

Novel Contaminant Transformation Pathways by Abiotic Reductants

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S Supporting Information

ABSTRACT: Environmentally relevant abiotic reductants, such as zerovalent iron (ZVI) and minerals containing divalent iron (DVI), react predominantly by electrontransfer 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 NaBH₄) 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,^{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 electrontransfer 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-

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Figure 1. Summary of the major reactions responsible for the interconversion of species derived from 2-chloroacetophenone (CAP) and 2chlorophenyl 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 NaBH₄ and pH 10.0 buffer, were prepared in an anaerobic chamber containing pure (99.999%) N₂ and <10 ppm O₂. 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 μ M. The spiked reactor was handshaken briefly and then mixed continuously during the rest of the experiment by end-over-end rotation at \sim 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 μ m 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 μ m, 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.

Letter

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), NaBH₄, 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.



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 NaBH₄ 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 Fe⁰ 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 Fe₂O₃/Fe^{II} and Fe₃O₄/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 NaBH₄) 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 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



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 (Fe₂O₃/Fe^{II} and Fe₃O₄/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.

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

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Abbrev- iation	Common Name (Manufacturer)	Standard Name (IUPAC)	CAS-RN	Supplier (Product No.)	Purity (%)	λ _{max} (nm)
САР	2-Chloro acetophenone	2-Chloro acetophenone	532-27-4	Sigma Aldrich	98	249.0
СРЕ	2-Chloro-1-phenyl ethanol	2-Chloro-1-phenyl ethanol	1674-30-2	Alfa Aesar	>97	256.5
ACN	Acetophenone	Acetophenone	98-86-2	Fluka	>99	245.0
SPE	sec-Phenyl ethanol	1-Phenyl ethanol	98-85-1	TCI	98	256.5
PED	1-Phenyl-1,2- ethanediol	1-Phenyl-1,2- ethanediol	93-56-1	Sigma Aldrich	97	256.0
SOX	Styrene oxide	2-Phenyloxirane	96-09-3	Sigma Aldrich	97	252.8

 Table S1. Summary of Contaminant/Probe/Analyte Properties.

 Table S2.
 Summary of Reductant Properties.¹

Name	Material	Supplier	Product	Description	Sieve + Particle Size	SSA ² (m ² /g)
ZVI-A	Zerovalent Iron, A	Hepure Claymont, DE	HCA-150 (now "Ferox Flow")	Sieved cast iron powder, >95% Fe	100-325 mesh, 15-500 μm	0.97 1.41
ZVI-B	Zerovalent Iron, B	Peerless Metal Powders & Abrasives Detroit, MI	50D	Iron aggregate	60-325 mesh, 0.9 μm	1.57 2.7
ZVI-C	Zerovalent Iron, C	Fisher Scientific Pittsburgh, PA	I-60	Electrolytic Powder, >99% Fe	>100 mesh, 0.2 μm	0.2,0.6 1.27
ZVI-D	Zerovalent Iron, D	Rio Tinto QMP Sorel -Tracy, Quebec	H2Omet 56	From ore not scrap >93% Fe	30-200 mesh 45-600 μm	0.21 0.25
ZVI-E	Zerovalent Iron, E	Hepure Claymont, DE	H200 (discontinued)	Sponge 95+ % Fe	100-325 mesh 70-80 μm	2.2
ZVZ	Zerovalent Zinc	Horsehead Corp. Monaca, PA	Zinc Dust 64	99.3% Zn (96.5% Zn ⁰)	>325 mesh 4.5 µm	0.62
Fe ₂ O ₃ /Fe ^{II}	Goethite + 1 mM FeSO ₄	Bayferrox ³	910 QE66	94-96% Fe	0.09 µm	
Fe ₃ O ₄ /Fe ^{II}	Magnetite + 1 mM FeSO ₄	Bayferrox ³	318 NM	92-93% Fe	<0.2 µm	
NaBH ₄	Sodium Borohydride	ACROS				

^l Property data as provide by manufacturer/supplier, unless indicated by italics. ² Specific surface area from BET N₂gas adsorption unless specified otherwise. ³ Refers to the iron oxide only. Ferrous iron was added and then allowed 24 hr to equilibrate with the oxide.



Figure S1. UV-vis spectra of the major analytes (CPE and transformation products). Blue curves are for standards obtained with a 1 cm path length quartz cuvette with a DI water blank. Red curves were obtained by DAD on the corresponding HPLC peaks (using actual product peaks for SPE, PED, and SOX.)



Figure S2. Representative chromatographs of the major analytes (CPE and transformation products): (**A**) HPLC Method 1, used for quantification of ACN and CAP; (**B**) HPLC Method 2, used for quantification of CPE and products.



Figure S3. Concentration vs. time plots for reaction of CPE with various zerovalent metal reductants (ZVI-A, -B, -C, -D, -E; and ZVZ). The metal dose was 50 mg/L in all cases.



Figure S4. Concentration vs. time plots for reaction of CPE transformation products (SPE, PDE, SOX) with adsorbed divalent iron (Fe_2O_3/Fe^{II} , Fe_3O_4/Fe^{II}); NaBH₄; and pH 10 borate buffer.



Figure S5. Concentration vs. time plots for reaction of SOX transformation products (SPE or PDE) with various reductants (ZVI-A, -B, Fe_2O_3/Fe^{II} , Fe_3O_4/Fe^{II} , $NaBH_4$) and unbuffered DIW.



Figure S6. Concentration vs. time plots for reaction of SPE and PED with various reductants.