



## Kinetics and mechanism of propachlor reductive transformation through nucleophilic substitution by dithionite

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### ABSTRACT

Chloroacetanilide herbicides are extensively used in the control of weeds and have widely resulted in nonpoint contamination of groundwater and soil resources. In the attempt to achieve better remediation for herbicide-contaminated resources, we investigated the reductive transformation of propachlor through nucleophilic substitution by dithionite ( $S_2O_4^{2-}$ ). Results showed that propachlor underwent rapid dechlorination in the presence of dithionite. The reaction was of second-order kinetics and strongly influenced by pH and temperature. At pH 7.0 and temperature 308 K, the rate constant of propachlor dechlorination was estimated at  $123.4 \pm 0.7 \text{ M}^{-1} \text{ h}^{-1}$ . Within the pH range tested (3.0–9.5), higher pH promoted the ionization of dithionite, resulting in a more active nucleophilic reagent of  $S_2O_4^{2-}$  to enhance the propachlor transformation rate. Similarly, higher reaction temperature overcame the activation barrier of steric hindrance in propachlor structure and accelerated the excitation of dithionite, in which higher rate constants of propachlor reductive dechlorination were obtained. Dechlorination was found to be the first and necessary step of propachlor nucleophilic substitution by dithionite. Sulfur nucleophile substituted compounds, including propachlor dithionite, propachlor ethanesulfonic acid (ESA), and hydroxyl propachlor, were identified as the dechlorination products of propachlor, indicating bimolecular nucleophilic substitution ( $S_N2$ ) as the mechanism for propachlor transformation initiated by dithionite.

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### 1. Introduction

Propachlor, 2-chloro-*N*-(1-methylethyl)-*N*-phenylacetamide (Fig. 1), is one of the important chloroacetanilide herbicides widely used in many countries for preventing the growth of weeds, such as annual grasses and some broadleaf plants, in agricultural cultivation (Kumari et al., 2009). Although the popularity of some chloroacetanilide herbicides, such as alachlor, has decreased in recent years, the use of others is increasing. Not surprisingly, excessive application of these herbicides has resulted in severe nonpoint contamination of groundwater and soil. In fact, chloroacetanilide herbicides are among the most frequently detected pollutants in groundwater and soil around the world (Kolpin et al., 2000).

Although chloroacetanilides readily undergo photolysis, oxidative degradation, and biotransformation, these processes are negligible or substantially slower in subsurface soil and groundwater due to the lack of certain key reaction condition(s) for these processes (Osano et al., 2003). Hydrolysis may be a fundamental process in controlling the fate of chloroacetanilides in the environment, but some transformation strategies still involve long degradation half-lives ranging from 1 to 7 years (Cavalier et al.,

1991; Zheng and Ye, 2001). Despite years of research on the environmental fate of these herbicides, information pertaining to the kinetics and mechanism of chloroacetanilide reductive transformation under environmentally relevant conditions is still limited (Boparai et al., 2006).

Exploring the potential rate enhancement of chloroacetanilide transformation through nucleophilic substitution in soil and groundwater has recently received considerable attention. Acidic and basic environments are generally more favorable for catalyzing the nucleophilic substitution for chloroacetanilide transformation, whereas these herbicides are more stable at neutral pH (Sharma, 2002; Carlson et al., 2006). Metal ions such as  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$  and  $Ni^{2+}$  are strong nucleophiles that increase the transformation rates of most chloroacetanilides through nucleophilic substitution reactions (Fife and Bembi, 1993). A heterogeneous reaction may further increase the chloroacetanilide transformation rates. For example, a much shorter half-life of less than 50 d was obtained from the heterogeneous nucleophilic substitution of acetyl alachlor by metal ions as catalysts at the interface of different homoionic clays (Liu et al., 2000). However, metal ions have also been reported to inhibit the nucleophilic substitution processes of those chloroacetanilides with carbonyl groups in their molecular structures, because the carbonyl groups block the intramolecular nucleophilic attack and induce deprotonation of the amide group to

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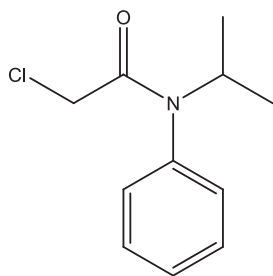


Fig. 1. Chemical structure of propachlor (2-chloro-N-(1-methylethyl)-N-phenylacetamide).

make the substrate less reactive toward nucleophilic attack (Huang and Stone, 1999).

Active nucleophiles accelerate the transformation and detoxification of pollutants. In particular, sulfur compounds are a large class of active nucleophiles useful in the process of herbicide transformation (Moran et al., 2011). Compounds containing single or multiple sulfur atoms were observed in the transformation of chloroacetanilides and resulted in shorter half-lives ranging from minutes to several hours. Nucleophilic sulfur compounds could thus exert a substantial influence on the fate of chloroacetanilide herbicides in aquatic environments (Loch et al., 2002). Several sulfur compounds, including thiosulfate (Cai et al., 2007), bisulfide (Loch et al., 2002), polysulfide (Loch et al., 2002), and bisulfite (Bian et al., 2009) have been reported to accelerate chloroacetanilide dechlorination.

Because of its high reducing potential in basic solutions ( $E^0 = -1.12$  eV), the dithionite ( $S_2O_4^{2-}$ ) can reductively dehalogenate organic halogenated pollutants and facilitate the reductive transformation of heavy metals (Nzengung et al., 2001; Geoffroy and Demopoulos, 2009). This environmentally benign compound also enhances the reactivity and reactive lifetime of other reducing agents, such as ferrous sulfate (Su and Ludwig, 2005), nanoscale zero-valent iron (Xie and Cwiertny, 2010), and clay minerals (Nzengung et al., 2001). Dithionite may also act as a nucleophile for reductive dechlorination of chloroacetanilides. Dithionite-treated sediments and soils reduce chloroacetanilide half-life to within 10 h (Boparai et al., 2006). However, few kinetics and mechanistic studies of dithionite-induced chloroacetanilide transformation have been carried out. This fundamental understanding of chloroacetanilide dechlorination, especially under varying conditions, is crucial to develop an effective treatment scheme for dithionite use in chloroacetanilide herbicide detoxification.

In this study, we investigated the reductive transformation of the chloroacetanilide herbicide propachlor by dithionite. The primary aims were to establish a kinetic model to predict the transformation rate of propachlor by dithionite and identify the reaction mechanism. To achieve these goals, experiments were conducted to: (i) determine the kinetics of the reaction between propachlor and dithionite; (ii) evaluate the reductive transformation of propachlor under different reaction conditions; and (iii) identify major transformation intermediates.

## 2. Experimental methods

### 2.1. Materials

Propachlor (99.9% purity) was obtained from Sigma–Aldrich (St. Louis, MO). The sodium dithionite and other chemicals were of analytical grade and purchased from BDH Chemicals (Poole, UK). Ultrapure water (18 M $\Omega$ -cm) generated from a Milli-Q water purification system was used to prepare the chemical solutions and for

the mobile phase of liquid chromatography. All chemicals were used as purchased without further purification.

### 2.2. Experimental procedures

A stock solution of 1.0 mM propachlor was prepared by dissolving 212 mg propachlor in 10 mL methanol and then diluting to 1 L with ultrapure water. Other stock solutions were prepared directly with ultrapure water, and all solutions were filtered through 0.22- $\mu$ m hydrophilic PTFE filters (Millipore, MA) before use. Aqueous solutions (20 mL) of propachlor (100  $\mu$ M) and dithionite (0–20 mM) were prepared in borosilicate glass serum bottles with phosphate buffer, (0.02 mol L $^{-1}$ ) at varying pH (3.0, 4.0, 5.0, 7.0, 9.5) and reaction temperatures (288 K, 298 K, 308 K, 318 K, and 328 K). After being covered with Teflon-lined butyl rubber septa and aluminum crimp seals, the reaction bottles were immediately placed onto a 150 rpm orbital shaker (LMS Cooled Incubators, Wolf Laboratories Limited, UK). At specified intervals, a 4-mL aliquot was collected from each bottle, and the reaction was quenched by immediately adding excess methanol (36 mL) (Goerke et al., 1971). The solutions were then passed through a 0.22- $\mu$ m PTFE filter before compositional analysis.

To elucidate the effect of atmosphere on the transformation of propachlor by dithionite, experiments were conducted using solutions prepared from water aerated with 99.999% nitrogen or 99.999% oxygen for 2 h. Before sealing, the reactions were aerated with the same nitrogen or oxygen gas for 20 min in the reaction bottles. These experiments were carried out at pH 7 and 308 K with 100  $\mu$ M propachlor and 10 mM dithionite. Each experiment was conducted in duplicate, and the mean values are reported in the results.

### 2.3. Analytical techniques

Propachlor concentrations in aqueous solutions were determined by a high performance liquid chromatography (HPLC) system (Shimadzu, Japan) equipped with a LC-10A pump, SIL-10A automatic injector, and SPD 10A-UV-vis detector. Propachlor separation was carried out with an Alltima<sup>TM</sup> C18 column (5  $\mu$ m beads, 250  $\times$  4.6 mm ID) and the mobile phase (70% methanol, 30% water) at a flow rate of 1.0 mL min $^{-1}$ . The detection wavelength for propachlor determination was set as 215 nm.

Chloride concentrations in the reaction solutions were analyzed by ion chromatography (IC, ICS-90, DIONEX, USA) coupled with a RFIC<sup>TM</sup> IonPac<sup>®</sup> AG14A-7  $\mu$ m Guard Column (4 mm, 50 mm), AMMS III micromembrane suppressor, IonPac<sup>®</sup> AS14A-7  $\mu$ m Analytical Column (4 mm, 250 mm), and a DS5 Detection Stabilizer conductivity detector. An eluent solution containing 8.0 mM Na<sub>2</sub>CO<sub>3</sub> and 1.0 mM NaHCO<sub>3</sub> was pumped at 1.0 mL min $^{-1}$ . The limits of detection and quantitation were 7 and 24  $\mu$ g L $^{-1}$ , respectively, and the relative standard deviation was within 5%.

Transformation products were analyzed by liquid chromatography/mass spectrometry (LC/MS) using a Shimadzu HPLC system with a Kromasil C18 column (250 mm  $\times$  4.6 mm i.d.), SIL-HT autosampler, LC-10 AT vacuum pump, and API 3000 mass analyzer. HPLC separation was performed at 0.5 mL min $^{-1}$  with a mobile phase of 85:15 water/acetonitrile ratio for 1.0 min, a 50:50 ratio for 2 min, with a linear change to the 10:90 ratio over 10 min and then held for 6 min, followed by re-equilibration at the initial condition (85:15 water/acetonitrile ratio) for 8.5 min. An electrospray interface (ESI) was used for the MS measurements in positive MS scan mode and full scan acquisition between  $m/z$  50 and 550. The other parameters were set as follows: the ESI was 4.0 kV, source block temperature was 80  $^{\circ}$ C, and the desolvation temperature was 400  $^{\circ}$ C. The flow rate of the desolvation gas (N<sub>2</sub>) was set at 400 L h $^{-1}$ , and argon was used as a cone gas at 50 L h $^{-1}$ .

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