# Pd-Catalyzed TCE Dechlorination in Water: Effect of [H<sub>2</sub>](aq) and H<sub>2</sub>-Utilizing Competitive Solutes on the TCE Dechlorination Rate and Product Distribution

GREGORY V. LOWRY AND MARTIN REINHARD\* Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020

The aqueous-phase  $H_2$  concentration ([H<sub>2</sub>](aq)) and the presence of H<sub>2</sub>-utilizing competitive solutes affect TCE dechlorination efficiency in Pd-based in-well treatment reactors. The effect of [H<sub>2</sub>](ag) and H<sub>2</sub>-utilizing competing solutes (cis-DCE, trans-DCE, 1,1-DCE, dissolved oxygen (DO), nitrite, nitrate) on the TCE transformation rate and product distribution were evaluated using 100 mg/L of a powdered Pd-on-Al<sub>2</sub>O<sub>3</sub> catalysts in batch reactors or 1.0 g of a 1.6-mm Pd-on- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in column reactors. The TCE dechlorination rate constant decreased by 55% from 0.034  $\pm$  0.006 to 0.015  $\pm$  0.001 min<sup>-1</sup> when the [H<sub>2</sub>](aq) decreased from 1000 to 100  $\mu$ M and decreased sharply to 0.0007  $\pm$  0.0003 min<sup>-1</sup> when the [H<sub>2</sub>](ag) decreased from 100 to 10 µM. Production of reactive chlorinated intermediates and C4-C6 radical coupling products increased with decreasing [H<sub>2</sub>](aq). At an [H<sub>2</sub>](aq) of 10  $\mu$ M (P/P<sub>0</sub> = 0.01), DCE isomers and vinyl chloride accounted for as much as 9.8% of the TCE transformed at their maximum but disappeared thereafter, and C4-C6 radical coupling products accounted for as much as 18% of TCE transformed. The TCE transformation rate was unaffected by the presence of *cis*-DCE (202  $\mu$ M), *trans*-DCE (89  $\mu$ M), and 1,1-DCE (91  $\mu$ M), indicating that these compounds do not compete with TCE for catalyst active sites. DO is twice as reactive as TCE but had no effect on TCE conversion in the column below a concentration of 370  $\mu$ M (11.8 mg/L), indicating that DO and TCE will not compete for active catalyst sites at typical groundwater DO concentrations. TCE conversion in the column was reduced by as much as a factor of 10 at influent DO levels greater than 450 mM (14.3 mg/L) because the  $[H_2](aq)$  fell below 100  $\mu$ M due to H<sub>2</sub> utilized in DO conversion. Nitrite reacts 2–5 times slower than TCE and reduced TCE conversion by less than 4% at a concentration of 6630  $\mu$ M (305 mg/L). Nitrate was not reactive and did not effect TCE conversion at a concentration of 1290 µM (80 mg/L).

## Introduction

Palladium (Pd)-based catalytic fixed-bed reactors show promise as a treatment technology for in situ destruction of halogenated groundwater contaminants. In deionized (DI) water, Pd catalysts rapidly dehalogenate a variety of commonly encountered halogenated groundwater contaminants including chlorinated ethylenes (PCE, TCE, DCE, vinyl chloride), chlorinated methanes (carbon tetrachloride, chloroform), chlorinated aromatic compounds (1,2-dichlorobenzene), chlorinated biphenyls (4-chlorobiphenyl), chlorofluorocarbons (Freon-113), and halogenated pesticides (1,2dibromo-3-chloropropane (DBCP) and lindane) without forming substantial amounts of chlorinated intermediate compounds (1-4). Common groundwater solutes such as bicarbonate, sulfate, and chloride have little effect on catalyst activity during the aqueous-phase destruction of TCE. Laboratory-scale column reactor experiments indicate that some groundwater solutes reduce catalyst activity, such as sulfite and bisulfide, but the adverse effects are reversible and catalyst activity is sustainable under groundwater treatment conditions (5). An in-well Pd-based pilot-scale fixed-bed reactor has been used to treat halogenated hydrocarbon contaminated groundwater for more than 1 year at Lawrence Livermore National Laboratory without significant loss of catalyst activity (6). All the research efforts mentioned above were performed under hydrogen-rich conditions, and no work has been published regarding the effects of the aqueous hydrogen concentration ([H<sub>2</sub>](aq)) on the contaminant transformation rate and product distribution or the conditions under which H<sub>2</sub> deficiencies might occur, such as the presence of additional H<sub>2</sub>-utilizing substrates.

Only trace quantities of undesirable halogenated intermediate compounds form under H<sub>2</sub>-rich conditions (1), but production may increase under hydrogen-limited conditions because the first step of the hydrodehalogenation reaction, removal of the halogen, is reversible (7). Trace amounts of butane and hexane have been observed during TCE transformation using palladized iron (8), and ethane and propane/ propene have been observed during transformation of carbon tetrachloride under H<sub>2</sub>-rich conditions (1), indicating that a free radical mechanism exists. Under H<sub>2</sub>-limited conditions, isomerization and polymerization side reactions may increase significantly and potentially lead to catalyst deactivation if these less reactive unsaturated C4–C6 hydrocarbon byproducts remain on the catalyst surface, effectively blocking active catalyst sites.

Groundwater contamination by halogenated hydrocarbons often involves multiple contaminants at one site, as in ref 6, rather than a single contaminant, and Pd catalysts readily transform many of these contaminants (1-4). Dissolved oxygen (DO) is also a constituent of most surface water and groundwater, and palladium catalyzes the rapid reaction between oxygen and hydrogen to form water (eq 1) (9):

**D** 1

$$2H_2 + O_2 \xrightarrow{Pd} 2H_2O \tag{1}$$

Similarly, Pd/Cu and Pd catalysts in the presence of dissolved  $H_2$  catalyze the aqueous-phase transformation of nitrate and nitrite to  $N_2$  (eqs 2 and 3) (10, 11):

$$2\mathrm{NO}_{3}^{-} + 5\mathrm{H}_{2} \xrightarrow{\mathrm{Pd/Cu}} \mathrm{N}_{2} + 2\mathrm{OH}^{-} + 4\mathrm{H}_{2}\mathrm{O} \tag{2}$$

$$2\mathrm{NO_2}^- + 3\mathrm{H_2} \xrightarrow{\mathrm{Pd}} \mathrm{N_2} + 2\mathrm{H_2O} + 2\mathrm{OH}^-$$
(3)

The presence of multiple contaminants, DO, nitrate, or nitrite may affect the catalyst's ability to transform TCE by competing with TCE for active catalyst sites if they utilize the same active sites as TCE for transformation or by depleting the

 $<sup>^{*}</sup>$  Corresponding author phone: (650)723-0308; fax: (650)723-7058; e-mail: reinhard@ce.stanford.edu.

#### TABLE 1. Headspace Reactor Operating Conditions

| temp (K)                | 295 ±0.2 |
|-------------------------|----------|
| total pressure (atm)    | 1.3      |
| vol (Ľ)                 | 2.0      |
| aq/vap                  | 1.5/0.5  |
| agitator speed (rpm)    | 1000     |
| [Cat] (g/L)             | 0.1      |
| [TCE] <sub>o</sub> (μM) | 140-180  |

reactor of  $H_2$  if their concentration and reactivity is significant. Diminished  $[H_2](aq)$  in the reactor or competitive sorption onto catalyst active sites may ultimately lead to a lower TCE transformation rate and increase production of unwanted halogenated reaction intermediates. For example, TCE conversion decreased significantly when the reactor influent  $H_2$  concentrations decreased ( $\boldsymbol{6}$ ), and DO was suggested to compete with TCE for  $H_2$  on the catalyst surface (12).

In this study, batch kinetic studies in model systems are used to (i) determine the effect of [H<sub>2</sub>](aq) on the TCE transformation rate, (ii) assess the potential for production of halogenated intermediate compounds and C4-C6 radical coupling products under H<sub>2</sub>-limited conditions, (iii) evaluate the role of C4-C6 radical coupling products in catalyst deactivation, and (iv) determine if the presence of *cis*-DCE, trans-DCE, and 1,1-DCE affects the TCE dehalogenation rate. Column reactors are used to quantify the H<sub>2</sub> requirements for DO, nitrate, and nitrite and to evaluate the effect of these solutes on the catalyst's ability to transform TCE to ethane. Batch studies indicate that the TCE transformation rate decreases sharply at [H<sub>2</sub>](aq) less than 100  $\mu$ M (P/P<sub>0</sub><0.1) and production of halogenated intermediates and radical coupling products increases as the  $[H_2](aq)$  decreases. The presence of cis-DCE, trans-DCE, and 1,1-DCE did not effect the transformation rate of TCE. Column reactor studies show that DO and nitrite are reactive solutes, utilize H<sub>2</sub>, and can sometimes interfere with the catalyst's ability to transform TCE to ethane.

### **Experimental Section**

**Chemicals.** All chemicals were reagent grade and 99+% pure unless noted. TCE was supplied by Fisher Scientific. 1,1-Dichloroethylene (DCE), *cis*-DCE (97%), and *trans*-DCE (98%) were supplied by Aldrich. Sodium nitrate (anhydrous) and sodium nitrite (anhydrous) were supplied by J. T. Baker. Pure hydrogen gas (zero grade), oxygen gas, and a 100 ppmv H<sub>2</sub> in N<sub>2</sub> gas standard were supplied by Praxair. Gas standards for vinyl chloride, 1-butene, *n*-butane, *cis*-2-butene, *trans*-2-butene, and 2-hexene were supplied by Scott Specialty Gases (Plumsteadville, PA).

**Catalysts.** Two prereduced commercially available 1 wt % Pd-on-Al<sub>2</sub>O<sub>3</sub> catalysts were used. A powdered  $(38-70 \,\mu\text{m})$  catalyst supplied by Aldrich was used in batch experiments. A spherical 1.6-mm edge-loaded (~70  $\mu$ m thickness) paladium-on- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst supplied by PMC (Precious Metals Corporation, Sevierville, TN) was used in the column experiments. The 1 wt % Pd content specified by the manufacturer was assumed to be accurate, and no special precautions were taken to avoid catalyst exposure to air prior to column experiments. Catalyst physical properties such as BET surface area, pore volume, and pore size distribution for the powdered and spherical catalysts are reported in refs *1* and *5*, respectively.

**Headspace Reactors.** The headspace reactor was a gastight 2.0-L glass and stainless steel batch reactor (Bioengineering AG, Wald, Switzerland) equipped with a magnetically driven mixer, temperature probe, heat exchanger, and pressure gauge as described in ref 1. Batch reactor operating conditions are given in Table 1. Complete details of the TABLE 2.  $H_2$  Partial Pressures and Corresponding [H<sub>2</sub>](aq) and Observed TCE Reaction Rate Constants and Half-Lifetimes in Headspace Reactors

| ( <i>P</i> / <i>P</i> <sub>o</sub> ) | [H <sub>2</sub> ](aq) (µM) | $k_{\rm obs}$ (min <sup>-1</sup> ) | t <sub>1/2</sub> (min) |
|--------------------------------------|----------------------------|------------------------------------|------------------------|
| 1.0                                  | 1000                       | $0.034 \pm 0.006^{a}$              | 20                     |
| 0.4                                  | 400                        | $0.025 \pm 0.004$                  | 28                     |
| 0.104                                | 100                        | $0.015 \pm 0.001$                  | 46                     |
| 0.04                                 | 40                         | $0.0037 \pm 0.0005$                | 187                    |
| 0.01                                 | 10                         | $0.0007 \pm 0.0003$                | 990                    |
|                                      |                            |                                    |                        |

<sup>a</sup> Errors represent 95% confidence intervals



FIGURE 1. Column experiment apparatus.  $V_{\text{EB}}$ , n, and  $\theta$  are the column empty-bed volume, porosity, and fluid retention time, respectively.

experimental procedure for the headspace reactor are described in ref 1, but a summary of the experimental procedure is as follows. The reactor was filled with DI water and sparged with pure  $H_2$  gas or a  $H_2/N_2$  gas mixture for 15 min to remove dissolved oxygen and provide a specific  $[H_2](aq)$ . Pure  $H_2$  gas  $(P/P_0 = 1)$  and  $H_2/N_2$  gas mixes of 40%, 10.4%, 4%, and 1% (*P*/*P*<sub>o</sub> = 0.4, 0.1, 0.04, and 0.01, respectively) were used to provide five [H<sub>2</sub>](aq) ranging from 10 to 1000  $\mu$ M as calculated using a Henry's constant of 5.34 imes 10<sup>7</sup> Torr (13). The H<sub>2</sub> partial pressures and corresponding calculated  $[H_2](aq)$  for the reactor total pressure are given in Table 2. After sparging, a saturated aqueous TCE (or TCE and DCE isomers) solution was quickly added to provide an initial reactant concentration of approximately 160  $\mu$ M (21 mg/L). Pentane (nonreactive) was also added as an internal standard. The reactants and pentane were agitated and equilibrated between the vapor and aqueous phase for 1 h before 0.1 g of powdered Pd-on-Al<sub>2</sub>O<sub>3</sub> was injected to begin the reaction. The H<sub>2</sub> partial pressure was held constant throughout the experiment to maintain a constant [H<sub>2</sub>](aq). Headspace samples (200  $\mu$ L) were taken from the reactor periodically during the experiment and analyzed for TCE as well as volatile reaction intermediates and products as described in ref 1.

**Column Reactors.** The reactors used in this study are identical to those in ref *5*, except that an inlet is inserted ahead of the column for easy addition of the nitrate or nitrite solution or dissolved oxygen (DO) in the column influent (Figure 1). Complete details of the reactor experimental setup and sampling protocol can be found in ref *5*, but a brief description follows. The feed tank contains DI water amended with TCE (4 mg/L) under hydrogen gas (1.24–1.27 atm). A positive displacement pump drives flow through the column in an upflow configuration at 1 mL/min. Concentrated nitrate or nitrite solutions are added using a 100-mL syringe and syringe pump (0.01 mL/min) to give the desired nitrate/ nitrite concentration in the column influent. A separate feed tank stores DI water amended with TCE (4 mg/L) under pure oxygen (1.5 atm). DO concentrations in the feed tank are

approximately 63 mg/L as calculated using a Henry's constant of  $3.3 \times 10^7$  Torr (13). DO is added to the column influent using a separate feed pump, and DO concentrations at the column influent are set by adjusting the flow rates on each feed pump (TCE/H<sub>2</sub> and TCE/O<sub>2</sub>) to maintain a total flow of 1 mL/min.

The reactors are stainless steel tubular fixed-bed reactors (1.27 cm  $\times$  9.8 cm,  $V_{\rm EB} = 10.5$  mL). A catalyst loading of 1.0 g was used to give approximately 50% steady-state TCE conversion. The moderate TCE conversion provides maximum sensitivity to small changes in TCE reactivity. Inert 1.6 mm diameter borosilicate glass beads were packed above and below the catalyst to improve the flow characteristics in the column by minimizing end and wall effects. Ideal plug flow is assumed. Column porosity was 0.44  $\pm$  0.02, giving a fluid residence time of 4.4  $\pm$  0.2 min in the column. Column influent and effluent samples were collected and analyzed for TCE, nitrate/nitrite, DO, and dissolved H<sub>2</sub>.

**Analytical Methods.** Headspace reactor samples ( $200 \mu L$ ) were analyzed for TCE and volatile reaction intermediates and products using GC/FID as described in ref 1. The instrument was calibrated daily using standards prepared from volumetric dilutions of a stock solution. Halogenated hydrocarbon (except vinyl chloride) response factors were calculated based on the total amount of compound added to the bottle (25% headspace/75% water). Calibrations for C2–C6 nonhalogenated reaction products and vinyl chloride were determined using certified gas standards (Scott Specialty Gases).

Column reactor influent and effluent samples (0.5 mL) were taken using a 1/4-28 threaded nose 2.5-mL gas-tight syringe (Unimetrics) and extracted into 1 mL of hexane containing 1.3 mg/kg PCE as an internal standard. One-microliter samples of the extract were analyzed for TCE using a HP 5890 series II GC equipped with an ECD as described in ref 1. Nonhalogenated reaction products were not measured using this method.

Column reactor influent and effluent samples were also periodically analyzed for halogenated reaction intermediates (*cis*-DCE, *trans*-DCE, 1,1-DCE, and vinyl chloride) and nonhalogenated reaction products (ethane and ethylene) to evaluate a carbon mass balance for the TCE transformation and to screen for the formation of undesired reaction intermediates. Aqueous 2.5-mL column influent and effluent samples were collected in a 5.0-mL gas-tight 1/4-28 threaded nose syringe (Unimetrics). A 2.5-mL headspace was created in the syringe and then capped and shaken to equilibrate the aqueous and gas phases. A 200- $\mu$ L headspace sample was withdrawn from the syringe and analyzed using GC/FID as described in ref *1*.

Column influent and effluent pH measurements were made using a Ross semi-microcombination pH electrode and EA940 ion analyzer (Orion Research, MA). The instrument was calibrated prior to each set of measurements using pH buffers of 4.01, 7.00, and 10.01. Column influent and effluent samples were collected in 4-mL glass vials, capped, and stored no longer than 15 days prior to analysis.

Nitrate and nitrite analysis was performed with a Dionex series 4000I ion chromatograph (Dionex, CA) equipped with a Dionex IonPac AS4A column ( $4 \times 250$  mm), an AG4A guard column ( $4 \times 50$  mm), and a conductivity detector. A 0.75 mM sodium bicarbonate/2.2 mM sodium carbonate solution was used as an eluent. The instrument was calibrated prior to analysis using volumetric dilutions of sodium nitrate and sodium nitrite stock solutions.

Dissolved oxygen measurements were made with a Hansatech DW1 oxygen electrode (Hansatech Instruments Ltd, Norfolk, England). A 2-mL column influent/effluent sample was collected in a 2.5-mL gas-tight syringe and carefully injected into the electrode cell for analysis. The electrode was calibrated using a 2-point calibration with  $N_2$ -sparged water as DO = 0 mg/L and air-saturated water as 8.8 mg/L. It was assumed that the electrode response was linear.

Dissolved hydrogen concentrations were analyzed using a KAPPA3 model E-001 reduction gas analyzer (Trace Analytical, Menlo Park, CA). A 2.0-mL column influent/ effluent sample was collected in a 1/4-28 threaded nose 5.0mL gas-tight syringe, a 2.0-mL headspace was created, and then the syringe was capped. The syringe was shaken to equilibrate the vapor and aqueous phases. A 250- $\mu$ L headspace sample was removed and diluted (1:100) in a 25-mL vial capped with a Mininert valve. A 50- $\mu$ L aliquot of the diluted headspace sample was then analyzed on the KAPPA3 reduction gas analyzer. The instrument was calibrated daily using 50–200- $\mu$ L samples of a 100 ppmv H<sub>2</sub> in N<sub>2</sub> gas standard supplied by Praxair (San Carlos, CA)

**Evaluation of Reaction Kinetics.** A Langmuir–Hinshelwood (L–H) kinetic formulation was used to model batch reactor experimental data that assumes noncompetitive equilibrium Langmuir type adsorption of TCE and adsorption of  $H_2$  (molecular or dissociative) and that a surface reaction between adsorbed species is the rate-controlling step:

$$-\frac{\mathrm{d}C_{\mathrm{TCE}}}{\mathrm{d}t\,c_{\mathrm{cat}}} = k_{\mathrm{rxn}} \left(\frac{K_{\mathrm{TCE}}C_{\mathrm{TCE}}}{1+K_{\mathrm{TCE}}C_{\mathrm{TCE}}}\right) \left(\frac{K_{\mathrm{H}_{2}}^{n}C_{\mathrm{H}_{2}}^{n}}{1+K_{\mathrm{H}_{2}}^{n}C_{\mathrm{H}_{2}}^{n}}\right)$$
(4)

In eq 4,  $k_{\rm rxn}$  is the apparent reaction rate constant;  $c_{\rm cat}$  is the catalyst concentration;  $K_{TCE}$  and  $K_{H_2}$  are the equilibrium adsorption constants for TCE and H<sub>2</sub>, respectively; C<sub>TCE</sub> and  $C_{\rm H_2}$  are the aqueous concentration of TCE and H<sub>2</sub>, respectively; and n is an integer exponent equal to 1/2 for dissociative adsorption of H<sub>2</sub> and equal to 1 for molecular adsorption of H<sub>2</sub>. A similar approach was successfully used to describe the kinetics of catalytic liquid-phase hydrogenation of aqueous nitrate solutions using a bimetallic Pd/Cu catalyst (14). TCE disappearance was first order in each experiment at fixed [H<sub>2</sub>](aq) ( $C_{o(TCE)} = 180 \,\mu$ M) and has been shown to transform via first-order kinetics for initial TCE concentrations as high as  $250 \,\mu M$  (1). This implies low surface coverage for TCE and that  $K_{\text{TCE}}C_{\text{TCE}} \ll 1$ . For a fixed [H<sub>2</sub>](aq), the last term in parentheses in eq 4 is constant. Using these simplifications and consolidating fixed constants yields a form useful for determining the influence of the [H<sub>2</sub>](aq) on the observed TCE transformation rate constant,  $k_{obs}$  (eqs 5 and 6):

$$\frac{\mathrm{d}C_{\mathrm{TCE}}}{\mathrm{d}t\,c_{\mathrm{cat}}} = k_{\mathrm{obs}}C_{\mathrm{TCE}} \tag{5}$$

where

$$k_{\rm obs} = k_{\rm rxn} K_{\rm TCE} \left( \frac{K_{\rm H_2}^n C_{\rm H_2}^n}{1 + K_{\rm H_2}^n C_{\rm H_2}^n} \right)$$
(6)

A kinetic modeling software package (Micromath Scientist v. 2.01), which minimizes the sum of the squared residuals, was used to model kinetic data obtained in the batch experiments. Reported errors are 95% confidence intervals.

In column experiments, substrate conversion through the column was calculated using

% conversion = 
$$\frac{(C_{\rm in} - C_{\rm eff})}{C_{\rm in}} \times 100$$
 (7)

where  $C_{in}$  and  $C_{eff}$  are the measured influent and effluent substrate concentrations, respectively. Transformation rate constants were calculated using eq 8 assuming pseudo-first-



Aqueous  $H_2$  Concentration ( $\mu$ M)

FIGURE 2. Effect of  $[H_2](aq)$  on TCE transformation rate constant determined in batch reactor. Solid line represents L–H model fit using eq 6. The value of *n* is fixed at 1/2.

order reaction kinetics and ideal plug flow as in ref 5:

$$k_{\rm obs} = \frac{-\ln\left(\frac{C_{\rm eff}}{C_{\rm in}}\right)}{\theta} \tag{8}$$

where  $k_{\text{obs}}$  is the observed pseudo-first-order TCE reaction rate constant and  $\theta$  is the fluid residence time in the column:

$$\theta = \frac{nV_{EB}}{Q} \tag{9}$$

In eq 9, *n* is the column porosity,  $V_{\text{EB}}$  is the column emptybed volume, and *Q* is the fluid flow rate through the column. The column porosity was calculated from gravimetric measurements. Details of the column porosity calculations are given in ref 5. It should be noted that  $\theta$  is calculated for the entire column rather than just the catalyst bed. The catalyst bed is approximately 30% of the total bed volume (Figure 1), so the actual fluid residence time in the catalyst bed is approximately 30% of the reported reactor residence time.

## **Results and Discussion**

Effect of [H2](aq) on TCE Transformation Rate. TCE transformation rates (t < 100 min) were measured in batch experiments at five different aqueous hydrogen concentrations ranging from 10 to 1000  $\mu$ M (P/P<sub>0</sub> = 0.01-1). The observed TCE transformation rate constant and half-lifetime for each [H<sub>2</sub>](aq) is given in Table 2. The TCE transformation rate constant only decreased by only a factor of 2 for [H<sub>2</sub>](aq) decreasing from 1000 to 100  $\mu$ M but decreased sharply for  $[H_2](aq)$  less than 100  $\mu$ M. At an  $[H_2](aq)$  of 40 and 10  $\mu$ M, the TCE transformation rate constant is 10% and 2% of the value at  $[H_2](aq) = 1000 \ \mu M$ , respectively. The TCE transformation rate appeared to be slowing in the lowest  $[H_2](aq)$ experiment ([H<sub>2</sub>](aq) = 10  $\mu$ M), and in fact, C/C<sub>o</sub> decreased to only 0.8 after 1100 min (data not shown). On the basis of the observed reaction rate constant for t < 100 min ( $k_{obs} =$  $0.0007 \pm 0.0003 \text{ min}^{-1}$ ), *C*/*C*<sub>o</sub> should reach 0.8 at some time between 220 and 560 min. This indicates that the reaction slows considerably ( $k_{obs} < 0.0002 \text{ min}^{-1}$ ) after the first 100 min of reaction. This is likely due to the buildup of unsaturated hydrocarbons such as ethylene and C4-C6 radical coupling products on the catalyst surface, effectively blocking catalyst active sites for TCE transformation.

The effect of aqueous hydrogen concentration on the TCE transformation rate and the best fit of the data using eq 6 is shown in Figure 2. The value of n was fixed at 1/2 because



FIGURE 3. Temporal concentration profile of total chlorinated intermediates for an [H<sub>2</sub>](aq) of 1000 and 40  $\mu$ M (*P*/*P*<sub>0</sub> = 1 and 0.04). *C*<sub>max</sub> occurs at different times.



FIGURE 4. Maximum amounts of chlorinated intermediates formed in batch reactors. Total bar height represents sum of chlorinated intermediates formed,  $C_{max}$ , as a percentage of the TCE mass transformed at the time  $C_{max}$  occurred.

dissociative adsorption of  $H_2$  onto active catalyst sites is expected and n = 1/2 was successfully employed in ref 14 using similar catalysts and hydrogen concentrations during the aqueous-phase reduction of nitrate solutions. The best fit was obtained by excluding data obtained at the lowest hydrogen concentrations as these rate constants are significantly lower than predicted based on the L–H model. This is consistent with catalyst deactivation occurring at  $H_2$ concentrations less than 100  $\mu$ M. Figure 2 also shows that the reaction order with respect to the [H<sub>2</sub>](aq) approaches zero order very slowly, indicating that significant increases in the [H<sub>2</sub>](aq) above 1000  $\mu$ M ( $P/P_0 = 1$ ) would result in only moderate increases in the TCE reaction rate. For instance, doubling the [H<sub>2</sub>](aq) from 1000 to 2000  $\mu$ M would increase  $k_{obs}$  by approximately 20%.

In previous batch studies under H<sub>2</sub>-rich conditions ([H<sub>2</sub>](aq) = 1000  $\mu$ M), transient production of chlorinated intermediates occurred (DCE isomers and vinyl chloride) but accounted for less than 3% of the TCE transformed at their maximum (1). Results reported here support this conclusion; however, the production of chlorinated intermediate compounds increases with decreasing [H<sub>2</sub>](aq). The time at which the total chlorinated intermediate concentration reached a maximum changed depending on the amount of H<sub>2</sub> available in each experiment (Figure 3). Figure 4 shows that chlorinated intermediates account for only 2.7% of the TCE transformed at the maximum under H<sub>2</sub>-rich conditions ([H<sub>2</sub>](aq) = 1000  $\mu$ M) but can account for as much as 9.8% of the TCE transformed under H<sub>2</sub>-poor conditions ([H<sub>2</sub>](aq) = 10  $\mu$ M). The values reported in Figure 4 are the maximum



FIGURE 5. Temporal concentration profile of individual DCE isomers and vinyl chloride for an [H<sub>2</sub>](aq) of 400  $\mu$ M (*P*/P<sub>0</sub> = 0.4). *C*<sub>max</sub> occurs at the same time for all chlorinated intermediates.

amount of chlorinated intermediates normalized by the total TCE transformed at that time such that the results from each experiment are directly comparable. Although the  $[H_2](aq)$  affects the total amount of chlorinated intermediates formed as a fraction of the TCE transformed, close examination of Figure 4 reveals that  $[H_2](aq)$  has little effect on the distribution of halogenated intermediates formed, with *cis*-DCE and 1,1-DCE accounting for approximately 80% of the halogenated intermediates formed, regardless of the  $[H_2](aq)$ .

Figure 5 shows the concentration profile of all three DCE isomers and vinyl chloride for an  $[H_2](aq)$  of 400  $\mu$ M (P/P<sub>o</sub> = 0.4). It is apparent that all three DCE isomers and vinyl chloride reach their maximum concentrations simultaneously, which is consistent with published results on the production of chlorinated intermediates using pure Pd metal as a catalyst (1). Experiments at other  $[H_2](aq)$  showed identical behavior (data not shown). The simultaneous peaking of DCE isomers and vinyl chloride indicate that their production is not due to sequential dechlorination (TCE  $\rightarrow$  $DCE \rightarrow vinyl chloride$ ) but rather a random process in which TCE has one (yielding a DCE isomer) or two (yielding vinyl chloride) chlorine molecules replaced by hydrogen before desorbing from the catalyst surface. The dominant transformation pathway however is the removal of all three chlorine atoms, as chlorinated intermediates account for only 9.8% of the TCE removed, even at the lowest  $[H_2](aq)$ . Attempts to model production of DCE isomers and vinyl chloride assuming sequential or parallel first-order production and decay were unsuccessful, which is additional evidence that formation of the DCE isomers and vinyl chloride is a transient process. Chlorinated intermediates were also never detected in laboratory-scale column studies (5) or a pilot-scale field experiment (6) under normal operation, indicating that production of chlorinated intermediates during TCE transformation may indeed be a transient phenomena, as suggested in ref 1. Ethane is the primary product in the Pd-catalyzed aqueous-phase reduction of TCE, but C4 and C6 radical coupling products are also observed. These include 1-butene, n-butane, cis-2-butene, trans-2butene, and 2-hexene. Figure 6 shows that production of C4-C6 radical coupling products increases with decreasing  $[H_2](aq)$  in the reactor and accounts for as much as 18% of the TCE converted at the lowest  $[H_2](aq)$ . The fully saturated C4 product, n-butane, is the primary radical coupling product at  $[H_2](aq)$  greater than 100  $\mu$ M ( $P/P_0 = 0.1$ ), but the product distribution shifts to undersaturated coupling products (1butene, cis-2-butene, trans-2-butene, and 2-hexene) at  $[H_2](aq)$  less than 100  $\mu$ M. The undersaturated products are reactive but less reactive than TCE. The catalyst deactivation observed at  $[H_2](aq)$  less than 100  $\mu$ M may be due to the presence of these undersaturated products if they sorb



FIGURE 6. Maximum amounts of C4–C6 radical coupling products (RCPs) formed in batch reactors. Maximum RCP production occurred at the end of each experiment, so total bar height represents the sum of RCPs formed as a percentage of the total TCE mass transformed in each experiment.

TABLE 3. Influent/Effluent [H\_2](aq) Concentrations and TCE and Oxygen Conversion through the Column

| [TCE] <sub>in</sub><br>(µM) | [O <sub>2</sub> ] <sub>in</sub><br>(µM) | TCE<br>conv<br>(%) | k <sub>tce</sub><br>(min⁻¹) | O₂<br>conv<br>(%) | <i>k</i> <sub>oxy</sub><br>(min <sup>-1</sup> ) | [H <sub>2</sub> ] <sub>in</sub><br>(µM) | [H <sub>2</sub> ] <sub>out</sub><br>(μΜ) |
|-----------------------------|---|--------------------|-----------------------------|-------------------|---|---|--|
| 32.5                        |   | 46.0               | 0.138                       |                   |   | 670                                     | 530                                      |
| 31.0                        | 250                                     | 45.8               | 0.137                       | 79                | 0.35  | 700                                     | 220                                      |
| 21.6                        | 370                                     | 42.3               | 0.123                       | 64                | 0.23  | 790                                     | 220                                      |
| 29.9                        | 450                                     | 13.4               | 0.032                       | 67                | 0.25  | 550                                     | 40                                       |
| 34.1                        | 600                                     | 4.4                | 0.010                       | 31                | 0.08  | 420                                     | 60                                       |
| 26.2                        | 540                                     | 44.8               | 0.133                       | 67                | 0.25  | 1150 <sup>a</sup>                       | 490                                      |

 $^{a}$  Influent [H\_2](aq) increased by increasing total H\_2 pressure on feed tank to 2.36 atm.

appreciably to catalyst reactive sites and effectively block access of TCE or  $H_2$  to those sites.

**Effect of Competing Halogenated Organic Compounds.** The TCE transformation rate was determined in batch reactors in the presence of competing halogenated organic substrates under H<sub>2</sub>-rich conditions ([H<sub>2</sub>](aq) = 1000  $\mu$ M). TCE (66  $\mu$ M), cis-DCE (202  $\mu$ M), trans-DCE (89  $\mu$ M), and 1,1-DCE (91  $\mu$ M) were simultaneously present in the reactor. The pseudo-first-order transformation rate constants for TCE, 1,1-DCE, *cis*-DCE, and *trans*-DCE were 0.040  $\pm$  0.006, 0.042  $\pm$  0.003, 0.052  $\pm$  0.002, and 0.050  $\pm$  0.004, respectively. The trends in reactivity (TCE = 1,1-DCE < *cis*-DCE = *trans*-DCE) are consistent with previously reported rates (1). The transformation rate of TCE was identical to that measured in the absence of competing halogenated substrates at  $[H_2](aq) = 1000 \,\mu M$  (Table 2) indicating that *cis*-DCE, *trans*-DCE, and 1,1-DCE do not compete with TCE for catalyst active sites. All substrates exhibited pseudo-first-order transformation behavior even though they were present at relatively high concentrations. This indicates that substrate coverage was low ( $K_iC_i \ll 1$  for all substrates) and may explain the absence of competition for active catalyst sites.

Effect of Dissolved Oxygen as a Competitive Solute. The effects of DO in the column influent are summarized in Table 3. DO transforms in the column and utilizes hydrogen approximately in the expected stoichiometric ratio of 2:1 (eq 1). Without H<sub>2</sub> limitations, DO conversion in the column typically ranges from 64% to 79%, which is greater than the TCE conversion (46%). The reaction rate constant for DO is approximately 2–2.5 times higher than that of TCE, indicating that the undesired reaction between H<sub>2</sub> and O<sub>2</sub> (eq 1) is faster than the desired TCE conversion. Despite this, DO in the

TABLE 4. TCE and Nitrate/Nitrite Conversion through the Column

| solute  | [solute] <sub>in</sub><br>(µM) | [TCE] <sub>in</sub><br>(µM) | TCE<br>conv<br>(%) | k <sub>tce</sub><br>(min <sup>-1</sup> ) | solute<br>conv<br>(%) | <i>k</i> <sub>solute</sub><br>(min <sup>-1</sup> ) |
|---------|--------------------------------|-----------------------------|--------------------|--|-----------------------|--|
| none    | 0                              | 26.6                        | 48.2               | 0.147                                    | 0                     | 0  |
| nitrate | 371                            | 30.1                        | 48.0               | 0.146                                    | 2                     | 0.005  |
|         | 1290                           | 31.0                        | 47.4               | 0.143                                    | 0                     | 0  |
| nitrite | 1565                           | 23.1                        | 44.0               | 0.129                                    | 23                    | 0.058  |
|         | 2609                           | 30.3                        | 43.3               | 0.127                                    | 10                    | 0.024  |
|         | 6630                           | 25.1                        | 44.4               | 0.131                                    |                       |  |

column influent has little or no effect (<10%) on the TCE transformation rate constant up to values of 370  $\mu$ M (11.8 mg/L), which is approximately an order of magnitude greater than the TCE concentration ( $\sim$ 30  $\mu$ M). The TCE transformation rate constant is reduced however at DO concentrations above 370 µM. The TCE transformation rate constant decreases by a factor of 4 at a DO concentration of 450  $\mu$ M (14.3 mg/L) and by a factor of 10 at a DO concentration of 600  $\mu$ M (19.2 mg/L). Additionally, the DO transformation rate constant,  $k_{oxy}$ , decreases by approximately a factor of 3 at the highest influent concentration (600  $\mu$ M, 19.2 mg/L). Although the presence of DO reduced TCE transformation in the column in some cases, it has no apparent effect on the product distribution. Ethane and trace amounts of ethene (<1%) are the only reaction products observed, and carbon mass balances of greater than 86% were obtained. This is consistent with previous results in the absence of DO (5).

In cases where the TCE transformation rate constant is reduced however, effluent [H2](aq) are 60 µM or lower (Table 3). Therefore, the reduced TCE conversion (and oxygen conversion) may be due to H<sub>2</sub> depletion in the system rather than oxygen out-competing TCE for active catalyst sites as this is consistent with results from the batch studies where  $k_{\rm rxn}$  decreased sharply at [H<sub>2</sub>](aq) less than 100  $\mu$ M. This hypothesis was tested by increasing the column influent  $[H_2](aq)$  to 1150  $\mu$ M but maintaining the DO concentration at 540  $\mu$ M (17.3 mg/L). By providing additional dissolved H<sub>2</sub>, the TCE conversion increased to 44.8%, indicating that DO and TCE do not compete for the same catalyst active sites, but rather that reduced TCE conversion in the presence of DO occurs as a result of H<sub>2</sub> limitations in the reactor. Batch data indicated that production of DCE isomers, vinyl chloride, and C4–C6 radical coupling products increases under H<sub>2</sub>limited conditions, but none of these products were detected in the reactor effluent.

Effects of Nitrate and Nitrite as Competitive Solutes. The effects of moderate to high concentrations of nitrate and nitrite on TCE conversion in the column are summarized in Table 4. The presence of nitrate at moderate (371  $\mu$ M, 23 mg/L) or high (1290  $\mu$ M, 80 mg/L) influent nitrate concentrations had no effect on TCE conversion in the column and conversion of nitrate through the column was essentially zero. Minor losses of nitrate (<5%) were observed the first day using the lowest nitrate concentration, but these losses ceased by the second day and are most likely due to adsorption of nitrate onto the catalyst support. The nonreactive behavior of nitrate using Pd-on-Al<sub>2</sub>O<sub>3</sub> catalysts is consistent with previous studies which reported that bimetallic catalysts such as Pd/Cu or Pd/Sn were required for the conversion of nitrate (10, 11, 14). Nitrate and TCE do not appear to compete for catalyst active sites because high concentrations of nitrate did not affect TCE conversion even though significant adsorption of nitrate to the catalyst surface is expected (14). Also, the presence of nitrate in the system did not lead to production of detectable chlorinated intermediates (DCE isomers and vinyl chloride) that may have occurred if adsorbed nitrate interfered with the adsorption

or reaction of TCE. Additionally,  $H_2$  consumption by nitrate is not a concern because nitrate is not reactive in the system.

Although nitrate transformation requires a bimetallic catalyst, nitrite has been shown to transform to N<sub>2</sub> (eq 3) using a Pd-on-Al<sub>2</sub>O<sub>3</sub> catalyst (*10*, *11*). The presence of nitrite in the column influent decreases TCE conversion in the column, but the effect is minor considering that the nitrite concentration is over 2 orders of magnitude higher than TCE at the highest influent nitrite concentration (Table 4). Influent nitrite concentrations ranging from 1565 (72 mg/L) to 6630  $\mu$ M (305 mg/L) decreased  $k_{TCE}$  approximately 10% to 13%, from 0.147 (value without nitrite present) to 0.13 min<sup>-1</sup>.

Steady-state nitrite conversion (eq 3) through the column ranged from 10% to 25%, with the lowest nitrite conversion occurring at highest influent nitrite concentration. Additionally, the column effluent pH increased from the normally measured value of 8.8 to 10.2 when nitrite was present in the influent, with no change in the column influent pH. The increase in effluent pH is consistent with the production of  $OH^{-}$  during the reduction of nitrite to  $N_2$  (eq 3) and is further evidence that nitrite reduction occurs. The lower percent conversion of nitrite at a higher nitrite concentration suggests that the nitrite transformation rate is approaching zero order with respect to nitrite, as might be expected at the high influent concentrations used. The minimal observed effect of nitrite on TCE transformation is therefore near the maximum expected as nitrite transformation is operating at or near saturation kinetics. The percent nitrite converted (10-25%) was always less than the percent TCE converted (43%), indicating that TCE is more reactive than nitrite in the system ( $k_{\text{TCE}}$  is approximately 2–5 times higher than  $k_{\text{nitrite}}$ ).

Increased reactor effluent pH, measured nitrite loss across the column, and a move toward zero-order nitrite transformation kinetics at high nitrite concentrations indicate that nitrite interacts significantly with the catalyst surface. However, the minor influence of nitrite on the observed TCE transformation rate constant (<13%) suggests that nitrite does not substantially compete with TCE for the same active catalyst sites. The lower reactivity of nitrite relative to TCE and the fact that nitrite concentrations in groundwater are typically very low indicate that nitrite will not lead to H<sub>2</sub> depletion in the reactor even though some H<sub>2</sub> is utilized for the reductive transformation of nitrite to N<sub>2</sub>.

In conclusion, the effect of  $[H_2](aq)$  on the TCE dehalogenation rate and product distribution is substantial, but complications such as production of chlorinated intermediate compounds and catalyst deactivation due to adsorbed radical coupling products can be avoided by maintaining  $[H_2](aq)$ at levels achieved by saturation at near ambient pressures (approximately 1000  $\mu$ M). The presence of dissolved oxygen expected in groundwater, even up to the saturation value of approximately 8.4 mg/L, will have little influence on the catalyst's ability to transform TCE as long as this  $[H_2](aq)$  is maintained above approximately 100  $\mu$ M. Similarly, nitrate and nitrite at concentrations expected under groundwater remediation conditions (<100 mg/L) will have little or no effect on the catalyst's ability to transform TCE.

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## Literature Cited

(1) Lowry, G. V.; Reinhard, M. *Environ. Sci. Technol.* **1999**, *33* (11), 1905.

- (2) Schüth, C.; Reinhard, M. Appl. Catal. B: Environ. 1998, 18, 215.
- (a) Schreier, C. G.; Reinhard, M. *Chemosphere* 1994, *29* (8), 1743.
   (4) Siantar, D.; Schreier, C.; Chou, C.; Reinhard, M. *Water Res.* 1996,
- 30 (10), 2315. (5) Lowry, G. V.; Reinhard, M. Environ. Sci. Technol. 2000, 34 (15), 3217.
- (6) McNab, W.; Ruiz, R.; Reinhard, M. Environ. Sci. Technol. 2000, 34 (1), 149.
- (7) Rylander, P. N. Hydrogenation Methods; Academic Press: New York, 1985.
- (8) Muftikian, R.; Fernando, Q.; Korte, N. Water Res. 1995, 29 (10), 2434.
- (9) Fogelberg, J.; Petersson, L. Surf. Sci. 1996, 350 (1-3), 91.
- (10) Horold, S.; Vorlop, K.-D.; Tacke, T.; Sell, M. Catal. Today 1993, 17 (1-2), 21.

- (11) Daub, K.; Emig, G.; Chollier, M.-J.; Callant, M.; Dittmeyer, R. Chem. Eng. Sci. 1999, 54 (10), 1577.
- (12) McNab, W.; Ruiz, R. Chemosphere 1998, 37 (5), 925.
- (13) Atkins, P. W. Physical Chemistry, 3rd ed.; W. H. Freeman and Company: New York, 1986.
- (14) Pintar, A.; Batista, J.; Levec, J.; Kajiuchi, T. App. Catal. B: Environ. **1996**, *11* (1), 81.

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