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# Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals

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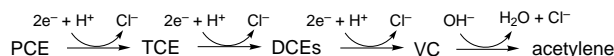
## Introduction

Reductive dehalogenation reactions are generally divided into two categories (1–3): hydrogenolysis (replacement of a halogen by a hydrogen) and reductive elimination (in which two halide ions are released). Both are accompanied by a net transfer of two electrons. Numerous examples of hydrogenolysis have been cited, including reduction of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) to 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD) (e.g., refs 4–8), CCl<sub>4</sub> to CHCl<sub>3</sub> (e.g., refs 9–12), and Cl<sub>2</sub>C=CCl<sub>2</sub> to Cl<sub>2</sub>C=CHCl (e.g., refs 13–17). An example of reductive elimination is Cl<sub>3</sub>C–CCl<sub>3</sub> reaction to Cl<sub>2</sub>C=CCl<sub>2</sub> (e.g., refs 18–22). Although CCl<sub>4</sub> reduction to CO and formate (9, 23–27) is occasionally cited as a third category, hydrolytic reduction, this term is misleading since hydrolysis is incidental to the actual reduction. In fact, this is another example of reductive elimination, albeit one in which the halogens are released from the same carbon (reductive  $\alpha$ -elimination) to form a carbene, which subsequently reacts with the solvent. To date, however, it does not appear to have been demonstrated in the literature that halogenated ethylenes can undergo reductive  $\beta$ -elimination to alkynes under environmental conditions. The purpose of this paper is to provide experimental evidence that such pathways may be involved in the reaction of chloroethylenes with zero-valent metals as well as to speculate on the significance of the products that may result.

The use of zero-valent metals to degrade contaminants represents an active research area (28–38). In large part, this was sparked by the suggestion of Gillham and co-workers that Fe(0) could be utilized as an immobilized reagent in a passive approach to groundwater remediation. Iron's utility in subsurface treatment walls for removing organohalides has been confirmed by controlled field

experiments by this group of researchers (39, 40). Several test installations have been completed at contaminated sites and more are planned (39–44). To date, the precise pathways through which metals reduce chloroethylenes have not been fully elucidated, nor have reaction products or intermediates been completely characterized. Such information is essential to the optimal design of remediation systems. Some of the observed products, such as vinyl chloride (28, 37, 45) are themselves of concern as drinking water contaminants, with very low maximum contaminant level values imposed by the U.S. EPA (46). Others, including *cis*-1,2-dichloroethylene as well as vinyl chloride, react relatively slowly in the presence of Fe(0) (28). The necessity of controlling the levels of such undesirable byproducts may dictate the overall design of metal-based remediation systems and thus the economic viability of this approach (42, 45). Any efforts to identify the routes through which such products are formed or which can account for their persistence would clarify the potential limitations of this promising technique or might even enable improved approaches to contaminant remediation.

One product reported in tetrachloroethylene and trichloroethylene reaction with Fe(0) is acetylene. Cipollone *et al.* (47) have speculated this arises through the sequential hydrogenolysis of tetrachloroethylene (PCE) to trichloroethylene (TCE), dichloroethylenes (DCEs), and then vinyl chloride (VC), followed by VC dehydrohalogenation to acetylene:



Although dehydrohalogenation does occur for haloethylenes (48–50), it requires extreme conditions in homogeneous solution. Thus, the second-order rate constant for OH<sup>−</sup> reaction with TCE in water at 25 °C is  $1.8 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  (51), yielding a half-life at pH 7 of 10<sup>6</sup> years. Even at the higher pH typical of Fe(0)-promoted reactions, reaction should still be slow, with a calculated half-life of 10<sup>3</sup> years at pH 10. Since base-promoted dehydrohalogenation reactions (which are likely to dominate over the pH-independent reaction for such substrates) are sensitive to inductive effects (52), they will undoubtedly proceed much more slowly for VC than for TCE. Such a pathway would therefore seem unlikely unless these reactions are somehow catalyzed by metal surfaces.

Calculations (shown in Table 1) indicate that reductive  $\beta$ -elimination reactions of chloroethylenes are in fact comparable energetically to hydrogenolysis at neutral pH. Experiments were therefore initiated to assess whether  $\beta$ -elimination reactions of chlorinated ethylenes could occur in the presence of two zero-valent metals, Fe and Zn.

## Experimental Section

**Reduction of Dichloroethylenes by Fe(0).** Experiments were conducted in 25-mL serum bottles capped with Teflon septa. Each bottle contained 1.7 g of Fe(0) (Fisher, 40 mesh)

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







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TABLE 1

Calculated Thermodynamic Reduction Potentials (Relative to Standard Hydrogen Electrode) for Two- and One-Electron Reduction of Selected Species in Aqueous Solution at 25 °C<sup>a</sup>

parent compd.	hydrogenolysis product	$E_H^\circ(W)$ (V) <sup>b</sup>	reductive elimination product	$E_H^\circ$ (V) <sup>c</sup>	other reduction product	$E_H^\circ(W)$ (V) <sup>d</sup>	one-electron reduction product	$E_1^\circ$ (V) <sup>e</sup>
PCE	TCE	0.592	$\text{ClC}\equiv\text{CCl}$	0.631				-0.36
TCE	<i>cis</i> -DCE	0.530	$\text{ClC}\equiv\text{CH}$	0.599				not available
TCE	1,1-DCE	0.513						-0.91
TCE	<i>trans</i> -1,2-DCE	0.509						-0.62
1,1-DCE	VC	0.423	NA <sup>f</sup>					-0.72
<i>cis</i> -DCE	VC	0.407	$\text{HC}\equiv\text{CH}$	0.568				-0.89
<i>trans</i> -DCE	VC	0.428	$\text{HC}\equiv\text{CH}$	0.589				-0.85
VC	$\text{H}_2\text{C}=\text{CH}_2$	0.481	NA <sup>f</sup>					-0.95
$\text{ClC}\equiv\text{CCl}$	$\text{ClC}\equiv\text{CH}$	0.56	NA <sup>f</sup>		<i>cis</i> -DCE	0.49		
$\text{ClC}\equiv\text{CCl}$					<i>trans</i> -DCE	0.47		
$\text{ClC}\equiv\text{CH}$	$\text{HC}\equiv\text{CH}$	0.50	NA <sup>f</sup>		VC	0.37		

<sup>a</sup> Calculations assume that Henry's law constant for  $\text{R}^*(\text{g}) \approx$  value for  $\text{R}-\text{H}(\text{g})$  (53),  $\{\text{H}^+\} = 10^{-7}$  M,  $\{\text{Cl}^-\} = 10^{-3}$  M, and that all other species are at unit activity. Gas-phase thermodynamic data from refs 54–57, corrected for air–water partitioning using Henry's law constants recommended by Mackay *et al.* (58), reported by ref 59, or estimated according to the method of Hine and Mookerjee (59). <sup>b</sup> Two-electron reduction potential corresponding to hydrogenolysis reaction:  $\text{RCI} + 2\text{e}^- + \text{H}^+ \rightleftharpoons \text{RH} + \text{Cl}^-$ . <sup>c</sup> Two-electron reduction potential corresponding to reductive  $\beta$ -elimination reaction:  $\text{RCI}=\text{RCI} + 2\text{e}^- \rightleftharpoons \text{R}=\text{R} + 2\text{Cl}^-$ . <sup>d</sup> Two-electron reduction potential corresponding to reduction of triple bond to double bond:  $\text{R}=\text{R} + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{HR}=\text{RH}$ . <sup>e</sup> One-electron reduction potential corresponding to reduction to radical species:  $\text{RCI} + \text{e}^- \rightleftharpoons \text{R}^* + \text{Cl}^-$ . <sup>f</sup> Not applicable; reductive  $\beta$ -elimination pathway does not exist for this compound.

and 34 mg of finely ground iron pyrite (Ward's Natural Science Est, Inc.), suspended in 1.7 mL of deoxygenated (Ar-sparged) deionized water (Milli-Q Plus UV, Millipore). Pyrite was included for consistency with studies reported elsewhere (36, 60). The iron was cleaned by washing in Ar-sparged 1 N HCl. Surface area analyses conducted via Kr BET adsorption using a Micromeritics Flowsorb II 2300 device indicated a surface area of 0.7 m<sup>2</sup>/g. Reaction mixtures were prepared in an anaerobic chamber (Coy Laboratory Products) containing an atmosphere of 10% H<sub>2</sub> in N<sub>2</sub>. Bottles were spiked with either 6.7  $\mu\text{L}$  of a solution of *trans*-DCE, 4.4  $\mu\text{L}$  of *cis*-DCE, 10  $\mu\text{L}$  of 1,1-DCE, or 30  $\mu\text{L}$  of VC in methanol (containing hexane as an internal standard) and were mixed on a rotator (Cole-Parmer) at 4 rpm. At selected intervals, 100- $\mu\text{L}$  headspace aliquots were removed (accompanied by injection of an equivalent volume of purified argon) and were injected in splitless mode onto a Fisons 8000 Series gas chromatograph (GC) equipped with a GS-Q PLOT column (J&W Scientific) and a flame ionization detector (FID). The possibility of mass transfer-limited air–water exchange of parent compounds and reaction products into the headspace in these systems forestalls a detailed kinetic analysis of the resulting data. Nevertheless, the high ratio of headspace to solution volume in these experiments provides an advantage in identifying reaction pathways, in that more highly volatile reaction products and intermediates will partition into the headspace rather than remaining in solution or sorbing to the metal

surface (36), thereby slowing their further reaction, enhancing their accumulation, and facilitating their detection.

**Reduction of Chlorinated Ethylenes by Zn(0).** Reactions were carried out in 1-L flasks equipped with a glass stopcock adapter, filled with 0.1 M deoxygenated NaCl solution to which 200 g of 30 mesh Zn(0) (100.5%, J. T. Baker) was added. Although a pH buffer was not employed, the pH remained relatively stable, diminishing at most from pH 7.1  $\pm$  0.1 to pH 6.7  $\pm$  0.1. The zinc was cleaned by washing with 400 mL of 0.4% H<sub>2</sub>SO<sub>4</sub>. Krypton BET analyses indicated a surface area of 0.035 m<sup>2</sup>/g. Note that in these experiments, essentially no headspace was initially present (to facilitate kinetic modeling of reaction pathways), although minor amounts (<20 mL) were eventually produced, presumably through H<sub>2</sub> evolution from the reaction of Zn with water. Flasks were spiked with 0.5 mL of a methanol solution of the target compound (either PCE, TCE, or *trans*-DCE) and were mixed by rotating about their long axes at 20–30 rpm. Aliquots of 1 mL were periodically removed using 2-mL glass syringes (equipped with three-way metal stopcock adapters, one end of which was plugged with an air-tight septum), accompanied by introduction of an equivalent volume of deoxygenated water. One milliliter of air was then injected through the septum into the syringe, as was 1  $\mu\text{L}$  of a methanol solution of hexane (as an internal standard). Syringes were shaken vigorously by hand, and 100- $\mu\text{L}$  headspace samples were analyzed by GC-FID as previously described. Results were modeled using the

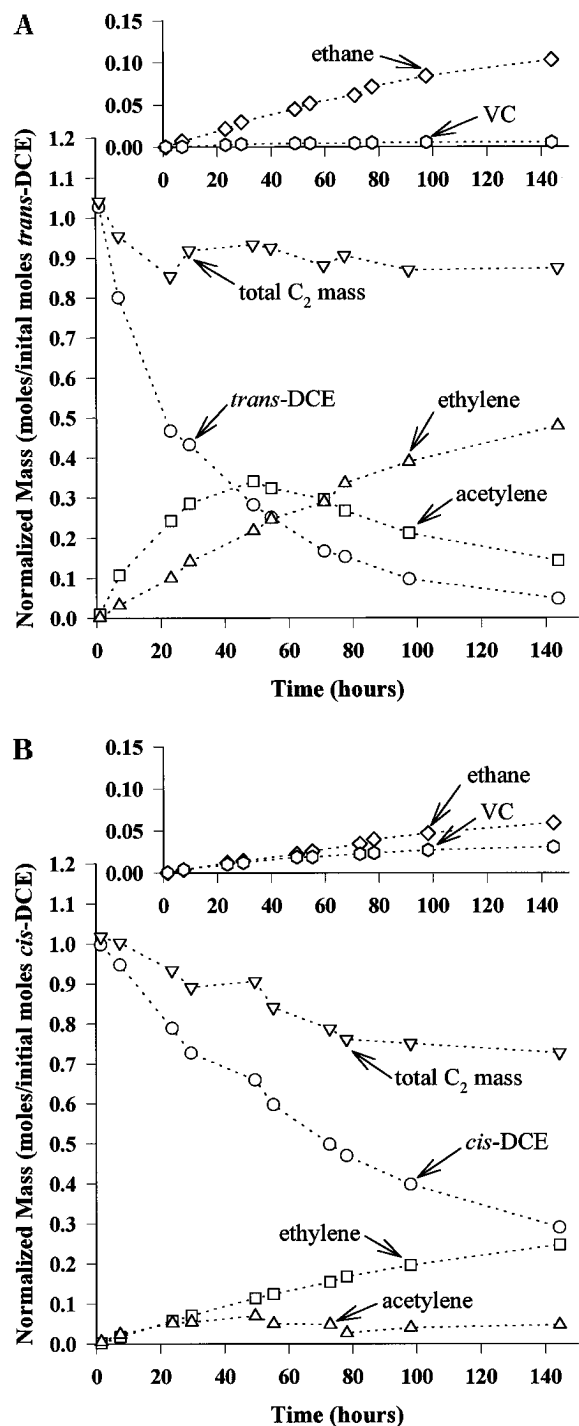
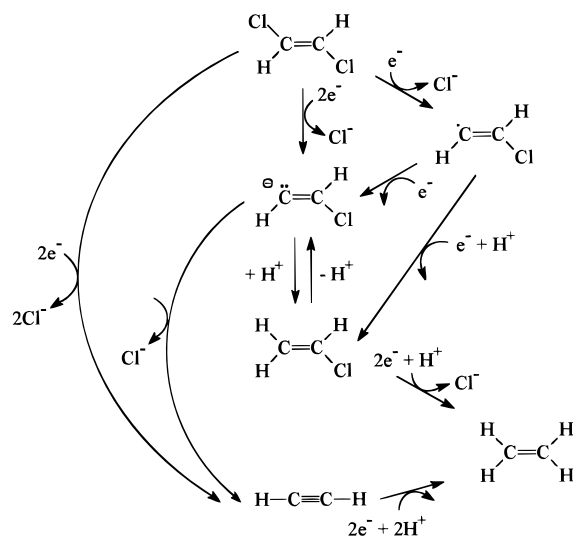


FIGURE 1. Reaction of *cis*- and *trans*-DCE in the presence of Fe(0) in high headspace system experiments. Results not corrected for sorption of dichloroethylenes onto Fe(0) (60): (A) results for *trans*-DCE; (B) results for *cis*-DCE. Initial DCE concentrations obtained by fitting DCE data to an exponential decay expression.

kinetic package *Scientist for Windows* v. 2.01 (Micromath Scientific Software, Inc., Salt Lake City, UT). This software package determines reaction rate constants and associated parameters by fitting experimental data to numerically integrated solutions of systems of differential rate expressions.

## Results and Discussion

Results for *trans*- and *cis*-DCE reaction with Fe(0) are shown in Figure 1. Both react primarily to acetylene and ethylene, with acetylene exhibiting accumulation and decay



**FIGURE 2.** Proposed pathways for reduction of *trans*-dichloroethylene by zero-valent metals.

typical of a reaction intermediate. Lesser amounts of ethane and VC were also observed, as were trace quantities of methane, propane, propene, butane, and 1-butene. In the absence of headspace, *trans*-DCE reacts with Fe(0)  $\sim 10\times$  faster than *cis*-DCE (60); this reactivity contrast is however muted in the presence of appreciable headspace due to the higher Henry's law constant of *trans*-DCE.

The results indicate a VC yield from *cis*-DCE approximately 7 times as great as from *trans*-DCE. Parallel experiments failed to evince any acetylene production in the reduction of VC or 1,1-DCE over the course of 10 days (during which 25% of the VC and 10% of the 1,1-DCE underwent transformation); rather, both reacted to ethylene and ethane as principal products. Nor was any acetylene observed in the absence of added organohalide.

A scheme that could account for these products is shown in Figure 2 for reduction of *trans*-DCE. In principle, reaction could proceed through transfer of a single electron to form a free radical. This could either undergo a second one-electron reduction to a vinyl carbanion or abstract a hydrogen atom from a suitable donor to yield VC. Alternatively, the reaction could occur by transfer of two electrons essentially in a single step. This two-electron transfer could yield a vinyl carbanion, or it could proceed in a concerted manner to produce acetylene directly.

It is known from experiments in homogeneous solution that vinyl carbanions are reversibly formed in haloethylene dehydrohalogenation. For example, the hydrogen of TCE can be exchanged with that of water (48, 61). Such vinyl carbanions are more stable than are alkyl carbanions due to the higher degree of *s* character in the  $sp^2$  hybrid orbital (62). Although the deprotonation step in dehydrohalogenation is slow, Miller and Lee (49) found that the free vinyl carbanion resulting from *cis*-1,2-dibromoethylene- $d_2$  deprotonation underwent reprotonation  $\sim 25$  times more rapidly than elimination. Thus, if reaction of chlorinated ethylenes were to proceed either via a free vinyl carbanion or a free radical intermediate, some of the corresponding hydrolysis product might be anticipated.

On the other hand, the vinyl carbanion could also undergo  $\beta$ -elimination to an alkyne. A characteristic of such reactions is that elimination of *trans* substituents is much more favorable than is *cis* elimination. In the absence

of isomerization of the vinyl carbanion, dehalogenation should therefore proceed more readily for substrates bearing a  $\beta$ -halogen *trans* to the lone pair on the  $\alpha$ -carbon than for substrates possessing a  $\beta$ -halogen only in the *cis* position. Such isomerization has previously been shown to be negligible for  $^-:\text{CCl}=\text{CHCl}$  carbanions (49). Acetylenes could also originate from the concerted elimination of an  $\alpha,\beta$ -dihaloolefin, especially if the halogens were *trans* to one another. The unavailability of a concerted reductive *trans*  $\beta$ -elimination pathway and the greater likelihood of carbanion protonation relative to *cis* elimination should together dictate that a higher yield of a hydrogenolysis product should result from reduction of a *cis*- $\alpha,\beta$ -dihaloolefin as compared to a *trans*-dihaloalkene. This prediction is in accordance with the results obtained with *cis*- and *trans*-DCE. In addition to geometric factors, whether or not a given compound might undergo reduction to a vinyl carbanion (part of which could protonate to the hydrogenolysis product) or alternatively undergo a concerted reaction to an alkyne may depend in part on factors that serve to stabilize the vinyl carbanion. These might include the presence of electron-withdrawing substituents such as halogens (62) or coordination by metal ions (possibly adsorbed at the metal surface).

A pathway analogous to Figure 2 would imply that PCE could be reduced to dichloroacetylene and TCE could be reduced to chloroacetylene, reactions potentially of environmental significance. Both dichloroacetylene and chloroacetylene are reported to be toxic (63, 64). The amounts that might accumulate would depend on rates of their production and subsequent transformation.

Limited evidence suggests that chlorinated acetylenes are unstable. Both are spontaneously flammable in air (63), and calculations (Table 1) indicate that their hydrogenolysis to form lesser halogenated acetylenes is plausible under appropriate conditions, as is their reduction to substituted ethylenes. An additional process chloroacetylenes might undergo is hydrolysis. Although the  $\text{sp}^2$ -hybridized carbon of chloroethylenes is resistant to hydrolysis, the C-Cl bond of  $\text{sp}$ -hybridized carbon of chlorinated acetylenes possesses unique features that render it susceptible to such reactions. Nucleophilic solvents can attack at Cl (rather than C) to yield the same lesser halogenated acetylene derivatives that result from hydrogenolysis (64, 65) plus HOCl (in the case of attack by  $\text{OH}^-$ ). Alternatively, the solvent can react with the halogenated acetylene derivative via an addition pathway to ultimately form carboxylic acids (63, 65). Thus, some acetate might be produced from chloroacetylene hydrolysis in aqueous solution; similarly, chloroacetate might be expected to result from dichloroacetylene hydrolysis.

Reduction of PCE by Zn(0) (Figure 3) provides indirect evidence that dichloroacetylene may represent an unstable intermediate. TCE represents the principal product, although lesser amounts of both *trans*-DCE and acetylene were also observed as well as traces of ethylene and *cis*-DCE. Parallel experiments confirmed that TCE and *trans*-DCE reacted at least an order of magnitude more slowly than PCE under these conditions. Attempts to model the *trans*-DCE and acetylene data by invoking sequential reduction of  $\text{PCE} \rightarrow \text{TCE} \rightarrow \text{trans-DCE} \rightarrow \text{acetylene}$  were unsuccessful (see inset in Figure 3); TCE and *trans*-DCE react too slowly to account for the rate of accumulation of their respective products. Modeling the data by invoking parallel reactions of PCE to TCE, *trans*-DCE, and acetylene,

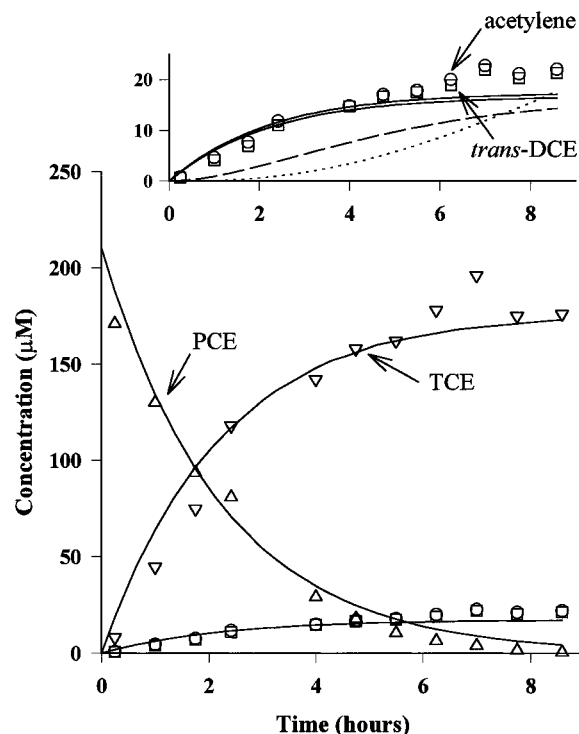


FIGURE 3. Reduction of PCE by Zn(0) in system containing 0.1 M deoxygenated NaCl solution with minimal headspace. Solid lines represent model fits assuming parallel reactions of PCE to TCE, *trans*-DCE, and acetylene, assuming all reaction products to be stable during the time frame of this experiment. Dashed line and dotted line in inset represent model fit to *trans*-DCE and acetylene data, respectively, assuming sequential reduction of  $\text{PCE} \rightarrow \text{TCE} \rightarrow \text{trans-DCE} \rightarrow \text{acetylene}$ .

however, captures most of the features of the early *trans*-DCE and acetylene data. This is consistent with the possibility that acetylene could be formed from the reduction of a transitory dichloroacetylene intermediate that undergoes rapid reduction to *trans*-DCE and chloroacetylene, the latter rapidly reacting further to acetylene. The true situation is likely to represent some combination of parallel and sequential reactions; more extensive studies will be required to assess the relative contributions of each.

There is some precedent for invoking chloroacetylenes as products of more highly chlorinated ethylene reduction. For example, one pathway to chloroacetylene synthesis involves the reduction of vicinal polyhaloalkanes or alkenes by zero-valent metals in organic solvents (66). Delavarenne and Viehe (65) note that a similar reduction in protic solvents is of limited practical value since the products often react further. One group of researchers (67) claims to have measured chloroacetylene (but not dichloroacetylene) in the electrochemical reduction of PCE in aqueous hexamethylphosphoramide solution. Interestingly, although the reaction of substituted acetylenes with  $\text{H}_2$  (hydrogenation) to the corresponding substituted olefins should preferentially follow a *cis* addition pathway, these researchers proposed that dichloroacetylene underwent reduction to *trans*-DCE. Castro and Stephens (68) have found that the reduction of substituted acetylenes by  $\text{Cr}^{2+}$  in aqueous solution results exclusively in *trans* rather than *cis*-olefins. This supports the possibility that the *trans*-DCE observed in PCE reduction by Zn(0) could have arisen from a dichloroacetylene intermediate. If chlorinated acetylenes were to be formed during PCE or TCE reduction by zero-valent metals, such reactions could thus at least partially

account for the production of VC and 1,2-DCE isomers. Very recently, Sivavek (69) has identified chloroacetylene in the reduction of TCE by Fe(0) in aqueous solution. We have also tentatively identified chloroacetylene as a trace product of TCE reduction by Fe(0), based on GC/MS analyses of headspace samples.

At present, insufficient information exists to prove whether electron transfer to chlorinated ethylenes is a one- or a two-electron process for reduction by zero-valent metals. Spin-trapping agents that might be useful in ESR analyses react readily with metals, possibly accounting for the lack of success reported to date (70). A comparison of the calculated one- and two-electron reduction potentials of chloroethylenes (Table 1) demonstrates that two-electron pathways (either hydrogenolysis or reductive  $\beta$ -elimination reactions) are favored over single-electron pathways, reflecting the relative instability of free radical intermediates in aqueous solution. We have found that the reductive elimination of probe compounds (*erythro* and *threo* isomers of 2,3-dibromopentane) by Zn(0), Fe(0), Al(0), and Cu(0) in aqueous solution at room temperature proceeds with virtually complete stereospecificity (71; Totten, unpublished data). This indicates that electron transfer from these metals to the substrates proceeds rapidly compared to the rate of rotation about the carbon-carbon bond, suggesting that at least some metal-promoted reductive  $\beta$ -elimination reactions can be viewed as an essentially concerted transfer of two electrons.

Further indirect evidence that tends to support a two-electron pathway comes from attempted linear free-energy relationships between reactivity in the Fe(0)-promoted reduction of chloroethylenes and thermodynamic reduction potentials. If regressions are conducted for reaction rate constants reported by Gillham and O'Hannesin (28) against the one- and two-electron reduction potentials shown in Table 1, the results indicate that the relationship between reactivity and one-electron reduction potential is very weak [ $R^2(\text{adj}) = -0.0754$ ]. In contrast, significantly better correlations are obtained by regressing reaction rate constants against two-electron reduction potentials, either for hydrogenolysis reactions [ $R^2(\text{adj}) = 0.749$ ] or  $\beta$ -elimination reactions [ $R^2(\text{adj}) = 0.808$ ]. Further proof of the one- versus the two-electron character of the reaction must await more detailed investigations.

If the reduction of halogenated ethylenes with zero-valent metals does show a strong preference for a concerted two-electron  $\beta$ -elimination pathway, this might account for the sluggish rates of reaction of chloroethylenes lacking the requisite *trans*- $\alpha,\beta$  pair of halogens, such as VC, 1,1-DCE, and *cis*-DCE, potentially accounting for their persistence in zero-valent metal-based remediation schemes. Although the reduction of PCE by Zn(0) does result in TCE as a major product, an observation inconsistent with a concerted reductive  $\beta$ -elimination pathway, this may simply reflect the greater degree of stabilization of a vinyl carbanion by the additional halogen substituents and may not signify a similar minor role for the concerted  $\beta$ -elimination of lesser halogenated ethylenes.

Reductive  $\beta$ -elimination may be mediated by species other than zero-valent metals. For example, Burris *et al.* (72) have found that the reduction of PCE and TCE by vitamin B<sub>12</sub> yields a significant amount of acetylene. It may be noteworthy that in these experiments, vitamin B<sub>12</sub> was reduced with titanium(III) citrate, which spectroscopic evidence has shown to reduce the metal center to the Co(I)

oxidation state (73). This raises the possibility that fully reduced vitamin B<sub>12</sub> could serve as a two-electron reductant. Strongly nucleophilic species are known to promote reductive elimination of vicinal dihaloalkanes through a process (involving nucleophilic attack on a halogen) that can be viewed as a two-electron reduction (74); in this respect, it may be worth noting that Co(I) corrinoids have been referred to as "supernucleophiles" (75). Belay and Daniels (76) have also reported acetylene production from 1,2-dibromoethylene (isomer unspecified) in pure cultures of methanogenic bacteria. These workers did not speculate as to the pathway involved. In light of the foregoing evidence, we consider reductive  $\beta$ -elimination to be a plausible explanation. Future investigations should consider the possibility of reductive  $\beta$ -elimination reactions of vicinal dihaloalkenes as well as the potential environmental significance of some of the intermediates of these reactions.

## Acknowledgments

This work was funded through Contract F08637 95 C6037 from the Department of the Air Force as well as through an NSF Young Investigator Award (Grant BES-9457260) to A.L.R. and an NSF Graduate Student Fellowship to L.A.T. Funding for D.R.B. and T.J.C. was provided, in part, by the Strategic Environmental Research and Development Program (SERDP) of the DoD, DoE, and EPA.

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Received for review December 29, 1995. Revised manuscript received April 17, 1996. Accepted April 22, 1996.

ES9509644