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

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A B S T R A C T
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 \((S_2O_2^2-)\). 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 M\(^{-1}\) 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 \(S_2O_2^2\) 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.

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...
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 ($S_2O_2^2-$) 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 MΩ·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-μm hydrophilic PTFE filters (Millipore, MA) before use. Aqueous solutions (20 mL) of propachlor (100 μM) 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-μm 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 99.99% 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 μM 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™ C18 column (5 μm beads, 250 × 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 an RFIC™ IonPac® AG14A-7 μm Guard Column (4 mm, 50 mm), AMMS III micromembrane suppressor, IonPac® AS14A-7 μm Analytical Column (4 mm, 250 mm), and a D55 Detection Stabilizer conductivity detector. An eluent solution containing 8.0 mM Na$_2$CO$_3$ and 1.0 mM NaHCO$_3$ was pumped at 1.0 mL min$^{-1}$. The limits of detection and quantitation were 7 and 24 μg 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 × 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 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°C, and the desolvation temperature was 400°C. The flow rate of the desolvation gas (N$_2$) was set at 400 L h$^{-1}$, and argon was used as a cone gas at 50 L h$^{-1}$.
3. Results and discussion

3.1. Reductive transformation of propachlor with dithionite

Propachlor is relatively stable and has a half-life in aqueous solution of up to 890 d if not disturbed (Carlson et al., 2006). In our study, propachlor was stable in phosphate buffer solution (pH 7) at 308 K (curve a in Fig. 2), which was further verified by low chloride concentrations throughout the testing period (curve c in Fig. 2). Dithionite exerted a strong effect on propachlor transformation, as demonstrated by curve d in Fig. 2. With 10 mM dithionite, propachlor (100 µM) achieved nearly complete transformation after 22 d.

Boparai et al. (2006) reported the reductive dechlorination of chloroacetanilide herbicides by dithionite, which is mediated by the Fe(II)/Fe(III) transformation pair in sediment/soil under anaerobic conditions. Our results indicate that dithionite induced the direct transformation of propachlor with high rates. Increasing chloride concentrations (curve b) demonstrate the generation of chloride ions throughout the propachlor transformation and the well-maintained mass balance of chlorine in the system. The curves e and f in Fig. 2 illustrate propachlor transformation under varying atmospheric conditions. We found that the propachlor transformation rate under anaerobic conditions (purged with nitrogen) was the same as that under aerobic conditions (purged with oxygen). This finding may indicate that with excess dithionite the effect of oxygen is negligible in the reductive dechlorination process, and the nucleophilic substitution of chlorine in propachlor is the first step of propachlor transformation initiated by dithionite.

3.2. Reaction order and rate constant

The transformation of propachlor initiated by dithionite was first analyzed using pseudo-first-order kinetics (i.e., at least 10:1 M ratio of dithionite to propachlor). The reaction between propachlor and dithionite can be written as follows:

\[ \text{Propachlor} + n\text{Na}_2\text{S}_2\text{O}_4 \rightarrow \text{products} \]  

Under pseudo-first-order conditions, the rate of propachlor transformation can be expressed by Eqs. (2) and (3):

\[ -d[\text{Propachlor}]/dt = k'[\text{Propachlor}] \]  

\[ \ln(k') = \ln(k) + n \ln([\text{Dithionite}]_0) \]  

where \( k' \) and \( k \) represent the reaction rate constants of first-order kinetics and second-order kinetics, respectively. A plot of \( \ln(k') \) versus \( \ln([\text{Dithionite}]_0) \) showed a strong linear relationship with a slope (n) nearly equal to 1.0 as the stoichiometric number (Fig. 3). Table 1 summarizes the estimated \( k' \) values corresponding to the initial dithionite concentrations. The overall reaction between propachlor and dithionite was of second-order, and was of first-order with respect to each reactant. With more than 10-fold excess dithionite, the initial concentration of propachlor should not affect the rate constant in the case of pseudo-first-order behavior. Using Eq. (3), a second-order rate constant of 123.4 ± 0.7 M\(^{-1}\) h\(^{-1}\) at pH 7.0 and 308 K was deduced from the transformation of 100 µM propachlor by 10 mM dithionite.

3.3. Effect of pH

The transformation of 100 µM propachlor by 10 mM dithionite at 308 K under different pH conditions is shown in Fig. 4. A previous study reported that acidic and basic conditions were more favorable for propachlor transformation than neutral conditions (Carlson et al., 2006). However, in the presence of dithionite, the reductive transformation rate of propachlor increased at higher pH conditions. Under acidic conditions, the half-life (\( t_{1/2} \)) of propachlor was 43.6 h at pH 3.0, 12.2 h at pH 4.0, and 2.8 h at pH 5.0. In neutral and basic environments, the \( t_{1/2} \) values of propachlor were found to decrease to 1.9 h at pH 7.0 and 1.4 h at pH 9.5.

The total Na\(_2\)S\(_2\)O\(_4\) concentration, [Na\(_2\)S\(_2\)O\(_4\)]\(_{total}\), represents the sum of H\(_2\)S\(_2\)O\(_4\), H\(_2\)S\(_2\)O\(_3\), and S\(_2\)O\(_3^2-\) species. This value, together with its speciation, is a function of pH (Boparai et al., 2008). Under acidic conditions, H\(_2\)S\(_2\)O\(_4\) and/or H\(_2\)S\(_2\)O\(_3\) are the predominant species, but at higher pH more H\(_2\)S\(_2\)O\(_3\) ions dissociate into S\(_2\)O\(_3^{2-}\), which is a more reactive species. Another reactive sulfuric species, thiosulfate, is also formed under high pH through the disproportionation of dithionite (Bian et al., 2009):

\[ 4\text{SO}_3^- \rightarrow 2\text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \]  

Therefore, the reaction mechanism between propachlor and S\(_2\)O\(_3^{2-}\) appeared to be a bimolecular nucleophilic substitution (SN2). The overall second-order reaction between S\(_2\)O\(_3^{2-}\) and...
were conducted at pH 7.0 and of propachlor initiated by dithionite at different initial concentrations. Experiments were conducted at pH 7.0 and T = 303 K.

Table 1
Pseudo-first-order rate constants (k') and correlation coefficients (R²) for the reaction of propachlor initiated by dithionite at different initial concentrations. Experiments were conducted at pH 7.0 and T = 303 K.

<table>
<thead>
<tr>
<th>[Propachlor]₀ (µM)</th>
<th>[S₂O₂⁻]₀ (mM)</th>
<th>k' × 10⁴ (h⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1</td>
<td>7.5</td>
<td>0.989</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>29.5</td>
<td>0.992</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>72.4</td>
<td>0.991</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>129.9</td>
<td>0.987</td>
</tr>
</tbody>
</table>

propachlor consisting of the hydrolytic dechlorination and the dithionite substitution confirmed the S₄O₂⁻ reaction mechanisms of propachlor transformation with dithionite.

3.4. Effect of reaction temperature

As illustrated in Fig. 5A, the effect of temperature on propachlor (100 µM) transformation in the presence of dithionite (10 mM) was evaluated from 288 to 328 K at pH 7. No transformation of propachlor was observed in the absence of dithionite at any temperature tested (data not shown). The transformation was more rapid at higher temperatures. The second-order rate constants (k) (and the corresponding t₁/₂ values) were 44.8 ± 0.3 M⁻¹ h⁻¹ (23.8 d) at 288 K, 79.4 ± 0.9 M⁻¹ h⁻¹ (6.7 d) at 298 K, 123.4 ± 0.7 M⁻¹ h⁻¹ (1.9 d) at 308 K, 176.4 ± 0.4 M⁻¹ h⁻¹ (1.4 d) at 318 K, and 214.4 ± 1.2 M⁻¹ h⁻¹ (1.1 d) at 328 K. The propachlor transformation rate constants were plotted in Fig. 5B to fit the linearized Arrhenius equation:

\[
\ln(k) = \ln(A) - \frac{E_a}{RT}
\]

where A is the pre-exponential factor, R is the gas constant, and T is temperature (K). The apparent activation energy (Eₐ) was thus calculated by means of the second-order rate constants at different temperatures. Plotting ln(k) versus 1/T yielded a linear curve with −Eₐ/R as the slope as shown in Fig. 5B. Therefore, the activation energy for propachlor transformation in the presence of dithionite was 31.01 kJ mol⁻¹.

The same data could also be fitted into a linearized version of the Eyring equation:

\[
\ln(k/T) = \ln(k_b/h) - \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

where k_b is Boltzman’s constant, h is Planck’s constant, R is the gas constant, T is temperature (K), and \(\Delta H^\circ\) and \(\Delta S^\circ\) are the enthalpic and entropic contributions, respectively, to the overall activation energy barrier \(\Delta G^\circ\). The regression result yielded the values of 85.6 kJ mol⁻¹ for \(\Delta H^\circ\), −69.5 J/mol K for \(\Delta S^\circ\), and 92.1 kJ mol⁻¹ for \(\Delta G^\circ\). The \(\Delta S^\circ\) is related to the reaction activity or latitude of orientation, configuration, and translation of the molecule. A negative \(\Delta S^\circ\) value usually suggests a transition state of a more ordered or rigid structure than the reactants in their ground states. The steric hindrance of the N-alkyl substituent in propachlor molecular may be responsible for the activation barrier inhibiting the nucleophilic attack by dithionite, which may be reflected by high temperature needed (Gan et al., 2002). Higher reaction temperatures can induce the excitation of propachlor to accelerate the nucleophilic substitution reaction, increasing the propachlor transformation rate.

3.5. Products of propachlor transformation

When treated with dithionite under neutral conditions, the first step of propachlor transformation is dechlorination through nucleophilic substitution with stoichiometric release of chloride ions (Fig. 2). The dissociation of chlorine from organic pollutants, an important step in the remediation of contaminated resources, creates products that are more easily degraded (Scheunert and Parlar, 1992). Therefore, dechlorinated chloroacetanilides should be more biodegradable than their parent compounds (Comfort et al., 2001). Reaction products other than chloride ions generated during propachlor transformation were determined by LC/MS (Fig. 6). The propachlor dithionite (C₁₁H₁₅NOS₂O₄, MW = 305), propachlor

Fig. 4. Reductive dechlorination of propachlor (100 µM) by dithionite (10 mM) under different pH conditions (controlled by phosphate buffer solution) at T = 308 K.

Fig. 5. Reductive dechlorination of propachlor (100 µM) by dithionite (10 mM) at pH 7.0 and different reaction temperatures (A). Arrhenius plot of the corresponding second-order rate constants for propachlor transformation at different temperatures (B).
ethanesulfonic acid ($C_{11}H_{15}NOSO_3$, MW = 257), and hydroxyl propachlor ($C_{11}H_{15}NO_3$, MW = 209) were identified in the positive ion mode with $[M + H]^+$ ion at $m/z$ 305, 257, and 209, respectively (Fig. 6). The main products of propachlor transformation initiated by dithionite were propachlor ethanesulfonic acid (ESA) and propachlor dithionite, along with a small amount of dechlorinated propachlor.

Dithionite can act as a nucleophile to substitute the chlorine in propachlor, producing propachlor dithionite. The S–S bond in dithionite is relatively weak (2.389 Å), and the dithionite anion can be regarded as a pair of SO$_2$ units linked by the weak S–S bond. Thiosulfate ions are also formed from the disproportionation of dithionite in aqueous solution as shown in Eq. (4). Chloroacetanilide herbicides can be transformed through chlorine substitution by thiosulfate, another strong nucleophile, producing thiosulfate-substituted herbicides (Cai et al., 2007). Propachlor ESA was formed not only through substitution of chlorine by thiosulfate, but also through transformation of propachlor by dithionite. The substituting dithionite in propachlor dithionite further dissociated, and the $-$SO$_2$ unit was substituted by hydroxyl ions in neutral and basic conditions. The hydroxyl propachlor may be formed during dechlorination and exist only as a transitional species.

In this study, reductive dechlorination was confirmed as the first step of propachlor transformation initiated by dithionite. Similar processes have been reported in the transformation of chloroacetanilide herbicides initiated by sulfur nucleophiles such as polysulfides (Lippa and Roberts, 2002), thiosulfate (Zheng et al., 2007; Cai et al., 2007), bisulfite (Bian et al., 2009), and thiourea (Zheng et al., 2004). Chloroacetanilide ESA is frequently detected at higher levels than its parent compounds (chloroacetanilides) in water and soils (Kolpin et al., 1996; Dagnac et al., 2002), indicating that this reaction may occur in natural environments. Understanding the mechanism by which dithionite initiates the dechlorination of propachlor is thus important. For example, reducing toxicity (i.e., higher lethal concentration 50 [$LC_{50}$]) may be explained by the generation of more readily biodegradable metabolites (Cai et al., 2007).

4. Conclusions

The results of this study suggest the active role of dithionite in controlling the fate of propachlor in the natural and engineering environments. In the presence of dithionite, propachlor underwent an efficient reductive dechlorination process accompanied by the release of chloride ions. The transformation of propachlor initiated by dithionite can be expressed using second-order kinetics. Alkaline conditions were found to be more favorable for the nucleophilic substitution of propachlor by dithionite due to the higher ionization of active dithionite species. Higher reaction temperatures increase the propachlor dechlorination rate by reducing steric hindrance and accelerating the excitation of dithionite. Reaction products of nucleophilic substitution of propachlor by dithionite and generated chlorine ions indicate reductive dechlorination and dithionite substitution as mechanisms for a SN$_2$ reaction.

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References


