

Kinetics of the Transformation of Trichloroethylene and Tetrachloroethylene by Iron Sulfide

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The transformation of trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,1-dichloroethylene (1,1-DCE) by 10 g/L (0.5 m²/L) FeS in aqueous solution at pH 8.3 was studied in batch experiments. TCE and PCE were transformed by FeS with pseudo-first-order rate constants, corrected for partitioning to the sample headspace, of $(1.49 \pm 0.14) \times 10^{-3} \text{ h}^{-1}$ (TCE) and $(5.7 \pm 1.0) \times 10^{-4} \text{ h}^{-1}$ (PCE). A 17% decrease in the concentration of 1,1-DCE was observed over 120 days; however, no reaction products were detected. TCE and PCE transformation data were fit to a rate law assuming transformation of TCE via parallel reaction pathways to acetylene and *cis*-1,2-dichloroethylene (*cis*-DCE) and transformation of PCE via parallel reaction pathways to acetylene and TCE. Acetylene was the major reaction product for both TCE and PCE. Determination of rate constants for each reaction pathway indicated that TCE was transformed to acetylene 11.8 ± 1.1 times faster than to *cis*-DCE and that PCE was transformed to acetylene 8.2 ± 1.8 times faster than to TCE. Additional minor reaction products were vinyl chloride (VC) for TCE and *cis*-DCE for PCE. Detection of acetylene as the major product of both TCE and PCE transformation by FeS contrasts with the sequential hydrogenolysis products typically observed in the microbial transformation of these compounds, making acetylene a potential indicator of abiotic transformation of TCE and PCE by FeS in natural systems.

Introduction

Trichloroethylene (TCE) and tetrachloroethylene (PCE) are common groundwater pollutants. For example, they were two of the three most frequently detected volatile organic compounds, other than trihalomethanes, in a U.S. Environmental Protection Agency sampling survey of 945 groundwater-based drinking water supplies (1). In addition, they were the second and fourth most frequently detected organic pollutants at U.S. National Priorities List (NPL) or Superfund sites (2), with TCE identified at 852 and PCE identified at 771 of the 1430 NPL sites as of September 1997. The widespread occurrence of these compounds in the aquatic environment has driven research to understand the transformations of these and related pollutants in natural and engineered systems.

At least two studies of the reaction of PCE with iron sulfide (FeS) have been reported (3, 4), but neither found significant transformation of PCE by FeS under the given experimental conditions. For TCE, one study (4) reported no transformation

by FeS, but two others (5, 6) found complete or nearly complete transformation of TCE by FeS (troilite). Acetylene was reported to be the major reaction product, and the C₃–C₆ hydrocarbons detected as minor products were attributed to coupling of radical intermediates formed in the TCE transformation process (5). Acetylene was also reported to be the major product of TCE degradation by magnetite (6) and iron metal (5), and it was a minor product in the transformation of PCE by zinc metal (7). In another study (8), acetylene was an intermediate that exhibited accumulation and decay in the transformation of TCE and PCE by iron metal. Acetylene was also detected as a product in the reaction of TCE and PCE with nickel and copper sulfides (4). Detection of significant quantities of acetylene as TCE and PCE reaction products contrasts with the sequential hydrogenolysis commonly observed in microbiological systems (e.g., ref 9), which has the potential to result in the accumulation of harmful intermediates such as vinyl chloride (VC).

Effective application of passive remediation technologies such as subsurface reactive barriers as well as prediction of the rates and products of TCE and PCE natural attenuation requires an understanding of the product distributions expected for these compounds in the presence of different environmental reductants as well as a quantitative treatment of the rates of transformation via competing reaction pathways. The goal of this work was to conduct such a study of the transformation of PCE and TCE by the soil mineral FeS. FeS is a common soil precipitate produced primarily as a result of microbial sulfate reduction (10) and has been identified in a number of aquatic systems (11–13). It is a potential reductant in the natural attenuation of chlorinated pollutants in sulfate-reducing environments, and it may have application as an additive to granular iron metal in certain passive remediation applications (14). Transformation of 1,1-dichloroethylene (1,1-DCE) by FeS was studied to understand its role as a possible product of TCE and PCE degradation by FeS.

Experimental Section

Procedures for maintenance of anaerobic conditions and sterilization of aqueous solutions and glassware are described elsewhere (15). All chemicals were commercially available reagent or ACS grade and were used as received. Water was distilled and then purified using a Milli-Q Plus water system (Millipore Corp., Bedford, MA). FeS was prepared and characterized as described previously (15) as poorly crystalline mackinawite with a specific surface area of 0.05 m²/g.

Kinetic experiments were conducted in individual 5-mL flame-sealed glass ampules (15) to maintain anaerobic conditions and to prevent losses of volatile organic compounds from individual samples during experiments of up to 4 months duration. After preparation, ampules were placed on Labindustries (Berkeley, CA) model T 415-110 rocking platform shaker at approximately 22 cycles/min in a temperature-controlled chamber at 25 °C in the dark. In each ampule, the aqueous phase volume was 5 mL, and the gas phase volume was approximately 2.82 mL.

All samples contained 10 g/L FeS, resulting in a surface area concentration of 0.5 m²/L. The pH was buffered at 8.3 with 0.05 M each of tris(hydroxymethyl)aminomethane (Tris) and Tris-HCl. Samples also contained 0.04 M NaCl and 0.01 N HCl, resulting in an ionic strength of 0.1 M. Where noted, certain samples contained 0.001 M cysteine. All rate constants reported here are pseudo-first-order rate constants for these conditions. Transformation of TCE and PCE was monitored over 2–3 half-lives, or when 0.001 M cysteine was present,

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for approximately 1 half-life. For 1,1-DCE, transformation by FeS was monitored over the course of 120 days, after which the experiment was stopped. For each compound, control experiments were concurrently performed using the ionic medium only and no FeS. There was no disappearance of any compound in the absence of FeS in the time scale of these experiments.

Samples were spiked with 50 μL of a 0.002 M solution of TCE, PCE, or 1,1-DCE that had been prepared in N_2 -sparged methanol so that the resulting aqueous solution contained 1% methanol by volume. Initial aqueous concentrations after partitioning to the ampule headspace, determined by measurement of the aqueous concentration in the ionic medium alone (i.e., no FeS), were 1.49×10^{-5} M (TCE), 1.27×10^{-5} M (PCE), and 1.21×10^{-5} M (1,1-DCE). Because methanol coeluted with VC, a potential reaction product, when using gas chromatography (GC) method B (described below), certain samples were spiked with a 0.002 M solution of TCE, PCE, or 1,1-DCE prepared in 2-propanol. These samples were analyzed alongside samples spiked with methanol solutions for the purpose of determining whether VC was a reaction product. Data from the 2-propanol-spiked samples were not used in rate constant determination.

At regular intervals during the course of the reaction, ampules were centrifuged at approximately 1000 rpm and broken open, and 100 μL of the supernatant was removed with a microsyringe and extracted with 0.4 mL of 2,2,4-trimethylpentane containing 3.2 μM tribromomethane as an internal standard. Extracted samples were analyzed for TCE, PCE, and 1,1-DCE using GC method A, which employed a Hewlett-Packard (HP) (Palo Alto, CA) 6890 GC with a J&W Scientific (Folsom, CA) DB-5 column (30 m \times 0.53 mm i.d. \times 1.5 μm film thickness) and an electron capture detector (ECD). Injector temperature was 250 $^\circ\text{C}$, and detector temperature was 275 $^\circ\text{C}$. Oven temperature was isothermal at 75 $^\circ\text{C}$ for 1 min and then ramped to 250 $^\circ\text{C}$ at a rate of 15 $^\circ\text{C}/\text{min}$. Concentrations of TCE, PCE, and 1,1-DCE were quantified by comparison of GC peak areas to a five-point standard curve. Samples were analyzed in duplicate, and the results typically agreed within 1% using GC method A.

A 1-mL volume of the aqueous supernatant from each sample was also analyzed for *cis*- and *trans*-1,2-dichloroethylenes (*cis*-DCE and *trans*-DCE), VC, ethane, ethene, and acetylene using GC method B, which employed a HP 5890 GC with a HP 19395 headspace autosampler and an analytical method described elsewhere (15). Concentrations of each compound were quantified by comparison of GC peak areas to a five-point standard curve. Samples were analyzed in duplicate, and the results typically agreed within 5% using GC method B.

Results and Discussion

Treatment of Kinetic Data. Values of pseudo-first-order rate constants (k_{obs}) were determined by best fit of measured aqueous concentrations as a function of time to a pseudo-first-order rate law. Evidence for fit of the data to such a rate law includes the relatively small uncertainties associated with the rate constants reported in Table 1 as well as the good agreement between experimental data and rate laws derived from the assumption of pseudo-first-order behavior. Additional evidence includes the fact that transformation of hexachloroethane (HCA) by 10 g/L FeS at similar HCA concentrations to the TCE, PCE, and 1,1-DCE concentrations studied here was shown to be first-order with respect to HCA (15).

Values of k_{obs} were corrected as described in other references (16–19) to account for the effects of partitioning of the reactant between the aqueous and gas phases, assuming that partitioning took place much more rapidly than FeS-mediated transformation reactions (a reasonable

TABLE 1. Pseudo-First-Order Rate Constants, Products, and Mass Recoveries for TCE, PCE, and 1,1-DCE Transformation by FeS^a

reactant	solution amend-ments	k_{obs} (h^{-1}) { k_{obs}' (h^{-1})}	products	mass recovery (as %) ^b
TCE	none	$(1.20 \pm 0.12) \times 10^{-3}$ { $(1.49 \pm 0.14) \times 10^{-3}$ }	acetylene	65
			<i>cis</i> -DCE	6
			VC	<1
			TCE remaining total	9
PCE	none	$(4.01 \pm 0.70) \times 10^{-4}$ { $(5.7 \pm 1.0) \times 10^{-4}$ }	acetylene	56
			TCE	1
			<i>cis</i> -DCE	1
			PCE remaining total	18
				76
TCE	10 ⁻³ M cysteine	$(3.46 \pm 0.40) \times 10^{-4}$ { $(4.28 \pm 0.49) \times 10^{-4}$ }	acetylene	41
			<i>cis</i> -DCE	4
			TCE remaining total	41
				86
PCE	10 ⁻³ M cysteine	$(1.07 \pm 0.26) \times 10^{-4}$ { $(1.53 \pm 0.37) \times 10^{-4}$ }	acetylene	19
			TCE	2
			<i>cis</i> -DCE	<1
			PCE remaining total	69
				90
1,1-DCE	none	not known ^c	1,1-DCE remaining ^d total	83

^a Uncertainties represent 95% confidence intervals. ^b Refer to the text for a description of how mass recoveries were calculated. ^c There was not sufficient transformation of 1,1-DCE over the course of the experiment (120 days) to determine a quantitative rate constant. ^d No reaction products were detected over the course of 120 days.

assumption for reactions with half-lives of one to several months). Corrected k_{obs} values, denoted k_{obs}' , are given by (16–19):

$$k_{\text{obs}}' = k_{\text{obs}} \left(1 + H_i \frac{V_g}{V_{\text{aq}}} \right) = k_{\text{obs}} f_r \quad (1)$$

where H_i is the dimensionless Henry's law constant for the reactant, V_g and V_{aq} are the volumes of the gas and aqueous phases in liters, and the variable f_r is defined as $(1 + H_i (V_g/V_{\text{aq}}))$.

Mass recoveries of reactants and products were also corrected to account for partitioning between the aqueous and gas phases. Mass recoveries of products were calculated by dividing the aqueous molar concentration of the product at the last time point of the experiment by the maximum possible aqueous molar concentration of the product, $C_{\text{p,aq,max}}$, and multiplying by 100%. The mass recovery of any reactant remaining at the last time point was determined in the same way. $C_{\text{p,aq,max}}$ is given by (19)

$$C_{\text{p,aq,max}} = \frac{C_{\text{r,aq,0}}(V_{\text{aq}} + H_r V_g)}{V_{\text{aq}} + H_p V_g} \quad (2)$$

where $C_{\text{r,aq,0}}$ is the initial aqueous molar concentration of the reactant, and H_p is the dimensionless Henry's law constant of the product.

Dimensionless Henry's law constants used in these calculations were averages of all experimentally determined values at approximately 25 $^\circ\text{C}$ that were reported in refs 20–26, except for $H_{\text{acetylene}}$, which was estimated rather than measured (27). These values are as follows: PCE, 0.764; TCE, 0.419; *cis*-DCE, 0.167; *trans*-DCE, 0.384; 1,1-DCE, 1.365; VC, 1.137; and acetylene, 0.887.

Table 1 reports rate constants, reaction products, and mass recoveries for the transformation of TCE, PCE, and 1,1-DCE by FeS. No *trans*-DCE, ethene, or ethane were

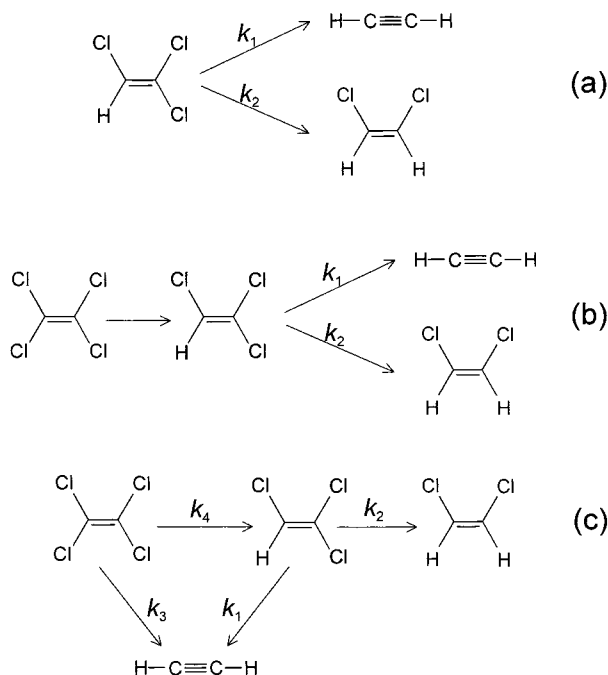


FIGURE 1. Hypothesized reaction pathways for transformation of TCE and PCE by FeS. Refs. for (a) and (c): 6–8, 16, 28, and 33.

detected as reaction products in any experiments. The incomplete mass recoveries reported in Table 1 and subsequent figures may be due to the formation of nonvolatile or water-soluble products that would not have been detected using the analytical methods employed here, inaccuracies in the Henry's Law constants used in calculating mass recoveries, adsorption of reactants and products to the FeS surface, and losses of volatile reactants and products during the sampling process.

Reductive Dechlorination of 1,1-DCE by FeS. An approximately 17% reduction in the concentration of 1,1-DCE was observed after 120 days in the presence of FeS; however, no reaction products were detected. The rate of disappearance of 1,1-DCE was not sufficient to calculate a quantitative rate constant based on these data. This result will not be discussed further, except in considering possible pathways for the transformation of TCE and PCE by FeS.

Kinetics of the Reductive Dechlorination of TCE by FeS. The corrected pseudo-first-order rate constant (k_{obs}) for TCE degradation by FeS was $(1.49 \pm 0.14) \times 10^{-3} \text{ h}^{-1}$, which is similar to the value of $1.15 \times 10^{-3} \text{ h}^{-1}$ predicted by the correlation reported by Sivavec et al. (5) for degradation of TCE in the presence of 0.5 m²/L FeS (troilite) in batch experiments. The principal reaction product for TCE transformation by FeS was acetylene, accounting for 71% of the transformed TCE, while *cis*-DCE accounted for 7%. VC was also detected at concentrations below 1% of the original TCE concentration after approximately 2000 h (83 days). Interpretation of graphical data in Sivavec and Horney (6) indicates a similar product distribution for transformation of TCE by FeS (troilite), with approximately 75% of TCE transformed to acetylene and 15–20% transformed to ethene, ethane, and other C₂–C₆ carbon products (a more specific product distribution was not given) in a column system.

Because acetylene and *cis*-DCE were detected simultaneously, experimental data were interpreted assuming parallel transformation of TCE to these two products, as illustrated in Figure 1a, with VC most likely forming from slow hydrogenolysis of *cis*-DCE. Parallel transformation of TCE to acetylene and *cis*-DCE, via one or more intermediates, has been proposed previously to explain product distributions in the reaction of TCE with FeS and magnetite (6), iron metal

TABLE 2. Acetylene/*cis*-DCE Product Distribution Ratio as a Function of Time for TCE Transformation by FeS

time (h)	$\frac{[\text{acetylene}]_{\text{aq}} f_{\text{acetylene}}}{[\text{cis-DCE}]_{\text{aq}} f_{\text{cis-DCE}}}$	
	no solution amendments	10 ⁻³ M cysteine ^a
164.4	9.94	
261.3	11.28	
363.4	11.30	
647.2	15.32	12.14
814.6	13.28	
1102	10.47	
1438	11.04	
1606	11.63	10.80
1942	11.82	11.12
2493	10.50	10.15
	mean 11.8 ± 1.1 ^b	mean 11.0 ± 1.3

^a Fewer values are reported in this column because substantial quantities of acetylene and *cis*-DCE were not detected as reaction products at early time points when 10⁻³ M cysteine was present in the reaction mixture. ^b Uncertainties in means are 95% confidence intervals.

(6, 8), and cobalamins in the presence of titanium(III) citrate (16, 28). The solution to the differential equations describing such a reaction scheme (29), modified to account for equilibrium partitioning of reactants and products between the aqueous and gas phases, is shown below. The transformation of *cis*-DCE to VC was ignored in this analysis due to its very slow rate. The integrated expression for pseudo-first-order decay of TCE in the aqueous phase is given by

$$[\text{TCE}]_{\text{aq}} = [\text{TCE}]_{\text{aq},0} e^{-k_{\text{obs,TCE}} t} \quad (3)$$

where $k_{\text{obs,TCE}}$ is the observed pseudo-first-order rate constant for TCE decay (Table 1). Equation 4 is the corresponding expression for accumulation of acetylene in the aqueous phase:

$$\frac{d[\text{acetylene}]_{\text{aq}}}{dt} = \frac{f_{\text{TCE}}}{f_{\text{acetylene}}} k_1 [\text{TCE}]_{\text{aq}} \quad (4)$$

Substituting eq 3 into eq 4 and integrating yields eq 5, which describes the aqueous concentration of acetylene at any time, t :

$$[\text{acetylene}]_{\text{aq}} = \frac{f_{\text{TCE}}}{f_{\text{acetylene}}} \frac{k_1 [\text{TCE}]_{\text{aq},0} (1 - e^{-k_{\text{obs,TCE}} t})}{k_{\text{obs,TCE}}} \quad (5)$$

The corresponding expression for $[\text{cis-DCE}]_{\text{aq}}$ can be obtained in the same manner:

$$[\text{cis-DCE}]_{\text{aq}} = \frac{f_{\text{TCE}}}{f_{\text{cis-DCE}}} \frac{k_2 [\text{TCE}]_{\text{aq},0} (1 - e^{-k_{\text{obs,TCE}} t})}{k_{\text{obs,TCE}}} \quad (6)$$

Dividing eq 5 by eq 6 and rearranging yields the following expression:

$$\frac{[\text{acetylene}]_{\text{aq}} f_{\text{acetylene}}}{[\text{cis-DCE}]_{\text{aq}} f_{\text{cis-DCE}}} = \frac{k_1}{k_2} \quad (7)$$

which relates the relative aqueous concentrations of acetylene and *cis*-DCE at any time to the ratio of the rate constants for decay of TCE to these two products. The left-hand side of eq 7 will be referred to as the acetylene/*cis*-DCE product distribution ratio, while the right-hand side is called the TCE branching ratio. The fact that the acetylene/*cis*-DCE product distribution ratio is approximately constant over the course of the experiment, as shown in Table 2, is evidence that

TABLE 3. Pseudo-First-Order Rate Constants (in h⁻¹) and Branching Ratios for Transformation of TCE and PCE by FeS^a

conditions	k_1 { k_1' }	k_2 { k_2' }	k_3 { k_3' }	k_4 { k_4' }	k_1/k_2^b	k_3/k_4^b
no organic amendments	$(1.11 \pm 0.11) \times 10^{-3}$ { $(1.37 \pm 0.13) \times 10^{-3}$ }	$(9.4 \pm 1.2) \times 10^{-5}$ { $(1.17 \pm 0.15) \times 10^{-4}$ }	$(3.57 \pm 0.62) \times 10^{-4}$ { $(5.11 \pm 0.89) \times 10^{-4}$ }	$(4.38 \pm 0.59) \times 10^{-5}$ { $(6.26 \pm 0.85) \times 10^{-5}$ }	11.8 ± 1.1	8.2 ± 1.8
10 ⁻³ M cysteine	$(3.17 \pm 0.36) \times 10^{-4}$ { $(3.92 \pm 0.45) \times 10^{-4}$ }	$(2.87 \pm 0.46) \times 10^{-5}$ { $(3.55 \pm 0.56) \times 10^{-5}$ }	$(9.4 \pm 3.4) \times 10^{-5}$ { $(1.34 \pm 0.49) \times 10^{-4}$ }	$(1.33 \pm 0.34) \times 10^{-5}$ { $(1.91 \pm 0.49) \times 10^{-5}$ }	11.0 ± 1.3	7.0 ± 3.2

^a k_1 – k_4 refer to the reactions shown in Figure 1a,c. Uncertainties in all values are 95% confidence intervals. ^b The ratios k_1/k_2 and k_3/k_4 are equal to k_1'/k_2' and k_3'/k_4' , respectively.

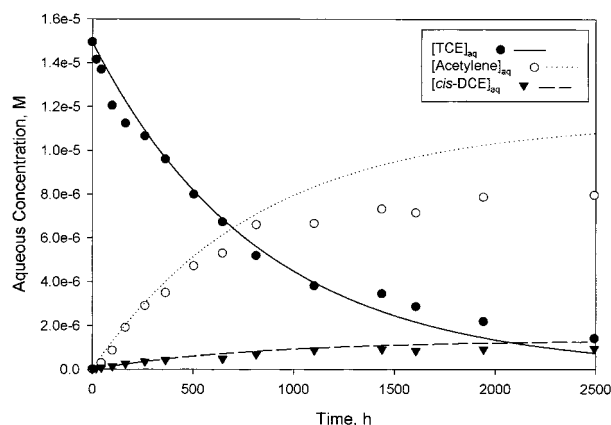


FIGURE 2. Aqueous concentrations of TCE, acetylene, and *cis*-DCE versus time. Data points represent experimentally measured values, and lines represent model fits based on the reaction scheme illustrated in Figure 1a.

acetylene and *cis*-DCE are produced by parallel reaction pathways since sequential pathways would result in accumulation of one product and depletion of the other over time. Assuming parallel transformation to acetylene and *cis*-DCE and no other products, the k_{obs} value for TCE reported in Table 1 equals the sum of the rate constants for decay of TCE to these two products, i.e.

$$k_{\text{obs,TCE}} = \frac{k_{\text{obs,TCE}}'}{f_{\text{TCE}}} = k_1 + k_2 \quad (8)$$

Combining eqs 7 and 8 and equating the TCE branching ratio (k_1/k_2) to the average value of the acetylene/*cis*-DCE product distribution ratio from Table 2 yields the values of k_1 and k_2 reported in Table 3. By eq 8, the pseudo-first-order rate constants for transformation of TCE to acetylene and *cis*-DCE in a headspace-free system, i.e., k_1' and k_2' , are equal to $k_1 f_{\text{TCE}}$ and $k_2 f_{\text{TCE}}$, respectively. Values of k_1' and k_2' are reported in Table 3 along with values of k_1 , k_2 , and k_1/k_2 . The value of 11.8 ± 1.1 for the TCE branching ratio means that transformation of TCE to acetylene by FeS was almost 12 times faster than transformation of TCE to *cis*-DCE under the conditions of these experiments, with the consequence that *cis*-DCE and VC were only minor reaction products. Figure 2 illustrates experimentally measured values of $[\text{TCE}]_{\text{aq}}$, $[\text{acetylene}]_{\text{aq}}$, and $[\text{cis-DCE}]_{\text{aq}}$ along with lines corresponding to the solutions to eqs 3, 5, and 6 that were obtained using the values of $k_{\text{obs,TCE}}$, k_1 , and k_2 reported in Tables 1 and 3.

Kinetics of the Reductive Dechlorination of PCE by FeS.

The corrected pseudo-first-order rate constant (k_{obs}) for PCE degradation by FeS was $(5.7 \pm 1.0) \times 10^{-4} \text{ h}^{-1}$. This value is smaller than the k_{obs} value for TCE ($(1.49 \pm 0.14) \times 10^{-3} \text{ h}^{-1}$), which is surprising since PCE has a more positive reduction potential than TCE (7, 30) and thus should be more susceptible to reduction reactions. There is no obvious explanation for the more rapid degradation of TCE versus PCE, but similar results have been reported for the trans-

formations of these compounds by iron metal (31, 32). The products of PCE transformation by FeS were acetylene, TCE, and *cis*-DCE. No VC was detected over the course of the experiment, which is likely due to only minimal accumulation of *cis*-DCE.

Two hypotheses were considered in interpreting the data for PCE transformation by FeS. First, PCE could be transformed to TCE, followed by parallel transformation of TCE to acetylene and *cis*-DCE as illustrated in Figure 1b. For such a process, the acetylene/*cis*-DCE product distribution ratio should have the same value as TCE (i.e., 11.8 ± 1.1). However, for PCE, the average value of this ratio for the time points when both acetylene and *cis*-DCE were present above quantitative detection limits was 109 ± 29 , suggesting that acetylene is being produced from PCE as well as TCE. This finding suggests interpretation of the data assuming parallel reaction of PCE to acetylene and TCE using a reaction scheme such as that illustrated in Figure 1c. Parallel transformation of PCE to acetylene and TCE, via one or more intermediates, has been proposed to explain product distributions in the reaction of PCE with iron (8), zinc (7), and cobalamins in the presence of titanium(III) salts (16, 33). The following set of differential equations applies to the reaction pathways illustrated in Figure 1c:

$$\frac{d[\text{PCE}]_{\text{aq}}}{dt} = -k_3[\text{PCE}]_{\text{aq}} - k_4[\text{PCE}]_{\text{aq}} \quad (9)$$

$$\frac{d[\text{TCE}]_{\text{aq}}}{dt} = -k_1[\text{TCE}]_{\text{aq}} - k_2[\text{TCE}]_{\text{aq}} + \frac{f_{\text{PCE}}}{f_{\text{TCE}}} k_4[\text{PCE}]_{\text{aq}} \quad (10)$$

$$\frac{d[\text{acetylene}]_{\text{aq}}}{dt} = \frac{f_{\text{TCE}}}{f_{\text{acetylene}}} k_1[\text{TCE}]_{\text{aq}} + \frac{f_{\text{PCE}}}{f_{\text{acetylene}}} k_3[\text{PCE}]_{\text{aq}} \quad (11)$$

$$\frac{d[\text{cis-DCE}]_{\text{aq}}}{dt} = \frac{f_{\text{TCE}}}{f_{\text{cis-DCE}}} k_2[\text{TCE}]_{\text{aq}} \quad (12)$$

Unlike the case of TCE, there is no exact analytical solution to this set of equations, so the following methodology was used to obtain an approximate solution. To determine k_3 and k_4 , measured values of $[\text{TCE}]_{\text{aq}}$ and $[\text{acetylene}]_{\text{aq}}$ were plotted as functions of time. The resulting data were approximated by polynomials, the derivatives of which were equated to the right-hand sides of eqs 10 and 11, respectively. Values of k_3 and k_4 were then approximated by nonlinear regression of the resulting equations using experimentally measured values of $[\text{TCE}]_{\text{aq}}$ and $[\text{PCE}]_{\text{aq}}$ as functions of time and the values for k_1 and k_2 determined previously, with the constraint that $k_3 + k_4 = k_{\text{obs,PCE}}$.

Once values for k_3 , and k_4 were determined, eqs 9–12 were solved using the program SigmaPlot 4.0 (SPSS Inc., Chicago IL), which employs a fourth-order Runge–Kutta algorithm. Experimentally measured values of aqueous concentrations of reactants and products as functions of time are plotted along with the numerical solutions to eqs 9–12 in Figure 3. The reasonable agreement between the experimental data and these equations is consistent with the reaction scheme illustrated in Figure 1c.

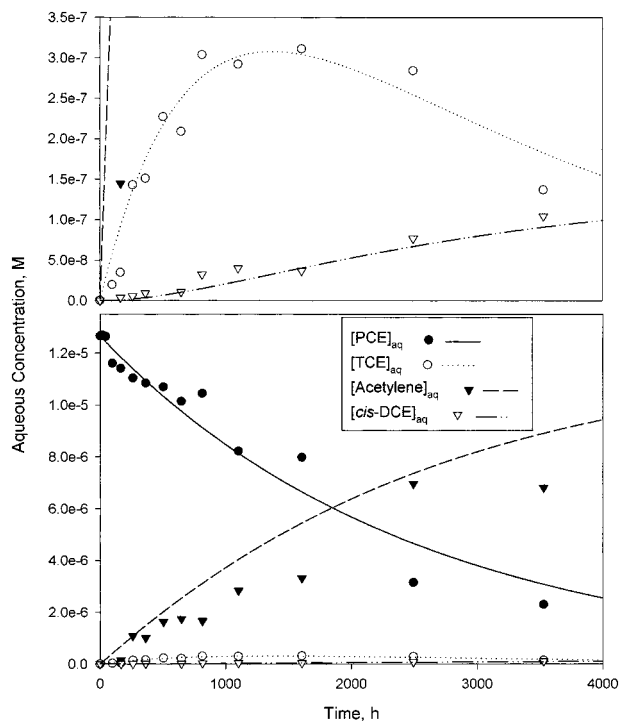


FIGURE 3. Aqueous concentrations of PCE, TCE, acetylene, and *cis*-DCE versus time. Data points represent experimentally measured values, and lines represent model fits based on the reaction scheme illustrated in Figure 1c.

Analogous to TCE, the pseudo-first-order rate constants for transformation of PCE to acetylene and TCE in a headspace-free system are defined as $k_3 f_{PCE}$ and $k_4 f_{PCE}$, respectively. Values of k_3 , k_4 , k_3' , and k_4' are reported in Table 3. The PCE branching ratio (k_3/k_4) of 8.2 ± 1.8 also reported in Table 3 indicates that, similarly to TCE, PCE is transformed by FeS to acetylene significantly faster than to TCE, with the result that *cis*-DCE was only a minor product and VC was not present above analytical detection limits.

Pathways for the Reductive Dechlorination of TCE and PCE by FeS. Figure 1, panels a and c, represent simple reaction schemes, and it possible or even likely that TCE and PCE are transformed by FeS via minor pathways not illustrated in these figures. For example, the transformation of *cis*-DCE to acetylene in the presence of iron metal has been reported (7, 34), and it is possible that *cis*-DCE is an intermediate in the transformation of TCE or PCE to acetylene. However, experimental evidence indicates that if *cis*-DCE was transformed by FeS to acetylene, the reaction was significantly slower than transformation of TCE and PCE to acetylene. This evidence includes the following: (a) the good fit of experimental data to rate laws derived from the reaction schemes illustrated in Figure 1a,c (Figures 2 and 3); (b) the relatively constant acetylene/*cis*-DCE product distribution ratio for TCE degradation (Table 2); and (c) the immediate accumulation of acetylene in the transformation of both TCE and PCE by FeS (Figures 2 and 3).

The possibility that TCE or PCE was transformed to 1,1-DCE followed by rapid decay to acetylene was also considered. The case of 1,1-DCE is especially relevant because Kästner (35) measured the appearance of 1,1-DCE in the transformation of PCE by activated sludge simultaneously with the growth of sulfidogenic bacteria and a change in the color of the culture medium to blackish, and he concluded that 1,1-DCE was formed by the microbial release of sulfide. In addition, 1,1-DCE was transformed to acetylene by cobalamin in the presence of titanium(III) citrate (18, 36). However, no acetylene (or any other product) was detected in this study in the transformation of 1,1-DCE by FeS over 120 days, eliminating the possibility that 1,1-DCE is a significant intermediate in the transformation of TCE or PCE to acetylene, since its slow rate of decay in the presence of FeS would have resulted in significant accumulation.

The potential for the intermediacy of *trans*-DCE in the transformation of TCE or PCE to acetylene was also considered, since transformation of *trans*-DCE to acetylene has been observed in the presence of iron (34), zinc (7), and cobalamins in the presence of titanium(III) salts (33). However, in a related study (19), transformation of 1,1,2,2-

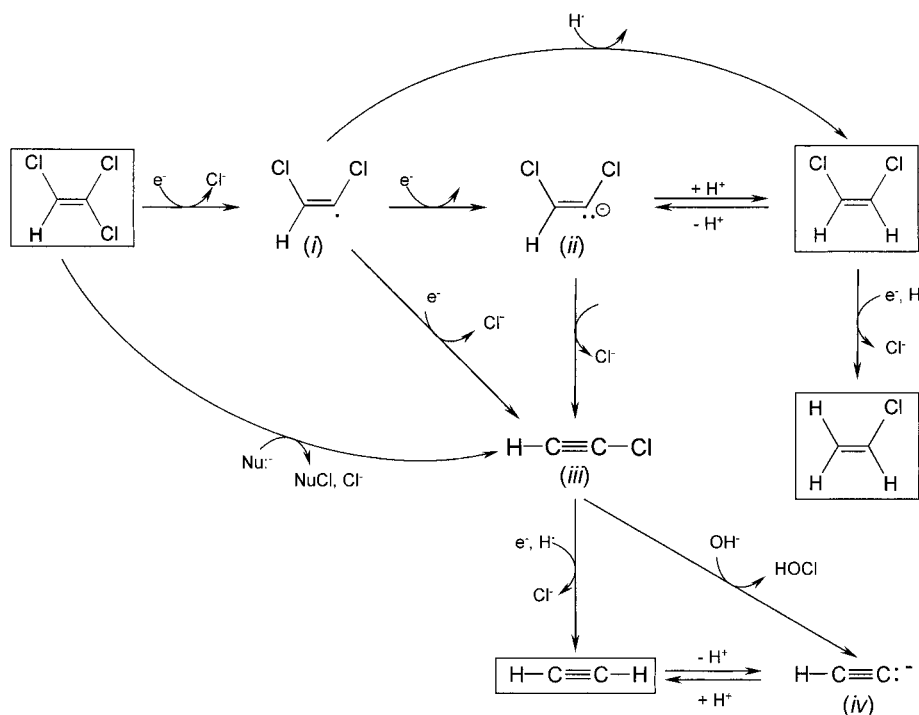


FIGURE 4. Possible pathways for transformation of TCE (6–8, 16, 28, 37, 38). Species in boxes were detected in the experiments reported here. Nu:⁻ means nucleophile.

tetrachloroethane by FeS produced among other products *trans*-DCE, which subsequently decreased in concentration no more than approximately 10% over the course of 7 days. This finding suggests that *trans*-DCE is not a significant intermediate in the transformation of TCE or PCE to acetylene, since it is transformed by FeS slowly enough that if it were an intermediate, it would be present above detection limits, and no *trans*-DCE was detected in these experiments at any time.

Several pathways for hydrogenolysis and reductive elimination of TCE and PCE have previously been proposed (6–8, 16, 28, 33, 37, 38). These pathways are illustrated for TCE in Figure 4, but analogous reaction pathways for PCE can also be considered. The detection of products of both hydrogenolysis (*cis*-DCE) and reductive elimination (acetylene) in the transformation of TCE by FeS suggests a pathway involving a common intermediate or intermediates such as the *cis*-dichlorovinyl radical (Figure 4(i)) or the *cis*-dichlorovinyl anion (Figure 4(ii)). Through isotope studies, Glod et al. (28) found evidence for the intermediacy of species similar to both (i) and (ii) in the transformation of TCE by cobalamin/titanium(III) citrate. Sivavec and Horney (6) detected hydrocarbon products hypothesized to arise from radical coupling reactions in the degradation of TCE by FeS (troilite).

Detection of both hydrogenolysis and reductive elimination products in the degradation of TCE (and PCE) by FeS suggests a common rate-limiting elementary reaction step with a common metastable intermediate such as (i) or (ii) (Figure 4). However, it is not possible, based on the evidence reported here, to disprove the hypothesis that the products of hydrogenolysis and reductive elimination are formed by independent pathways that do not share a common reaction intermediate. It is possible, for example, that dichloroelimination of TCE to chloroacetylene takes place in a single elementary reaction step that does not share a common intermediate with pathways for *cis*-DCE formation. Evidence was recently reported that the initial step in the reductive elimination of chloroethylenes by zero-valent metals is an essentially concerted two-electron reduction (7). Nucleophiles such as sulfides and polysulfides have been shown to promote related dihaloelimination reactions (39–43 and references cited therein) by pathways that may involve a single two-electron reduction reaction (44), and it is certainly possible that the sulfide functional groups in FeS promote such a reaction. Such a pathway is illustrated for TCE in Figure 4. However, the following observations are not consistent with the idea of a concerted two-electron reduction of TCE or PCE by FeS. Addition of 1 mM cysteine to FeS slurries produced diminished rates of disappearance of both TCE and PCE. This is consistent with previous results (15) in which the transformation of hexachloroethane by FeS was significantly slowed by cysteine, speculated to be due to adsorption of cysteine to surface iron atoms. Despite the expected decrease in the values of k_{obs} and $k_1 - k_4$ for TCE and PCE in the presence of cysteine (calculated as described previously and shown in Tables 1 and 3), cysteine did not significantly affect the TCE and PCE branching ratios (Table 3). This suggests a common rate-limiting elementary reaction step in the formation of acetylene and *cis*-DCE from TCE and in the formation of acetylene and TCE from PCE, since it seems unlikely that addition of cysteine would affect the rates of two independent rate-limiting steps to the same extent. Additional studies are needed to gain further evidence for this hypothesis.

Application of Results. The principal product in the reaction of TCE and PCE by FeS was acetylene. Consequently, detection of acetylene in sulfate-reducing environments contaminated with TCE or PCE may be indicative of abiotic degradation by FeS, since microbial decay of these compounds by sulfate-reducing bacteria typically yields hydro-

genolysis products (e.g., ref 45). While the detection or nondetection of acetylene is potentially confounded by the numerous pathways for transformation of this compound in natural systems, including hydrolysis and hydrogenation, analysis for acetylene in addition to other potential TCE and PCE reaction products in samples from contaminated sites may provide insight into the pathway(s) of TCE and PCE degradation in the environment.

The results described here also illustrate the utility of calculating and reporting TCE and PCE branching ratios to allow quantitative evaluation of the relative rates of TCE and PCE hydrogenolysis and reductive elimination reactions and expected product distributions. Such information is very relevant for understanding the natural transformation of TCE and PCE and for evaluating the suitability of a particular reductant for a treatment application.

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