

## REDUCTION OF 1,2-DIBROMOETHANE IN THE PRESENCE OF ZERO-VALENT IRON

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**Abstract**—The degradation reaction of 1,2-dibromoethane (ethylene dibromide or EDB) in water was studied in the presence of zero-valent iron (acid-cleaned, cast iron) in well-mixed batch aqueous systems. The observed products were ethylene and bromide ions. Carbon and bromine mass recoveries of >95% were obtained. Bromoethane and vinyl bromide were not observed. The reduction rates of bromoethane and vinyl bromide with iron indicate that they should have been observed if they were significant reaction intermediates for EDB. The results indicate that reductive  $\beta$ -elimination may be the dominant reaction pathway. Reaction kinetics are rapid and pseudo-first order. The activation energy was determined to be 50 kJ/mol, indicating that the reaction rate may not be aqueous phase diffusion controlled but rather controlled by the chemical reaction rate on the iron surface. Metallic iron may be a suitable treatment approach for EDB-contaminated groundwater in above-ground, as well as in situ applications, due to rapid kinetics and nontoxic products.

**Keywords**—1,2-Dibromoethane    Ethylene dibromide    Kinetics    Zero-valent iron    Reductive elimination

## INTRODUCTION

Over the past several decades 1,2-dibromoethane (also known as ethylene dibromide or EDB) was used as a pesticide and fuel additive. It is a potential carcinogen and can cause liver and kidney damage [1]. Ethylene dibromide has found its way into groundwater due to subsurface releases. The environmental chemistry of EDB in soil and groundwater has been reviewed by Pignatello and Cohen [2]. It has been shown to be persistent within aquifers for decades in some cases. In addition, the regulatory action levels for EDB in water are extremely low (0.1  $\mu\text{g/L}$  or lower) [2], which can present a treatment challenge.

Zero-valent metals have recently been shown to be effective for the treatment of halogenated organic contaminants in groundwater [3–5]. Among these metals, iron has received the most attention. The surface-mediated reduction of trichloroethylene (TCE) and tetrachloroethylene (PCE) by zero-valent (metallic) iron produces nontoxic end products, primarily ethylene and ethane, as well as several chlorinated reactive intermediates [6,7]. The treatment of TCE- and PCE-contaminated groundwater by metallic iron has been limited to in situ application due to required residence times (i.e., the reaction rates tend not to be sufficiently fast for aboveground applications).

The purpose of the present study was to evaluate the efficacy of zero-valent iron as a treatment approach for groundwater contaminated with EDB. Possible reaction pathways for the reduction of EDB by metallic iron are shown in Figure 1. These potential pathways include reductive  $\beta$ -elimination, hydrogenolysis, and dehydrohalogenation. The present study was conducted to evaluate these potential pathways in the reduction of EDB by metallic iron in well-mixed aqueous batch systems. In addition, EDB reduction kinetics of these systems was also determined.

## MATERIALS AND METHODS

*Chemicals*

The chemicals used were 1,2-dibromoethane and bromoethane (Chemservice, West Chester, PA, USA), ethylene (Scott Specialty Gases, Plumsteadville, PA, USA), 1,2-dichloroethane and vinyl bromide (1 M in THF) (Aldrich Chemical Company, Milwaukee, WI, USA), pentane (pesticide grade, Baxter Healthcare Corporation, McGraw Park, IL, USA), iron (40 mesh, cast iron, Fisher Scientific, Pittsburgh, PA, USA), and KBr (Sigma Chemical Company, St. Louis, MO, USA). The metallic iron was acid washed to remove iron oxides from the surface as described in Campbell et al. [7]. Iron surface area is 1.2  $\text{m}^2/\text{g}$  [7].

*Kinetic experiments*

Crimp-top borosilicate glass serum vials (Wheaton, Millville, NJ, USA) with internal volumes of 160 ml were used. Each kinetic run consisted of three bottles, one of which was a control containing EDB and no iron. Each of the bottles contained 100 ml of Ar-sparged distilled deionized Milli-Q (Millipore, Bedford, MA, USA) water. The control bottle also contained 1.9 g of glass beads to compensate for the headspace displaced by 5 g of iron in the reaction bottles. Ampoules (1 ml) containing 5 g iron were filled with argon, sealed under vacuum, and were transferred to the reaction bottles. Vials were crimp-sealed in an anaerobic chamber (10%  $\text{H}_2$  in  $\text{N}_2$ ) with teflon-lined septa (Supelco, Bellefonte, PA, USA). Control and reaction vials were spiked with 5  $\mu\text{l}$  of EDB and 1  $\mu\text{l}$  3.5 M pentane in methanol as internal standard. In separate experiments it was shown that the amount of pentane in the system does not change over the time period of the reaction nor does it affect the EDB reduction kinetics. The bottles were placed on a roller drum and rotated vertically with vials laid in the horizontal position at 16 rpm unless otherwise specified. The temperature of the reaction was 20°C unless otherwise specified. When EDB solubilized and vapor–water partitioning reached equilibrium, the reaction bottles were vigorously shak-

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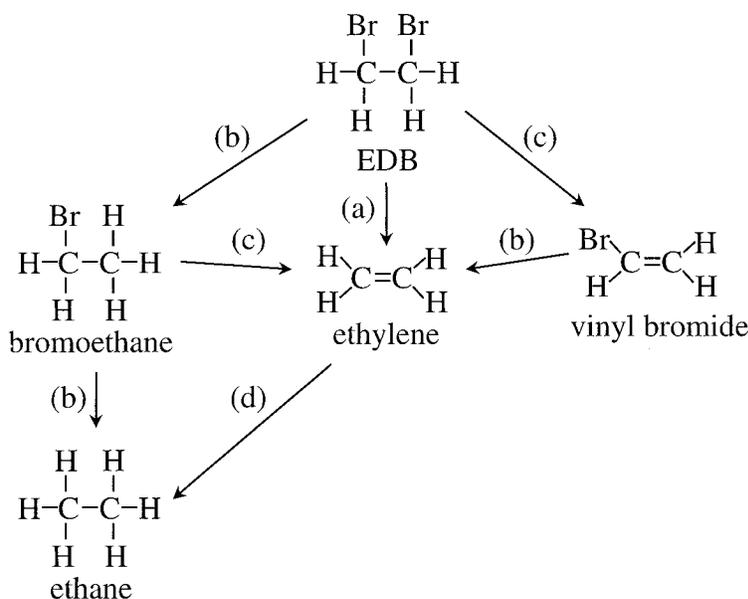


Fig. 1. Potential reaction pathways for the reduction of ethylene dibromide by zero-valent iron: (a) reductive  $\beta$ -elimination, (b) hydrogenolysis, (c) dehydrohalogenation, and (d) reduction of alkene to alkane.

en to break the glass ampoules containing iron, thus releasing the iron to the vapor-water system. Headspace samples (200  $\mu\text{l}$ ) taken from the control and reaction vials were analyzed by GC (described below).

The EDB mass balance experiment was carried out in a similar manner. After the headspace sampling at each time point, 5-ml aliquots of aqueous samples were taken from the reaction bottles for bromide analysis (described below). A separate reaction vial was used for each sampling point due to sampling for bromide. The bromoethane and vinyl bromide mass balance/kinetic experiments were conducted in a similar fashion with the following exceptions: duplicate vials only, 8 g Fe, and no sampling for  $\text{Br}^-$ .

The kinetics of EDB degradation in the presence of iron and absence of headspace was also carried out with one control and two reaction vials (160 ml). Each reaction vial contained 8 g of iron (to maintain the same iron:water ratio) in two sealed ampoules. These vials were filled with Milli-Q water in an anaerobic chamber with no headspace and crimp-sealed with teflon-lined septa. Each vial was spiked with 8  $\mu\text{l}$  EDB, allowed to solubilize, and ampoules were broken to start the reaction. This resulted in approximately 2 ml of head space due to air in the ampoules. This small amount of headspace was insignificant considering the dimensionless Henry's constant,  $H_v$ , for EDB at 20°C is 0.035. This experiment was considered essentially headspace-free. At each sampling time, a 50- $\mu\text{l}$  aliquot of aqueous phase was transferred from the 160-ml vials to a GC autosampler vial containing a 250- $\mu\text{l}$  insert and 100  $\mu\text{l}$  of acetonitrile containing *o*-dichlorobenzene (internal standard). The vial was placed on a vortex mixer for 1 min and analyzed by GC using a GSQ-PLOT column and electron-capture detection (ECD) as described below.

#### Analytical methods

The analysis of headspace samples (200  $\mu\text{l}$ ) was carried out using GC with flame ionization detection using a dual-column sequence reversal technique [8]. Relative response factors were determined for the components of interest by preparing and analyzing standards prepared by equilibrating

known masses of analytes and internal standard at 20°C in 160-ml vials containing the same vapor:water ratio as the reaction vials. This allowed determination of the mass of analyte in the vapor-water portion of the system, thus accounting for vapor-water partitioning. Ethylene was confirmed as the primary carbon-containing product by GC-MS.

Aqueous samples from low initial EDB concentration runs were analyzed by purge and trap using an HP 6890 GC with flame ionization. The column used was a DB-624 (30 m  $\times$  0.53-mm i.d., film thickness 13  $\mu\text{m}$ ). The inlet temperature was 120°C, detector at 200°C, and the temperature program used was: initial temperature of 40°C, hold for 5 min, 8.5°C/min to 200°C, then 50°C/min to 250°C. The analyses of aqueous samples for the no headspace experiments were done on an HP 5890 GC using a HP-1 column (15 m, 0.53 mm i.d., Hewlett Packard, Wilmington, DE, USA) with ECD detection. Bromide was analyzed using an HP series 1050 HPLC system with Maxsil 10 SAX column (250 mm  $\times$  4.60 mm, Phenomenex, Torrance, CA, USA). The mobile phase was a 9:1 ratio of a 0.5 M phosphate buffer and acetonitrile. Ultraviolet detection was at 205 nm.

#### RESULTS AND DISCUSSION

A time course of EDB reduction by metallic iron and product formation is shown in Figure 2. The loss of EDB in the control was less than 10% over the course of the experiment. Minor  $\text{C}_1$  to  $\text{C}_5$  hydrocarbons (<1% of EDB carbon added) were observed in the reaction and control vials and are not included. These hydrocarbons were previously determined to be due to carbon present in the cast iron [9]. The main products observed were ethylene and bromide ions. Carbon and bromine mass recoveries were 95% or greater.

Ethylene may be obtained from the reduction of EDB by three possible routes (see Fig. 1): (1) reductive  $\beta$ -elimination, (2) hydrogenolysis followed by dehydrohalogenation, and (3) dehydrohalogenation followed by hydrogenolysis. The second route requires the formation of bromoethane as a reactive intermediate. Bromoethane was not observed (approximate detection limit 0.5  $\mu\text{mol}$ ). The reduction of bromoethane by me-

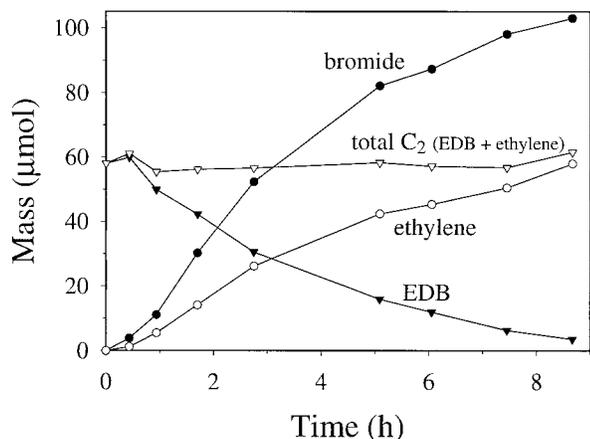


Fig. 2. Masses of ethylene dibromide and daughter products in a 160-ml closed vapor:water (60:100) batch system at 20°C containing metallic iron (5 g). Separate reaction vials used for each sampling event. Loss in controls (no iron) was less than 10%.

tallic iron is shown in Figure 3 (representative time series run). Negligible loss in control vial was observed. Both ethane and ethylene were observed as reduction products for bromoethane, but only ethylene was observed for EDB. Bromoethane reaction kinetics were sufficiently slow that it should have been observed if it was a significant reactive intermediate. It is interesting to note that both dehydrohalogenation and hydrogenolysis occur to form ethylene and ethane, respectively (see Fig. 1). Similarly for the third route, vinyl bromide was not observed (approximate detection limit 0.5  $\mu\text{mol}$ ). The reduction of vinyl bromide by iron is shown in Figure 4 (representative time series run) and shows ethylene as the main reduction product. Negligible loss in the control vial was observed. Vinyl bromide reaction kinetics were also sufficiently slow that it should have been observed if it was a significant reaction intermediate. The results suggest that the production of ethylene from the reduction of EDB by metallic iron is predominantly due to the reductive  $\beta$ -elimination route.

Reaction kinetics were observed to vary between batches of cleaned iron by a factor of less than two. For consistency in the interpretation of EDB kinetic results, a single batch of iron was used for the remaining kinetic experiments and this batch

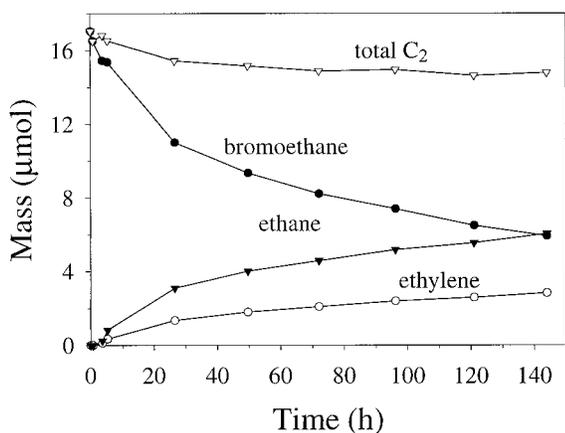


Fig. 3. Masses of bromoethane and daughter products in a 160-ml closed vapor:water (60:100) batch system at 20°C containing metallic iron (8 g) (representative time series). Loss in controls (no iron) was less than 10%.

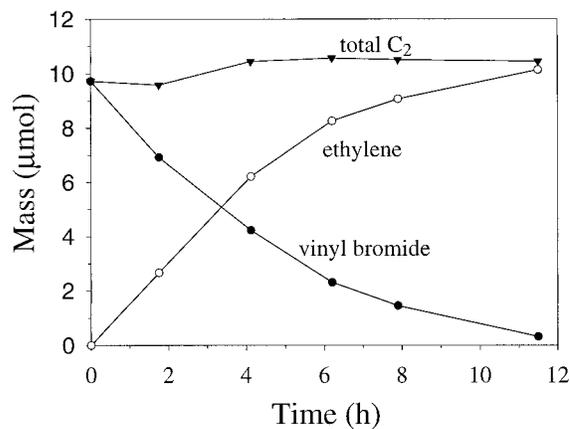


Fig. 4. Masses of vinyl bromide and daughter product in a 160-ml closed vapor:water (60:100) batch system at 20°C containing metallic iron (8 g) (representative time series). Loss in controls (no iron) was less than 10%.

was different than the iron used in the experiments above. Figure 5 shows a representative kinetic plot for the reduction of EDB by zero-valent iron. This reaction was carried out in sealed 160-ml vials with 100 ml water, 5 g iron, and 58  $\mu\text{mol}$  EDB (approximately 100 ppm in aqueous phase) at 16 rpm. The data exhibited first-order kinetics over a span of greater than four half-lives ( $t_{1/2} = 1.44$  h; average  $t_{1/2}$  of two kinetic runs under these conditions = 1.30 h). The reduction of EDB by zero-valent iron is very rapid compared to the reduction of chlorinated ethylenes. Campbell et al. [7], in a similar batch system with zero-valent iron, showed that the half-lives for TCE and PCE to be approximately 1 d and greater than 5 d, respectively. In addition, the complete dehalogenation of TCE and PCE requires even more time because several chlorinated reactive intermediates are formed. In contrast, EDB is rapidly dehalogenated to ethylene, a benign product. The observed rapid reaction kinetics with iron suggests that an aboveground treatment application for EDB may be possible.

The effect of rotor speed was examined to determine if the batch system was well mixed, an important experimental parameter because the reaction was rapid and surface mediated. The reaction was carried out at rotor speeds of 1, 8, 16, and 24 rpm (data not shown). Reaction rates at 8 rpm and above

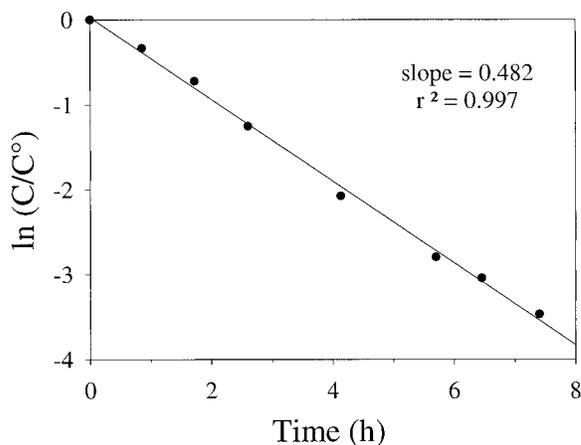


Fig. 5. Representative pseudo-first-order rate plot for the reduction of ethylene dibromide in a 160-ml well-mixed, closed vapor:water (60:100) batch system containing metallic iron (5 g) at 20°C.

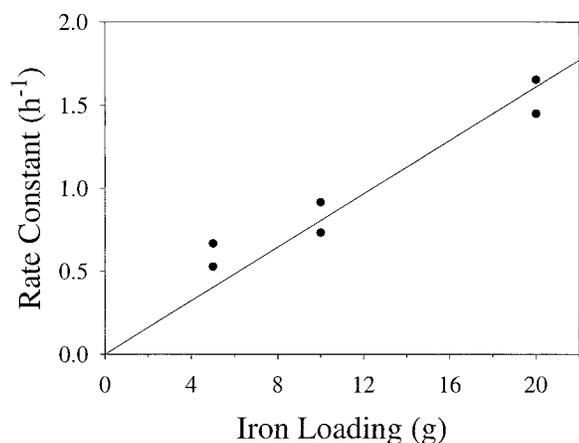


Fig. 6. Pseudo-first-order rate constants for the reduction of ethylene dibromide in a 160-ml well-mixed, closed vapor:water (60:100) batch system containing metallic iron at 20°C as a function of iron loadings.

were relatively constant, suggesting that the 16 rpm used in the remaining experiments provided a well-mixed system.

The kinetic experiments were carried out in head-space systems due to the ease of head-space sampling and analysis. A batch system without head-space was also examined and the kinetic results indicated that there was no difference between the two systems in terms of kinetics. This was expected due to the high fraction of EDB mass in the aqueous phase.

The effect of iron loading on reaction kinetics was studied and the results are shown in Figure 6. There is an increase in rate with increasing iron loading. This type of behavior is expected for surface-mediated reactions and can be exploited in flow-through systems of iron where the proportion of iron to water is very high.

First-order rate constants were determined for the reaction carried out at five different temperatures (ranging from 4 to 40°C). Using the method of Gossett [10] to determine Henry's constant values between 4 and 30°C, it was determined that the portion of EDB mass in the vapor phase of the system varied only from 2.8 to 6.5%, thus the effect of vapor-liquid partitioning was not expected to impact significantly the rates determined. An Arrhenius plot was generated for the EDB reaction with zero-valent iron. The activation energy for the reduction of EDB by Fe<sup>0</sup> was calculated as  $51 \pm 7$  kJ/mol (95% confidence limits). Lasaga [11] suggested that aqueous heterogeneous reactions that have an activation energy >20 kJ/mol may not be considered to be diffusion controlled. Hence, the reaction of EDB with zero-valent iron in the system examined appears to be controlled by the intrinsic reaction rate on the iron surface as opposed to aqueous phase diffusion to the surface. Similar results and conclusions were obtained by Scherer et al. [12] for the reduction of carbon tetrachloride and hexachloroethane with iron.

The reduction kinetics of the chlorine analog of EDB, 1,2-dichloroethane, was examined for comparison. For the reaction of 100 ppm of 1,2-dichloroethane with 5 g of iron and 100 ml Milli-Q water in a 160-ml bottle vapor-water batch system, a conversion of less than 5% was observed after a period of 4 d. The reactivity of the chlorine analog is significantly lower than the bromine compound. A reasonable mechanism of the dehalogenation reaction involves two electron transfers to EDB and two halogen ions leaving. A possible explanation

for the low relative reactivity of 1,2-dichloroethane would be that bromide is a better leaving group than chloride.

The experiments reported thus far used an initial EDB concentration of 100 ppm, whereas groundwater concentrations are commonly observed in the ppb range. Preliminary column experiments (results not presented) indicate that at low ppb EDB concentrations there is significant nonreactive sorption of EDB to cast iron. This type of nonreactive sorption has been observed with chlorinated ethenes on cast iron [13,14] and has been attributed to inclusions of graphite within the cast iron [14]. Batch kinetic results at low ppb EDB levels have been difficult to interpret due to this nonreactive sorption. This sorption was not observable at the higher EDB levels, indicating highly nonlinear sorption, similar to that observed for the chlorinated ethenes [13,14].

The reduction of EDB by metallic iron was evaluated in this study. Reductive  $\beta$ -elimination appears to be the primary reaction pathway yielding ethylene and bromide ions as the reaction products. The EDB reduction kinetics with iron are rapid, especially relative to rates for TCE and PCE. The rapid kinetics and formation of benign transformation products suggests that the use of metallic iron to treat EDB-contaminated waters may be practical in aboveground as well as in situ applications.

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