Chemosphere 82 (2011) 592–596

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Technical Note

Batch reactor kinetic studies on the reductive dechlorination of chlorinated ethylenes by *tetrakis*-(4-sulfonatophenyl)porphyrin cobalt

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ARTICLE INFO

Article history:
Received 1 October 2010
Received in revised form 3 November 2010
Accepted 4 November 2010
Available online 4 December 2010

Keywords:
Chlorinated ethylenes
Reductive dechlorination
Cobalt porphyrin
Kinetic studies

ABSTRACT

Tetrakis-(4-sulfonatophenyl)porphyrin cobalt was identified as a highly-active reductive dechlorination catalyst for chlorinated ethylenes. Through batch reactor kinetic studies, degradation of chlorinated ethylenes proceeded in a step-wise fashion with the sequential replacement of Cl by H. For perchloroethylene (PCE) and trichloroethylene (TCE), the dechlorination products were quantified and the C_2 mass was accounted for. Degradation of the chlorinated ethylenes was found to be first-order in substrate. Dechlorination trials with increasing catalyst concentration showed a linearly increasing pseudo first-order rate constant which yielded rate laws for PCE and TCE degradation that are first-order in catalyst. The dechlorination activity of this catalyst was compared to that of another water-soluble cobalt porphyrin under the same reaction conditions and found to be comparable for PCE and TCE.

1. Introduction

Perchloroethylene (PCE) and trichloroethylene (TCE) have been the focus of interest due to their common presence in groundwater systems (Squillace et al., 2004), long-lived stability, and carcinogenic and toxicology profiles (Henschler, 1994; Doherty, 2000a,b). Environmental contamination by PCE results from its widespread use as a dry cleaning solvent while TCE contamination is a consequence of improper disposal of metal degreasing solvents (Doherty, 2000a,b). Removal and degradation of PCE and TCE to less chlorinated or hydrocarbon compounds have been areas of long-standing interest where a number of strategies have been employed including degradation by microbial-based approaches (Hirl and Irvine, 1998; Damborsky, 1999; Banerjee and Ragsdale, 2003; Smidt and de Vos, 2004), reduction by zero valent metals (Roberts et al., 1996; Kim and Carraway, 2002, 2003; Song and Carraway, 2008), and dechlorination by transition metal catalysts (Gantzer and Wackett, 1991; Burris et al., 1996, 1998; Glod et al., 1997a,b; Dror and Schlautman, 2003; Fritsch and McNeill, 2005). These and other methods are of continuing interest (Pratt and Van der Donk, 2006; Song and Carraway, 2008; Cheng and He, 2009; Kliegman and McNeill, 2009; Liang et al., 2009; Aeppli et al., 2010).

Aqueous-phase reductive dechlorination of PCE and TCE by vitamin B_{12} has been well studied due to the importance of cobalamin in biological systems and its rich mechanistic pathways in degrading chlorinated ethylenes (CEs) (Banerjee and Ragsdale, 2003; Kliegman and McNeill, 2008). In batch reactor studies, vitamin B_{12} in the presence of a bulk reducing agent (*e.g.* titanium(III) citrate) catalyzes the dechlorination of CEs through reaction with the super-reduced cob(I)alamin (Glod et al., 1997a). Cobalt(I) is the active oxidation state for reductive dechlorination and is obtained through reduction by titanium(III) citrate. Cobalt(I) is classified as a “super nucleophile” and is also a powerful reducing agent (Schrauzer et al., 1968; Schrauzer and Deutsch, 1969). With the cobalt(I) stabilizing corrin ligand, cob(I)alamin is able to degrade PCE and TCE which contain highly-oxidized sp^2 hybridized carbon centers (Burris et al., 1996, 1998; Glod et al., 1997a).

In addition to the native vitamin B_{12} system, several studies have identified and characterized synthetic complexes that mimic the reductive dechlorination activity of cob(I)alamin. While metal centers and supporting ligand systems have varied, synthetic catalysts often have major structural and reactivity similarities to cobalamin including tetradentate coordination by a macrocycle and low oxidation state metal centers that are stable in aqueous solutions (Gantzer and Wackett, 1991; Dror and Schlautman, 2003; Fritsch and McNeill, 2005). Cobalt porphyrin complexes have been demonstrated to be highly-active in homogenous, aqueous phase catalysis where solubility was imparted by the presence of co-solvent (dimethyl formamide) or *meso*-substituted, ionic aryl groups (*e.g.* *N*-methyl pyridinium and benzoate, **1**, $R = CO_2^-$) (Dror and Schlautman, 2003, 2004a,b; Fritsch and McNeill, 2005).

With the small pool of synthetic cobalt reductive dechlorination catalysts studied, we sought to identify, and study in-depth, a new,

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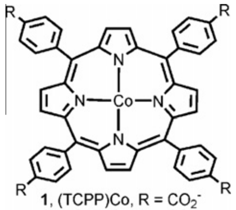
doi:10.1016/j.chemosphere.2010.11.015



1, (TCPP)Co, R = CO_2^-
2, (TSPP)Co, R = SO_3^-

water-soluble cobalt porphyrin complex to determine if substituent effects at the periphery of the porphyrin macrocycle affected catalytic activity. We employed batch reactor dechlorination studies in sealed, deoxygenated glass vials to monitor CE reductive dechlorination with kinetic time courses via headspace gas sampling. Here, we report on the identification and catalytic reductive dechlorination activity of 5,10,15,20-*tetrakis*-(4-sulfonatophenyl)-porphyrin cobalt(II) ((TSPP)Co, **2**, $R = SO_3^-$) for the degradation of CEs in aqueous solution. This complex shows superior catalytic dechlorination activity relative to the vitamin B_{12} complex and is of comparable activity relative to another previously studied synthetic water-soluble cobalt porphyrin.

2. Materials and methods

2.1. Materials

The following chemicals were purchased commercially and used without further purification. 5,10,15,20-*Tetrakis*-(4-sulfonatophenyl)-porphyrin cobalt(II) tetrasodium salt ((TSPP)Co) and 5,10,15,20-*tetrakis*-(4-carboxyphenyl)-porphyrin cobalt(II) ((TCPP)-Co) were purchased from Porphyrin Systems. PCE and TCE were purchased from Aldrich. Tris(hydroxymethyl)aminomethane (Tris) was purchased from Fisher Scientific. Trisodium citrate monohydrate, *trans*-dichloroethylene, and titanium(III) chloride (20% wt in 2 N HCl), were purchased from Acros. C*is*-dichloroethylene was purchased from Pfaltz & Bauer. Titanium(III) citrate was prepared with an adapted method (Smith and Woods, 1994).

2.2. Instrument settings

Gas chromatography coupled with flame ionization detection (GC–FID, SRI 8610C) utilizing a MXT-1 column (30 m × 0.5 mm, 5 μm film thickness, Restek) equipped with a split/splitless injector was used to analyze the headspace gas samples from the reaction vials in the splitless mode. The inlet temperature was 150 °C, detector temperature was 200 °C, and a helium flowrate of $1\ mL\ min^{-1}$ was used. Isothermal oven temperatures varied depending on the CE substrate: PCE 100 °C, TCE 80 °C, and both dichloroethylenes (DCEs) 40 °C. CEs were identified by retention time and quantified by peak area comparison to standard samples. An isothermal oven temperature of 40 °C was utilized for hydrocarbon detection. GC coupled with mass spectrometry was performed on a Hewlett Packard 5890 GC, equipped with an HP-5MS column (30 m × 0.250 mm i.d, 0.25 μm film thickness, Agilent Technologies) and a Hewlett Packard 5972 Mass Selective Detector.

2.3. CE dechlorination kinetic trials

The reductive dechlorination reactions were conducted in 42 mL septum-sealed vials. A stock solution of (TSPP)Co (200 μM) was prepared in deionized H_2O. A 110 mM stock solution of Tris buffer was prepared in water and adjusted to pH 8.5 with hydrochloric acid. Individual CE stock solutions were prepared in methanol. PCE and TCE were 4.5 mM CE substrate with 25 mM toluene internal standard and the DCEs were 4.5 mM cDCE or tDCE with 23 mM pentane internal standard. Dechlorination reaction vials were prepared by adding 9 mL of Tris buffer, an aliquot of (TSPP)Co solution to yield in-vial concentrations from 0.27 to 10.0 μM, and a stir bar. Vials were deoxygenated by sparging with N_2 for 20 min. The CE substrate was added via syringe from the CE stock solutions yielding in-vial substrate concentrations of 250 μM for PCE and TCE and 150 μM for cDCE and tDCE. Headspace and aqueous phase concentrations of substrate were equilibrated in a 35 °C water bath for 1 h. The dechlorination reaction was initiated by syringe addition of titanium(III) citrate (500 μL of a 640 mM stock solution) after collection of a time zero headspace sample for GC–FID analysis. The addition of the acidic titanium(III) citrate solution to the vial yielded a reaction pH 8. The reaction pH was verified by sacrificing vials to determine the initial pH and measuring the pH of each vial after the time course was completed. Headspace samples (50 μL) were collected and analyzed at regular intervals. CE peak areas were compared to the internal standard and reaction headspace samples were compared to authentic standards to determine each CE concentration. The pseudo first-order rate constant for the degradation of a substrate was determined by first-order kinetic analysis based on its concentration at each time point over the course of reaction.

2.4. Catalyst concentration studies

Kinetic trials were prepared with the procedure above with (TSPP)Co varying in concentration from 0.27 to 2.0 μM for PCE and from 2.8 to 9.3 μM for TCE. The observed rate constant (k_{obs}) for degradation at each catalyst concentration was determined by first-order kinetic analysis based on the substrate concentration at each time point over the course of reaction.

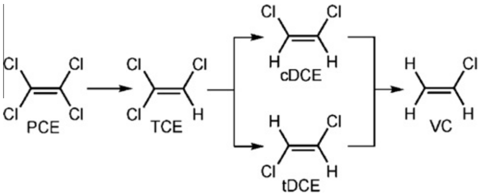
2.5. Comparison of cobalt catalysts

Reaction vials were prepared as above with vials containing either (TSPP)Co or (TCPP)Co to compare their dechlorination rate constants under the same reaction conditions. For PCE, the in-vial catalyst concentration used was 1.5 μM, while for TCE it was 4.2 μM.

3. Results and discussion

3.1. (TSPP)Co mediated chlorinated ethylene degradation

The catalytic reductive dechlorination of the CEs by (TSPP)Co was explored in batch reactions at pH 8 in the presence of a bulk reducing agent, titanium(III) citrate at 35 °C. The degradation of the CEs followed a sequential, step-wise replacement of Cl by H (Eq. (1)).



(1)

Reductive dechlorination of PCE with (TSPP)Co yielded the concomitant formation of TCE as the only dechlorination product (Fig. 1). The presence of cDCE in the reaction vial was determined to be due to the subsequent dechlorination of TCE by (TSPP)Co. The reaction was monitored at regular time intervals through the sampling of the headspace above the reaction solution. The kinetic data