



# Catalytic oxidation of 2,4,6-tribromophenol using iron(III) complexes with imidazole, pyrazole, triazine and pyridine ligands



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## ARTICLE INFO

### Article history:

Received 4 November 2015

Received in revised form

19 December 2015

Accepted 21 December 2015

Available online 28 December 2015

### Keywords:

Non-heme

Terpyridine

Catalytic oxidation

2,4,6-Tribromophenol

Humic acid

## ABSTRACT

Five types of non-heme iron complexes, coordinated with imidazole, pyrazole, triazine and pyridine ligands, which had been previously synthesized, were used in the following studies. Among these complexes, the *mer*-[FeCl<sub>3</sub>(terpy)] complex showed the highest catalytic activity for the oxidative degradation of 2,4,6-tribromophenol (TrBP) using KHSO<sub>5</sub> as an oxygen donor. The turnover numbers for the degradation and debromination of TrBP in the *mer*-[FeCl<sub>3</sub>(terpy)]/KHSO<sub>5</sub> catalytic system were estimated to be 1890 ± 1 and 4020 ± 216, respectively. The catalytic activity was significantly inhibited at pH 4–7 in the presence of a humic acid, a major component of landfill leachates. However, the percent of TrBP degradation and debromination increased at pH 8. GC/MS analyses showed that a major oxidation product was 2,6-dibromo-*p*-benoquinone (DBQ) and its level decreased with increasing reaction time, suggesting that organic acids (identified by LC/TOF-MS) are formed via the ring-cleavage of DBQ. Mineralization to CO<sub>2</sub> was observed to be 15% as a result of the oxidation for a 3 h period, where TOC values before and after the reaction were measured. Absorption spectra of *mer*-[FeCl<sub>3</sub>(terpy)] with *m*-chloroperoxybenzoic acids as an oxygen donor in acetonitrile showed that a center metal, Fe, formed a peroxide complex with the oxygen donor.

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## 1. Introduction

2,4,6-Tribromophenol (TrBP) is used in the production of fungicides, wood preservatives [1] and an intermediate in the production of brominated flame retardants (BFRs) [2]. TrBP is eluted from landfills where wastes derived from electrical devices including BFRs are disposed of, and this leads to water pollution [3]. In particular, humic acids (HAs) are present in landfill leachates in the form of dissolved organic matter and interactions with HA can enhance water solubility and inhibit the oxidative degradation of organic pollutants [4,5]. Because TrBP has been reported to have endocrine disrupting effects, the TrBP in landfill leachates must be reduced.

Previous studies suggest that Fe(III)-porphyrins, a model of heme enzymes, can be effective for the oxidative degradation of bromophenols and chlorophenols [6–18]. Among the halogenated phenols, bromophenols are relatively resistant to oxidative degradation and dehalogenation [8]. However, mineralization to CO<sub>2</sub> has

been reported in the case of a heterogeneous Fe(III)-porphyrin catalyst, which was introduced into an ionic liquid supported Fe<sub>3</sub>O<sub>4</sub> [19]. However, in a homogeneous catalytic system, mineralization is minimal, because of catalyst self-degradation.

On the other hand, non-heme enzymes, such as methane monooxygenase, rubeo dioxygenase, lipooxygenase and catechol dioxygenase, involve iron as a center metal. These enzymes can be activated by an oxygen donor, and organic substrates are oxidized by active species such as L<sup>•+</sup>-Fe(IV)=O, L-Fe(IV)=O and HO<sup>•</sup> that are produced in such systems [18]. Stable non-heme iron complexes with tetradentate ligands had been synthesized and applied as catalysts for the selective oxidation of olefins [19–24]. However, there are no reports, regarding the catalytic oxidation of halogenated phenols using non-heme iron complexes. Catechol dioxygenases can oxidize catechol, a phenol derivative, via ring-cleavage [20]. In particular, Dhanalkshmi et al [25]. reported that iron complexes, when coordinated with tridentate ligands, such as pyridine-2,6-dicarboxylic acid, 2,2':6,2''-terpyridine (terpy) and 2,6-bis(benzimidazol-2'-yl) pyridine, showed higher activities for the oxidation of catechol. This finding suggests that a non-heme

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iron complex with a tridentate ligand might be effective for the oxidation of phenol derivatives.

Five types of non-heme iron complexes with monodentate imidazole, pyrazole and tridentate nitrogen ligands (Fig. 1), which had been previously synthesized and their structures determined by X-ray crystallography [26], were prepared. In the present study, the catalytic activities of the non-heme iron complexes for the oxidative degradation of TrBP and the influence of HA on the oxidation of TrBP were investigated. In addition, to characterize the oxidation products of TrBP produced by the non-heme catalyst, the reaction mixtures and  $\text{CH}_2\text{Cl}_2$  extracts derived from them were analyzed by LC/TOF-MS and GC/MS, respectively. The detection of the activated species of the non-heme complex by the oxygen donor was examined by observing the visible absorption spectrum.

## 2. Materials and methods

### 2.1. Materials

Imidazole (im), 1-methylimidazole (meim) (Wako Pure Chemical Industries), 3-methylpyrazole (mepy), 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz), terpy and TrBP (Tokyo Chemical Industry) were used without further purification. An iron(III) chloride anhydride was obtained from Nacalai Tesque.  $\text{KHSO}_5$  was obtained as a triple salt,  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$  (Merck). Other reagents were obtained from Wako Pure Chemical Industries and were used without further purification. An HA used in this study was extracted from Shinshinotsu peat soil, as described in a previous report [27]. The elemental compositions of the HA were as follows: C 54.5%, H 5.35%, N 2.17%, S 0.66%, O 35.1%, ash 2.22% [28].

### 2.2. Synthesis and characterization of non-heme iron complexes

Five types of non-heme iron complexes (Fig. 1) were prepared based on the methods previously reported by Cotton et al [26]. The detailed procedures for their preparation can be found in Supplementary Material (Text SM-1). The FT-IR spectra of the synthesized complexes were measured using an FT/IR 600-type spectrophotometer (Japan Spectroscopic Co., Ltd.). Elemental analyses (C, H, N and Cl) of the complexes were carried out by the Instrumental Analysis Division, Equipment Management Center Creative Research Institution, Hokkaido University (Sapporo, Japan). The Fe contents of the complexes were determined using an inductively coupled plasma-atomic emission spectrophotometer (ICPE9000 type, Shimadzu) after wet digestion with a mixture of  $\text{HNO}_3/\text{HCl}$  and the appropriate dilution with ultra-pure water. Analytical data, product yields, elemental composition and FT-IR spectra for each complex were as follows: *mer*- $[\text{FeCl}_3(\text{meim})_3]$ , yield 13.4%; elemental analysis, observed (calculated), %C 35.03 (35.27), %H 4.27 (4.44), %N 20.44 (20.57), %Cl 26.08 (25.43), %Fe 13.7 (13.38); IR spectrum,  $\nu(\text{C-H})$  2952 and  $1420\text{ cm}^{-1}$ ,  $\nu(\text{C-N})$   $1108\text{ cm}^{-1}$ ;  $[\text{FeCl}_2(\text{im})_4]\text{Cl}$ , yield 53.8%; elemental analysis, observed (calculated), %C 32.04 (35.45), %H 3.66 (3.96), %N 24.80 (20.67), %Cl 24.9 (35.45), %Fe 13.0 (11.80); IR spectrum,  $\nu(\text{C-H})$   $3050\text{ cm}^{-1}$ ,  $\nu(\text{C-N})$   $1261$  and  $1055\text{ cm}^{-1}$ ;  $[\text{FeCl}_2(\text{mepy})_4]\text{Cl}$ , yield 7.48%; elemental analysis, observed (calculated), %C 38.90 (39.16), %H 4.78 (4.93), %N 22.79 (22.84), %Cl 21.84 (21.72), %Fe 11.40 (11.45); IR spectrum,  $\nu(\text{C-H})$  2964 and  $1442\text{ cm}^{-1}$ ,  $\nu(\text{C-N})$  1103 and  $1049\text{ cm}^{-1}$ ; *mer*- $[\text{FeCl}_3(\text{tptz})]$ , yield 75.7%; elemental analysis, observed (calculated), %C 43.51 (43.10), %H 2.97 (2.79), %N 16.94 (16.51), %Cl 21.04 (21.03), %Fe 11.00 (11.45); IR spectrum,  $\nu(\text{C-H})$  1523 and  $1468\text{ cm}^{-1}$ ,  $\nu(\text{C=C, C=N})$  1523 and  $1468\text{ cm}^{-1}$ ; *mer*- $[\text{FeCl}_3(\text{terpy})]$ , yield 71.8%; elemental analysis, observed (calculated), %C 45.50 (45.6), %H 2.77 (2.81), %N 10.61 (10.63), %Cl 26.78 (26.93), %Fe 13.70 (13.40); IR spec-

trum,  $\nu(\text{C-H})$  3047 and  $767\text{ cm}^{-1}$ ,  $\nu(\text{C=C, C=N})$  1610, 1468 and  $1453\text{ cm}^{-1}$ .

### 2.3. Assay for TrBP degradation

A 10-mL aliquot of 0.02 M  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  buffer (pH 4–8) was placed in a 50-mL Erlenmeyer flask and a 50  $\mu\text{L}$  aliquot of 0.01 M TrBP in acetonitrile was then added to the solution. Aqueous catalysts were added to be produced concentrations of 0.1–10  $\mu\text{M}$ , and a 0.1 mL aliquot of 0.1 M  $\text{KHSO}_5$  or  $\text{H}_2\text{O}_2$  was then added to the mixture to start the reaction. After shaking for 30 min, a 1 mL aliquot of the reaction mixture was placed in a glass vial, and 0.5 mL 2-propanol was then added. A 20  $\mu\text{L}$  aliquot of the mixture was injected into a PU980-type HPLC pumping system (JASCO) to analyze the remaining TrBP in the reaction mixtures. The mobile phase was a mixture of methanol and water (78:22 in volume), which was acidified with aqueous 0.08%  $\text{H}_3\text{PO}_4$ , and the stationary phase was a COSMOSIL 5C18-AR-II column ( $4.6 \times 250\text{ mm}$ ). The flow rate of the eluent, the column temperature and the detection wavelength were set at  $1.0\text{ mL min}^{-1}$ ,  $50^\circ\text{C}$  and 290 nm, respectively.

The  $\text{Br}^-$  that is released as a result of the oxidation was analyzed by an ion chromatography (Dionex IC-120 type, Thermo-Fishers) with conductivity detection. The mobile phase was an aqueous solution of 2.7 mM  $\text{Na}_2\text{CO}_3/0.3\text{ mM NaHCO}_3$ , and the separation column was an IonPacAS12A analytical column ( $4 \times 200\text{ mm}$ , Thermo-Fishers) with an IonPacAG12A guard column ( $4 \times 50\text{ mm}$ ). The flow rate and column oven temperature were set at  $1.5\text{ mL min}^{-1}$  and  $35^\circ\text{C}$ , respectively. To evaluate the percent mineralization to  $\text{CO}_2$ , the concentration of total organic carbon (TOC) in the reaction mixture was analyzed before and after the reaction using a TOC-V CSH type analyzer (Shimadzu). In this test, a stock solution of 0.01 M TrBP was prepared using aqueous 0.01 M NaOH.

### 2.4. Identification of oxidation products by GC/MS

A 30 mL aliquot of a 0.02 M phosphate buffer (pH 7) containing 200  $\mu\text{M}$  TrBP and 2.7  $\mu\text{M}$  catalyst was placed in a 100-mL Erlenmeyer flask. A 300  $\mu\text{L}$  aliquot of 0.1 M  $\text{KHSO}_5$  was added and the flask subjected to shaking at room temperature for 1 min, 30 min and 24 h. After the reaction period, a 1 mL aliquot of 1 M ascorbic acid and a 0.5 mL aliquot of 1 mM anthracene in hexane and acetone (1:1) as an internal standard (ISTD) were then added. To adjust the pH of the solution to 11–11.5, a 15 mL aliquot of  $600\text{ g L}^{-1}\text{ K}_2\text{CO}_3$  was added, and 5 mL of acetic anhydride was then added dropwise into the mixture to acetylate the phenolic hydroxyl groups in the TrBP and the oxidation products. This solution was then extracted 3 times with 20 mL of  $\text{CH}_2\text{Cl}_2$ . After dehydration of the organic phase with  $\text{Na}_2\text{SO}_4$  anhydride, the  $\text{CH}_2\text{Cl}_2$  was removed by flushing with a stream of dry  $\text{N}_2$  gas at  $35^\circ\text{C}$  and the resulting residue was re-dissolved in 300  $\mu\text{L}$  of  $\text{CH}_2\text{Cl}_2$ . A 1  $\mu\text{L}$  aliquot of the solution was injected into a GC-17A/QP5050 type GC/MS (Shimadzu). Separation was accomplished with a 100% methylsiloxane capillary column (0.25  $\mu\text{m}$  thickness, 0.25 mm i.d.  $\times$  25m). Temperature gradient:  $65^\circ\text{C}$  (1.5 min);  $65\text{--}120^\circ\text{C}$  ( $35^\circ\text{C min}^{-1}$ );  $120\text{--}130^\circ\text{C}$  ( $4^\circ\text{C min}^{-1}$ );  $300^\circ\text{C}$  (10 min).

### 2.5. Identification of organic acids using LC/TOF-MS

A 0.1 mL aliquot of aqueous 0.1 M  $\text{KHSO}_5$  was added to an ammonium formate buffer (pH 8), which contained 50  $\mu\text{M}$  TrBP and 10  $\mu\text{M}$  catalyst. After a 30 min reaction period, a 1 mL aliquot of the reaction mixture was pipetted into a glass vial and 0.5 mL methanol was then added. The organic acids in the reaction mixture were identified and using a 1200 type LC/TOF-MS (Agilent). The stationary phase was a ZORBAX Extend-C18 column ( $2.1 \times 100\text{ mm}$ ,

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