NBA) could be also oxygenated nearly 85% detected by UV–vis, HPLC in the similar conditions. The degradation components of RhB and NBA were analyzed by GC–MS and IR. The mineralization rate of RhB and NBA were 12 and 11.1% after reaction for 24 h respectively.

Metallo-porphyrazines (MPz) and relative derivatives are a kind of porphyrin-like complexes, which are of excellent stabilities to light, heat and chemicals and with easier synthetic procedure, so these molecules have potential applications in the cases of photo-sensitization, photo-catalysis, and molecular recognizing for exterior substrates.[1] Some experiments have shown that the iron(III) tetra-sulfo-phthalocyanine (Fe(PcS))/H$_2$O$_2$ system can efficiently degrade organic pollutants in a mixed aqueous solution with acetonitrile,[2,3] and an efficient degradation of organic pollutants employing (Fe(PcS))/H$_2$O$_2$ in aqueous solutions without acetonitrile and with visible light irradiation has also been observed.[4,5] However, these systems are not yet able to activate molecular oxygen for oxidative degradation of organic pollutants in aqueous solutions. Recently, a new complex photo-catalysis system with iron(II) bipyridine carried on ion-exchange resin as bio-mimetic oxygenase enzyme mode has been successfully developed,[6] which allows direct use of molecular oxygen dissolved in water for pollutants treatment with visible light at ambient temperature.

Here we report a novel catalyst, iron(II)–tetra(1,4-dithin)-porphyrazine (FePz(dtn)$_4$) carried on ion-exchange resin, which is used as bio-mimetic oxygenase enzyme to activate molecular oxygen for degrading the organic pollutants in the aqueous solutions. To our knowledge, this is the first report for activating molecule oxygen using the FePz(dtn)$_4$ in water without light excitation. The synthesis and characterizations of FePz(dtn)$_4$ are listed in the reference.[7] The oxygenation degradation of two non-biodegradable organic compounds, such as Rhodamine B (RhB) and *p*-nitrobenzoic acid (NBA) as the target pollutants have been studied in the presence of FePz(dtn)$_4$ at ambient temperature.

10.0 mg of FePz(dtn)$_4$ carried on the ion-exchange resin (Amberlite resin type CG400, size 200 mesh, FePz(dtn)$_4$/resin = 0.7%, w/w) was mixed in 5 mL of buffer (phosphate pH 6.86, citrate pH 3, or borate pH 9.2 were used respectively) with 5 mL RhB aqueous solution (1.0×10^{-5} mol/L) or 5 mL NBA aqueous solution (1.0×10^{-3} mol/L), respectively. The reaction mixtures were bubbled first with nitrogen for adsorption equilibration in the first 30 min, and then, the oxygenation reaction carried out in ambient temperature and under different pH conditions with constant bubbling of oxygen. Reaction processes were monitored by UV–vis spectroscopy (Perkin Elmer USA, Lamberda-Bio35) and HPLC (Hitachi L7000, Turner (Kromasil) C$_{18}$ column, Japan) after filtering the catalyst on the ion-exchange resin in the different time intervals.

The reaction products with unreacted reactant were analyzed by GC–MS (HP8986, HP-5MS column) or GC (GC-17AATF, OV225 column, Shimadzu, Japan) and by IR (Nexus 470 FTIR, USA) during different time intervals after filtering the catalyst and removing the water from the degraded species under the reduced pressure and treating the samples with esterifying or silicifying reagent.

The oxidative degrading trend of RhB described by UV–vis spectral changes (absorbance) with different oxygen-bubbling time intervals in the presence of FePz(dtn)$_4$ in borate buffer (pH 9.2) is shown in Figure 1, during which the absorption peak at 550 nm was decreasing gradually in the first 5 h, and an obvious dropping of this peak appeared at after 7 h, while the absorption peak around 200 nm rapidly increased corresponding with the peak at 550 nm decreasing. It means that the aromatic ring of the RhB has been broken during the oxygen bubbling and the formed smaller molecules have a large absorbance around the 200 nm. The peak further dropping around 200 nm during the oxygen bubbling appears the degraded species in mineralizing.

The degraded species of RhB in aqueous in the presence of FePz(dnt)$_4$/O$_2$ are also analyzed by IR spectroscopic changes

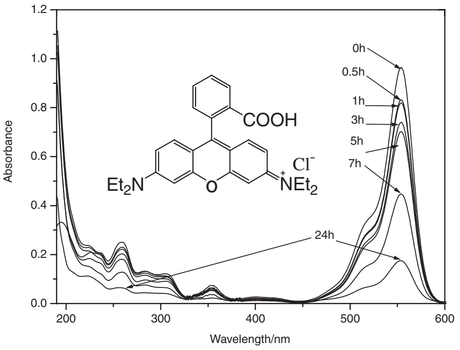

Figure 1. UV–vis spectral changes of Rodamine B (1×10^{-5} M) as a function of different oxygen-bubbling time interval in the presence of FePz(dtn)$_4$.

after oxygen bubbling for 24 h. There are some new absorption peaks to be observed, for example, the new strong absorption at 2360 cm^{-1} is attributed to –C≡N of an aliphatic fragment. The new strong absorptions between 2800–3100 cm^{-1} should be attributed to the stretch vibration of $-\mathrm{CH}_2-$ and $-\mathrm{CH}_3$ of aliphatic fragment cleaved from aromatic ring and the new strong absorptions at 1466 and 1389 cm^{-1} are attributed to their bend vibration. The new absorption at 3379 cm^{-1} is designated to some fragment containing –OH or –NH groups. The new absorption peaks of C–H bonds of di-substituted benzene are designated to 833 and 586 cm^{-1}, which appeared the benzopyran ring to have been fragmented. The absorption peak at 1713 cm^{-1} is attributed to a C=O group other than in the RhB at 1759 cm^{-1}, a strengthened absorption at this position means that there are some conjugated carboxylic fragments generated during the oxygenating degradation.

The fragmental species of the RhB in the oxygenation degradation were further confirmed by GC–MS analysis after reacting for 24 h and esterificating of the fragments in ethanol, in which there are nine peaks to be observed in the GC analysis. These fragments have been identified by MS analysis as degraded small molecules and some substituted benzenes, such as 1-isocyano-4-methylbenzene (Retention time $t_\mathrm{R} = 5.57$ min), 5-pyrrolidin-2-ylidenmethyl-3,4-dihydropyrorol-2-one ($t_\mathrm{R} = 6.21$ min), 2-furancarboxylic acid ($t_\mathrm{R} = 6.65$ min), 2-methyl-3-oxo cyclohex-1-enyloxyacetic acid ethanol ester ($t_\mathrm{R} = 9.15$ min), 4-methyl-2*H*-1-benzopyran-2-one ($t_\mathrm{R} = 12.25$ min), 3-methyl-3-phenyl-2-propenal ($t_\mathrm{R} = 14.36$ min), 5-hydroxytryptophan ($t_\mathrm{R} = 14.86$ min), 2-cyanohexanoic acid ethyl ester ($t_\mathrm{R} = 16.0$ min) and 5-hydroxy-1*H*-indole-3-ethanol ($t_\mathrm{R} = 20.24$ min). These fragmental species are rearranged oxidative products from RhB.

Combing the analyses of the GC–MS and IR data indicated that the oxygenation degradation of RhB in the presence of $\mathrm{FePz(dtn)_4/O_2}$ without light irradiation produced a broken of the pyran-ring and benzene ring to form small molecule species in the oxidative processes. The mineralization rate of RhB determined by chemical oxygen demand values ($\mathrm{COD_{Cr}}$ method[8,9]) is about 12% after reacting for 24 h. The catalytic activity of the $\mathrm{FePz(dtn)_4}$ in the degradation of RhB was maintained effectively after 10 recyclic experiments (ca. 40 h) if 7 h is as a cycle run. The IR spectra of the catalyst carried on the resin appeared no changes before and after 10 cycle runs. It means that the $\mathrm{FePz(dtn)_4}$ carried on the resin is able to be used repeatedly and stable, which is strongly adsorbed on the carrier without obvious desorption during the oxygenating degradation reaction. So the catalyst $\mathrm{FePz(dtn)_4}$ as bio-mimetic oxygenase enzyme to activate molecular oxygen dissolved in water for degrading organic pollutants is efficient at ambient temperature.

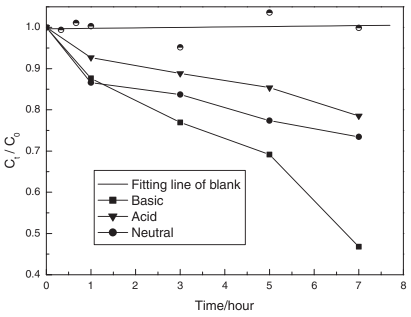

Figure 2. The variation of relative concentration of Rodamine B (1×10^{-5} M) versus different oxygen-bubbling time interval and different pH (citrate pH 3.0, phosphate pH 6.86, borate pH 9.18) in the presence of $\mathrm{FePz(dtn)_4}$, The fitting line in the top is a blank experiment in the absence of $\mathrm{FePz(dtn)_4}$ in borate buffer.

The variations of relative concentration of RhB versus different oxygen-bubbling time interval at different pH conditions in the presence of $\mathrm{FePz(dtn)_4}$ are shown in Figure 2, which indicates that the oxidative degradations of RhB were significant either in acidic and neutral aqueous, or in basic aqueous solutions. The degradation rates calculated from the variations of relative concentration of RhB with initial concentration (1×10^{-5} mol/L) are about 20–22% in acidic and neutral aqueous and 52% in basic aqueous solutions in the 7 h oxygen bubbling. It demonstrated that the $\mathrm{FePz(dtn)_4}$ as a kind of novel catalyst, is able to oxygenate degrading organic pollutants in an extensive pH conditions.

In order to further examine the role of $\mathrm{FePz(dtn)_4}$ in the oxygenation reaction, the degradation components of the NBA was also investigated by HPLC in the similar conditions. According to the peak intensity variations of the NBA during the oxygenating degradation, above 85% (in aqueous phase) of the NBA has been degraded by oxygen bubbling for 24 h in the presence of $\mathrm{FePz(dtn)_4}$. The IR data of the degraded species indicated that the benzene ring of the NBA has been broken by the catalysis oxygenation. Further, the GC data of the degraded products of the NBA silicified by chlorotrimethylsilane was compared with silicified standard samples to demonstrate that the NBA has been degraded to form small molecule compounds such as fumaric acid and maleic acid and mineralized products in the presence of $\mathrm{FePz(dtn)_4/O_2}$ system. The mineralization of the NBA is 11.1% after reacting for 24 h.

This work introduced a novel $\mathrm{FePz(dtn)_4/O_2}$ system, which can activate molecular oxygen and degradate toxic organic pollutants without light excitation in an extensive pH regions in aqueous solution at ambient temperature.

The work was supported by the National Science Foundation of China (No. 29771025) and (No. 20377053); The authors also appreciate for the support of The State Key Projection (No. 29833090).

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Published on the web (Advance View) December 15, 2003; DOI 10.1246/cl.2004.34