This is an open access article published under an ACS AuthorChoice License, which permits copying and redistribution of the article or any adaptations for non-commercial purposes.

Environmental Science & Technology Letters

Letter

pubs.acs.org/journal/estlcu

Novel Contaminant Transformation Pathways by Abiotic Reductants

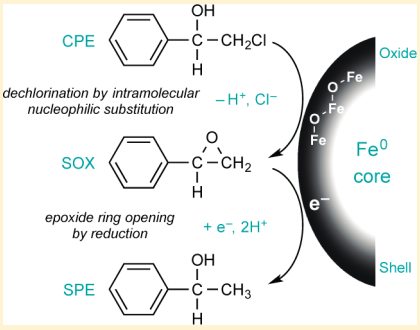
Shengwen Chen,[†] Dimin Fan,[‡] and Paul G. Tratnyek*,[‡]

[†]School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University (SSPU), Shanghai 201209, People's Republic of China

[‡]Institute of Environmental Health, Oregon Health & Science University, Portland, Oregon 97239, United States

Supporting Information

ABSTRACT: Environmentally relevant abiotic reductants, such as zerovalent iron (ZVI) and minerals containing divalent iron (DVI), react predominantly by electron-transfer mechanisms with a variety of contaminant and probe compounds. Other reduction mechanisms involving activated forms of hydrogen (H_{ads} or H^-) have been suggested, but most evidence for these is only from systems containing noble metals that catalyze hydrogen activation (e.g., Pd). Here, 2-chlorophenylethanol and relatives of this aromatic halohydrin are used as probe compounds to show that ZVI can affect reduction by several novel pathways that are not observed with DVI minerals. These pathways include dechlorination by intramolecular nucleophilic substitution and epoxide ring opening by reduction. The former appears to be catalyzed by hydroxyl groups associated with oxides on actively corroding ZVI, and the latter can arise from hydride transfer (from $NaBH_4$) or electron transfer (from ZVI).



INTRODUCTION

Despite a few attempts to define broadly the range of abiotic reduction reactions involving organic contaminants,[1−3] the vast majority of interest in these transformation processes has been focused on dehalogenation of chlorinated solvents and nitro reduction of energetic compounds. More recently, there has been diversification in the classes of contaminants that have been shown to be susceptible to abiotic reduction—e.g., various pesticides[4,5] and pharmaceutical and personal care products (PPCPs)[6,7] versus divalent iron (DVI) minerals and zerovalent iron (ZVI)—but the pathways and mechanisms involved are still relatively limited. One distinctive organic compound that we have studied is 2-chloroacetophenone (CAP), which is a minor environmental contaminant,[8,9] a model for metabolites of a variety of other contaminants,[10,11] and a probe compound for distinguishing between electron-transfer and hydride-transfer mechanisms in environmental media.[12,13]

In previous work, we showed that CAP in suspensions of zerovalent iron gives almost exclusively the expected electron-transfer reduction product [acetophenone (ACN)],[13] but anoxic sediments also give substantial yields of the putative hydride-transfer reduction product [2-chlorophenyl ethanol (CPE)].[12] These pathways are shown in Figure 1, as reactions 1 and 2, respectively. In some cases, the mass balance was incomplete (even after accounting for adsorption), leaving the question of what other products are formed. With one type of ZVI, hydrolysis of CAP to 2-hydroxyacetophenone was the dominant reaction, but this was an exceptional case.[13] With other types of ZVI, preliminary data suggested *sec*-phenyl ethanol (SPE) might eventually form from CAP, possibly by either hydride transfer via ACN or dechlorination by electron transfer via CPE (reaction 3 or 4, respectively, in Figure 1).[13]

The possibility of further transformation of CPE has not been investigated even though it may be of interest for several reasons: (i) as a probe for novel or diagnostic contaminant transformation reactions under reducing conditions, (ii) as a probe for chiral selectivity in contaminant reduction reactions, and (iii) as a model for transformation pathways of other β-halohydrins (e.g., various alkyl chlorohydrins[14,15]). This letter is focused mainly on the first of these concerns, although it also provides a basis for further work on the second and third aspects. The results demonstrate several modes of reactivity, with respect to the reductant and reductate,[13] that have not been well-defined by previous work and that may broaden the range of contaminant transformation reactions that can be achieved by chemical reduction under environmental conditions.

EXPERIMENTAL SECTION

Chemicals and Materials. The chemical reagents used in this study, and their essential meta-data, are given as Supporting Information (in Table S1 for organic analytes and in Table S2 for ZVI and other reductants). All reagents were used as received, without further purification, size fractionation, etc. Solutions were prepared in deionized (DI) water that was deoxygenated by being sparged with N_2 for at least 1 h. For high-performance liquid chromatography (HPLC), the mobile-

Received: August 29, 2014
Revised: September 19, 2014
Accepted: September 22, 2014
Published: September 22, 2014

 © 2014 American Chemical Society

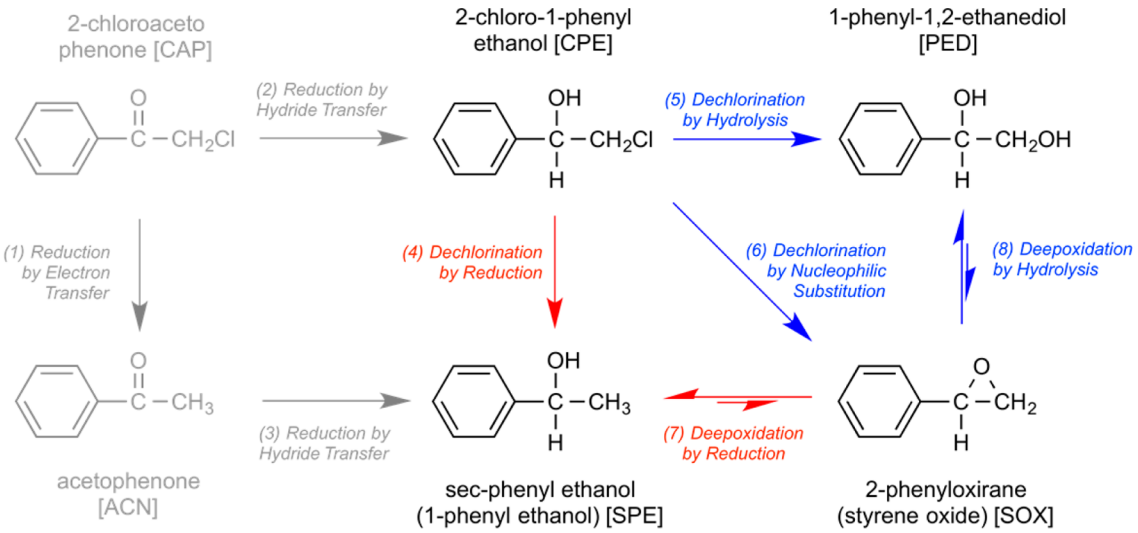


Figure 1. Summary of the major reactions responsible for the interconversion of species derived from 2-chloroacetophenone (CAP) and 2-chlorophenyl ethanol (CPE) in environmentally relevant reducing media.

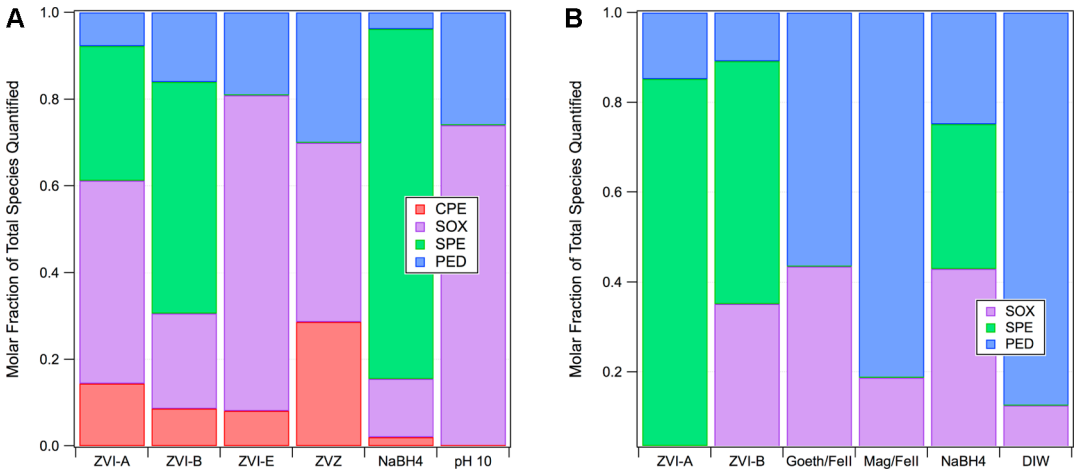


Figure 2. Summary of products at the termination of batch experiments that exposed (A) 2-CPE and (B) SOX to various types of reductants and control media. Only media that gave significant reaction are shown.

phase components were DI water and HPLC-grade methanol (Fisher Scientific, Waltham, MA).

Batch Experiments and Analysis. All experiments were performed in batch reactors composed of 60 mL serum vials sealed with butyl rubber septa (Thermo Scientific) and aluminum crimp caps. All batch experiments, except those with $NaBH_4$ and pH 10.0 buffer, were prepared in an anaerobic chamber containing pure (99.999%) N_2 and <10 ppm O_2. Most reactors were filled with 2 g of particulate material and 40 mL of deoxygenated DI water. These mixtures were allowed 20−28 h of "pre-exposure" time with mixing by end-over-end rotation at ∼9 rpm. Then, 1.00 mL of the analyte stock solution (4 mM, in DO/DI water) was added, to achieve initial analyte concentrations of 100 μM. The spiked reactor was hand-shaken briefly and then mixed continuously during the rest of the experiment by end-over-end rotation at ∼9 rpm. All aspects of the experiments were performed at room temperature (∼23 °C).

Periodically throughout each experiment, 2.5 mL of the reaction medium was removed from the batch reactor and filtered through 0.45 μm syringe filters into autosampler vials for analysis by HPLC. HPLC was performed on a Varian ProStar system with a photodiode array detector, using a Platinum C18 5 μm, 250 mm × 4.6 mm column (Grace, Deerfield, IL). The mobile phases were 20:80 and 35:65 DI water/methanol mixtures (methods 1 and 2, respectively) pumped at a flow rate of 1 mL min^{-1}. Analyte peaks were identified by matching retention times to those of commercially available standards, comparing the UV−vis spectra of the peaks to spectra of the standards (obtained with a PerkinElmer Lambda Max 20 instrument in a medium similar to the HPLC eluent). UV−vis spectra for each analytical standard and sample HPLC chromatographs for methods 1 and 2 are given as Supporting Information (Figures S1 and S2, respectively). Quantification of analytes was performed on the basis of the absorbance at 220 nm, using multipoint calibration curves.

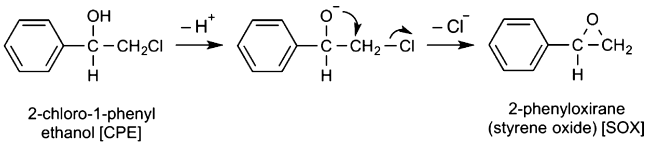
■ RESULTS AND DISCUSSION

Concentration versus time plots for CPE, SOX, and their transformation products are presented as Supporting Information (Figures S3−S6). The distributions of products observed at the end of experiments that gave significant reaction are summarized in Figure 2.

Reactions of CPE. In our previous work using CAP to probe the relative reactivities of various types of ZVI,[13] we speculated that the progressive declines in mass balance based on formation of ACN, which we observed in most cases, might be due to formation of other reduction products, such as CPE and SPE. In this study, we confirmed CPE reacts to form substantial concentrations of SPE with two of the five types of ZVI studied (ZVI-A and -B) (Figure 2A and Figure S3 of the Supporting Information). The three types of ZVI that were most reactive with CPE (ZVI-A, -B, and -E) produced two additional products that we had not considered in previous work: 2-phenyloxirane (SOX), which was the major product initially and then declined slowly, and PED, which accumulated slowly throughout most experiments (Figure S3 of the Supporting Information). Additional experiments with zerovalent zinc (ZVZ), $NaBH_4$, and pH 10 borate buffer also produced SOX as the initial product and SPE and/or PED toward the end of each experiment (Figure 2A and Figures S3F and S4C,D of the Supporting Information). In contrast, CPE did not react significantly with Fe_2O_3/Fe^{II} or Fe_3O_4/Fe^{II} (Figure S4A,B of the Supporting Information).

The facile formation of SOX from CPE suggests a direct reaction (Figure 1, reaction 6), which most likely occurs by intramolecular nucleophilic substitution, as shown in Scheme 1.

Scheme 1



According to this mechanism, any factor that makes the hydroxyl group in CPE more nucleophilic (such as dissociation to the oxido group) should favor formation of the epoxide by displacement of chloride. This is consistent with the high yield of SOX from CPE in pH 10 borate buffer (Figure 2A and Figures S2A and S4D of the Supporting Information) and may also explain the formation of SOX in the $NaBH_4$ solution, which had a pH of ∼10.8 because of the hydrolysis of the borohydride.[16] The latter is reminiscent of results obtained with bromohydrins and Raney nickel, which gives reductive debromination (in this case, by hydrogenation), but also epoxidation (because of residue from the alkali used to activate the catalyst).[17]

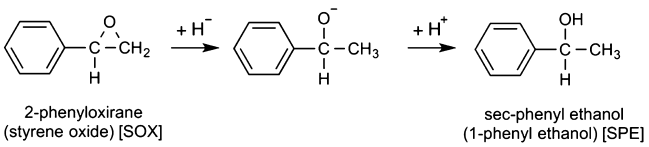
Apart from solution-phase hydroxide at high pH, the most thoroughly studied mechanism for catalyzing the intramolecular nucleophilic displacement shown in Scheme 1 involves halohydrin dehalogenase enzymes.[18,19] Within the reactive site of these enzymes, a combination of several amino acids provides sufficient Lewis basicity to abstract the hydroxyl proton of various halohydrins, thereby catalyzing formation of the corresponding epoxides. An analogous proton abstraction mechanism may be responsible for the formation of SOX that we observed from CPE in the presence of zerovalent metals (Figure 2A). In this case, we propose that deprotonated hydroxyls on metal oxide surfaces are responsible for the initial abstraction of the hydroxyl proton of CPE. This effect should be significant only when deprotonated surface hydroxyls are prevalent, such as when corrosion of underlying zerovalent metal increases the interfacial pH above the point of zero charge for the metal oxides that comprise the passive films on the metals (their pH_{pzc} is ∼8).[20] Many studies have shown that the interfacial pH during aqueous corrosion of metals can be greater than bulk pH's.[21−23] In contrast, iron oxides in the absence of Fe^0 presumably do not develop the elevated interfacial pH caused by metal corrosion, and because the bulk solution pH in our experiments (∼7.0) was below the pH_{pzc} of the passive film, this combination of factors may account for the lack of SOX formed by Fe_2O_3/Fe^{II} and Fe_3O_4/Fe^{II} (Figure S4A,B of the Supporting Information).

The transformations of CPE directly to SPE and PED (reactions 4 and 5, respectively) are not favorable under any of the conditions studied here. Reaction 4 would be hydrogenolysis of a monochloroalkane, which generally is much slower than hydrogenolysis of per-halogenated compounds,[24] and reaction 5 involves direct hydrolysis of the chloromethyl moiety, which is not likely to be as favorable as the intramolecular pathway (reaction 6).[25] These expectations are supported by the data obtained in this study. (i) Initially, the main product from CPE was always SOX, with SPE and PED arising to various degrees only later in the experiments (Figures S3 and S4 of the Supporting Information). (ii) Significant accumulations of SPE or PED were observed only after SOX concentrations had peaked and, in some cases, begun to decline (Figures S3A,B,E and S4C,D of the Supporting Information). (iii) Experiments initiated with SPE and PED showed negligible transformation over the range of conditions tested (Figure S6 of the Supporting Information). Therefore, when significant concentrations of SPE and PED were formed from CPE, this most likely occurred via SOX (i.e., by reactions 7 and 8).

Reactions of SOX. Most of the media that reacted significantly with CPE were tested for reactivity with SOX, and the results are shown in Figure 2B and Figure S5 of the Supporting Information. In DIW, there was only conversion of SOX to PED, suggesting that ring opening of this epoxide by hydrolysis (reaction 8) is moderately facile even at circumneutral pH. In general, the hydrolysis of epoxides is substantially acid- and base-catalyzed,[25] but we did not investigate the effect of pH in this case.

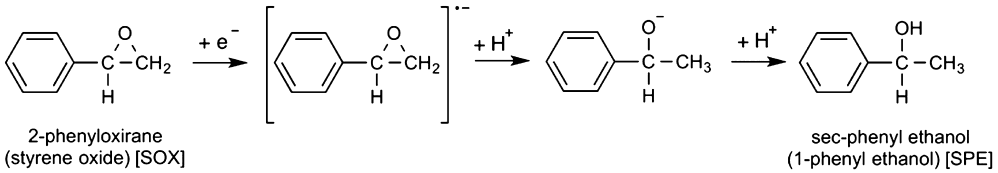
In addition to hydrolysis of SOX to PED, the three reducing media tested (ZVI-A and -B and $NaBH_4$) yielded significant concentrations of SPE (Figure 2B). The transformation of SOX to SPE suggests epoxide ring opening by a reductive pathway (reaction 7), a reaction that appears to have been overlooked as a possible route of contaminant transformation. Reduction of epoxides to alcohols is performed synthetically, however, by catalytic hydrogenation or with soluble hydrides.[17] The latter presumably involves the mechanism shown in Scheme 2.

Scheme 2



Scheme 2 easily explains the formation of SPE by $NaBH_4$ (Figure S5C of the Supporting Information), but it may not be sufficient to explain the appearance of SPE as the major product of SOX reaction with ZVI (Figure S5A,B of the Supporting Information). While a number of studies have concluded that hydride contributes to the reduction of contaminants by

Scheme 3



ZVI,[26−28] most data do not require this pathway, and a few specific arguments have been made against a significant role for hydride.[13,29] One of these arguments is based on the lack of CPE formed upon addition of CAP to batch reactors containing ZVI.[13] For this study, we confirmed that only ACN was formed from CAP using ZVI-A and -B (data not shown), which is consistent with reduction by electron transfer and not hydride.

An alternative mechanism for reducing SOX to SPE is electron transfer via a free radical intermediate (Scheme 3) or possibly an organometallic surface species.[30] In either case, the electron-transfer pathway could lead to radical coupling and other side reactions that likely would yield products that could not be detected using the analytical methods we used. This would be consistent with the relatively poor mass balances obtained in these two experiments (Figure S5A,B). The balance of products might be influenced by experimental conditions, such as the presence of hydrogen donors to trap the radical intermediates,[30,31] but addition of 100 mM isopropyl alcohol to the reaction medium did not change the results obtained with SOX or ZVI-A and -B (data not shown). Interpretation of such chemical effects may be complicated by the interfacial character of reactions on ZVI. Another approach to evaluating the mechanism proposed in Scheme 3 is to utilize the chirality of the α-carbon in the species involved, which will be addressed as part of a broader study of chiral selectivity in reduction by zerovalent metals.

Implications for Contaminant Fate and Remediation. The two new pathways of contaminant transformation by ZVI identified here, hydrolysis catalyzed by oxides under conditions of active corrosion and epoxide ring opening by electron transfer from reduced iron, may help to expand the range of contaminants that can be treated by ZVI to include more PPCPs, pesticides, and other specialty chemicals. It may also explain a few reports of contaminant degradation by ZVI (under anoxic conditions) in which a facile reductive pathway (like dechlorination) is not available.[32,33] The two novel contaminant transformation pathways described here do not appear to be produced by the less strongly reducing, divalent iron minerals (Fe_2O_3/Fe^{II} and Fe_3O_4/Fe^{II}) that are of renewed interest because of their contribution to *in situ* chemical reduction (ISCR).[34]

■ ASSOCIATED CONTENT

Supporting Information

Identifiers and meta-data for the materials used and concentration versus time plots for representative experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tratnyek@ohsu.edu. Phone: (503) 346-3431. Fax: (503) 346-3427.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the Cultivate Discipline Fund of the Shanghai Second Polytechnic University (XXKPY1303) and the Shanghai Cooperative Center for WEEE Recycling (ZF1224-15).

■ REFERENCES

(1) Macalady, D. L.; Tratnyek, P. G.; Grundl, T. J. Abiotic reduction reactions of anthropogenic organic chemicals in anaerobic systems. *J. Contam. Hydrol.* **1986**, *1*, 1−28.

(2) Wolfe, N. L.; Macalady, D. L. New perspectives in aquatic redox chemistry: Abiotic transformations of pollutants in groundwater and sediments. *J. Contam. Hydrol.* **1992**, *9*, 17−34.

(3) Tratnyek, P. G.; Macalady, D. L. Oxidation-reduction reactions in the aquatic environment. In *Handbook of Property Estimation Methods for Chemicals: Environmental and Health Sciences*; Mackay, D., Boethling, R. S., Eds.; Lewis: Boca Raton, FL, 2000; pp 383−415.

(4) Eykholt, G. R.; Davenport, D. T. Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. *Environ. Sci. Technol.* **1998**, *32*, 1482−1487.

(5) Hakala, J. A.; Chin, Y.-P. Abiotic reduction of pendimethalin and trifluralin in controlled and natural systems containing Fe(II) and dissolved organic matter. *J. Agric. Food Chem.* **2010**, *58*, 12840−12846.

(6) Mohatt, J. L.; Hu, L.; Finneran, K. T.; Strathmann, T. J. Microbially mediated abiotic transformation of the antimicrobial agent sulfamethoxazole under iron-reducing soil conditions. *Environ. Sci. Technol.* **2011**, *45*, 4793−4801.

(7) Chen, J.; Qiu, X.; Fang, Z.; Yang, M.; Pokeung, T.; Gu, F.; Cheng, W.; Lan, B. Removal mechanism of antibiotic metronidazole from aquatic solutions by using nanoscale zero-valent iron particles. *Chem. Eng. J.* **2012**, *181−182*, 113−119.

(8) Forgang, J. A.; McIntosh, K. R. Case study: Fate, transport, and remediation of tear gas. *Hazard. Ind. Wastes* **1996**, 1044-0631.

(9) Andrulewicz, E. Chemical weapons dumped in the Baltic Sea. In *Assessment of the Fate and Effects of Toxic Agents on Water Resources*; Gonenc, I. E., Koutitonsky, V., Rashleigh, B., Ambrose, R., Jr., Wolflin, J., Eds.; NATO Security through Science Series; Springer: Dordrecht, The Netherlands, 2007; pp 299−319.

(10) Havel, J.; Reineke, W. Microbial degradation of chlorinated acetophenones. *Appl. Environ. Microbiol.* **1993**, *59*, 2706−2712.

(11) Moonen, M. J. H.; Kamerbeek, N. M.; Westphal, A. H.; Boeren, S. A.; Janssen, D. B.; Fraaije, M. W.; Van Berkel, W. J. H. Elucidation of the 4-hydroxyacetophenone catabolic pathway in *Pseudomonas fluorescens* ACB. *J. Bacteriol.* **2008**, *190*, 5190−5198.

(12) Smolen, J. M.; Weber, E. J.; Tratnyek, P. G. Molecular probe techniques for the identification of reductants in sediments: Evidence for reduction of 2-chloroacetophenone by hydride transfer. *Environ. Sci. Technol.* **1999**, *33*, 440−445.

(13) Miehr, R.; Tratnyek, P. G.; Bandstra, J. Z.; Scherer, M. M.; Alowitz, M.; Bylaska, E. J. The diversity of contaminant reduction reactions by zero-valent iron: Role of the reductate. *Environ. Sci. Technol.* **2004**, *38*, 139−147.

(14) Yang, R. S. H. Propylene chlorohydrins: Toxicology, metabolism, and environmental fate. In *Reviews of Environmental Contamination and Toxicology*; Ware, G., Ed.; Springer: New York, 1987; Vol. *99*, pp 47−59.

(15) Matthew, B. M.; Anastasio, C. Determination of halogenated mono-alcohols and diols in water by gas chromatography with electron-capture detection. *J. Chromatogr., A* **2000**, *866*, 65−77.
(16) Retnamma, R.; Novais, A. Q.; Rangel, C. M. Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: A review. *Int. J. Hydrogen Energy* **2011**, *36*, 9772−9790.
(17) Hudlicky, M. *Reductions in Organic Chemistry*; American Chemical Society: Washington, DC, 1996.
(18) You, Z.-Y.; Liu, Z.-Q.; Zheng, Y.-G. Properties and biotechnological applications of halohydrin dehalogenases: Current state and future perspectives. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 9−21.
(19) Schallmey, M.; Floor, R. J.; Hauer, B.; Breuer, M.; Jekel, P. A.; Wijma, H. J.; Dijkstra, B. W.; Janssen, D. B. Biocatalytic and structural properties of a highly engineered halohydrin dehalogenase. *ChemBioChem* **2013**, *14*, 870−881.
(20) Stumm, W. *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface of Natural Systems*; Wiley: New York, 1992.
(21) Han, J.; Brown, B. N.; Young, D.; Nesic, S. Mesh-capped probe design for direct pH measurements at an actively corroding metal surface. *J. Appl. Electrochem.* **2010**, *40*, 683−690.
(22) Deslouis, C.; Frateur, I.; Maurin, G.; Tribollet, B. Interfacial pH measurement during the reduction of dissolved oxygen in a submerged impinging jet cell. *J. Appl. Electrochem.* **1997**, *27*, 482−492.
(23) Tada, E.; Sugawara, K.; Kaneko, H. Distribution of pH during galvanic corrosion of a Zn/steel couple. *Electrochim. Acta* **2004**, *49*, 1019−1026.
(24) Scherer, M. M.; Balko, B. A.; Gallagher, D. A.; Tratnyek, P. G. Correlation analysis of rate constants for dechlorination by zero-valent iron. *Environ. Sci. Technol.* **1998**, *32*, 3026−3033.
(25) Larson, R. A.; Weber, E. J. Hydrolysis. In *Reaction Mechanisms in Environmental Organic Chemistry*; Lewis: Chelsea, MI, 1994; Chapter 2, pp 103−167.
(26) Khudenko, B. M. Feasibility evaluation of a novel method for destruction of organics. *Water Sci. Technol.* **1991**, *23*, 1873−1881.
(27) Odziemkowski, M. S.; Gui, L.; Gillham, R. W. Reduction of N-nitrosodimethylamine with granular iron and nickel-enhanced iron. 2. Mechanistic studies. *Environ. Sci. Technol.* **2000**, *34*, 3495−3500.
(28) Li, T.; Farrell, J. Electrochemical investigation of the rate-limiting mechanisms for trichloroethylene and carbon tetrachloride reduction at iron surfaces. *Environ. Sci. Technol.* **2001**, *35*, 3560−3565.
(29) Scherer, M. M.; Westall, J. C.; Tratnyek, P. G. Discussion on "Electrochemical and Raman spectroscopic studies of the influence of chlorinated solvents on the corrosion behaviour of iron in borate buffer and in simulated groundwater" [Corrosion Science 42 (2000) 1921−1939]. *Corros. Sci.* **2001**, *44*, 1151−1157.
(30) RajanBabu, T. V.; Nugent, W. A. Selective generation of free radicals from epoxides using a transition-metal radical. A powerful new tool for organic synthesis. *J. Am. Chem. Soc.* **1994**, *116*, 986−997.
(31) Balko, B. A.; Tratnyek, P. G. Photoeffects on the reduction of carbon tetrachloride by zero-valent iron. *J. Phys. Chem. B* **1998**, *102*, 1459−1465.
(32) Ghauch, A. Degradation of benomyl, picloram, and dicamba in a conical apparatus by zero-valent iron powder. *Chemosphere* **2001**, *43*, 1109−1117.
(33) Ghauch, A.; Gallet, C.; Charef, A.; Rima, J.; Martin-Bouyer, M. Reductive degradation of carbaryl in water by zero-valent iron. *Chemosphere* **2001**, *42*, 419−424.
(34) Tratnyek, P. G.; Johnson, R. L.; Lowry Gregory, V.; Brown, R. A. In situ chemical reduction for source zone remediation. In *Chlorinated Solvent Source Zone Remediation*; Kueper, B. H., Stroo, H. F., Vogel, C. M., Ward, C. H., Eds.; SERDP and ESTCP Remediation Technology Monograph Series; Springer: New York, 2014; Vol. 7, pp 307−351.