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Pathways of Chlorinated Ethylene and Chlorinated Acetylene Reaction with Zn(0)

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To successfully design treatment systems relying on reactions of chlorocarbons with zero-valent metals, information is needed concerning the kinetics and pathways through which transformations occur. In this study, pathways of chlorinated ethylene reaction with Zn(0) have been elucidated through batch experiments. Data for parent compound disappearance and product appearance were fit to pseudo-first-order rate expressions in order to develop a complete kinetic model. Results indicate that reductive β-elimination plays an important role, accounting for 15% of tetrachloroethylene (PCE), 30% of trichloroethylene (TCE), 85% of *cis*-dichloroethylene (*cis*-DCE), and 95% of *trans*-dichloroethylene (*trans*-DCE) reaction. The fraction of PCE, TCE, *trans*-DCE, and *cis*-DCE transformation that occurs via reductive elimination increases as the two-electron reduction potential (E_2) for this reaction becomes more favorable relative to hydrogenolysis. In the case of PCE and TCE, reductive elimination gives rise to chlorinated acetylenes. Chloroacetylene and dichloroacetylene were synthesized and found to react rapidly with zinc, displaying products consistent with both hydrogenolysis and reduction of the triple bond. Surface area-normalized rate constants (k_{SA}) for chlorinated ethylene disappearance correlate well with both one-electron (E_1) and two-electron (E_2) reduction potentials for the appropriate reactions. Correlation with E_2 allows prediction of the distribution of reaction products as well as the rate of disappearance of the parent compound.

Introduction

The use of zero-valent metals as reductants of chloroalkanes and chloroethylenes represents a promising new approach for treating groundwater contaminated with such solvents. Removal of the parent compound, however, may not be sufficient to attain drinking water standards as partially dechlorinated reaction products or intermediates may also pose human health risks. For example, some moderately persistent species, such as *cis*-dichloroethylene (*c*is-DCE) and vinyl chloride (VC), which have been detected as products of tetrachloroethylene (PCE) (*1*) and trichloroethylene (TCE) (*1−4*) reduction by iron, are themselves of concern as contaminants. The necessity of controlling effluent levels of such species may dictate the overall design of metal-based treatment systems (*5−7*). To develop process models that could be used to optimize the design of in situ or ex situ treatment systems, information is needed concerning the rates and pathways through which chlorinated intermediates are formed and subsequently degrade.

Zinc was selected in the present study in order to gain insight into pathways through which one possible candidate metal reacts with chlorinated ethylenes. Zinc has previously been studied for use as a reductant of carbon tetrachloride (*8*, *9*), as well as lindane (γ-hexachlorocyclohexane), 1,1,1-trichloroethane, and chloroform (*10*). Methyl parathion has also been found to undergo reduction when contaminated soil is mixed with zinc metal (*11*). Although oxidation of zinc metal might be anticipated to release Zn(II) species, which might be of concern in drinking water, Carraway and co-workers (*12*) have recently demonstrated that dissolved Zn^{2+} concentrations generated in the reaction of PCE with Zn(0) can be minimized by adding hydroxyapatite, onto which the Zn(II) is presumably removed via adsorption (*12−14*).

Our previous work (*1*, *15*) has shown that chlorinated ethylene reduction by zero-valent metals, such as iron and zinc, proceeds via two parallel pathways: hydrogenolysis and reductive β-elimination. In the case of ethylenes bearing an α,β pair of chlorines, reductive elimination gives rise to substituted acetylenes. A third reaction that may occur in these systems is the reduction of multiple bonds. This creates the possibility that a particular intermediate may arise from multiple pathways. For example, vinyl chloride may be produced via hydrogenolysis of the dichloroethylenes or alternatively by reduction of the triple bond of chloroacetylene. The existence of such competing reactions greatly complicates the modeling of transformation pathways. A scheme that accounts for reactions of chlorinated ethylenes and other possible intermediates with zinc is detailed in Figure 1 (*1*, *15*). Although our prior work established the overall plausibility of this scheme, the data reported by us (*1*, *15*) and others (*2−4*, *16−18*) have not been sufficiently detailed as to determine the rate constants associated with each of these reactions for either Zn(0) or Fe(0). The principal objective of this work was to measure the kinetics of chlorinated ethylene reaction with Zn(0) through detailed measurements in batch systems.

A second question relates to our ability to develop quantitative structure−activity relationships (QSARs) through which rates and products might be predicted for the reaction of other organohalides with metals. Johnson et al. (*19*) proposed that surface area-normalized rate constants (k_{SA} values) could be correlated with two-electron reduction potentials for hydrogenolysis, even though many of the species employed in their correlation could potentially react to a significant extent via competing reductive β-elimination. Without detailed knowledge of the product distributions in the experiments compiled by ref *19*, it has not been possible to properly account for the contributions of such competing reactions. Reduction potentials for hydrogenolysis and reductive elimination can be quite different (see Table 1 and ref *15*); failure to correctly account for the pathways by which different species react may influence the success of such attempted correlations. In undertaking this study, we also sought to assess whether QSARs could be improved through separate correlations of the two types of reductive dehalogenation as well as through correlation of reaction rate constants with one-electron reduction potentials.

Experimental Section

Chemicals. The following chemicals were used as received: tetrachloroethylene (99.9%, HPLC grade, Aldrich), trichlo-

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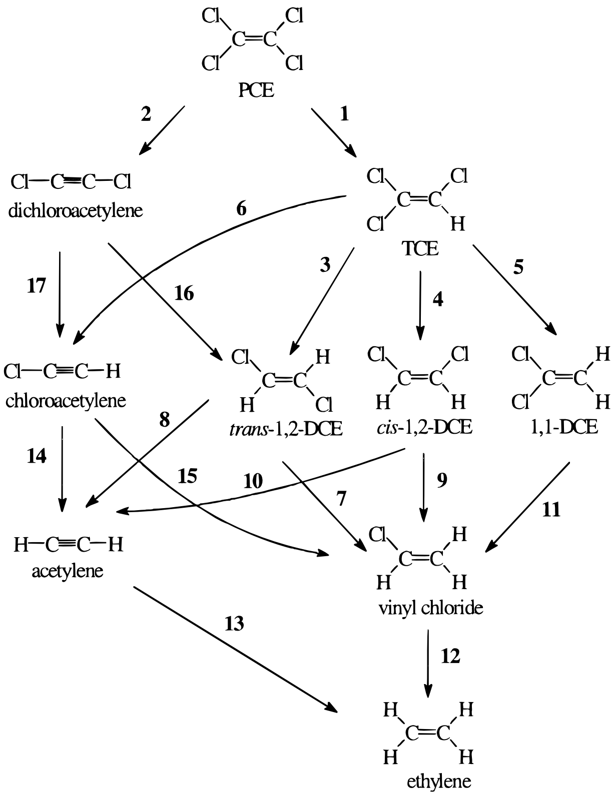

FIGURE 1. Hypothesized reaction sequence (*1*, *15*) for reduction of chlorinated ethylenes and related compounds. Reaction numbers correspond to rate constants given in Table 1.

roethylene (99.5+%, Aldrich), *cis*-dichloroethylene (97+%, Aldrich), *trans*-dichloroethylene (*trans*-DCE, Supelco), 1,1-dichloroethylene (1,1-DCE, 99%, Aldrich), vinyl chloride in methanol (Chem Service, 2000 μg/mL), 10% ethylene in helium (Scott Specialty gas), and 1% acetylene in helium (Scott Specialty gas). Methanolic (HPLC grade, J. T. Baker) spiking solutions were prepared for PCE, TCE, and the DCE isomers.

Acid solutions for cleaning metals were prepared using deoxygenated, deionized water (Milli-Q Plus UV, Millipore). Solutions were deoxygenated by sparging (1 h/L) with argon, which was purified using an in-line molecular sieve and oxygen traps. Reaction bottles were filled with deoxygenated solutions containing 0.1 M NaCl (99%; J. T. Baker) and 50 mM Tris buffer [tris(hydroxymethyl)aminomethane, reagent grade; Sigma], pH 7.2. The high (relative to typical groundwater) NaCl concentration was employed to poise the chloride content in the system, as chloride ion is released during reductive dechlorination. Chloride is known to accelerate corrosion by weakening the passive oxide film on metals (*20*), and its presence has been shown to increase the rate of carbon tetrachloride reduction by iron (*21*).

Synthesis of Chlorinated Acetylenes. Chloroacetylene and dichloroacetylene were synthesized from *cis*-DCE and TCE, respectively. Potassium hydride (35% in mineral oil, Aldrich) was rinsed twice with pentane (J. T. Baker) and once with freshly distilled dry tetrahydrofuran (THF). Dehydrohalogenation of *cis*-DCE or TCE was induced by potassium hydride and a catalytic amount of methanol in dry THF as described by ref *22*. Verification of the identities of the synthesis products was conducted via gas chromatography/mass spectrometry (GC/MS). The resulting solutions of the chlorinated acetylenes in THF were used as spiking solutions. No purification of these reportedly explosive (*22*−*24*) gases was attempted.

Metal Preparation. The zinc metal (J. T. Baker, 30 mesh) was cleaned with 0.4% H_2SO_4 to remove surface oxides (*25*) using the procedure described in ref *26*. The cleaned metal was used within 24 h, for it was found that the reactivity of the metal steadily decreased by a factor of 3 over a period of 3 weeks, even when stored in an anaerobic chamber. The surface area was 0.035 m^2/g as measured via Kr adsorption using a Micromeritics Flowsorb II 2300.

Experimental Systems. Reaction bottles were filled with deoxygenated 0.1 M NaCl/50 mM Tris buffer within an anaerobic chamber. Depending on the reactivity of the compound being studied, varying quantities of metal were added to the flask, with higher zinc loadings being used to increase the reaction rate of less reactive compounds. Reactions of PCE were studied using 5 g of zinc in 125-mL (nominal volume) glass bottles with glass stopcock adapters. The stopcock outlets were fitted with an NMR septum (Aldrich) to facilitate sampling while excluding oxygen. The glass stopcocks isolated the flask contents from the potentially sorptive NMR septum except during the brief sampling intervals. The bottles were mixed by rotating about their longitudinal axes on a rotator (Cole-Parmer) at 56 rpm; incubations were conducted at room temperature (23 ± 1 °C).

Reactions of all other species were carried out in 160-mL serum bottles sealed with Teflon-faced butyl rubber septa (Wheaton). Serum bottles were used in preference to the 125-mL bottles used for PCE because the pressure buildup caused by hydrogen gas evolution at high metal loadings or over long reaction times causes the glass stopcock adapters on the 125-mL reactors to leak. For the remaining chlorinated ethylenes, acetylene, and ethylene, 25 g of zinc was used, and bottles were rotated at 36 rpm. Reaction bottles used for chloroacetylene and dichloroacetylene contained 1 and 0.5 g of zinc, respectively, and were rotated at 56 rpm. The chlorinated acetylenes and PCE were substantially more reactive than any of the other species. Experiments conducted with PCE suggested that a possible mass transfer limitation existed at lower mixing speeds for this species; experiments with the most highly reactive species were thus conducted at a high mixing rate in an attempt to overcome this problem. Reaction rate was independent of mixing speed between 15 and 45 rpm for the less reactive species.

Chlorinated ethylenes were introduced to the reactors via a methanolic spike (resulting in 0.003− 0.06% methanol by weight) and the chlorinated acetylenes via the THF solution in which they were synthesized (resulting in 0.03% THF by weight). Spiking solutions of acetylene or ethylene were made by equilibrating the appropriate gas/helium mixture with deoxygenated buffer in a 1-L syringe (Hamilton). The syringe was then transferred to an anaerobic chamber where aliquots of the equilibrated solution were introduced to the reaction flasks to achieve the desired starting concentration. Reactions were performed at various initial concentrations ranging from 3 to 80 μM for acetylene, 3−30 μM for vinyl chloride, and 15−350 μM for the dichloroethylenes, TCE, and PCE. At specified intervals, 1-mL samples were withdrawn from the reactors while simultaneously injecting 1 mL of deoxygenated buffer. This made it possible to avoid introducing headspace to the bottle during sampling, allowing anoxic conditions to be maintained.

Analytical Methods. Aqueous samples were transferred to 2.5-mL (nominal volume) autosampler vials. Headspace samples were analyzed by gas chromatography (GC) with flame ionization detection (FID) using the system described in ref *26*. The THF solutions containing the chlorinated acetylenes were analyzed via cold on-column GC using an Rt_x-1 column (30 m × 0.32 mm i.d., 3 μm film thickness, Restek) and an FID detector.

Calibration curves were generated using aqueous standards (0.1 M NaCl/50 mM Tris, pH 7.2) of PCE, TCE, and the DCE isomers prepared in 20-mL glass syringes. These

TABLE 1. Surface Area-Normalized Rate Constants for Chlorinated Ethylenes and Their Reaction Products[a]

	reaction	k_{SA} (L m^{-2} h^{-1})[b]	n[c]	E_1 (V)[d,e]	E_2 (V)[d]
1	PCE → TCE	0.3(±0.01)	9	−0.358	0.582
2	PCE → dichloroacetylene	4.5(±0.7) × 10^{-2}	9	−0.358	0.631
3	TCE → *trans*-DCE	1.5(±0.1) × 10^{-3}	5	−0.597	0.534
4	TCE → *cis*-DCE	6.0(±1.0) × 10^{-4}	5	−0.578	0.543
5	TCE → 1,1-DCE	6.8(±9.1) × 10^{-5}	5	−0.840	0.523
6	TCE → chloroacetylene	9.4(±1.2) × 10^{-4}	5	−0.578	0.609
7	*trans*-DCE → VC	6.4(±8.2) × 10^{-7}	2	−0.880	0.488
8	*trans*-DCE → acetylene	1.3(±0.1) × 10^{-5}	2	−0.880	0.573
9	*cis*-DCE → VC	5.2(±1.5) × 10^{-7}	2	−0.898	0.478
10	*cis*-DCE → acetylene	3.0(±0.2) × 10^{-6}	2	−0.898	0.564
11	1,1-DCE → VC	4.1(±0.3) × 10^{-5}	3	−0.773	0.498
12	VC → ethylene	1.0(±0.5) × 10^{-4}	3	−0.954	0.375
13	acetylene → ethylene	5.0(±1.4) × 10^{-4}	5		
14	chloroacetylene → acetylene	6.5(±0.7)	1		
15	chloroacetylene → VC	0.50(±0.3)	1		
16	dichloroacetylene → *trans*-DCE	20.6(±0.9)	4		
17	dichloroacetylene → chloroacetylene	4.4(±0.3)	4		

[a] Reaction numbers pertain to those illustrated in Figure 1. [b] Uncertainties represent 95% confidence limits. [c] Number of replicate experiments used to determine rate constants. [d] Calculations assume the Henry's law constant for a radical species is the same as that of the hydrogenated parent (*28*), $\{H^+\} = 10^{-7}$ M, $\{Cl^-\} = 1$ mM, and that all other species are present at unit activity. Gas-phase thermodynamic data are from refs *29*−*31*, corrected for air−water partitioning using Henry's law constants recommended by refs *32* and *33*. The small changes in the E_1 and E_2 values as compared to those previously reported (*15*) result from differences in the source of thermodynamic data. [e] E_1 values are for the formation of the appropriate radical species. Reactions shown with identical one-electron reduction potentials produce the same radical intermediates.

standards were analyzed using the same method as samples. Acetylene, ethylene, and vinyl chloride were calibrated using gas standards (Scott Specialty Gas). The gas standards were mixed in a 2-mL syringe (with a wetted barrel) equipped with a three-way stopcock, one end of which was fitted with a septum. Gas samples (200 μL) were withdrawn and injected manually. Aqueous concentrations were calculated using the "dimensionless" Henry's law constants [(mol/L_{air})/(mol/L_{water})] determined via a modified EPICS method (*27*) at 60 °C (the temperature of the autosampler oven) in the buffer solution. The values obtained were 1.1 for acetylene, 1.1 for vinyl chloride, and 8.7 for ethylene. Due to the lack of commercial availability of the chlorinated acetylenes and uncertainty as to the exact yield obtained in the syntheses, calibrations for these species could not be conducted directly.

Bottles were initially filled without headspace. As much as 6 mL of headspace evolved during the longer incubations, presumably attributable to the reduction of protons by the metal to form hydrogen gas. For most species observed in these experiments, less than 4% of the mass would have been lost via partitioning to the headspace at 25 °C. Ethylene, however, has a substantially higher Henry's law constant than the other species, and losses of over 25% of the mass of this species into the headspace could be incurred for the reactions of long duration. Reported aqueous ethylene concentrations, therefore, include the calculated fraction that partitioned into the headspace. As ethylene is stable under the conditions employed, its partitioning into the headspace does not affect its subsequent behavior. Partitioning of all other species into the headspace was minimal, so reported aqueous concentrations were not corrected.

The identities of all reaction products detected were confirmed by GC/MS analysis. Samples were placed in 2.5-mL autosampler vials and shaken by hand for 3 min. A 50−200-μL headspace sample was then withdrawn and manually injected (via splitless injector) on a Hewlett-Packard (HP) 5890 GC equipped with an HP 5970 mass spectrometer detector and a GS-Q PLOT column (30 m × 0.32 mm i.d.; J&W Scientific). The THF solutions containing the chlorinated acetylenes were analyzed on the same GC/MS using the Rt_x-1 column previously described.

The pH of the aqueous medium was measured before and after the reaction, using a Ross combination electrode (Orion). The pH during the reduction of PCE (which reacted completely in ~8 h) was stable at pH 7.3. The solution pH did rise slightly during the longer incubations required for other species, however, starting at pH 7.3 and ending at 7.6.

Kinetic Modeling. Pseudo-first-order rate constants were calculated using the software package Scientist for Windows (v. 2.01, Micromath, Salt Lake City, UT). The relevant system of differential equations is given by

$$\frac{dC_i}{dt} = -(\sum_{j=1}^{N_j} k_{ij})C_i \qquad (1)$$

$$\frac{dC_j}{dt} = (\sum_{i=1}^{N_i} k_{ij})C_i - (\sum_{m=1}^{N_m} k_{jm})C_j \qquad \text{(for all } j) \qquad (2)$$

where C represents aqueous concentrations and k values are pseudo-first-order rate constants. Equation 1 pertains to the reaction of the parent species, i, forming all possible daughter products, j. In eq 2, the daughter product, j, may be produced by multiple parents, i, and can itself react to other species, m, according to rate constants k_{jm}.

Given experimental data, differential rate expressions, and initial conditions, Scientist calculates the selected parameters (in this case, k_{ij} and the initial concentration of the parent compound) via a least-squares fit of the data to numerically integrated solutions of the system of rate expressions. By computing each k_{ij} value according to the distribution of products, the model apportions the overall rate constant for parent compound disappearance into the contributions for the competing reactions. When calculating the k_{ij} values for a given species, the rate constants (k_{jm}) for reactions of daughter products that were detected in a given experiment were constrained to be equal to those determined in independent experiments in which the daughter products were introduced as the starting material.

Results

Pseudo-first-order rate constants for each reaction shown in Figure 1 were divided by the metal surface area per liter of solution to obtain k_{SA} values. These k_{SA} values are given in Table 1 along with the corresponding one- and two-electron reduction potentials.

Different initial concentrations of organohalide did not have a significant effect on the observed rate constants; thus, the values in Table 1 represent averages of the rate constants determined at each initial concentration. Confidence limits were calculated by propagating the errors associated with the model-calculated uncertainties obtained from several different timecourses. For the majority of the reactions listed in Table 1, the rate constants could be determined with a fair degree of precision ($\pm$15%, based on the 95% confidence limits). Substantially greater uncertainty arose, however, for some of the minor reactions that result in only trace product accumulation (e.g., reactions 5, 7, and 9).

Preliminary experiments conducted at lower mixing speeds with PCE had suggested a dependence of reaction rate on initial concentration (*34*). This effect, however, was not observed at the higher mixing rates employed in the present study. Competitive inhibition effects were systematically investigated for the two most reactive species, PCE and TCE. For example, 15 μM PCE was added to each of six reaction bottles. One bottle contained no competitor, and each of the others contained a 200 μM concentration of one of the other chlorinated ethylenes (TCE; *cis*-, *trans*-, or 1,1-DCE; VC). Similar experiments were performed with TCE. No significant decrease in the rate of reaction of PCE or TCE was observed under these conditions, indicating that competitive effects, if present, were too small to detect.

Carbon mass balances at the end of the experiments were >90% of the regressed initial parent compound concentration. No losses were observed in zinc-free blanks, suggesting that sorption to the Teflon-faced septa and losses through needle punctures were minimal. Further experimental results and modeling details are discussed in the following sections.

Effect of Metal Loading. Normalization of rate constants by metal surface area assumes that a linear relationship exists between observed rate constant and metal loading. Results of some investigations with iron (*35*, *36*) have, however, suggested that reaction rate might not be directly proportional to metal loading. Scherer and Tratnyek (*35*), for example, found that the rate of carbon tetrachloride reaction reached a plateau as iron loading was increased. A similar relationship between TCE reduction rate and iron loading was observed by Gotpagar et al. (*36*). Such a nonlinear dependence on metal loading was not encountered in the present study; rather, the pseudo-first-order rate constant for parent compound disappearance was found to increase linearly with metal loading (data not shown), giving r^2 values of 0.983 for PCE (at zinc loadings from 6 to 56 g/L), 0.993 for TCE, and 0.994 for acetylene (the latter two over a range of 65−240 g/L of zinc).

Vinyl Chloride and Acetylene. Both of these species reacted to form ethylene. No subsequent reduction of ethylene to ethane was observed. Pseudo-first-order rate constants were calculated by simultaneously fitting the disappearance of the parent compound and the production of ethylene. It should be noted that no acetylene was observed in the reduction of vinyl chloride. From the measured rates of disappearance of vinyl chloride and acetylene, substantial accumulation of acetylene would be anticipated if it were an intermediate in the reduction of vinyl chloride to ethylene.

Dichloroethylenes. Reaction of *cis*- and *trans*-DCE with Zn(0) produced acetylene, vinyl chloride, and ethylene. Only the latter two products were observed from the reaction of 1,1-DCE. For the DCE isomers, reaction proceeded so slowly (with a $t_{1/2}$ >125 days) at a zinc loading of 25 g/160 mL that accurate determination of the rate of disappearance of the parent compound was not feasible. Rate constants reported in Table 1 were therefore based on the rate of appearance of the reaction products under pseudo-zero-order conditions, assuming the concentration of the parent compound to be invariant at very low conversions.

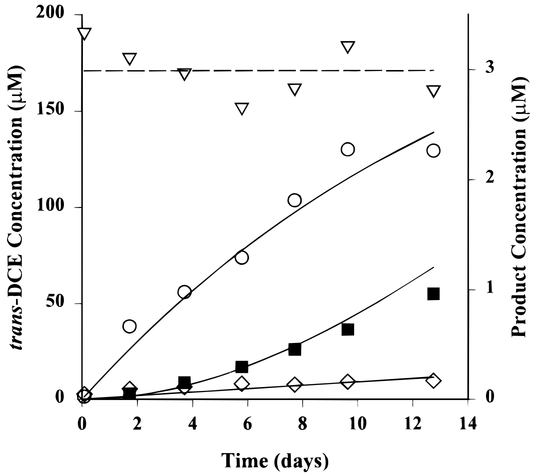

FIGURE 2. Reduction of *trans*-DCE (▽) by 25 g of Zn(0) in 160 mL of 0.1 M NaCl/0.05 M Tris buffer (pH 7.2). Solid lines are model fits to reaction products acetylene (○), ethylene (■), and vinyl chloride (◇). The dashed line represents the mean concentration of *trans*-DCE determined by averaging the data points shown.

A representative plot of experimental results obtained for *trans*-DCE is given in Figure 2. The solid lines are the model fits with rate constants for vinyl chloride and acetylene reaction constrained to equal values determined in independent experiments. Due to the pressure buildup from hydrogen gas evolution, venting of the reactors was necessary for the last few samples. This action may have resulted in a stripping of the highly volatile ethylene and a loss of some of the mass contained in the headspace, accounting for the slight overprediction by the model of the measured ethylene concentrations at the end of the experiment.

TCE and PCE. Example time courses obtained for TCE and PCE along with the corresponding model fits are shown in Figures 3 and 4, respectively. The pseudo-first-order rate constants were calculated by simultaneously fitting the disappearance of the parent compound and the appearance of the daughter species, constraining subsequent reactions of daughter species as previously described. Reaction of TCE with zinc gave rise to the three dichloroethylene isomers, vinyl chloride, acetylene, and ethylene. It is interesting to note that even though *cis*-DCE is the thermodynamically favored species (Table 1) and is often the preferred product of microbial TCE reduction (*37*), *trans*-DCE was the predominant DCE isomer formed from TCE reduction by zinc. Modeling the results of TCE reduction (Figure 3) again results in overprediction of the ethylene concentration, most likely due to the venting that occurred toward the end of the experiment (to which we attribute the 4% loss in mass balance observed for this experiment). The predicted concentrations of vinyl chloride are also higher than the observed values. This is a reflection of the high degree of uncertainty associated with the rate constant for formation of vinyl chloride from chloroacetylene (reaction 15; see below).

The major products of PCE reduction are TCE, *trans*-DCE, and acetylene (Figure 4). Trace amounts of *cis*-DCE, vinyl chloride, and chloroacetylene (not shown) were also observed. Experiments with PCE were relatively short in duration; as a result, no headspace evolved.

The acetylene observed in the experiments with both PCE and TCE appeared too rapidly to originate from the reductive elimination of the *cis*- or *trans*-DCE observed as daughter products in these systems. Attempts to model the data via a sequence such as PCE → TCE → DCEs → acetylene proved unsuccessful, as previously demonstrated by Roberts et al.

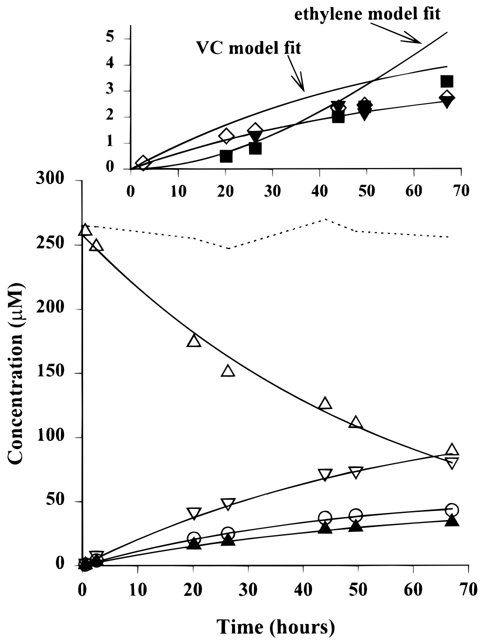

FIGURE 3. Reduction of TCE (△) in 160 mL of 0.1 M NaCl/0.05 M Tris buffer (pH 7.2) by 25 g of Zn(0). Major products are *trans*-DCE (▽), acetylene (○), and *cis*-DCE (▲). Inset shows trace products 1,1-DCE (▼), ethylene (■), and vinyl chloride (◇). The dotted line represents the observed C$_2$ mass balance, while solid lines are model fits.

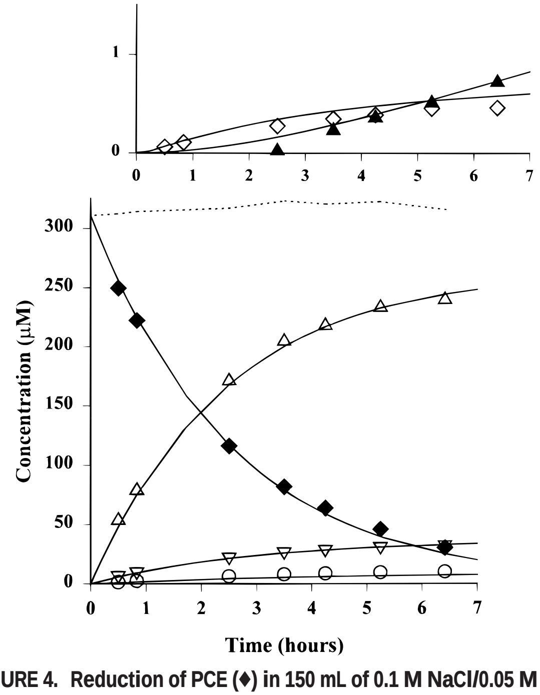

FIGURE 4. Reduction of PCE (♦) in 150 mL of 0.1 M NaCl/0.05 M Tris buffer (pH 7.2) by 5 g of Zn(0). Major products are TCE (△), *trans*-DCE (▽), and acetylene (○). Inset shows trace products *cis*-DCE (▲) and vinyl chloride (◇). The dotted line represents the observed C$_2$ mass balance, while solid lines are model fits.

(*15*). Such a sequence would predict curves for acetylene that were concave upward, in sharp contrast to the observed results. In a similar manner, the rate of appearance of vinyl chloride from TCE reduction (Figure 3) as well as that of *trans*-DCE formation from PCE reduction (Figure 4) were too rapid to be attributable to a sequence of hydrogenolysis reactions of the sort TCE → *trans*-DCE → VC or PCE → TCE → *trans*-DCE.

Further evidence that the acetylene and vinyl chloride observed in TCE reduction did not arise from reactions of dichloroethylenes was provided by computing product yields as a function of time. For example, when TCE is the starting material, *cis*- and *trans*-DCE (as well as 1,1-DCE) are formed. If the observed acetylene and vinyl chloride were secondary products derived from these DCE isomers, their yields relative to the DCEs would increase over time. During the reduction of TCE (Figure 3), however, the yields of acetylene and vinyl chloride relative to *cis*- and *trans*-DCE were constant. The yield of vinyl chloride was also constant relative to 1,1-DCE. This suggests that the vinyl chloride and acetylene observed during TCE reduction are produced via a highly reactive intermediate through a pathway that operates concurrently to hydrogenolysis of TCE to DCEs (and their subsequent reactions). Yields of acetylene and *trans*-DCE (relative to TCE) were also constant during PCE reduction (Figure 4), again consistent with their formation through a highly reactive intermediate or intermediates.

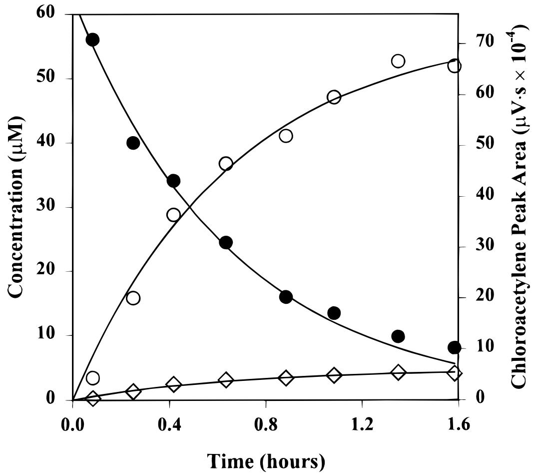

FIGURE 5. Reduction of chloroacetylene in 0.1 M NaCl/0.05 M Tris buffer (pH 7.2) by 1 g of Zn(0). Solid symbols (●) represent chloroacetylene peak areas, while open symbols for acetylene (○) and vinyl chloride (◇) reflect measured concentrations. The model fit for the chloroacetylene data represents model-calculated concentrations.

Chlorinated Acetylene Reduction. As the chlorinated acetylenes do not make up a significant portion of the mass balance in the reduction of PCE or TCE, reductive elimination to such species could only be a significant pathway if these react too rapidly to enable their accumulation. Independent confirmation was therefore sought by synthesizing dichloro- and chloroacetylene and measuring their rates and products of reaction. On the basis of our attempts to model the reduction of TCE, we anticipated that chloroacetylene would react to form acetylene and vinyl chloride via reactions 14 and 15 (see Figure 1) if it were the intermediate responsible for the generation of these species. Dichloroacetylene could give these same products after first being reduced to chloroacetylene via reaction 17; alternatively, reduction of the triple bond could result in *trans*-DCE via reaction 16 or (in principle) *cis*-DCE.

Analysis of the chloroacetylene solution via GC/MS revealed no contaminant peaks other than those expected (unreacted *cis*-DCE and residual pentane from washing of the potassium hydride). Results obtained for chloroacetylene reaction with zinc are shown in Figure 5. Measured rates of chloroacetylene reaction were sufficiently rapid that no detectable accumulation would be predicted to result from TCE reduction. The sole observed products of chloroacetylene reaction were acetylene and vinyl chloride, as anticipated. Note that at this zinc loading (1 g/160 mL as compared to the 25 g/160 mL used for the experiments with the DCE isomers), reaction of the *cis*-DCE present to these products

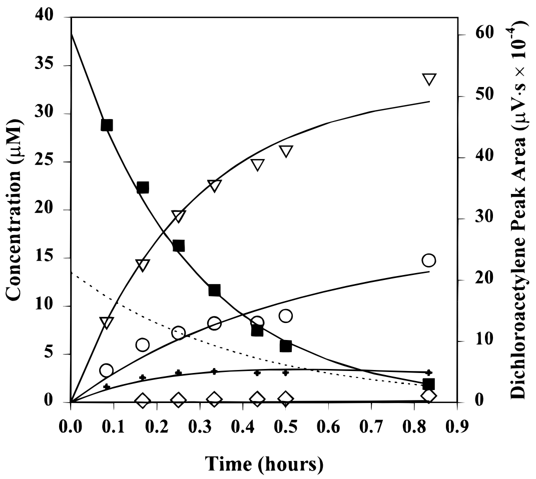

FIGURE 6. Reduction of dichloroacetylene in 0.1 M NaCl/0.05 M Tris buffer (pH 7.2) by 0.5 g of Zn(0). Solid symbols (■) represent dichloroacetylene peak areas. The model fit for the dichloroacetylene data represents model-calculated concentrations. Open symbols for *trans*-DCE (▽), acetylene (○), and vinyl chloride (◊) are measured concentrations. The chloroacetylene concentration (+) was calculated using the relationship between peak area and aqueous concentration developed in Figure 5. The dashed line represents the calculated concentration of a hypothesized contaminant assumed to react to form acetylene.

is extremely slow. In principle, water may add to the triple bond of chloroacetylene to form an α-halo vinyl alcohol (*23*). This can rearrange to acetate after addition of a second water molecule. Experiments in the absence of zinc, however, failed to reveal any significant loss of chloroacetylene that might be attributed to hydrolysis over a 24-h period.

Due to a lack of quantitative standards, concentrations of chloroacetylene could not be directly determined. A rate constant for chloroacetylene reaction was therefore computed by simultaneously fitting the chloroacetylene peak area and the concentrations of the reaction products as a function of time. This was accomplished by expressing the differential equation for the disappearance of chloroacetylene (see eq 1) in terms of peak area. An additional equation was included in which a linear coefficient relating peak area to concentration was treated as a fitting parameter. The model fit through the chloroacetylene peak areas shown in Figure 5 therefore represents the aqueous chloroacetylene concentration values calculated by the model.

Justification for this approach is provided by computing molar response factors from the results. Using the modified EPICS method (*27*), dimensionless Henry's law constants at 60 °C in the 50 mM Tris/0.1 M NaCl solution were found to be 2.4 for chloroacetylene and 3.5 for dichloroacetylene (see below). From these Henry's law constants, the model-derived aqueous concentrations, and the known air:water ratio in the vials, the total mass of chlorinated acetylene injected onto the GC, and thus the molar FID response factor (μV-s/nmol injected), could be calculated at each time point. For chloroacetylene and dichloroacetylene, the FID molar response factors (relative to acetylene) were estimated as 1.07 and 1.12, respectively. The similarity of these response factors to that of acetylene gives independent confirmation of the validity of the model-derived concentrations. We note that FID molar response factors for the chlorinated ethylenes display a similar trend with increasing chlorination.

Results obtained for the reaction of dichloroacetylene with zinc are displayed in Figure 6. No hydrolysis of dichloroacetylene was observed in the absence of zinc over a period of 24 h. Dichloroacetylene reaction rates in the presence of zinc were sufficiently rapid so that no detectable accumulation of dichloroacetylene and only traces of chloroacetylene would be anticipated from PCE reduction, consistent with our observations. Dichloroacetylene reacted to form *trans*-DCE, chloroacetylene, acetylene, and vinyl chloride as the only observed reaction products. Reaction of residual TCE was not a significant source of these products at this metal loading. The observed acetylene concentration, however, was much too high to arise from the sequential reaction of dichloroacetylene → chloroacetylene → acetylene or from the other known acetylene precursors (*trans*-DCE, TCE) present. Modeling the data suggested that acetylene was also being produced by reaction of another species. The concentration of this hypothesized contaminant(s), as calculated by the model, is given by the dotted line in Figure 6. Direct analysis of the THF solution via GC/MS and GC/FID revealed several contaminant peaks besides the expected TCE and pentane, most likely arising from side reactions during the synthesis. These peaks were not detectable via the headspace analysis method employed in monitoring the reaction kinetics. The largest of these peaks has a mass spectrum consistent with that given for 1,2-dichloro-1-methoxyethylene (*38*).

TABLE 2. Percentage of Reaction Occurring via Reductive Elimination

species	% reductive elimination	$\Delta E_2 = (E_{\text{red. elim}} - E_{\text{hydrogenolysis}})$
PCE	15(±2)[a]	0.049
TCE	30(±4)	0.075[b]
cis-DCE	85(±8)	0.086
trans-DCE	95(±2)	0.085

[a] Uncertainties represent 95% confidence limits. [b] Using the value for the reduction of TCE to *trans*-DCE (the principal observed DCE isomer).

Discussion

Factors Influencing Reaction Products. Based on the rate constants given in Table 1, the fraction of the overall reaction that occurs via reductive elimination may be calculated for each chlorinated ethylene possessing an α,β pair of chlorine atoms. This percentage was calculated by comparing the rate constant for reductive elimination to that for overall parent compound disappearance (reductive elimination + hydrogenolysis). Error limits were obtained by propagating the errors associated with the different rate constants. As the results summarized in Table 2 reveal, reductive elimination is an important contributor and cannot be ignored in pathway modeling under the conditions employed in the present experiments. Additional studies (beyond the scope of the present investigation) will be required to address the impact of reaction conditions (e.g., electrolyte composition and concentration; pH; concentration of potential hydrogen atom donors such as methanol, THF, and natural organic matter; temperature; metal cleaning or aging of the metal surface) on product branching ratios.

Note that as the reductive elimination reaction becomes more thermodynamically favorable relative to hydrogenolysis, the percentage of reaction occurring through reductive elimination increases. If we assume that the thermodynamic data for the reductive elimination and hydrogenolysis reactions are of comparable accuracy, it does not appear that the reaction products are purely under thermodynamic control. If the E_2 values for hydrogenolysis and reductive elimination were identical, a 50:50 split of reaction products would be expected, while it is clear that even with reductive elimination favored thermodynamically (e.g., for PCE and TCE), only 15−30% of the reaction proceeds via this route.

Product distributions are affected not only by the competition between the reductive elimination and hydrogenolysis pathways for the chlorinated ethylenes but also by the branching ratio between hydrogenolysis and reduction of the triple bond for the chlorinated acetylenes. Only 8% of chloroacetylene is reduced to form vinyl chloride. With dichloroacetylene, however, 82% of the reaction proceeds via reduction of the triple bond to form *trans*-DCE.

Hydrogenation (reduction of triple bonds to double bonds by H_2) is usually thought to occur via cis addition, giving rise to *cis*-olefins. For example, we have found in our laboratory that 2-butyne is reduced to *cis*-2-butene by iron (*26*). Zinc has also been shown to promote the stereospecific reduction of substituted alkynes to *cis*-alkenes in ethanol (*39*, *40*) or THF/MeOH/H_2O (*41*); a strong preference for cis reduction has also been observed for the zinc–copper couple in ethanol (*42*). Our results with zinc, however, indicate that the reduction of the dichloroacetylene triple bond forms *trans*-DCE rather than the cis isomer. There are precedents for reduction of substituted acetylenes to *trans*-olefins by certain dissolving metal reductants. For example, reaction of sodium metal in ammonia produces *trans*-olefins from substituted acetylenes (*43*–*45*), and the zinc–copper couple produces a mixture of the cis and trans isomers (3:5) for reduction of phenylpropiolic acid ($C_6H_5C{\equiv}CCOOH$) to cinnamic acids ($C_6H_5CH{=}CHCOOH$) in an ammonium chloride–ammonia solution (*46*). Zinc has also been cited for use in the semireduction of alkynes to *trans*-alkenes (*47*).

When PCE or TCE react with zinc, several of the products (namely, *trans*-DCE, vinyl chloride, and acetylene) may arise through more than one route. For example, vinyl chloride may be produced via hydrogenolysis (reaction 7, 9, or 11) or via reduction of chloroacetylene (reaction 15). On the basis of the rate constants given in Table 1, we can determine the percentage of the *trans*-DCE, vinyl chloride, and acetylene that originates from an initial reductive elimination of PCE or TCE via reactions 2 or 6. At relatively low conversions (<25%) of TCE, greater than 99.7% of the vinyl chloride and acetylene observed arise from an initial reductive elimination reaction of TCE to form chloroacetylene via reaction 6. At longer times (92% TCE conversion), the DCE daughter products have begun to react to form acetylene and vinyl chloride, but >97% of vinyl chloride and acetylene present still results from an initial reductive elimination to chloroacetylene. Similar results are obtained for PCE. For 92% conversion of PCE, 95% of the *trans*-DCE observed is produced via a dichloroacetylene intermediate. At shorter times, the percentage is higher, for hydrogenolysis of TCE has not yet contributed appreciably to the observed *trans*-DCE accumulation. Virtually all of the acetylene and vinyl chloride observed during PCE reduction arise either from the reductive elimination of PCE to dichloroacetylene or else from the subsequent reductive elimination of the initial daughter product (TCE) to chloroacetylene.

Linear Free Energy Relationships. If reaction were to occur via an outer-sphere single electron-transfer pathway, a good correlation between one-electron reduction potential (E_1) and the relevant rate constant might be anticipated (*48*). Our results indicate that rate constants do correlate well with one-electron reduction potentials, as shown in Figure 7a. The calculated regression equation is $\log(k_{SA}) = 8.23(\pm 1.79) \times E_1 + 2.21(\pm 1.30)$, where stated errors represent 95% confidence limits. The regression reported excludes the data point for vinyl chloride (as with regressions against E_2, see below). The good correlation of rate constants with reduction potential is consistent with electron transfer as the limiting factor dictating chloroethylene reactivity with zinc (rather than mass transfer, adsorption, or desorption as a rate controlling step).

Although one-electron reduction potentials could be used to predict the overall rate constant pertaining to disappearance of a particular species, this descriptor does not provide any insight as to the distribution of reaction products that will result. Separate correlation of hydrogenolysis rate constants and rate constants for reductive elimination against two-electron reduction potentials furnishes a means of predicting reaction products as well as rates. Figure 7b displays correlations of k_{SA} versus two-electron reduction potential (E_2) values for the hydrogenolysis component of the reaction $[\log(k_{SA}) = 53.56(\pm 15.06) \times E_2 - 31.85(\pm 7.86)]$ and the reductive elimination component $[\log(k_{SA}) = 60.39(\pm 15.09) \times E_2 - 39.58(\pm 8.97)]$, where stated errors again represent 95% confidence limits. The high rate constant for vinyl chloride reaction to ethylene (filled circle) seems to be anomalous and was excluded from the relevant regression.

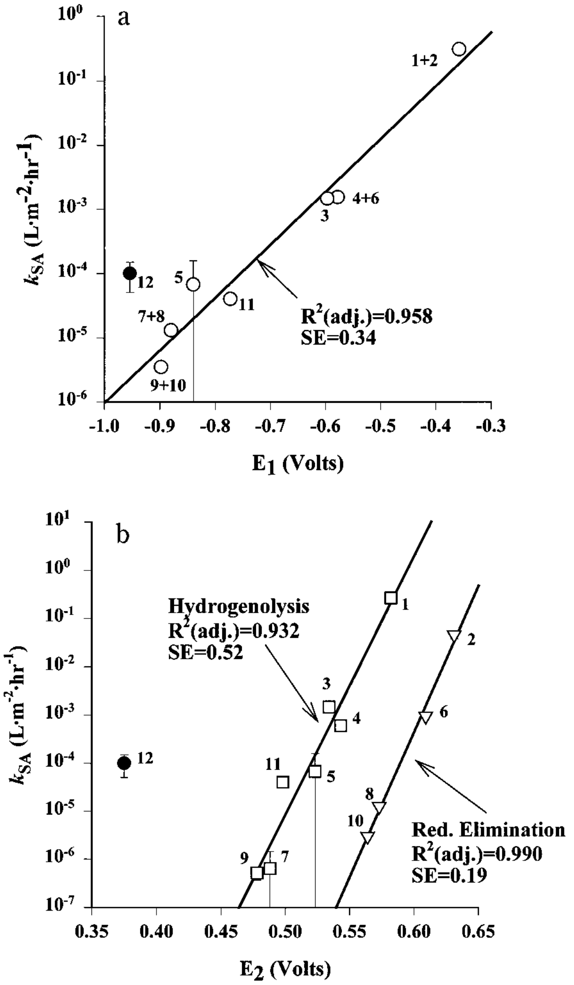

FIGURE 7. Correlation of surface area-normalized rate constants (k_{SA}, Table 1) (a) with one-electron reduction potentials and (b) with two-electron reduction potentials. Numbering corresponds to the reactions indicated in Table 1. Regression lines exclude the data point for vinyl chloride (filled circle, reaction 12). If no error bar is shown, it is smaller than the symbol.

Environmental Significance of Reductive Elimination. At first glance, reductive elimination of PCE or TCE may not seem overly beneficial. For example, the subsequent reduction of dichloroacetylene produces *trans*-DCE, a relatively persistent byproduct as compared to the parent species, PCE. This reaction pathway, however, partially circumvents TCE formation, a product that undergoes reduction in part to 1,1-DCE (a species that reacts only to vinyl chloride) and to *cis*-DCE (which produces approximately three times more vinyl chloride per mole as does *trans*-DCE). Mathematical simulations of the reactions of saturated PCE and TCE solutions with zinc reveal that *cis*-DCE, by virtue of being the least reactive species in the system, represents a bottleneck to attaining the drinking water limit for vinyl chloride. Reductive elimination of PCE reduces the amount of TCE formed, decreasing the amounts of *cis*-DCE, 1,1-DCE, and finally vinyl chloride produced.

Recent work has investigated the uncertainty associated with barrier design based on variations in rate constants, flow rates, and other transport processes (*7*, *49*, *50*). In these studies, however, the branching ratio between hydrogenolysis and reductive elimination was not explicitly known, making it difficult to quantitatively assess the importance of reductive elimination reactions. The results of the present study should facilitate more definitive investigations. We can further demonstrate the environmental significance of reductive elimination by comparing model predictions using the rate constants determined in this work with those obtained from a model that assumes the disappearance of any given species can be described by the same overall rate constant, but with reaction only occurring through hydrogenolysis. In other words, PCE is assumed to react solely to TCE via a rate constant obtained by summing reactions 1 and 2, TCE is assumed to react solely to a mixture of the three DCE isomers (68.7% *trans*-DCE, 28.1% *cis*-DCE, and 3.2% 1,1-DCE) with an overall rate constant equal to the sum of reactions 3−6, and *cis*- and *trans*-DCE react only to vinyl chloride via a sum of the rate constants for reactions 9 plus 10 or 7 plus 8, respectively. For a saturated solution of PCE, the model that constrains all transformations to a sequence of stepwise hydrogenolysis reactions requires hydraulic residence times (for a plug flow reactor) to reach the drinking water limit for vinyl chloride (2 μg/L, ref *51*) that are 76% greater than if reductive elimination reactions are incorporated. Similar calculations indicate hydraulic residence times that are 41% greater to attain the vinyl chloride drinking water limit from a saturated TCE solution when reductive elimination reactions are routed into the hydrogenolysis pathway.

Despite the production of undesirable species from subsequent reactions of chlorinated acetylenes, we note that if reductive elimination did not occur, all PCE or TCE initially present would be converted to vinyl chloride. Even though chlorinated acetylenes are toxic (*22*−*24*), their rapid rate of reaction with zinc does not allow accumulation to high concentrations, decreasing the likelihood that these species will be of toxicological concern in the effluent from a metal-based treatment scheme. This suggests that reductive elimination, by partially circumventing the formation of persistent, undesirable products, should be viewed as an environmentally desirable reaction.

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