Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles

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ABSTRACT

Benzotriazoles (BTs) are high production volume chemicals with broad application in various industrial processes and in households, and have been found to be omnipresent in aquatic environments. We investigated oxidation of five benzotriazoles (BT: 1H-benzo-triazole; 5MBT: 5-methyl-1H-benzotriazole; DMBT: 5,6-dimethyl-1H-benzotriazole hydrate; 5CBT: 5-chloro-1H-benzotriazole; HBT: 1-hydroxybenzotriazole) by aqueous ferrate (Fe(VI)) to determine reaction kinetics as a function of pH (6.0–10.0), and interpreted the reaction mechanism of Fe(VI) with BTs by using a linear free-energy relationship. The pK_a values of BT and DMBT were also determined using UV–Visible spectroscopic method in order to calculate the species-specific rate constants, and they were 8.37 ± 0.01 and 8.98 ± 0.08 respectively. Each of BTs reacted moderately with Fe(VI) with the k_{app} ranged from 7.2 to 103.8 $M^{-1}s^{-1}$ at pH 7.0 and $24 \pm 1\,°C$. When the molar ratio of Fe(VI) and BTs increased up to 30:1, the removal rate of BTs reached about >95% in buffered milli-Q water or secondary wastewater effluent. The electrophilic oxidation mechanism of the above reaction was illustrated by using a linear free-energy relationship between pH-dependence of species-specific rate constants and substituent effects (σ_p). Fe(VI) reacts initially with BTs by electrophilic attack at the 1,2,3-triazole moiety of BT, 5MBT, DMBT and 5CBT, and at the N–OH bond of HBT. Moreover, for BT, 5MBT, DMBT and 5CBT, the reactions with the species $HFeO_4^-$ predominantly controled the reaction rates. For HBT, the species H_2FeO_4 with dissociated HBT played a major role in the reaction. The results showed that Fe(VI) has the ability to degrade benzotriazoles in water.

1. Introduction

Benzotriazoles (BTs) are high production volume chemicals that find broad application in various industrial processes and in household products as anti-corrosion agents (Weiss et al., 2006). BTs are a class of polar heterocyclic compounds containing the benzotriazole skeleton with a benzene ring on which a vicinal pair of carbon atoms covalently bonded to three nitrogen atoms in a five membered ring. BTs are characterized by high water solubility (3–70 g/L), low octanol water distribution coefficients (log K_{ow} 0.11–2.26), and low soil adsorption coefficient (log K_{oc} 1.2–2.2) and they are also weakly basic compounds (pK_a 7.39–8.98) (US EPA, 2008), thus they are expected to be quite mobile in the aquatic environment.

BTs are classified as toxic to aquatic organisms. The acute toxicity EC_{50} or LC_{50} of BTs to aquatic organisms (Microtox bacteria, fathead minnow and water flea) are in the range of

0.72–118 mg/L (Cancilla et al., 1997; Pillard et al., 2001). BT has been shown to exhibit antiestrogenic activity in vitro in a yeast assay but not in vivo to fish (Harris et al., 2007). Moreover, it can interfere with the regulation of embryo development in protochordates such as *Ciona Intestinalis* (Kadar et al., 2010). BTs in aquatic environment may cause negative effects in the aquatic organisms. Therefore, it is necessary to remove BTs in effluents by applying various treatment technologies.

BTs have been incompletely removed in conventional wastewater treatment plants due to their resistance to biodegradation (Weiss and Reemtsma, 2005; Weiss et al., 2006; Giger et al., 2006). Due to their incomplete removal and discharge of effluents, BTs have been reported in various aquatic environments. The concentration levels of BTs ranged from 0.01 to 0.2 μg/L in drinking water samples (van Leerdam et al., 2009) and between 0.1 and 6.3 μg/L in surface waters (Giger et al., 2006) as well as 0.8–18 μg/L in effluents of sewage treatment plants (Weiss and Reemtsma, 2005; Weiss et al., 2006; Reemtsma et al., 2010). 1H-Benzotriazole (BT) has been listed as one of the most widely detected polar organic pollutants in European surface water and ground water during pan-European reconnaissance (Loos et al., 2009, 2010).

Various oxidation processes have been studied in the laboratory for BTs. Ozonation has been found quite effective in removal of BT from the treatment plant effluent (Weiss et al., 2006). The second-order rate constants for BT with molecular ozone were determined to be $36.4 \, M^{-1}s^{-1}$ (the log-reduction of BT with ozone in excess) or $18.4 \, M^{-1}s^{-1}$ at pH 2 and $22.0 \, M^{-1}s^{-1}$ at pH 5 (the competition kinetic model) (Vel Leitner and Roshani, 2010), but the rate constants were found to be above $10^9 \, M^{-1}s^{-1}$ for the reaction of hydroxyl radicals with BT using the pulse radiolysis technique (Naik and Moorthy, 1995). Photoelectrocatalytic degradation of BT by liquid phase deposited TiO_2 film mainly proceeds by cleavage of the azo bond leading to decolorization, followed by opening of the benzene ring to form small molecular organic products (Ding et al., 2010). BT can also be degraded by UV irradiation in aqueous solution (Andreozzi et al., 1998; Hem et al., 2003; Wang et al., 2000). Reaction kinetics in photochemical transformation are significantly affected by pH because of its influence upon benzotriazole dissociation (Andreozzi et al., 1998). Moreover, previous studies of oxidation processes have mainly focused on BT, but few on its derivatives.

Ferrate (Fe(VI)) is another powerful oxidizing agent in water treatment, which has the oxidation-reduction potential of 2.20 V at acidic pH condition and 0.57 V at basic pH condition (Lee et al., 2004). Due to its dual functions of an oxidant and a subsequent coagulant/precipitant as ferric hydroxide (Fe(III)) (Jun and Wei, 2002), Fe(VI) is regarded as an environmentally friendly oxidant in water and wastewater treatment process (Jiang and Lloyd, 2002; Sharma, 2002, 2010; Jiang, 2007). However the instability of Fe(VI) has limited its use in water treatment applications, but recent development in the production of Fe(VI) in situ using the electrochemical method makes it a promising oxidant for the real application of Fe(VI) in water and wastewater treatment plants (Yu and Licht, 2008; Alsheyab et al., 2009; Macova et al., 2009). As the oxidant of iron series, Fenton reactions compose reactions of peroxides with iron ions to form active oxygen species at the low pH of 2.8–3.0 that limit their

widespread usage (Pignatello et al., 2006), but Ferrate works well in a broader pH range. At circumneutral pH solution, H_2FeO_4, $HFeO_4^-$, FeO_4^{2-} are the predominant species with the oxidizing power of these oxidants increasing in the order nonprotonated ferrate < monoprotonated ferrate < diprotonated ferrate (Kamachi et al., 2005). These pH-dependent variations of Fe(VI) reaction with organic contaminants could be explained by considering species-specific reactions between Fe(VI) species and acid-base species of an ionizable substrates (Lee et al., 2005a; Sharma et al., 2006). Fe(VI) has been known to react with electron-rich organic moieties (ERM) through electrophilic oxidation mechanism (Lee et al., 2009). The proposed mechanism for the oxidation of aniline (Huang et al., 2001b) or phenol (Huang et al., 2001a) by Fe(VI) involves a free radical reaction mechanism through an associative type of mechanism with hydrogen bond formation in the activated complex accompanied by intermolecular electron transfer. Nevertheless, there has so far been no study on the oxidation of BTs by Fe(VI) available in the literature, especially on their reaction mechanisms.
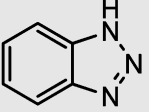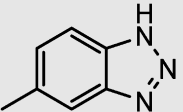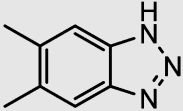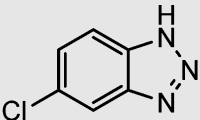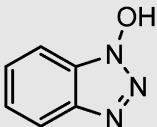
The objectives of the present study were to assess the potential of Fe(VI) oxidation of five benzotriazoles (BT: 1H-benzotriazole; 5MBT: 5-methyl-1H-benzotriazole; DMBT: 5,6-dimethyl-1H-benzotriazole hydrate; 5CBT: 5-chloro-1H-benzotriazole; HBT: 1-hydroxybenzotriazole) and determine the reaction rate constants. A linear free-energy relationship was used to explain the reaction mechanism of Fe(VI) with BTs. Besides, the pK_a values of BT and DMBT were also determined by UV–Visible spectroscopic method in order to calculate the species-specific rate constants.

2. Experimental section

2.1. Standards and reagents

1H-Benzotriazole (BT, 99%) was purchased from Tokyo chemical industry (Tokyo, Japan). 5-Methyl-1H-benzotriazole (5MBT, 98%), 5,6-dimethyl-1H-benzotriazole hydrate (DMBT, 99%) and 5-chloro-1H-benzotriazole (5CBT, 99%) were purchased from Acros Organics (New Jersey, USA). 1-Hydroxybenzotriazole anhydrous (HBT, 98%) was purchased from J & K Chemical (Guangzhou, China). The basic physiochemical information on the five benzotriazoles is listed in Table 1. Diammonium 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonate) (ABTS, 98%) was obtained from Tokyo chemical industry (Shanghai, China). Potassium ferrate (Fe(VI)) was prepared by wet chemical synthesis (Delaude and Laszlo, 1996). It has a purity of above 95% as Fe(VI) (w/w), which was determined by the direct 510 nm method ($\varepsilon = 1150 \, M^{-1} \, cm^{-1}$) at the pH value of 9.1 ± 0.1 (5 mM K_2HPO_4/1 mM borate) (Rush and Bielski, 1986). All solutions were prepared with Milli-Q water from a Millipore Water Purification System. Buffer chemicals and all other reagents used for solutions were of analytical grade. Stock solutions of Fe(VI) (0.8–1.5 mM) was prepared by dissolving solid potassium ferrate in Milli-Q water (pH ≈ 9.2) and used immediately. Stock solutions of BT and HBT were prepared in Milli-Q water at concentrations of 100 mg/L. Stock solutions of 5MBT, DMBT and 5CBT were prepared in Milli-Q water assisted by 2% (v/v) acetonitrile at

Table 1 — Species-specific second-order rate constants for the reactions of Fe(VI) with benzotriazoles in the pH range of 6.0–10.0 and at 24 ± 1 °C.

Benzotriazoles	Chemical name	pK_a	σ_p[d]	k_{12}	k_{21}	k_{22}	R^2	k_{app} at pH 7.0 $(M^{-1}s^{-1})$	$t_{1/2}$ (s)[e]
	1H-benzotriazole (BT)	8.37[a]	0		$1.9(\pm0.4)\times10^1$	$1.9(\pm0.2)\times10^2$	0.95	19.9	689.8
	5-Methyl-1H-benzotriazole (5MBT)	8.5[b]	−0.17		$2.7(\pm0.5)\times10^1$	$4.3(\pm0.5)\times10^2$	0.95	28.2	486.1
	5,6-Dimethyl-1H-benzotriazole (DMBT)	8.98[a]	−0.34		$8.5(\pm1.7)\times10^1$	$7.3(\pm1.4)\times10^2$	0.91	76.5	179.6
	5-Chloro-1H-benzotriazole (5CBT)	7.5[b]	0.23		$2.0(\pm0.2)\times10^0$	$6.6(\pm0.6)\times10^1$	0.88	7.2	1917.3
	1-Hydroxybenzotriazole (HBT)	7.39[c]	−0.37	$1.6(\pm0.1)\times10^6$		$7.7(\pm0.6)\times10^1$	0.99	103.8	132.3

a Supplementary Information, SI-word.
b Hart et al. (2004).
c http://www.chemicalbook.com/ProductMSDSDetailCB2420172_EN.htm.
d σ_p values were obtained from the literature (Hansch et al., 1991).
e Estimated by assuming pseudo-first-order conditions with a Fe(VI) excess ([Fe(VI)] = 10 mg/L, pH = 7.0).

concentrations of 100 mg/L. In Fe(VI) degradation processes, the experiments were not affected by the presence of trace acetonitrile (Lee et al., 2009).

A secondary wastewater effluent was grab sampled from the Liede municipal wastewater treatment plant which uses primary sedimentation and activated sludge treatment. The plant is the biggest wastewater treatment plant which serves 2 million people in metropolitan Guangzhou, China. The pH, UV_{254}, DOC, conductivity and alkalinity of the effluent were 6.88, 0.08, 4.93 mg/L, 512 μS/cm and 3 mM as HCO_3^-, respectively. The samples were filtered with a 0.45 μm cellulose-nitrate membrane and used within 24 h. Besides, the trace pollutants did not interfere the experiments because of the high spiked concentrations for each target compound of BTs (10 μM).

2.2. Determination of pK_a values of BT and DMBT

The absorbencies of BT and DMBT in different pH buffer solutions were determined by a UV–VIS spectrophotometer at the wavelength of 280 nm at room temperature (24 ± 1 °C) (Castro et al., 2003; Fagel and Ewing, 1951). For detailed information of determination of pK_a values of BT and DMBT, please refer to Supplementary Information, Text S1.

2.3. Kinetics of BTs oxidation by Fe(VI)

Second-order rate constants for the reaction of Fe(VI) with the five BTs were determined in the pH range of 6.0–10.0. Reagents 10 mM phosphate/acetic acid were used as the pH 6.0–9.0 buffer solutions and 10 mM phosphate/NaOH used to adjust the pH 9.5 and 10.0 of reaction solutions. The kinetics of BTs oxidation by Fe(VI) was conducted under pseudo-first-order conditions with Fe(VI) in excess to BTs. In the 150 mL reaction mixture solutions, the initial concentration of Fe(VI) was 100 μM while the concentration for each of BTs was 2 μM. The experiments were performed in a 200 mL beaker equipped with a magnetic stirrer (500 r/min) at the room temperature (24 ± 1 °C). The Fe(VI) stock solution was quickly filtered through a 0.45 μm hydrophilic polyethersulfone (PES) syringe filter (Shanghai ANPEL, China) and then standardized spectrophotometrically at 510 nm. Reactions were initiated by adding an aliquot of the Fe(VI) stock solution to suspensions containing each of BTs under rapid mixing. At proper time intervals, 5 mL of the reaction solution with an ABTS solution to measure residual Fe(VI) concentrations using a ABTS method at 415 nm (Lee et al., 2005b), and 1 mL of the reaction solution was sampled and quenched with a thiosulfate solution (5 mM, 0.1 mL) to measure residual concentrations of BTs. The absorbance was measured with a Lambda 850 spectrophotometer (PerkinElmer, USA). The pH values were determined using a Thermo Orin 5 star pH meter (Thermo Fisher Scientific, USA), which was calibrated using standard buffers (pH 4.0, 7.0, and 10.0, Thermo China). The pH variation was below 0.1 units during the experiments.

Each of BTs was analyzed on an Agilent 1200 series high performance liquid chromatography (HPLC) fitted with a diode array detector (Santa Clara, CA). An SGE C18 RS column (100 × 4.6 mm, 5 μm) (Melbourne, Australia) with a guard column (C18, 4.6 × 7.5 mm, 5 μm) was used for the separation. The column temperature was set at 30 °C. Methanol and water

(acidified with 0.1% acetic acid) were used as the mobile phase. The eluent ratio for BT, 5MBT, DMBT, 5CBT and HBT was 30:70, 40:60, 50:50, 50:50 and 20:80, respectively. The injection volume was 100 μL and the flow rate was set at 1 mL/min. The UV wavelength for BT, 5MBT, DMBT, 5CBT and HBT was 254 nm, 260 nm, 265 nm, 265 nm and 204 nm, respectively. The limit of quantitation of each target compound was 10 μg/L.

2.4. Elimination of BTs at various Fe(VI) dose

The elimination level of BTs at various Fe(VI) dose was determined in buffered milli-Q water (10 mM phosphate buffer) and secondary wastewater effluent (20 mM borate buffer) at pH 8.0 and room temperature (24 ± 1 °C). In a series of 25 mL amber volumetric flasks, 10 μM for each of BTs was spiked in the buffer solution and then the filtered and standardized stock solution of Fe(VI) was added to yield the various concentrations of 0, 50, 100, 200 and 300 μM. The solutions were shaken to have sufficient reaction. Reaction time was 3 h in the darkness. One milliliter of the reaction solution was sampled and quenched with 100 μL of a thiosulfate solution (50 mM). If the reaction solution had iron-precipitates, the treated samples were quenched and centrifuged at 4000 r/min to remove the precipitates. The residual concentration for each of BTs was then determined by the HPLC methods as described above. All experiments were performed in triplicate.

3. Results and discussion

3.1. Kinetics for the reaction of BTs with Fe(VI)

According to the previous studies on Fe(VI) reaction with electron-rich organic moieties (ERM) (Lee et al., 2005a; Sharma et al., 2006; Lee et al., 2008; Hu et al., 2009; Lee et al., 2009), second-order reaction kinetics for the reaction of Fe(VI) with BTs were designed under pseudo-first-order conditions with Fe(VI) in excess to BTs ($[Fe(VI)]_0 = 50 \times [BTs]_0$, and $[BTs]_0 = 2$ μM). Second-order reaction rate law can be described by eq (1).

$$-d[BTs]/dt = k_{app}[Fe(VI)][BTs] \qquad (1)$$

Eq (1) is rearranged and d[BTs]/[BTs] is integrated to become eq (2).

$$\ln([BTs]/[BTs]_0) = -k_{app}\int_0^t [Fe(VI)]dt \qquad (2)$$

Where the term $\int_0^t [Fe(VI)]dt$ is the Fe(VI) exposure, the time integrated concentration of Fe(VI) due to the instability (Lee et al., 2005a) and k_{app} is the apparent second-order rate constant. As a representative example, Fig. 1 (a) shows the oxidation of BT (2 μM) by excess Fe(VI) (100 μM) at pH 7.5 and 24 ± 1 °C. The present study used the second-order rate constant (k_{self}, eq (3)) for the Fe(VI) self-decomposition to predict the Fe(VI) self-decomposition as a function of time (Lee et al., 2009).

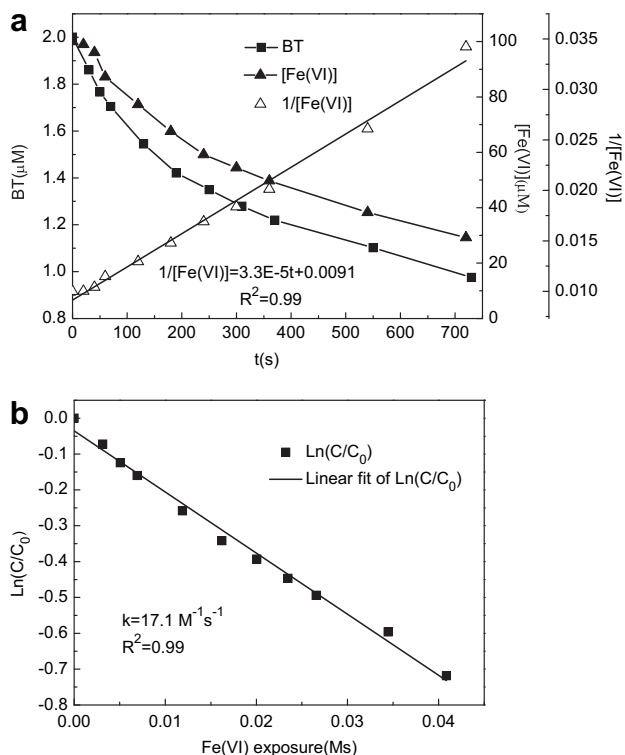$$-d[Fe(VI)]/dt = k_{self}[Fe(VI)]^2 \qquad (3)$$

a

b

Fig. 1 – (a) Fe(VI) oxidation of 1H-benzotriazole.
$[BT]_0 = 2$ μM, $[Fe(VI)]_0 = 100$ μM, pH 7.5, 24 ± 1 °C. (b) Fit of
1H-benzotriazole oxidation by Fe(VI) with second-order
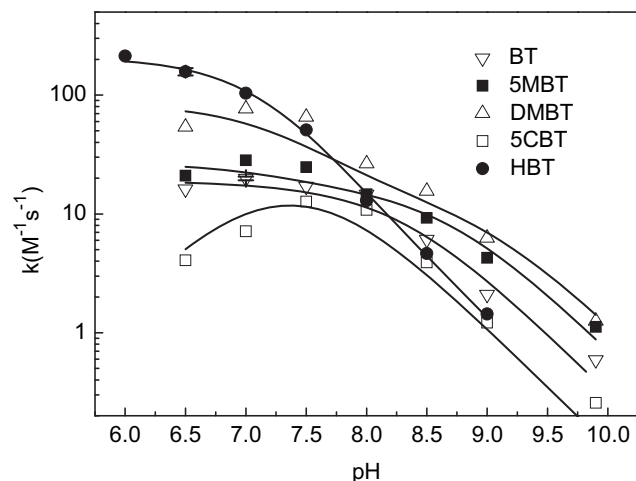reaction kinetics (eq (2)).

Fig. 2 – Apparent second-order rate constants and
associated model simulation for the reactions of
benzotriazoles with Fe(VI) as a function of pH (6.0–10.0) at
the room temperature (24 ± 1 °C).

Accordingly separating the variables and integrating give
eq (4) (Fig. 1 (a)).

$$1/[Fe(VI)] = k_{self}t + C \quad (4)$$

Then substituting eq (4) into Fe(VI) exposure leads to eq (5).

$$\int_0^t [Fe(VI)]dt = \frac{1}{k_{self}}\ln\left(1 + \frac{k_{self}}{C}t\right) \quad (5)$$

Therefore the slope of the plots gave the k_{app} as 17.1 $M^{-1}s^{-1}$
($R^2 > 0.99$) at pH 7.5 and 24 ± 1 °C (Fig. 1 (b)). The values of rate
constants k_{app} for the reaction of Fe(VI) with BTs as a function
of pH (6.0–10.0) are presented in Fig. 2. The rate constants of
the reaction decreased with increasing pH values except
5CBT. The oxidation rate of 5CBT showed a general increase
with decreasing pH between pH 10.0 and 7.5, but the rates
decreased obviously with a decrease in acidic media with
a maximum at pH 7.5 as Fe(VI) reaction with glycine
(Noorhasan et al., 2010). These pH-dependent variations in
k_{app} could be distributed by considering species-specific
reactions between Fe(VI) species (, $pK_{a,H2FeO4} = 3.50$ (Rush
et al., 1996), $pK_{a,HFeO4} = 7.23$ (Sharma et al., 2001)) and acid-
base species of an ionizable BTs (pK_a, Table 2) by eqs (6–12).

$$k_{app}[Fe(VI)]_{tot}[BTs]_{tot} = \sum_{\substack{i = 1,2,3 \\ j = 1,2}} k_{ij}\alpha_i\beta_j[Fe(VI)]_{tot}[BTs]_{tot} \quad (6)$$

$$\alpha_1 = [H_2FeO_4]/[Fe(VI)]_{tot} = [H^+]^2/T \quad (7)$$

$$\alpha_2 = [HFeO_4^-]/[Fe(VI)]_{tot} = [H^+]K_{a,H2FeO4}/T \quad (8)$$

$$\alpha_3 = [FeO_4^{2-}]/[Fe(VI)]_{tot} = K_{a,H2FeO4}K_{a,HFeO4-}/T \quad (9)$$

$$T = [H^+]^2 + [H^+]K_{a,H2FeO4} + K_{a,H2FeO4}K_{a,HFeO4-} \quad (10)$$

$$\beta_1 = [BTs]/[BTs]_{tot} = [H^+]/([H^+] + K_{a,BTs}) \quad (11)$$

$$\beta_2 = [BTs^-]/[BTs]_{tot} = K_{a,BTs}/([H^+] + K_{a,BTs}) \quad (12)$$

Where $[Fe(VI)]_{tot} = [H_2FeO_4] + [HFeO_4^-] + [FeO_4^{2-}]$, $[BTs]_{tot} = [BTs] + [BTs^-]$. α_i and β_j represent the respective species
distribution coefficients for Fe(VI) and BTs, i and j represent
each of the three Fe(VI) species and BTs species respectively,
and k_{ij} represents the species-specific second-order rate

**Table 2 – The determined k_{app} values for reactions of BT
with various oxidants.**

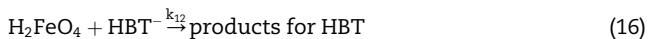| Oxidants	pH	k_{app} ($M^{-1}s^{-1}$)	Reference
Fe(VI)	7.0	19.9	This study
	9.8	0.6	This study
O_3	2.0	$18.4^a/36.4^b$	Vel Leitner and Roshani, 2010
	5.0	22.0	Vel Leitner and Roshani, 2010
•OH	2.0	1.7×10^{10}	Vel Leitner and Roshani, 2010
	10.2	6.2×10^9	Vel Leitner and Roshani, 2010
	5.8	7.6×10^9	Naik and Moorthy, 1995
	10.5	9.0×10^9	Naik and Moorthy, 1995

a : the competition kinetic model.
b : the log-reduction of BT with ozone in excess.

constant for the reaction between the Fe(VI) species i with the BTs species j.

Based on previous investigations (Lee et al., 2005a; Lee et al., 2008; Hu et al., 2009; Lee et al., 2009), the reactions of FeO_4^{2-} species with the compounds studied were omitted due to the low reactivity of FeO_4^{2-} species, and did not significantly affect the model accuracy. For BT, 5MBT, DMBT and 5CBT, eqs (13–15) were used to model the kinetics. Hence the species-specific second-order rate constants, k_{21} and k_{22}, were calculated from least-squares nonlinear regressions of the experimental k_{app} data by using the software SigmaPlot 10.0 (Systat Software Inc.). The model could explain the experimental k_{app} well ($R^2 = 0.88$–0.95). Table 1 summarizes the determined k_{21} and k_{22} values for BTs except HBT. k_{22} was magnitude higher than k_{21} because the deprotonated species are better electron donors. However just like Fe(VI) reaction with 4-cyanophenol and 4-nitrophenol (Lee et al., 2005a), the model kinetics (eqs (13–15)) could not interpret the observed pH dependency of k_{app} for HBT. The k_{app} of HBT steadily increases even at the whole investigated pH range. Thus we also utilized the eq (16,17) between H_2FeO_4 species and the dissociated HBT species ($k_{12}\alpha_1\beta_2$) to explain the pH dependency of k_{app} of HBT.

$$HFeO_4^- + BTs \xrightarrow{k_{21}} products \qquad (13)$$

$$HFeO_4^- + BTs^- \xrightarrow{k_{22}} products \qquad (14)$$

$$k_{app} = k_{21}\alpha_2\beta_1 + k_{22}\alpha_2\beta_2 \text{ for BT, 5MBT, DBMT, 5CBT} \qquad (15)$$

$$H_2FeO_4 + HBT^- \xrightarrow{k_{12}} products \text{ for HBT} \qquad (16)$$

$$k_{app} = k_{12}\alpha_1\beta_2 + k_{21}\alpha_2\beta_1 + k_{22}\alpha_2\beta_2 \qquad (17)$$

Fig. 3 shows a successful model for the observed pH dependency of k_{app} for HBT ($R^2 = 0.99$) using eq (16,17) by least-squares nonlinear regressions. The k_{12} and k_{22} values were 1.6

(± 0.1) $\times$ 10^6 $M^{-1}s^{-1}$ and 7.7(± 0.6) $\times$ 10^1 $M^{-1}s^{-1}$ for HBT respectively. But the value of k_{21} could not be determined accurately because of low contribution of protonated Fe(VI) with undissociated HBT. Besides the k_{12} is 10^4 times higher than k_{22}, which indicates H_2FeO_4 has a higher reactivity than $HFeO_4^-$ (Kamachi et al., 2005).

As a consequence, each of BTs can be oxidized at circumneutral pH, with $t_{1/2}$ ranging from 132 s to 1917 s for an Fe(VI) concentration of 10 mg/L at pH 7.0 and 24 $\pm$ 1 °C. In addition, the second-order rate constants for BT reaction with Fe(VI) (19.9 $M^{-1}s^{-1}$, pH 7.0) are similar to that with molecular ozone which was determined to be 36.4 $M^{-1}s^{-1}$ (the log-reduction of BT with ozone in excess) or 18.4 $M^{-1}s^{-1}$ at pH 2 and 22.0 $M^{-1}s^{-1}$ at pH 5 (the competition kinetic model) (Vel Leitner and Roshani, 2010), but magnitude lower than that with the hydroxyl radicals during ozonation (Vel Leitner and Roshani, 2010) or the pulse radiolysis (Naik and Moorthy, 1995). The second-order rate constants of the BT reaction with the hydroxyl radicals were determined to vary from 6.2 $\times$ 10^9 $M^{-1}s^{-1}$ to 1.7 $\times$ 10^{10} $M^{-1}s^{-1}$. The determinted k_{app} values for reactions of BT with various oxidants were shown in Table 2.

3.2. Linear free-energy relationships

A linear free-energy relationship was performed to predict the effect of the substituents on the species-specific second-order rate constants of the BTs reaction with Fe(VI). Although other Hammett parameters (i.e., σ^+) have previously been used to test substituted phenols reactivity with Fe(VI) (Lee et al., 2005a), the present study used σ_p as free-energy descriptors on account of their suitability for characterizing electrophilic reactions. The σ_p terms for BTs were obtained from the literature (Hansch et al., 1991). Fig. 3 shows the obtained Hammett-type correlations for k_{21} versus σ_p and for k_{22} versus σ_p (except for HBT). The linear regressions for both the undissociated and the dissociated BTs are

$$\log(k_{21}) = 1.00(\pm 0.08) - 2.86(\pm 0.38)\sigma_p \quad R^2 = 0.95 \, n = 4 \qquad (18)$$

$$\log(k_{22}) = 2.27(\pm 0.02) - 1.94(\pm 0.10)\sigma_p \quad R^2 = 0.99 \, n = 4 \qquad (19)$$

A negative Hammett slope (ρ) illustrated the electrophilic oxidation mechanism. The magnitude of the ρ value reflects the sensitivity of the reaction to the substituent effect (Hansch et al., 1991). However, the reaction between $HFeO_4^-$ with the undissociated BTs (-2.86) is more sensitive to the substituent effect than that with the dissociated BTs(-1.94).The Hammett constant (σ) reflects the effects of substituents on the electron density of the aromatic ring by inductive and resonance effects. Fig. 3 indicates that electron-donating substituents ($\sigma < 0$) activate the BT structures toward attack by Fe(VI), whereas electron-withdrawing substituents ($\sigma > 0$) result in deactivation. With the increasing amount of methyl substituents of BT, the stronger the activation, and the higher the reaction rate of BTs with Fe(VI) except HBT. Thus, with the success of the linear free-energy relationships (eq (18,19)) we can suppose that Fe(VI) reacts initially with BT by electrophilic attack at the 1,2,3-triazole moiety. For HBT, it deviates from the fitted straight line. Because the hydroxyl replaces
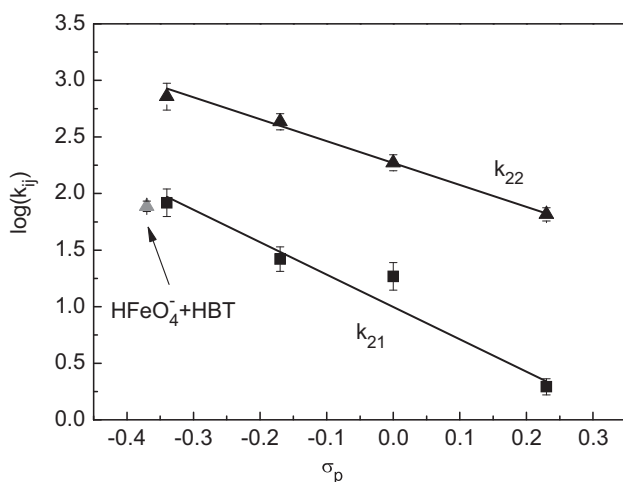

Fig. 3 – Correlations between the second-order rate constants of the reactions between $HFeO_4^-$ with the undissociated benzotriazoles(k_{21}) and the dissociated benzotriazoles (k_{22}) vs Hammett constants.

hydrogen atom connecting with nitrogen rather than the benzene ring, the reaction mechanism is electrophilic attack at the N–OH bond of HBT by Fe(VI).

3.3. BTs degradation by Fe(VI)

Fig. 4 demonstrates the degradation efficiency of BTs oxidation by Fe(VI) individually under different molar ratios in buffered milli-Q water (Fig. 4 (a)) and secondary wastewater effluent (Fig. 4 (b)) at pH 8.0 and 24 ± 1 °C. With the dosage of Fe (VI) gradually increasing, the concentration of each BTs was decreasing. Due to the competition reaction occurred between BTs and wastewater matrix, the removal rate of each BTs in secondary wastewater effluent was less then in buffered milli-Q water when the dosage of Fe(VI) was lower than 100 μM (Fig. 4). However, when the dosage of Fe(VI) was more than 100 μM, the competition disappeared after the wastewater matrix were consumed (Lee and von Gunten, 2010), the removal rate of each BTs in secondary wastewater effluent was similar to that in buffered milli-Q water. With the molar ratio of Fe(VI) and BTs increasing up to 30:1, the removal rate of each BTs reached about >95% in buffered milli-Q water or secondary wastewater effluent. Besides, intermediates of the oxidation of benzotriazole by Fe(VI) were investiagted and independently determined by gas chromatography-mass spectrometry (GC–MS) and rapid resolution liquid chromatography-tandem mass spectrometry (RRLC-MS/MS), for detailed information of byproducts identification, please refer to Supplementary Information, Text S2. But no obvious intermediates were found in the present study.

The present study and previous studies (Lee and von Gunten, 2010; Noorhasan et al., 2010; Sharma, 2010) showed that Fe(VI) can react with dissolved organic nitrogen compounds. Oxidation of nitrogen-containing compounds by Fe(VI) can proceed through either one-electron or two-electrons processes to yield non-hazardous oxidation products (Sharma, 2010). The k values decrease in the order of aniline > glycine (primary amine) > dimethylamine (secondary amine) > trimethylamine (tertiary amine) in the pH range 6–8 (Lee and von Gunten, 2010; Noorhasan et al., 2010). The present study demonstrated that Fe(VI) can also react with the nitrogen-containing heterocyclic compounds BTs. The k of BTs are found ranging between secondary amine and tertiary amine, depending on the substituents on BTs. In a word, BTs can be degraded by Fe(VI) oxidation completely.

4. Conclusions

Second-order reaction kinetics was used to model the data obtained from the Fe(VI) oxidation of BTs and species-specific second-order rate constants were determined for the reaction as a function of pH. For BT, 5MBT, DMBT and 5CBT, the reactions with the species $HFeO_4^-$ predominantly controled the rates. For HBT, the species H_2FeO_4 with dissociated HBT played a major role in the reaction. Each of BTs reacted moderately with Fe(VI) with the half life ($t_{1/2}$) ranged from 132 s to 1917 s as estimated by assuming pseudo-first-order conditions with a Fe (VI) excess. When the molar ratio of Fe(VI) and BTs increasing up to 30:1, the removal rate of BTs reached about >95% in buffered milli-Q water and secondary wastewater effluent. A linear free-energy relationship could interpret the electrophilic oxidation mechanism. Fe(VI) reacts initially with BTs by electrophilic attack at the 1,2,3-triazole moiety of BT, 5MBT, DMBT and 5CBT, and at the N–OH bond of HBT.
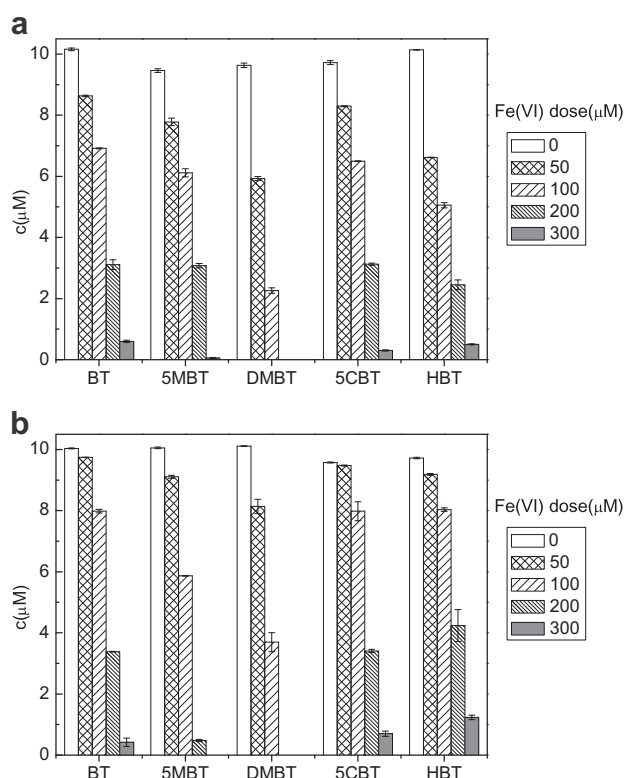

Fig. 4 – Oxidation of benzotriazoles in buffered milli-Q water (a, 10 mM phosphate buffer) and secondary wastewater effluent (b, 20 mM borate buffer) as a function of the Fe(VI) dose (0–300 μM). Experimental conditions: pH = 8.0, T = 24 ± 1 °C, [BTs]$_0$ = 10 μM, and contact time 3 h.

Appendix. Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.watres.2011.01.022.

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