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Oxidative removal of diclofenac by chlorine dioxide: Reaction kinetics and mechanism

Yingling Wang [a,b], Haijin Liu [b], Youhai Xie [b], Tianjun Ni [a], Guoguang Liu [b,c,*]

[a] School of Basic Medical Sciences, Xinxiang Medical University, Xinxiang 453003, PR China
[b] School of Environment, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Key Laboratory for Yellow River and Huaihe River Water Environment and Pollution Control, Ministry of Education, Xinxiang 453007, PR China
[c] Faculty of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, PR China

HIGHLIGHTS

- The reaction kinetics of diclofenac oxidation via ClO_2 was investigated.
- The influences of pH and temperature on reactivities were elucidated.
- Quenching experiments were employed to establish a kinetics model.
- The degradation mechanism involved two tentative routes: ClO_2 oxidation and $O_2^{\cdot}$ oxidation.

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ABSTRACT

Diclofenac (DCF) is one of the most widely used anti-inflammatory drugs, which has been frequently detected in the aquatic environment. In this work, the detailed kinetics and mechanism of DCF degradation via ClO_2 under simulated water disinfection conditions were investigated. Experimental results demonstrated that DCF may be rapidly and completely oxidized with excess ClO_2. The reaction had first-order dependence with respect to DCF and ClO_2, and the largest apparent second-order rate constant, k_{app}, was $1.51(\pm0.017) \times 10^3\ M^{-1}\ s^{-1}$ at pH 7.0. Within the studied pH (5–10) and temperature (278–308 K) ranges, the small variation of k_{app} exhibited very slight pH and temperature dependence. The degradation of DCF was significantly inhibited (36.07(±0.36)%) through the addition of an $O_2^{\cdot-}$ scavenger (chloroform), but not by a $HO^{\cdot}$ scavenger (isopropanol). This indicated that $O_2^{\cdot-}$ played a key role during the DCF removal process. Based the obtained results, a kinetics model for DCF degradation by ClO_2 was established, which involved electron transfer from DCF to ClO_2 molecules to form $DCF^{\cdot}$ and subsequent $O_2^{\cdot-}$ radicals. A tentative mechanism that accounted for the kinetics model was proposed and validated, involving the two major pathways: direct oxidation by ClO_2 and indirect oxidation by $O_2^{\cdot-}$.

1. Introduction

Chlorine dioxide is a powerful one-electron oxidant (E_a = 0.936 V), known for its ability to oxidize organic [1] and inorganic pollutants [2]. ClO_2 is also known for its anti-bacterial [3] and anti-viral properties [4]. It is commonly employed in the pulp and paper industry [5], as well as in water treatment systems [6]. Previous studies have reported the oxidative degradation of several pharmaceutical contaminants via ClO_2 such as estrogenic 17α-ethinylestradiol, antibiotic sulfamethoxazole, roxithromycin, β-lactams and fluoroquinolones [7–9]. As a highly selective oxidant, ClO_2 has the advantages of comparable biocidal efficacy, along with less pH-dependence and the reduced potential of disinfectant by-products formation, in comparison to free chlorine [6,10]. In view of the increasing use of ClO_2 in domestic water treatment, it is of great interest to elucidate the specific reactions of ClO_2 with extensively consumed pharmaceutical drugs, which have been detected in groundwater, as some partially degraded products may be hazardous on release into the ecosystem [11,12].

Diclofenac (DCF, 2-[(2,6-dichlorophenyl) amino] phenylacetic acid), a non-steroidal anti-inflammatory drug, is one of the most frequently detected pharmaceuticals in the effluents emanating

* Corresponding author at: School of Environment, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Key Laboratory for Yellow River and Huaihe River Water Environment and Pollution Control, Ministry of Education, Xinxiang 453007, PR China. Tel.: +86 373 3325971; fax: +86 373 3326335.
E-mail address: liugg@gdut.edu.cn (G. Liu).

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from hospitals and sewage treatment plants (STPs) [13], as well as in surface waters [14]. Since typically, only 20–30% of DCF loads are removed by conventional STPs, the remainder is subsequently introduced through STP-discharges into ambient surface waters, such as rivers and lakes [15,16]. Over the last several years, various advanced oxidation processes (AOPs) for the degradation of DCF have been studied under diverse experimental conditions, encompassing photocatalysis with TiO_2 [17] or Fenton reagents [18], ozonation [19] and sonolysis, either in isolation or when combined with UV–Vis irradiation in the presence of TiO_2 [20,21]. However, all of these AOPs, except for photo-Fenton processes, typically suffer from high operational costs and the only partial degradation of pharmaceuticals [22], a relatively high concentration of DCF was still detected in STP-effluents and ambient surface waters at level of up to 4.7 and 1.2 $\mu g\ L^{-1}$, respectively [19,23].

Several studies have revealed that the DCF residues in the environment pose threats to both human health and ecosystems. For example, the harmful effects of DCF on different organisms in realistic aquatic environments have been demonstrated [24]. DCF may also cause renal failure in the Indian Gyps vultures and gills alterations in rainbow trout, with these observed effects taking place at concentrations as low as 1 $\mu g\ L^{-1}$ [25,26]. According to Hernando et al. [27], based on the EC_{50} values reported in the literature, DCF may be considered as very toxic to bacteria ($EC_{50} < 1\ mg\ L^{-1}$) and to invertebrates and algae ($EC_{50} = 1–10\ mg\ L^{-1}$). In the year 2000, DCF was included into the EU priority list of compounds that are known to pose a significant risk to aquatic ecosystems [28]. As a result, novel and reactive disinfectant are required for the rapid and complete degradation of DCF during potable water treatment, while producing little or no toxic by-products.

From the foregoing, the structure of the DCF molecule contains phenyl ring, carboxyl and amine moieties and thus is likely to be susceptible to attack by oxidants such as ClO_2. A better understanding of the reaction kinetics and transformation pathways of DCF with ClO_2 will be useful to better predict the fate of DCF in water treatment. Furthermore, the simulation of actual water environments through variations of pH and temperature might ultimately validate the practical application of ClO_2. The primary objectives of this study were to both investigate the reaction kinetics of DCF oxidation and evaluate the influences of initial pH and temperature on this reactivity under simulated water disinfection conditions. A further step was to identify the major transformation pathways and degradation mechanism of the parent compound via quenching experiments, and through the establishment of a kinetics model.

2. Materials and methods

2.1. Standards and reagents

DCF, 2-[(2,6-dichlorophenyl) amino] benzeneacetic acid, sodium salt (98% purity), was purchased from J&K Chemical Co. Ltd. (Beijing, China). Sodium chlorite (90% purity), isopropanol (99.7%, AR) and chloroform (99.5%, AR) were obtained from Tianjin Guangfu Chemical Reagents Co. Ltd. (Tianjin, China). A pure solution of ClO_2 was generated from gaseous ClO_2 by slowly adding dilute H_2SO_4 to a $NaClO_2$ solution. Impurities such as chlorine were removed from the N_2 gas stream by a $NaClO_2$ scrubber and the gaseous ClO_2 was introduced into ultra-pure water and stored in a brown bottle at 4 °C in a dark refrigerator to slow decomposition [29]. Isopropanol and chloroform were used as hydroxyl radical (HO) and superoxide radical ($O_2^{\cdot-}$) scavengers, respectively. High performance liquid chromatography (HPLC)-grade methanol was obtained from Suqian Guoda Chemical Reagents Co. Ltd. (Jiangsu, China). Other employed reagents ($Na_2S_2O_3$, KI, phosphate, etc.) were of analytical grade and used without further purification. 18.2 MΩ cm of ultrapure water (Millipore, USA) was used throughout the experimental procedures and chromatographic analyses.

2.2. Experimental setup

Kinetics experiments involving DCF oxidation by ClO_2 were carried out in 250 mL circulating jacket beaker on a collector-type magnetic stirrer in the dark. To prevent the DCF from auto-oxidation/photolysis, the DCF reaction solution (250 mL) was freshly prepared by spiking 0.25 mL of its stock solution (3.00 mM) to attain a concentration of 3.00 μM. The pH of the tested aqueous solutions was adjusted to the desired level through the addition of either NaOH or phosphoric acid. Preliminary experiments to determine the reaction orders and rate constants were conducted with an initial DCF concentration (3.00 μM), and different volumes of ClO_2 stock solution (20–45 μL) were then added to initiate the reaction.

According to the factorial experiment design, the reactivity as a function of pH (5–10) and temperature (278–308 K) were systematically investigated. At preselected time intervals, 2.00 mL of the reaction liquid was transferred using an Eppendorf pipette, from the jacket beaker to the HPLC vial, which contained 50 μL of preloaded $Na_2S_2O_3$ (0.01 M), to immediately terminate the reaction [30,31]. Samples were further analyzed using HPLC to determine the remaining DCF concentration. All trials were performed in triplicate and mean values were quoted as results. The relative standard deviation (RSD) of three separate measurements was never higher than 20%.

2.3. Analytical methods

The concentrations of the DCF solutions were determined via a reversed-phase HPLC system, which consisted of two Waters 1525 Binary HPLC pumps and Waters 2998 Photodiode Array detector (Waters, Massachusetts, USA). Analytical column temperatures were controlled with a Model 1500 Column Heater (Waters, and product of Singapore). The analytical column was a 150 mm × 4.6 mm Waters C18 column, (particle size 5 μm). A Waters guard column (C18, 4.6 mm × 20 mm, particle size 5 μm) was employed to protect the analytical column (both purchased from Waters) , and the injection volume was 20 μL. The mobile phase was a mixture of 75% HPLC-grade methanol and 25% Milli-Q-water (containing 1% acetic acid) at a constant flow rate of 1.0 mL min^{-1}, with the detection wavelength set at 276 nm.

The high concentration of ClO_2 stock solution was standardized just prior to application by idometric titration with a standard sodium thiosulfate solution [32] and the low concentrations of ClO_2 reaction solutions were determined spectrophotometrically based on the molar absorption coefficient of ClO_2, $\varepsilon_{359\ nm} = 1230\ M^{-1}\ cm^{-1}$ at 359 nm [33]. The pH of the solution was measured using a Mettler Toledo Delta 320 pH, whereas, the reaction temperatures were simultaneously controlled by a HX-08 Cryostat (Shanghai Bilon Instruments Co. Ltd., China).

3. Results and discussion

3.1. Kinetic parameters for DCF-ClO_2 reaction

In the ClO_2 oxidation of organic contaminants, second order kinetics has generally been observed [10,11,34]. However, in some cases, the decay of ClO_2 might follow the mixed-order or second-order kinetics [35,36]. Initially, the experiments were conducted at pH 7.0 and 298 K to determine the rate law of the

reaction between ClO_2 and DCF. The rate expression for the reaction of ClO_2 with DCF may be described as the following equation:

$$-\frac{d[DCF]}{dt} = k_{app}[DCF]^m[ClO_2]^n \quad (1)$$

where $[ClO_2]$ and [DCF] are the concentrations of ClO_2 and DCF, m and n are the orders of the reaction with respect to the concentrations of ClO_2 and DCF, respectively, and k_{app} is the apparent reaction rate constant. The kinetic experiments were designed under the condition of ClO_2 in excess of DCF ($[DCF]_0$ = 3.00 μM, and $[ClO_2]_0$ = 18.9–42.6 μM). When the initial ClO_2 concentration was added from 18.9 μM to 42.6 μM, the removal rate of DCF was increased from 81.9% to 98.0% after 60 s of reaction time, while the ClO_2 consumed during the kinetic investigation was varied correspondingly from 7.29% to 4.08% as observed at 359 nm on an UV–Vis spectrophotometer [33], confirming the negligible amount of ClO_2 loss throughout the experiments. Eq. (1) can be rewritten as:

$$-\frac{d[DCF]}{dt} = k_{obs}[DCF]^m \quad (2)$$

$$k_{obs} = k_{app}[ClO_2]^n \quad (3)$$

The loss of DCF as a function of time could be fitted nicely to single exponential decay, in the presence of ClO_2 (18.9 μM) as illustrated in Fig. 1a, which indicated that the rate was first-order with respect to the concentration of DCF, i.e., m = 1. Different values of pseudo first-order rate constants (k_{obs}, s^{-1}) were determined from the slopes of the linear time-course plots of $\ln([DCF]/[DCF]_0)$ for each initial concentration of ClO_2.

For a constant concentration of DCF (3.00 μM), k_{obs} increased linearly with increasing ClO_2 concentrations from 18.9 μM to 42.6 μM (Fig. 1b). The plot of $\ln k_{obs}$ vs. $\ln[ClO_2]_0$ was linear (R^2 = 0.9951) and a slope of 1.03 (±0.032) (Fig. 1b) was obtained, which implied that the reaction was also of the first-order with respect to the ClO_2 concentration, i.e., n = 1. To summarize, the oxidation kinetics of DCF by ClO_2 could be described by the following second-order rate equation:

$$-\frac{d[DCF]}{dt} = k_{app}[DCF][ClO_2] \quad (4)$$

For each experiment (performed with different concentrations of ClO_2), k_{app} values were determined by considering Eq. (3). The value of k_{app} was calculated to be 1.51(±0.017) × 10^3 M^{-1} s^{-1} with a ClO_2 concentration of 18.9 μM, which is little less than the results (k_{app} 1.05 × 10^4 M^{-1} s^{-1}) reported by Huber, et al. [37]. However, it is about 10^3 times higher that of chlorination (k_{app} = 3.89 ± 1.17 M^{-1} s^{-1} at pH 7.0) [38]. The half-life of DCF degradation was determined by ClO_2 treatment within 24.3(±0.27) s, while only 50% of DCF was removed by chlorination with a total chlorine concentration of 1 mg L^{-1} in 215 s. The other phenolic moiety of 17α-ethinylestradiol (k_{app} = 1.8 × 10^6 M^{-1} s^{-1}), the aromatic amine moieties of sulfamethoxazole (k_{app} = 7.9 × 10^3 M^{-1} s^{-1}) [7] and the phenolic-diketone groups of tetracycline (k_{app} = 1.26 × 10^6 M^{-1} s^{-1}) [10] were considered as favorable sites for attack by ClO_2. Comparatively, ibuprofen (k_{app} < 0.1 M^{-1} s^{-1}), atenolol (k_{app} ≈ 1 M^{-1} s^{-1}) [39] and ciprofloxacin (k_{app} = 7.9 M^{-1} s^{-1}) [9] typically had lower rates than the above-mentioned pharmaceuticals.

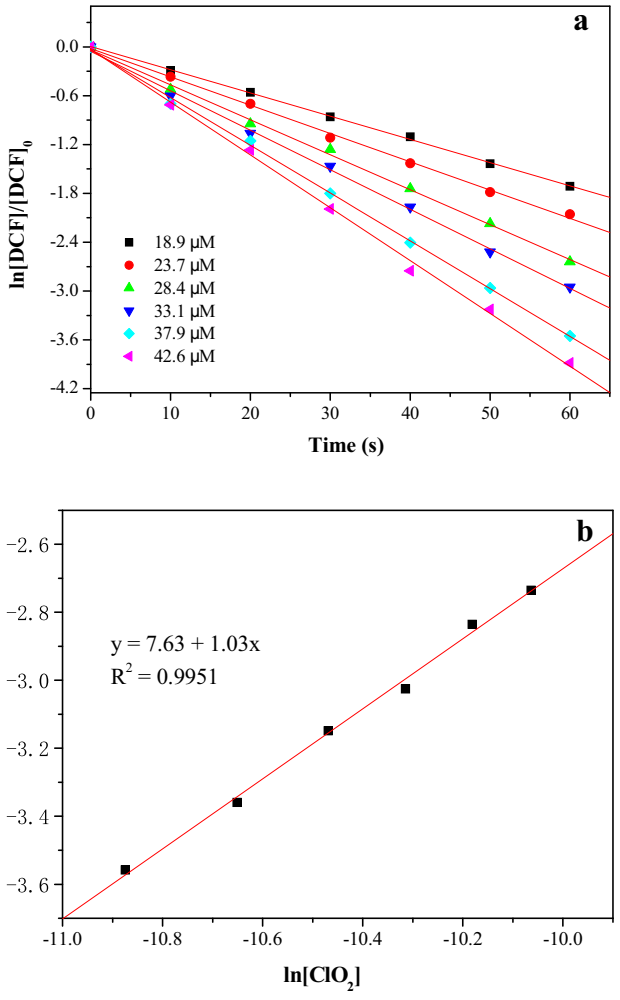


Fig. 1. Determination of reaction order for DCF oxidation by ClO_2: (a) plot of $\ln([DCF]/[DCF]_0)$ vs. reaction time at different initial ClO_2 concentrations; and (b) plot of $\ln(k_{obs})$ vs. $\ln[ClO_2]_0$. $[DCF]_0$ = 3.00 μM, pH = 7.0, T = 298 K.

3.2. Effect of pH on DCF oxidation

Similar experiments were also performed to determine the values of k_{app} at different pH levels at 298 K. Fig. 2 indicated that the oxidation of DCF (3.00 μM) by ClO_2 (18.9 μM) was slightly dependent on pH. From pH 5.0 to 10.0, k_{obs} initially increased from 1.75(±0.036) × 10^{-2} s^{-1} to 2.78(±0.054) × 10^{-2} s^{-1} and subsequently decreased slightly from 2.78(±0.054) × 10^{-2} s^{-1} to 1.94(±0.035) × 10^{-2} s^{-1} with the maximum value of 2.78(±0.054) × 10^{-2} s^{-1} at pH 7.0. According to k_{obs} at the setting

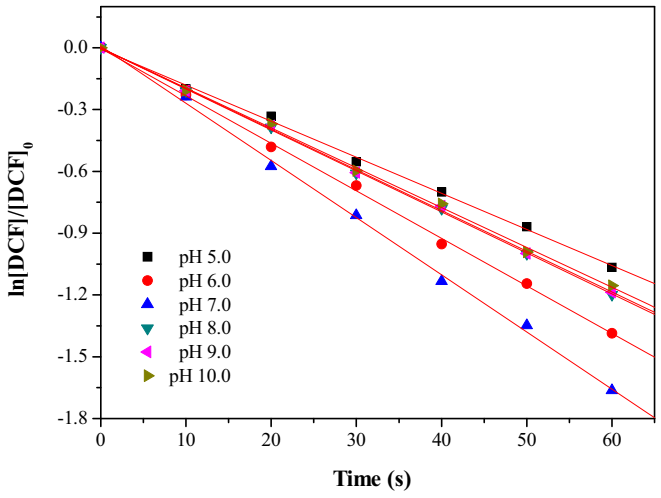


Fig. 2. Plot of $\ln[DCF]/[DCF]_0$ vs. reaction time under different pH conditions. $[DCF]_0$ = 3.00 μM, $[ClO_2]_0$ = 18.9 μM, pH = 7.0, T = 298 K.

Table 1
Oxidation kinetic parameters of DCF under different pH. $[DCF]_0$ = 3.00 μM, $[ClO_2]_0$ = 18.9 μM, pH = 7.0, T = 298 K.

pH	k_{app} (M^{-1} s^{-1})	Dynamic equation	Half-life ($t_{1/2}$, s)	Correlation coefficient (R^2)
5.0	9.25×10^2	$\ln[DCF]/[DCF]_0 = -0.0175t - 0.00574$	39.6	0.9974
6.0	1.22×10^3	$\ln[DCF]/[DCF]_0 = -0.0231t - 0.00256$	30.1	0.9985
7.0	1.47×10^3	$\ln[DCF]/[DCF]_0 = -0.0278t + 0.00802$	25.0	0.9978
8.0	1.05×10^3	$\ln[DCF]/[DCF]_0 = -0.0199t - 8.71E-4$	34.8	0.9993
9.0	1.04×10^3	$\ln[DCF]/[DCF]_0 = -0.0198t - 8.57E-5$	35.1	0.9988
10.0	1.02×10^3	$\ln[DCF]/[DCF]_0 = -0.0194t - 0.00164$	35.8	0.9981

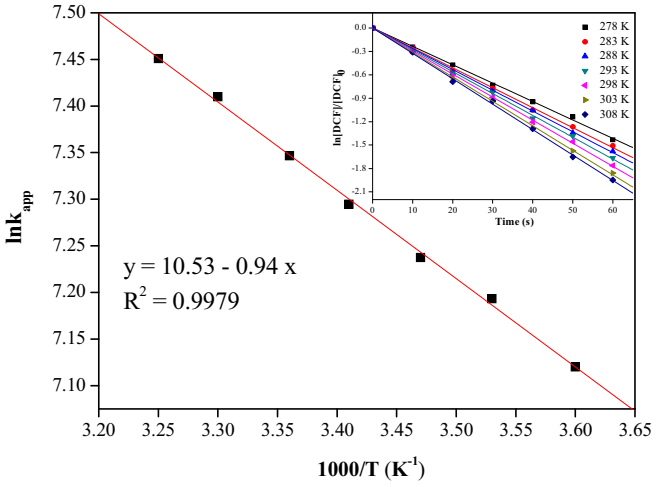


Fig. 3. Arrhenius plot of $\ln k_{app}$ vs. $1/T$ (insert: plot of $\ln[DCF]/[DCF]_0$ vs. reaction time under different temperature). $[DCF]_0$ = 3.00 μM, $[ClO_2]_0$ = 18.9 μM, pH = 7.0.

pH and Eq. (3), the k_{app} value of DCF with ClO_2 could be readily calculated. As shown in Table 1, less pH-dependence was observed for an average value of k_{app} at ~$1.12(\pm0.016) \times 10^3$ M^{-1} s^{-1} and k_{obs} at ~$2.13(\pm0.032) \times 10^{-2}$ s^{-1} within the studied pH range, which was primarily attributed to the properties of ClO_2, such as its high solubility, low reactivity with water and hydrolysis resistance. However, the slight difference in the rate constant with changing pH might be ascribed to the varying of reaction species of DCF and ClO_2. The existent form of DCF and ClO_2 may be described by the following Eqs. (5) and (6):

$$DCF \rightleftharpoons DCF^- + H^+ \quad pK_a = 4.2 \quad [37] \tag{5}$$

$$ClO_2 \overset{+e^-}{\rightarrow} ClO_2^- \overset{+2e^-}{\rightarrow} ClO^- \overset{+2e^-}{\rightarrow} Cl^- \quad [33] \tag{6}$$

where pK_a of $HClO_2$ is 1.96 and pK_a of HClO is 7.5 at 298 K. From pH 5.0 to 7.0, DCF^-, ClO_2, ClO_2^- and HClO are the major species in solution due to the above pK_a value. The HClO species is a much stronger electrophile than ClO_2^- and ClO^- [33], thus it may promote the oxidation of DCF by increasing the fraction of deprotonated DCF and HClO in the reaction system. Above pH 7.0, the reaction rates gradually slowed down, as the pH was increased from 7.0 to 10.0, although the fraction of DCF^- and ClO^- increased, which maybe due to the unfavorable repulsion between ClO^- and DCF^- anions.

According to the redox potential of ClO_2, it is known that chlorine dioxide is typically more reactive under acidic conditions than in neutral and alkaline media [40,41]. However, in some studies, the reaction rates between ClO_2 and aromatic systems, such as tetracycline antibiotics [10], methiocurb [11] and amaranth [42] have been favored by elevated pH, which gave rise to an opposite pH independence. In conclusion, these facts verified that pH played multiple roles in the ClO_2 mediated oxidation of targets.

3.3. Effect of temperature on DCF oxidation

The oxidation of DCF was dependent on temperature since the k_{app} of DCF destruction by ClO_2 was increased gradually from $1.24(\pm0.022) \times 10^3$ to $1.72(\pm0.028) \times 10^3$ M^{-1} s^{-1} with elevated temperatures from 278 K to 308 K, as depicted in Fig. 3 (insert).

According to the Arrhenius equation:

$$\ln k_{app} = \ln A - \frac{E_a}{RT} \tag{7}$$

where E_a is the apparent activation energy, R is the universal gas constant, and A is the Arrhenius pre-exponential constant. Plotting $\ln(k_{app})$ vs. $1/T$ would show a linear relationship between calculated kinetic constants and the reciprocal of absolute temperature (T), as shown in Fig. 3. E_a was determined to be $7.87(\pm0.14)$ kJ mol^{-1} by fitting Eq. (7) to the experimental data. The fit-derived value of E_a fell at the lower end of the range expected for reactions under chemical control, which indicated rather small temperature dependence. The enthalpic (ΔH^{++}) and entropic (ΔS^{++}) contributions to the activation energy were also determined to be $5.38(\pm0.17)$ kJ mol^{-1} and $-165.75(\pm3.03)$ J mol^{-1} K^{-1}, respectively, by fitting the temperature-dependent kinetic data with the Eyring Eq. [43]:

$$\ln\frac{k_{app}}{T} = -\frac{\Delta H^{++}}{R} \times \frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{++}}{R} \tag{8}$$

where k_B is Boltzmann's constant and h is Planck's constant.

The E_a and ΔH values indicated a subtle energy difference between the transition state and the reactants, because of the relative high reactivities between ClO_2 and DCF, which suggested the electrophilic attack by ClO_2. The abstraction of an electron on the nitrogen atom of DCF would be likely to produce DCF radicals (DCF·).

3.4. Effect of oxygen concentration on DCF oxidation

Dissolved oxygen experiments were conducted to investigate the effect of oxygen concentration on the degradation of DCF, for which three conditions were required, i.e., using N_2 or O_2 as a purging gas (200 mL min^{-1}), or under magnetic stirring.

As can be seen from Fig. 4, the higher the oxygen content, the more rapid the reaction rate. The fitting rate constants (k_{obs}) were $2.63(\pm0.058) \times 10^{-2}$, $3.51(\pm0.067) \times 10^{-2}$ and $2.84(\pm0.051) \times 10^{-2}$ s^{-1} in the absence and presence of O_2, or under magnetic stirring, respectively. These results led to the conclusion that dissolved oxygen promoted the oxidation of DCF. Therefore, it is possible that the DCF oxidation process involved dissolved oxygen participation in the reaction solution via reactive oxygen species (ROS), such as ·OH, $^1O_2$ and $O_2^{\cdot-}$.

3.5. Kinetics model and mechanism for DCF oxidation

To ascertain the generation of ROS and study the mechanism underlying DCF oxidation by ClO_2, quenching experiments for

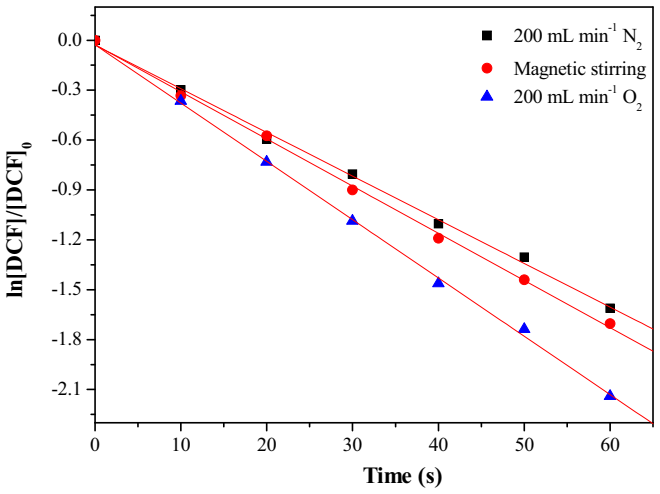


Fig. 4. Kinetics of DCF oxidation by ClO_2 at various dissolved oxygen contents. $[DCF]_0$ = 3.00 μM, $[ClO_2]_0$ = 18.9 μM, pH = 7.0, 298 K.

hydroxyl radicals [44] and superoxide anion radicals [18] were performed via the addition of isopropanol and chloroform, respectively. Fig. 5 shows the role of the resultant ·OH and $O_2^{\cdot-}$ in the ClO_2-mediated oxidation of DCF at pH 7.0 at 298 K. It was clear that the addition of isopropanol had no effect on the degradation of DCF, while chloroform served to suppress its oxidation significantly. Experimental results suggested that $O_2^{\cdot-}$ was the most probable ROS in this system.

According to the previous research [45], the contribution of ·OH and $O_2^{\cdot-}$ toward the overall oxidation of DCF may be estimated as follows:

$$R_{\cdot OH} = \frac{k_{\cdot OH}}{k} \approx \frac{k - k_{isopropanol}}{k} \quad (9)$$

$$R_{O_2^{\cdot-}} = \frac{k_{O_2^{\cdot-}}}{k} \approx \frac{k - k_{chloroform}}{k} \quad (10)$$

where $R_{\cdot OH}$ and $R_{O_2^{\cdot-}}$ are the contribution rates of oxidation of DCF via ·OH and $O_2^{\cdot-}$, respectively; $k_{\cdot OH}$ and $k_{O_2^{\cdot-}}$ are the corresponding rate constants; $k_{isopropanol}$ and $k_{chloroform}$ are the rate constants for the addition of isopropanol and chloroform in the reaction system; k is the rate constant for DCF oxidation with ClO_2 in the absence of free radical scavengers. Calculations revealed that $R_{\cdot OH}$ was 2.73(±0.14)%, while $R_{O_2^{\cdot-}}$ was 36.07(±0.36)%. The direct oxidation of DCF via ClO_2 accounted for the principal dissipation of DCF due to the considerable inhibition of the degradation via the addition of $O_2^{\cdot-}$ scavenger.

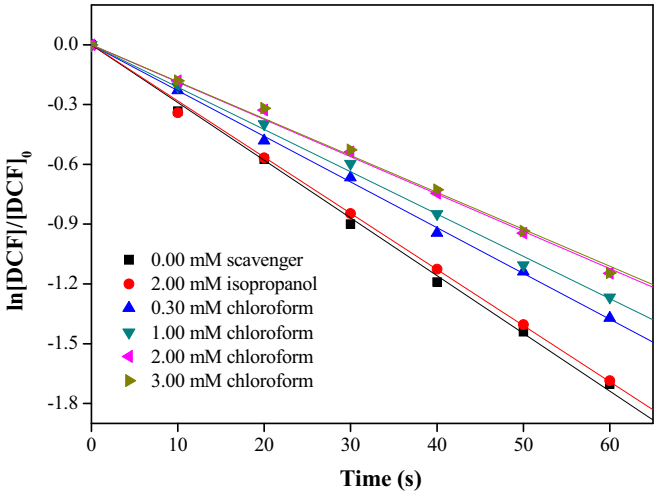


Fig. 5. Effects of isopropanol and chloroform on kinetics of DCF (3.00 μM) oxidation by ClO_2 (18.9 μM) at pH 7.0 and 298 K.

Because chlorine dioxide exists as a free radical monomer (ClO_2) [42], the above results may be interpreted on the basis of the following kinetics model for the $O_2^{\cdot-}$oxidation of DCF:

$$DCF + ClO_2 \xrightarrow[slow]{k_1} DCF^{\cdot} + ClO_2^- \quad (11)$$

$$DCF^{\cdot} + O_2 \xrightarrow{k_2} DCF^+ + O_2^{\cdot-} \quad (12)$$

$$O_2^{\cdot-} \xrightarrow{k_3} O_2 \quad (13)$$

$$O_2^{\cdot-} + DCF \xrightarrow{k_4} products \quad (14)$$

$$DCF^{\cdot} + ClO_2 \xrightarrow[fast]{k_5} products \quad (15)$$

where k_1 is the second-order rate constant of electron transfer from the DCF zwitterion to ClO_2 to produce $DCF^{\cdot}$ and ClO_2^-, k_2 is the second-order rate constant between $DCF^{\cdot}$ and O_2, k_3 is the first-order rate constant for physical quenching of $O_2^{\cdot-}$ by water, k_4 is the second-order rate constant between $O_2^{\cdot-}$ and DCF, and k_5 is the direct oxidation rate constant between $DCF^{\cdot}$ and ClO_2. Reaction (14) is the indirect oxidation via $O_2^{\cdot-}$; Reaction (15) is the direct oxidation process via ClO_2.

Considering the contribution of $O_2^{\cdot-}$, the rate expression (Eq. (4)) should be rewritten:

$$-\frac{d[DCF]}{dt} = k_1[DCF][ClO_2] + k_4[DCF][O_2^{\cdot-}] \quad (16)$$

The steady-state approximation for $DCF^{\cdot}$ is:

$$\frac{d[DCF^{\cdot}]}{dt} = k_1[DCF][ClO_2] - k_2[DCF^{\cdot}][O_2] - k_5[DCF^{\cdot}][ClO_2] = 0 \quad (17)$$

Rearranging Eq. (17) yields:

$$[DCF^{\cdot}] = \frac{k_1[DCF][ClO_2]}{k_2[O_2] + k_5[ClO_2]} \quad (18)$$

The steady-state approximation for $O_2^{\cdot-}$ is:

$$\frac{d[O_2^{\cdot-}]}{dt} = k_2[DCF^{\cdot}][O_2] - k_3[O_2^{\cdot-}] - k_4[DCF][O_2^{\cdot-}] = 0 \quad (19)$$

Rearranging Eq. (19) yields:

$$[O_2^{\cdot-}] = \frac{k_2[DCF^{\cdot}][O_2]}{k_3 + k_4[DCF]} \quad (20)$$

Substituting Eqs. (18) and (20) into Eq. (16) yields:

$$-\frac{d[DCF]}{dt} = \frac{k_1k_2k_4[O_2][ClO_2]}{(k_2[O_2] + k_5[ClO_2])(k_3 + k_4[DCF])}[DCF]^2 + k_1[DCF][ClO_2] \quad (21)$$

Rearranging Eq. (21) yields:

$$k_{obs} = -\frac{d[DCF]}{dt[DCF]} = \frac{k_1k_2k_4[O_2][ClO_2]}{(k_2[O_2] + k_5[ClO_2])(k_3 + k_4[DCF])}[DCF] + k_1[ClO_2] \quad (22)$$

According to Eq. (22), the various initial $[DCF]_0$ were the function of corresponding k_{obs}. The experimental results presented in Fig 6 showed an imperfect linear relationship between DCF concentration and k_{obs}, where the y-intercept of line was the k_{obs} of direct oxidation by ClO_2. Increasing initial DCF concentration led

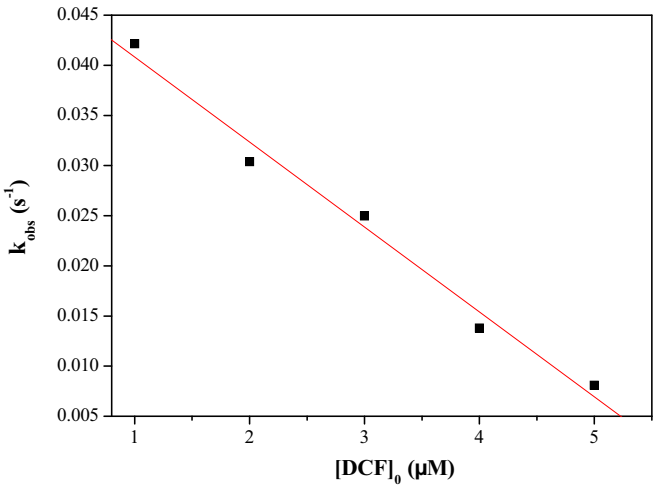


Fig. 6. k_{obs} for the reactions of DCF with ClO_2 (18.9 μM) as a function of initial DCF concentration (1.00–5.00 μM) at pH 7.0 and 298 K.

to a decline in the kinetic rate constants, which were found to be $4.21(\pm0.13)\times10^{-2}$, $3.04(\pm0.085)\times10^{-2}$, $2.50(\pm0.054)\times10^{-2}$, $1.38(\pm0.039)\times10^{-2}$ and $8.09(\pm0.21)\times10^{-3}\ s^{-1}$ at DCF concentrations of 1.00, 2.00, 3.00, 4.00 and 5.00 μM, respectively. From Fig. 6, the k_{obs} of the direct oxidation resulting from the extrapolation to $[DCF]_0 = 0$, the corresponding k_{obs} and k_{app} of direct oxidation were $4.96(\pm0.018)\times10^{-2}\ s^{-1}$ and $2.61(\pm0.094)\times10^{3}\ M^{-1}\ s^{-1}$, respectively.

According to the results of the quenching experiments in DCF solutions, the heuristic mechanism for the initial reaction of DCF with ClO_2 may account for the oxidation pathways (Scheme 1):

(1) The first step involves a single electron transfer from the nitrogen atom of DCF to the ClO_2 radical, to form a DCF· radical and ClO_2^-.

(2) During the direct oxidization of DCF· by ClO_2, the oxidant is initially reduced to ClO, then to HClO, and subsequently to Cl^- [33]. Therefore, four tentative routes may contribute to the direct oxidization, and occur through oxygen transfer process [31,46]:

$$DCF^{\cdot} + ClO_2 \rightarrow DCF - OH + ClO \quad (23)$$

$$DCF^{\cdot} + ClO_2 \rightarrow \text{decarboxyl} - DCF + ClO \quad (24)$$

$$DCF^{\cdot} + H^+ + ClO \rightarrow DCF^+ + HOCl \quad (25)$$

$$DCF^{\cdot} + HOCl \rightarrow DCF - Cl + H_2O \quad (26)$$

In agreement with these profiles, decarboxyl-DCF, hydroxyl-DCF and chloro-DCF have been verified in our published work [29], which suggested that direct electron transfer and oxygen transfer process occurred simultaneously.

(3) DCF· concurrently transfers an electron to dissolved oxygen in solution with the formation of $O_2^{\cdot-}$ and other ROS.

(4) DCF may be indirectly oxidized by either $O_2^{\cdot-}$ or other free radicals, which simultaneously accompany the physical quenching of free radicals.

Good correlations between the experimental data and the model verified that ClO_2 oxidation and $O_2^{\cdot-}$ oxidation coexisted during the DCF degradation process.

4. Conclusions

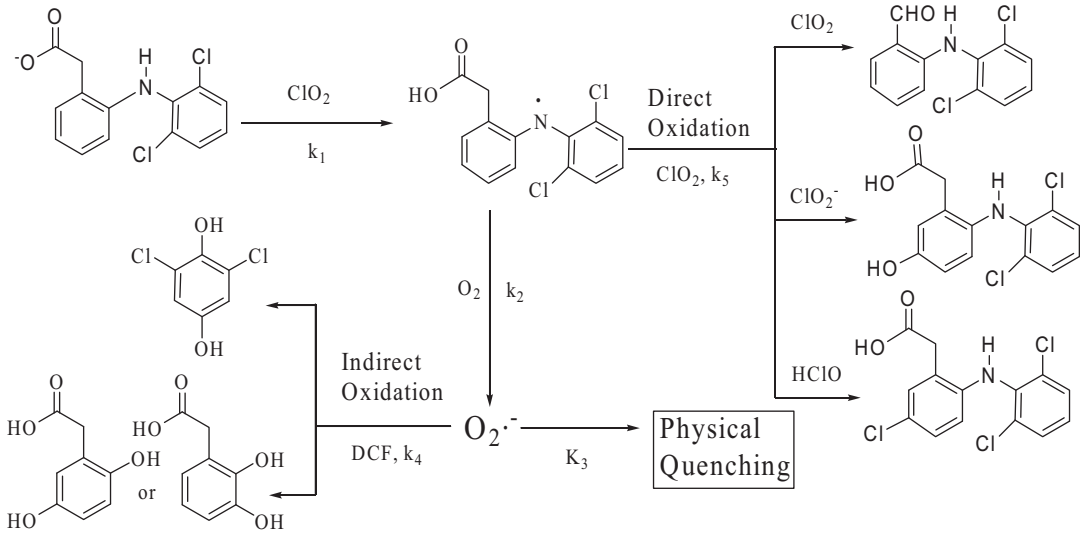
The kinetics and mechanism of DCF degradation by aqueous ClO_2 were investigated under simulated water treatment conditions. The following conclusions can be drawn:

(1) DCF may be rapidly and completely oxidized by the presence of excess ClO_2. All of the reactions followed pseudo first-order with respect to each reactant, and k_{app} under different conditions were determined.

(2) The slight variation of k_{app} under different pH and temperature exhibited relatively lower dependent on pH and temperature, with a maximum value of $1.51(\pm0.017)\times10^3$ at pH 7.0. The activation energy, enthalpy and entropy were $7.87(\pm0.14)\ kJ\ mol^{-1}$, $5.38(\pm0.17)\ kJ\ mol^{-1}$ and $-165.75(\pm3.03)\ J\ mol^{-1}\ K^{-1}$, respectively.

(3) The degradation of DCF was significantly inhibited (36.07%) through the addition of $O_2^{\cdot-}$ scavengers (chloroform), but not by HO· scavengers (isopropanol), indicating that DCF was partially oxidized by the $O_2^{\cdot-}$ that was generated by the reaction system.

(4) The kinetics model for DCF degradation by ClO_2 was established on the basis of the experimental results obtained. The proposed mechanism proceeded through two tentative routes: direct oxidation via ClO_2 and indirect oxidation via $O_2^{\cdot-}$.



Scheme 1. Proposed mechanism for the initial reactions between DCF and ClO_2.

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