Angewandte Chemie

Water Treatment

Efficient Degradation of Organic Pollutants by Using Dioxygen Activated by Resin-Exchanged Iron(II) Bipyridine under Visible Irradiation**

*Wanhong Ma, Jing Li, Xia Tao, Ju He, Yiming Xu, Jimmy C. Yu, and Jincai Zhao**

The treatment of persistent organic pollutants in water by green chemical processes has been a very active research topic in recent years.[1] To mimic the oxidative characteristics of iron-containing oxygenase enzymes such as cytochrome P450 and non-heme methane monooxygenase (MMO), several synthetic analogues that allow the use of environmentally friendly oxidants (O_2 or H_2O_2) in pollution treatment have been developed.[2–8] For example, Meunier and coworkers reported that 2,4,6-trichlorophenol (TCP) in a CH_3CN/water solvent mixture could be efficiently degraded in the presence of H_2O_2 and iron phthalocyaninesufonate (FePcS), resulting in a 14% mineralization of TCP.[3,4] However, when water was used as the only solvent, the conversion rate was greatly decreased. Taking advantage of the strong absorption of FePcS in the visible range, we showed recently that visible-light irradiation can accelerate the degradation of salicylic acid, orange II, and rhodamine B in the presence of FePcS and H_2O_2 without the addition of CH_3CN.[7,8] In some organic synthetic processes, dioxygen can be used as an oxidant.[9,10] However, an additional reducing reagent such as zinc metal, ferrocene, ascorbate, or hydrogen/colloidal platinum is required in these systems to reduce the second oxygen atom of O_2 to H_2O (the Gif system).[11–13] The requirement of sacrificial reagents causes problems in separation and may even be considered as secondary contamination if these methods are used for the treatment of water.

Elimination of organic pollutants in water by oxidation with molecular oxygen and sunlight is the most environmentally friendly pollution-treatment method. Herein we show that FeBR, an iron(II) complex of 2,2′-bipyridine ($[Fe^{II}(bpy)_3]^{2+}$) supported on a commercial cationic ion-exchange resin (amberlite IRA 200), is an efficient catalyst for the activation of O_2 at room temperature to degrade organic pollutants including rhodamine B (RhB), malachite

---

[*] Prof. J. Zhao, Dr. W. Ma, Dr. J. Li, Dr. X. Tao, Dr. J. He, Dr. Y. Xu
Center for Molecular Sciences, Institute of Chemistry
Chinese Academy of Science
Beijing 100080 (China)
Fax: (+86) 10-6255-9373
E-mail: jczhao@infoc3.icas.ac.cn

Dr. J. C. Yu
Department of Chemistry and Environmental Science Programme
The Chinese University of Hong Kong
Shatin, N.T., Hong Kong (China)

[**] This work was supported by NSFC (Nos. 20133010, 20077027, 20277038, and 4001161947), CAS, and the China National Ministry for Science and Technology.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

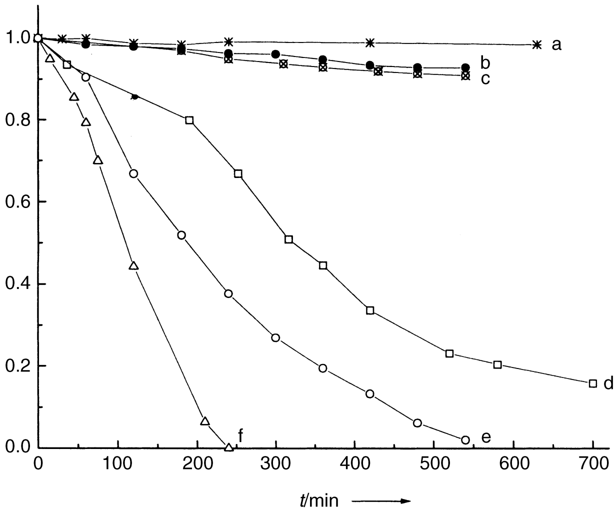


Figure 1. Concentration changes of substrates (50 mL) as a function of irradiation time under different conditions. a) Homogenous solution of RhB (20 μM) and [Fe^{II}(bpy)$_3$]$^{2+}$ (10 μM) at pH 2.6 under visible-light irradiation; b) heterogeneous dispersion of RhB (20 μM) and FeBR (5 mg) at pH 2.6 in the dark; c) deaerated heterogeneous dispersion of RhB (20 μM) and FeBR (5 mg) at pH 2.6 under visible-light irradiation; d) heterogeneous dispersion of DMA (100 μM) and FeBR (5 mg) at pH 4.6 under visible-light irradiation; e) heterogeneous dispersion of RhB (20 μM) and FeBR (5 mg) at pH 2.6 under visible-light irradiation; f) heterogeneous dispersion of MG (100 μM) and FeBR (5 mg) at pH 5.0 under visible-light irradiation.

green (MG), and *N,N*-dimethylaniline (DMA) in aerated aqueous solutions under visible-light irradiation ($\lambda > 420$ nm) (Figure 1). The catalytic reaction with FeBR proceeded efficiently without addition of any sacrificial reagents. The total organic carbon (TOC) removal yield reached 60% for RhB (20 μM, pH 2.6), 58% for MG (400 μM, pH 5.0), and 75% for DMA (100 μM, pH 4.6). The catalytic activity of the FeBR catalyst in the degradation of RhB was maintained effectively even after 22 repeated experiments (~100 h) (Figure 2). Another advantage of the proposed system is that the FeBR catalyst can be separated from the solution simply by filtration. Control experiments 1) with the catalyst in the dark, 2) in the absence of the catalyst, under irradiation, 3) with the resin itself, under irradiation, 4) with the iron(II)/resin (or iron(III)/resin), under irradiation, and 5) with a homogeneous, aqueous [Fe^{II}(bpy)$_3$]$^{2+}$ solution under visible-light irradiation all showed no significant degradation of the organic species. In aqueous solutions purged with nitrogen or helium gas the photodegradation rate of RhB was greatly decreased. These results demonstrated that both molecular oxygen and visible-light irradiation are necessary for the degradation of organic compounds.

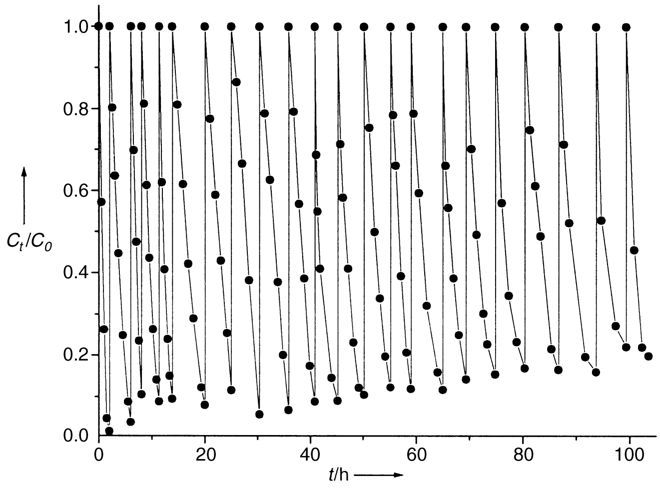
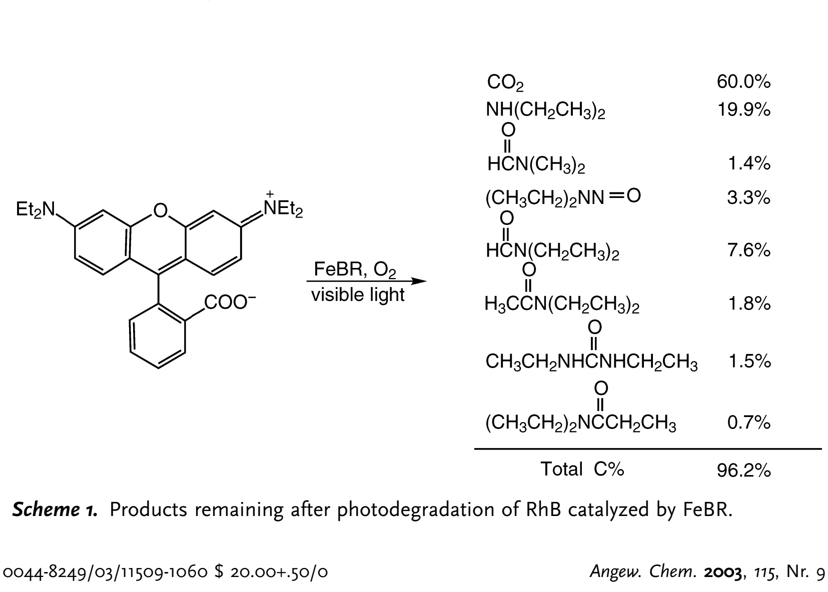


Figure 2. Cycling runs in the photodegradation of RhB in the presence of FeBR under visible-light irradiation. FeBR (10 mg/100 mL); addition of RhB (5 μmol/run).

The catalyst displays a broad absorption band in the region of 240–700 nm with a maximum located at 522 nm. Such extended coverage in the visible spectrum makes it possible to utilize most of the energy from sunlight. The quantum yield was 2.1×10^{-2} at 500 ± 5 nm for the degradation of MG.[14] Notably, Figure 1 shows substantial degradation of DMA (which does not absorb at wavelengths longer than 310 nm) under visible-light irradiation in the presence of the FeBR catalyst. This rapid degradation of DMA illustrates that the photoexcitation of FeBR initiates the photocatalytic degradation process and that the photosensitization process induced by the photoexcitation of substrates does not play a major role.

In the RhB photodegradation process, infrared spectroscopy (IR) and GC–MS were used to monitor the reaction and to identify the products. The IR study revealed ring opening as shown by the decrease and final disappearance of the vibration peaks of the aromatic ring at 1648, 1589, 1548, and 1527 cm^{-1}. The main degradation by-products identified by GC–MS (see Supporting Information) are shown in Scheme 1. About 60% of the organic carbon was mineralized into CO_2; the remaining by-products were mainly small molecular compounds such as *N,N*-diethylamine and *N,N*-diethylformamide, which are known to be biologically degradable. As expected, no hydroxylated or degraded species resulting from the photooxidation of the bipyridine ligands in FeBR were detected by GC–MS.



Scheme 1. Products remaining after photodegradation of RhB catalyzed by FeBR.

The X-ray photoemission spectra (XPS) of the FeBR catalyst before and after photoreaction are virtually identical. They all show the presence of only the iron(II) species (2p3 BE 708.85 eV). Unlike $[Ru^{II}(bpy)_3]^{2+}$ and $[Os^{II}(bpy)_3]^{2+}$, $[Fe^{II}(bpy)_3]^{2+}$ in solution did not exhibit the ability to activate dioxygen because of the extremely rapid deactivation of the excited states of the iron(II) bipyridine complex.[15,16] However, $[Fe^{II}(bpy)_3]^{2+}$ supported on amberlite could activate molecular oxygen efficiently to oxidize substrates under visible-light irradiation. This suggests that the resin not only acts as a support for the $[Fe^{II}(bpy)_3]^{2+}$ exchange, but also provides a unique framework that significantly alters the photochemical properties of $[Fe^{II}(bpy)_3]^{2+}$. Just as hydrogen bonds are instrumental in regulating chemical processes, including those observed in respiratory proteins and metal-containing hydrolases,[17] the interaction between the resin and $[Fe^{II}(bpy)_3]^{2+}$ may play an important role in prolonging the lifetime of the FeBR excited state and thus enhancing the probability of its transferring electrons to O_2. The fluorescence measurements provided direct evidence for the interaction between $[Fe^{II}(bpy)_3]^{2+}$ and the resin. FeBR clearly exhibited fluorescence at $\lambda_{max}^{ex} = 522$ nm and $\lambda_{max}^{em} = 588$ nm, while both $[Fe^{II}(bpy)_3]^{2+}$ in solution and the resin itself were nonluminescent.

The reactive oxygen species formed in the photoreaction process were examined by spin-trapping ESR spectroscopy. Experiments were carried out for the degradation of RhB (20 μM) both in water and in methanol. The formation of $^{\bullet}$OH radicals would be expected in the aqueous system, whereas $^{\bullet}OOH/O_2^{\bullet-}$ radicals that are unstable in water at room temperature should appear in methanol.[18] Upon visible-light irradiation, the ESR signals of DMPO–$^{\bullet}OOH/O_2^{\bullet-}$ adducts with the characteristic six peaks were observed in the methanol system, and the intensity increased slightly with irradiation time. These results confirm that $^{\bullet}OOH/O_2^{\bullet-}$ radicals are formed through the activation of molecular oxygen in the photocatalytic process. However, $^{\bullet}$OH radicals were not found during photoreactions in either aqueous or methanolic solutions. In another experiment, it was found that addition of 2-propanol, a known scavenger of $^{\bullet}$OH radicals,[19] to the photoreaction system did not cause any apparent changes in the degradation rate of RhB. This indicates that $^{\bullet}$OH radicals are not the main active oxygen species involved in the photoreaction catalyzed by FeBR. The formation of H_2O_2 was also observed during the photodegradation of both RhB and MG. However, when we directly introduced H_2O_2 (100 μM) into the RhB degradation system we did not find any acceleration in the degradation of RhB. It may be concluded that H_2O_2 is formed in a side reaction and is not the main active oxygen species involved in the photodegradation of RhB in the presence of FeBR. Therefore the photodegradation of organic pollutants catalyzed by FeBR must mainly involve the superoxide (resin–$[Fe^{III}(bpy)_3O_2^{\bullet-}]$ and the oxoiron (resin–$[Fe^{IV}(bpy)_3{=}O]$) as the active oxygen species, rather than $^{\bullet}$OH radicals (Fenton mechanism[20]). Mechanisms involving similar intermediates have been proposed by other groups for the oxidation of organic species, catalyzed by iron complexes in organic solvents.[21–23]

This work introduces a simple and green heterogeneous photocatalytic approach for the degradation of organic pollutants. It may also provide useful insight for the development of new routes in synthetic chemistry.

Experimental Section

The FeBR catalyst was prepared by an ion-exchange method. Amberlite IRA 200 resin (Alfa Aesar Co. ~1.0 mmol g^{-1} saturated loading) was ground and then sieved to a size of ~200 mesh. These resin particles were washed with alcohol, HCl, and NaOH to remove any possible contaminants. An appropriate amount of the resin was added to a $[Fe^{II}(bpy)_3]^{2+}$ solution at a suitable concentration at pH 4 and was stirred until all $[Fe^{II}(bpy)_3]^{2+}$ ions were exchanged. Different loadings of $[Fe^{II}(bpy)_3]^{2+}$ catalysts (20 %, 50 %, 75 %, and 100 % of the saturated exchange amount) were prepared. The FeBR catalyst of 50 % loading (i.e. $[Fe^{II}(bpy)_3]^{2+} = 0.5$ mmol g^{-1} resin) exhibited the highest activity (with relative rates for the degradation of RhB of 0.61 for 20 %, 1.0 for 50 %, 0.50 for 75 %, and 0.03 for 100 % of saturated loading), and therefore was used for all experiments.

The reaction system containing the catalyst and the substrate was magnetically stirred in a pyrex glass vessel and irradiated with a 500 W halogen lamp. A pyrex jacket with water circulation was used to cool the lamp. A light filter was placed outside the pyrex jacket to completely cut out light below 420 nm and guarantee irradiation with visible light. ESR spectroscopic experiments were carried out at ambient temperature (298 K) with a Bruker ESP 300E spectrometer. XPS was performed on a 220I-XL multifunctional spectrometer (VG Scientific England) using $Al_{K\alpha}$ radiation. GC–MS analysis was carried out on a Trio 2000 (Micromass UK Ltd).

Received: October 16, 2002 [Z50381]

---

[1] B. Meunier, *Science* **2002**, *296*, 270–271.

[2] B. Meunier, *Chem. Rev.* **1992**, *92*, 1411–1456.

[3] A. Sorokin, J. L. Séris, B. Meunier, *Science* **1995**, *268*, 1163–1166.

[4] A. Sorokin, B. Meunier, *J. Chem. Soc. Chem. Commun.* **1994**,1799–1800.

[5] C. P. Horwitz, D. R. Fooksman, L. D. Vucolo, S. W. Gordon-Wylie, N. J. Cox, T. J. Collins, *J. Am. Chem. Soc.* **1998**, *120*, 4867–4868.

[6] S. S. Gupta, M. Stadler, C. A. Noser, A. Ghosh, B. Steinhoff, D. Lenoir, C. P. Horwitz, K. W. Schramm, T. J. Collins, *Science* **2002**, *296*, 326–328.

[7] X. Tao, W. Ma, T. Zhang, J. Zhao, *Angew. Chem.* **2001**, *113*, 3103–3105; *Angew. Chem. Int. Ed.* **2001**, *40*, 3014–3016.

[8] X. Tao, W. Ma, T. Zhang, J. Zhao, *Chem. Eur. J.* **2002**, *8*, 1321–1326.

[9] R. A. Sheldon, I. W. C. E. Arends, G. J. ten Brink, A. R. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781.

[10] G-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639.

[11] D. H. R. Barton, D. Doller, *Acc. Chem. Res.* **1992**, *25*, 504–512.

[12] P. Stavropoulos, R. Celenligil-Cetin, A. E. Tapper, *Acc. Chem. Res.* **2001**, *34*, 745–752.

[13] B. Singh, J. R. Long, F. Fabrizi de Biani, D. Gatteschi, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 7030–7047.

[14] E. E. Wegner, A. W. Adamson, *J. Am. Chem. Soc.* **1966**, *88*, 394–404.

[15] S. Ferrere, *Chem. Mater.* **2000**, *12*, 1083–1089.

[16] J. Phillps, J. A. Koningstein, C. H. Langford, R. Sasseville, *J. Phys. Chem.* **1978**, *82*, 622–623.

[17] W. N. Lipscomb, N. Sträter, *Chem. Rev.* **1996**, *96*, 2375–2433.

[18] D. T. Sawyer, J. S. Valentine, *Acc. Chem. Res.* **1981**, *14*, 393–400.

[19] C. Kormann, D. W. Bahnemann, M. Hoffmann, *Environ. Sci. Technol.* **1988**, *22*, 998 – 1004.
[20] C. Walling, *Acc. Chem. Res.* **1975**, *8*, 125 – 131.
[21] L. Weber, R. Hommel, J. Behling, G. Haufe, H. Hennig, *J. Am. Chem. Soc.* **1994**, *116*, 2400 – 2408.
[22] C. E. MacBeth, A. P. Golombek, V. G. Young, Jr., C. Yang, K. Kuczera, M. P. Hendrich, A. S. Borovik, *Science* **2000**, *289*, 938 – 941.
[23] T. J. Collins, *Acc. Chem. Res.* **2002**, *35,* 782 – 790.

0044-8249/03/11509-1062 $ 20.00+.50/0