



CATALYTIC HYDRODEHALOGENATION OF CHLORINATED ETHYLENES USING PALLADIUM AND HYDROGEN FOR THE TREATMENT OF CONTAMINATED WATER

Cindy G. Schreier and Martin Reinhard*

Department of Civil Engineering

Stanford University

Stanford, CA 94305-4020, USA

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ABSTRACT

A kinetic model is presented for the catalytic hydrodehalogenation of chlorinated ethylenes using Pd and H₂ under water treatment conditions. All five chlorinated ethylenes, including tetrachloroethylene (PCE) and vinyl chloride, were completely removed from tap water within 10 minutes at room temperature by 0.5 g of 0.5% Pd on alumina and 0.1 atm H₂. Ethane accounted for 55-85% of the mass balance in these systems. Ethene was a reactive intermediate whose maximum concentration accounted for less than about 5% of the initial substrate. Palladium on granular carbon was also an effective catalyst, although ethane yield for PCE was somewhat lower than with Pd-alumina (55% versus 85%). The transformation of PCE was first order with respect to both substrate and amount of metal, with a half-life of $t_{1/2} = 9$ min for 0.055 μ mole Pd (583 μ g of 1% Pd on powdered activated carbon). Addition of ~10 mg/L of nitrite to the water decreased the rate constant by about 50%. The nitrite concentration decreased by about 25% over the course of the reaction. Addition of nitrate or sulfate had smaller effect on the rate of PCE transformation; chloride had no effect. The presence of oxygen greatly reduced the amount of ethane produced regardless of the catalyst support. Bisulfide poisoned the catalyst.

INTRODUCTION

Background

Widespread contamination of water supplies with chlorinated solvents and pesticides has spurred an intense effort to find efficient and cost effective treatment methods. Conventional methods for volatile organics removal include granular activated carbon (GAC) treatment or air stripping, which are non-destructive. These treatment methods simply transfer the contaminants from water into another medium (i.e. GAC or air) which must then be treated at an additional cost. Treatment methods that transform the contaminants into harmless products are, potentially, preferable since no secondary waste streams are produced. Currently, there are few technologies available which destroy halogenated compounds without producing harmful products. Oxidative and thermal processes are expensive and require the use of expensive chemicals and/or a high energy input. Moreover, both processes are prone to produce halogenated by-products which themselves may be hazardous.

Biological processes may be effective, but they require well controlled growth conditions for the microorganisms and, thus, may not always be practical.

The hydrodehalogenation (replacement of halide by hydrogen) of organic compounds using hydrogen gas and a noble metal catalyst is a widely used process in chemical synthesis (Rylander, 1985, 1979). The procedure effectively transforms a broad range of compound classes, including chlorinated aliphatics, olefins, and aromatics, which constitute the majority of the halogenated environmental contaminants. Despite this apparent versatility, the potential use of this process to treat hazardous waste or contaminated water has not received wide attention. Recently, however, Kovenklioglu et al. (1993), Balk et al. (1993), and Miyabe et al. (1993) disclosed in patents similar processes involving a metal (several were suggested, but palladium was preferred) and a reducing agent such as hydrogen gas, for the hydrodehalogenation of compounds in contaminated water and aqueous waste streams. The substrates considered included chlorinated ethanes, ethylenes, benzenes and phenols. In addition, Marques and co-workers (1993, 1994) demonstrated that chlorinated benzenes could be dehalogenated using Pd-on-carbon and H₂, aqueous base, and a phase-transfer catalyst. Tests in our laboratory have shown that chlorinated ethylenes (Schreier and Reinhard, 1995) and 1,2-dibromo-3-chloropropane (DBCP) (Siantar et al., 1995) are rapidly dechlorinated in drinking water with hydrogen gas as the primary reductant and palladium-on-carbon or palladium-on-alumina pellets as the catalyst.

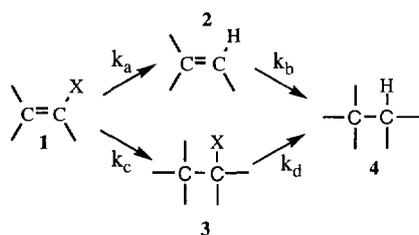
In addition to treatment of halogenated organics, catalytic hydrodehalogenation may be potentially useful for the treatment of reducible inorganic ions such as nitrate, selenate and arsenite. Sell et al., 1983, reported the removal of nitrate from drinking water using hydrogen gas and Pd-on-Cu as a catalyst. Organics removal was not observed, possibly because these authors optimized their process for nitrate removal (by limiting the amount of hydrogen supplied to the feed water). It is unclear yet whether or how nitrate or other contaminants affects the transformation of chlorinated compounds.

The work reported herein describes the ability of supported palladium and H₂ to transform chlorinated ethylenes. The type of support--alumina and granular or powdered carbon--was investigated as was the amount of metal required and the effect of some water quality parameters (specifically oxygen, nitrite, nitrate, and sulfate) on the rate of transformation. Catalytic hydrodehalogenation differs from the dehalogenation reactions recently reported by us and others (Schreier and Reinhard, 1994; Matheson and Tratnyek, 1994; Gillham and O'Hannesin, 1994; Lipczynska-Kochany et al., 1994) which use zero-valent iron or manganese powder in that the catalytic surface (Pd) and the electron donor (H₂) are supplied as two separate reagents. Consequently, this process may have significant advantages over the iron process because both the catalytic effect and the electron donor concentration can be optimized independently.

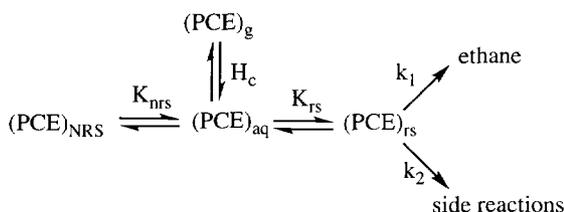
Mechanism and Pathway of Catalytic Hydrodehalogenation

In the presence of Pd and H₂, a halogenated vinylic compound, **1**, may undergo hydrodehalogenation and hydrogenation of the double bond to yield the alkane, **4**, as shown in Scheme 1 below (based on Rylander, 1985). Metals such as Pt and Rh can also catalyze hydrogenation, but they are usually less effective toward hydrodehalogenation. Nickel can be used, but it is more susceptible to poisoning. The first step of the transformation may be either hydrodehalogenation, to yield **2**, or hydrogenation to yield **3**. Compounds **2** and **3** may then react further via hydrogenation and dehalogenation, respectively, to give **4**. Both pathways are possible and may be competitive, because Pd is capable of dehalogenating alkyl halides even though they are more difficult to transform than vinylic, benzylic, or aryl halides (Rylander, 1985). For polyhalogenated ethylenes, the scheme can be extended with competitive pathways after each hydrodehalogenation step.

The mechanism of hydrogenation is thought to be a multi-step process in which two H atoms (formed by dissociative adsorption of H₂ on the catalyst) are sequentially transferred to the sorbed olefin. Sorption of H₂ and the olefin and transfer of the first H atom are reversible (Rylander, 1985). Consequently, if transfer of the second H atom is slow (as might occur under hydrogen-poor conditions) side reactions such as isomerization, coupling, or reaction with other organic contaminants may occur. The mechanism of the hydrodehalogenation step is uncertain, but Kraus and Bazant (1973) have suggested that it involves S_N2-type attack by an hydridic species.



Scheme I



Scheme II

Kinetic Models

The two pathways for substrate disappearance are summarized for tetrachloroethylene (PCE) in Scheme II. In addition to transformation to ethane (which is represented as the conversion of PCE to ethane since an exact mechanism is not known) and the side reactions mentioned above, partitioning of the substrate from the aqueous phase (aq) onto catalyst reactive sites (rs) and non-reactive sites (nrs) also occurs. Partitioning into the gas phase (g) was included because of the experimental procedure used involved headspace analyses. These partitioning steps are assumed to be in rapid equilibrium.

Assuming both reactions of PCE disappearance are pseudo-first order with respect to PCE, the rate of PCE disappearance is given by

$$-\frac{d\text{PCE}_T}{dt} = (k_1 + k_2)\{\text{PCE}\}_{rs} M_{\text{met}} \quad \text{Eqn. 1}$$

where PCE_T is the total moles of PCE, k_1 and k_2 are the pseudo-first order rate constants defined in Scheme II, $\{\text{PCE}\}_{rs}$ is the concentration of PCE on reactive sites (in mole/g of metal on the catalyst) and M_{met} is the mass of metal catalyst. Total PCE is given by $\text{PCE}_T = [\text{PCE}]_g V_g + [\text{PCE}]_{\text{aq}} V_{\text{aq}} + \{\text{PCE}\}_{rs} M_{\text{met}} + \{\text{PCE}\}_{\text{nrs}} M_{\text{sup}}$ where $[\]$ denotes moles/L, $\{\ \}$ is mole/g, V is volume, and M_{sup} is the mass of catalyst support. Using the equilibrium relations $H_c = [\text{PCE}]_g / [\text{PCE}]_{\text{aq}}$, $K_{\text{nrs}} = \{\text{PCE}\}_{\text{nrs}} / [\text{PCE}]_{\text{aq}}$ and $K_{\text{rs}} = \{\text{PCE}\}_{rs} / [\text{PCE}]_{\text{aq}}$ this equation becomes

$$\text{PCE}_T = (\{\text{PCE}\}_{rs} / K_{rs}) (H_c V_g + V_{\text{aq}} + K_{rs} M_{\text{met}} + K_{\text{nrs}} M_{\text{sup}}) \quad \text{Eqn. 2a}$$

$$\text{PCE}_T = (\{\text{PCE}\}_{rs} / K_{rs}) B \quad \text{Eqn. 2b}$$

where $B = (H_c V_g + V_{\text{aq}} + K_{rs} M_{\text{met}} + K_{\text{nrs}} M_{\text{sup}})$. Taking the derivative of both sides of Eqn. 2b and substituting $d\text{PCE}_T/dt$ into Eqn. 1 yields, upon rearrangement,

$$-\frac{d\{PCE\}_{rs}}{dt} = \frac{(k_1 + k_2)K_{rs}M_{met}\{PCE\}_{rs}}{B} \quad \text{Eqn. 3}$$

Assuming that $\{PCE\}_{rs}$ is proportional to $[PCE]_{aq}$, Eqn. 3 becomes

$$-\frac{d[PCE]_{aq}}{dt} = \frac{(k_1 + k_2)K_{rs}M_{met}[PCE]_{aq}}{B} \quad \text{Eqn. 4}$$

Note that this equation predicts that PCE transformation is first order in both substrate and the amount of metal. Eqn. 4 can be integrated to give

$$[PCE]_{aq} = [PCE]_{aq,0} \exp(-k_{obs}t) \quad \text{Eqn. 5}$$

where $[PCE]_{aq,0}$ is the aqueous phase concentration at $t = 0$ and $k_{obs} = (k_1 + k_2)K_{rs}M_{met}/B$.

If the initial reaction of PCE is rate-limiting, and there is no build-up of intermediates, then the rate of ethane appearance (in moles) is

$$\frac{d(\text{ethane})}{dt} = k_1 M_{met} \{PCE\}_{rs} = k_1 K_{rs} M_{met} [PCE]_{aq}$$

Substituting Eqn. 5 into this equation and integrating yields

$$\frac{\text{ethane}}{PCE_{T,0}} = \frac{k_1}{k_1 + k_2} (1 - e^{-k_{obs}t}) \quad \text{Eqn. 6}$$

where ethane is in moles, and $PCE_{T,0}$ is the initial total moles of PCE. Note that as the reaction progresses, $(1 - e^{-k_{obs}t}) \rightarrow 1$ and $k_1/(k_1 + k_2) \rightarrow \text{ethane}/PCE_{T,0}$, the yield of ethane.

The pseudo-first order rate constant, k_{obs} , is a function of experimental parameters such as the headspace and aqueous phase volumes as well as the Henry's constant of the substrate. A more fundamental rate constant for comparison purposes is $k_{catalyst}$, defined as

$$k_{cat} = (k_1 + k_2)K_{rs} = k_{obs}B/M_{met} \quad \text{Eqn. 7}$$

which is a function only of the type of catalyst employed. The constant, B (Eqn. 2b) can be estimated for a carbon catalyst support. Specifically, because the mass of metal is typically much smaller than the mass of the support (Pd is 1% by weight in these experiments) and because carbon is known to strongly sorb PCE, the $K_{rs}M_{met}$ term in Eqn. 2 is assumed to be negligible compared to the $K_{nrs}M_{sup}$ term. B , therefore, becomes

$$B = (H_c V_g + V_{aq} + K_{nrs}M_{sup}) \quad \text{Eqn. 8}$$

where $K_{nrs} = (\text{moles of PCE/g support})/[PCE]_{aq}$. If the degree of PCE sorption is known, K_{nrs} , and thus B and k_{cat} can be calculated.

Catalyst Support

In order to maximize surface area and minimize the amount of metal (and hence, cost) required, metal catalysts are often finely dispersed onto supports. Numerous materials may be used for this purpose including

alumina and carbon. Because changing from one support to another may have a fairly small effect on catalyst properties or may be critical to its activity (Smith, 1992) we investigated two types of commonly available catalyst--palladium on alumina (Pd-alumina) and palladium on carbon. The latter is available as palladium on granular activated carbon (Pd-GAC) or as palladium on powdered activated carbon (Pd-PAC).

Catalyst Inhibition and Poisoning

A reduction in catalyst activity (ability of a catalyst to transform a given substrate) or selectivity (ability of a catalyst to transform a substrate to a specific product) can occur in the presence of certain compounds. Although several compounds may potentially poison a metal catalyst, there is generally no method of predicting which, if any, will actually cause problems for a given reaction (Rylander, 1985). Some potential catalyst inhibitors or poisons include molecules containing elements such as N, P, As, Sb, O, S, Se and Te; compounds of catalytically toxic metals such as Hg, Pb, Bi, Sn, Zn, Cd and Cu; and molecules containing multiple bonds such as CO, cyanogen compounds, and strongly adsorbing organic molecules (Hughes, 1984). In this work we investigated some potential poisons/inhibitors likely to be found in water, specifically, oxygen, nitrite, nitrate, and sulfate.

EXPERIMENTAL

Procedures

Pd-alumina/Pd granular carbon: Experiments were conducted in 125 mL glass bottles equipped with cork-style Mininert™ valves. The bottles were filled with 60 mL of tap water which had been deoxygenated by purging with N₂ (this resulted in 60mL of headspace when the bottles were corked) and placed either in a glovebox containing a 90% N₂/10% H₂ atmosphere or in a glovebag with a 100% N₂ atmosphere. Then 0.5 g of either 0.5% Pd-alumina (Aldrich Chemical Co.) or 1% Pd on granular carbon (Pd-GAC) (4-8 mesh; Aldrich Chemical Co.) was added and the bottles were capped, removed from the anaerobic chamber, spiked with 1.0-1.1 μmoles of substrate (in 3.5 μL of methanol), and immediately placed on an orbital shaker (400 rpm). (Addition of 1.0 μmoles of substrate to a bottle yielded aqueous phase concentrations of about 10-16 μM (~1 mg/L), depending upon the Henry's constant of the compound. Note that the initial H₂ partial pressure was 0.1 atm if the bottles were filled in the glovebox and 0atm if they were filled in the N₂-containing glovebag.) Headspace samples were analyzed periodically for chlorinated ethylenes, ethene and ethane. Hydrogen additions were made by injecting H₂ into the aqueous phase via syringe. For some experiments, the catalyst was pre-reduced (exposed to hydrogen prior to reaction) by storing it in the glovebox (90% N₂/10% H₂ atmosphere) for at least 12 hours before use.

Pd-activated carbon powder: Experiments were conducted in 125 mL serum bottles to which aqueous phase and catalyst were added. The catalyst (1% Pd-PAC; Aldrich Chemical Co.) was added in the form of a slurry which was prepared immediately before it was to be used. The total aqueous phase was 60 mL. The bottles were then purged with nitrogen for 20-30 minutes to remove oxygen. Unless otherwise noted, the bottles were capped, 5 mL (200 μmoles) of H₂ was added to the aqueous phase via syringe and the bottles shaken at 400 rpm for 15 minutes to pre-reduce the palladium. The bottles were then spiked with PCE (1.1 μmoles in 3.5 μL of methanol) and shaking resumed. Headspace samples were taken periodically and analyzed for PCE and ethane. In some cases 100 μL aqueous samples were taken and analyzed for nitrite, nitrate, and sulfate.

Analyses

Headspace samples were analyzed for chlorinated compounds using gas chromatography with electrolytic conductivity detection (GC/ELCD). Headspace samples were analyzed for ethene and ethane using

GC/flame ionization detection (GC/FID). Nitrite, nitrate, and sulfate were quantified by analyzing 100 μ L aqueous samples using ion chromatography (IC).

RESULTS AND DISCUSSION

Effect of Catalyst Support on Product Distribution

The reduction of PCE to ethane in water by Pd-alumina was facile at room temperature even at the low hydrogen partial pressure of 0.1 atm (Figure 1a). Figure 1 depicts the normalized total μ moles of PCE and ethane in the bottle as a function of time when the catalyst was pre-reduced and the initial H_2 partial pressure was approximately 0.1 atm. Removal of PCE began immediately with the amount decreasing by 75% within 5 minutes. Concurrently and without a measurable delay, the amount of ethane increased and reached 85% of the initial PCE concentration within 10 minutes. Trace amounts (< approx. 2%) ethene were also observed, but disappeared by 30 minutes (data not shown). Clearly, at least some of the chlorinated substrate reacted via the upper pathway (k_a and k_b) in Scheme I. After 30 minutes the bottle was respiked with PCE. Two minutes later ($t=32$ minutes), the PCE was 98% removed while the amount of ethane increased again by 85% of the added PCE. The respiking procedure was repeated once more without apparent loss of reactivity. The reason for the apparent loss of 20% of the mass is unclear but could be due to side reactions which are unknown.

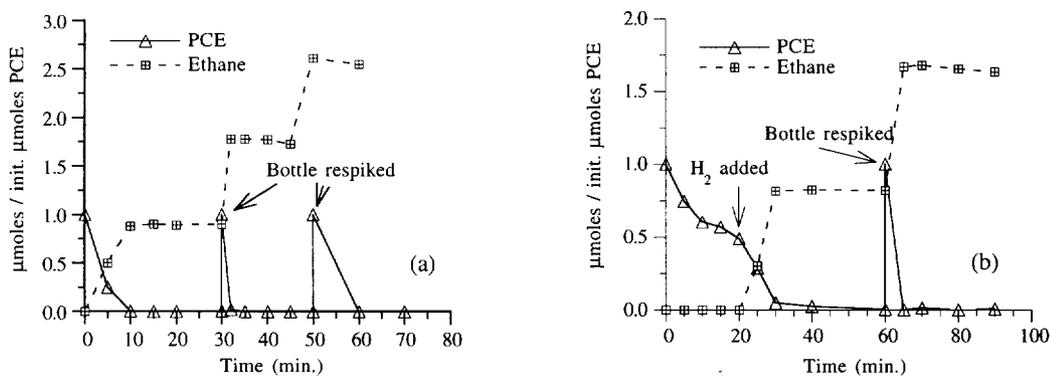


FIGURE 1. a) Removal of PCE and formation of ethane in N_2 -purged tap water containing 0.5g of 0.5% Pd-alumina (pre-reduced) and 0.1 atm initial H_2 . Respiked after 30 and 50 minutes. b) Same as (a) except Pd not pre-reduced and no initial H_2 ; H_2 added after 20 minutes; respiked after 60 minutes. Conditions: 400 rpm shaking, room temperature.

The role of H_2 was investigated by starting the reaction in a bottle in which both the catalyst and the water were stored under N_2 --that is, neither was exposed to H_2 and no oxygen was present. The data are shown in Figure 1b. As expected, ethane was not formed in the absence of H_2 ; the partial loss of PCE at this stage was presumably due to sorption. After 20 minutes, 5 mL of H_2 were added to the bottle resulting in a partial pressure of 0.08 atm. Ethane production commenced immediately, accounting for approximately 80% of the initial PCE within 10 minutes ($t=30$ minutes). Ethene was a trace, transient intermediate (data not shown); no vinyl chloride or other chlorinated ethylenes were observed. No loss of reactivity was observed when the bottle was respiked after 60 minutes. Similar results were obtained for trichloroethylene (TCE), *cis*- and *trans*-

dichloroethylene (cis-DCE, trans-DCE), and vinyl chloride (VC). The yield of ethane was slightly lower (70-75%) with these substrates compared to PCE, except for trans-DCE which was 55%. The maximum amount of ethene observed (approx. 5%) was greater than for PCE. The data for VC is shown in Figure 2 as an example.

The possibility of using carbon rather than alumina as the catalyst support was investigated because Pd-GAC is often used in chemical syntheses, is readily available, and because carbon is used to remove (via adsorption) organics from water. An experiment was conducted which was identical to the one depicted in

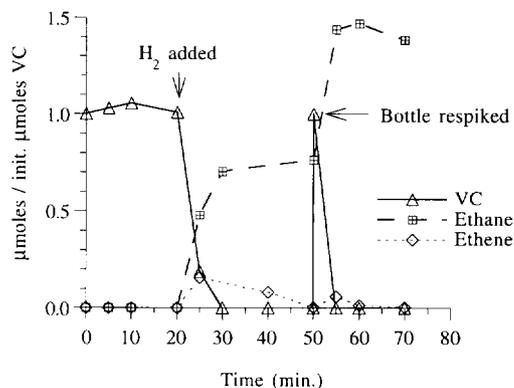


FIGURE 2. Removal of vinyl chloride and formation of ethane N_2 -purged tap water containing 0.5 g of 0.5% Pd-alumina (stored under N_2) and no initial H_2 ; 5.0 mL H_2 added after 20 minutes; respired after 60 minutes. Conditions: 400 rpm shaking, room temperature.

Figure 1a except that the pre-reduced catalyst was Pd-GAC rather than Pd-alumina. The results, shown in Figure 3a, were similar to those of the Pd-alumina case except that the yield of ethane was approximately 55% rather than 85%. The lower yield may be due to an increase in side reactions caused by the change in catalyst support. It is probably not due irreversible adsorption since in tests using Pd-PAC the amount of ethane produced was the same regardless of whether or not PCE was pre-adsorbed (see below).

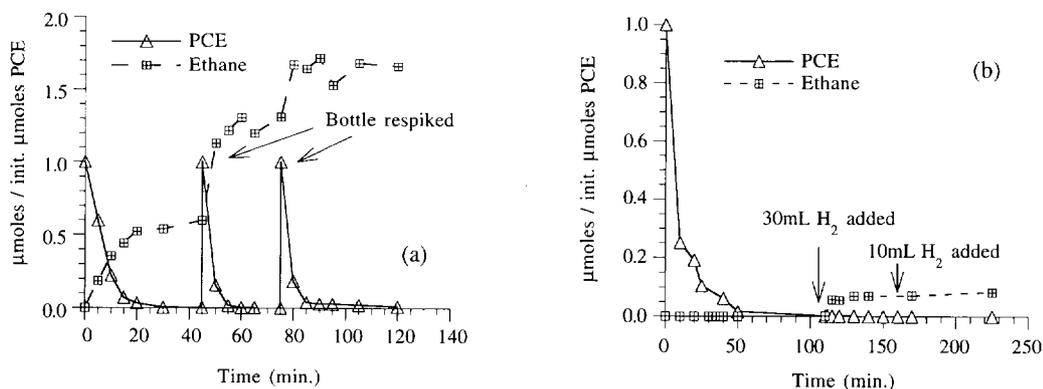


FIGURE 3. a) Removal of PCE and formation of ethane in N_2 -purged tap water containing 0.5g of 1% Pd-granular carbon (pre-reduced) and 0.1 atm initial H_2 . Respiced after 50 and 75 minutes. b) Removal of PCE and formation of ethane in air-purged tap water containing 0.5g of 1% Pd-granular carbon (pre-reduced) and no initial H_2 . 30 mL H_2 added after 110 minutes; additional 10 mL supplied after 160 minutes. Conditions as in Figure 1.

Effect of Oxygen on Product Distribution

The slightly slower reaction of substrate after the initial spike (compared to respikes) was repeatedly observed and was probably due to competitive reaction of Pd and H₂ with trace amounts of oxygen in the system. The reaction of Pd and H₂ with oxygen to form water is well-known and is, for instance, used to maintain anaerobic conditions in gloveboxes. In an experiment (data not shown) using air-saturated water and Pd-alumina which had only been exposed to air, PCE did not disappear. However, after the addition of 40 mL (1800 μmoles) of H₂, PCE was >99% removed within 10 minutes. The volume of H₂ added was approximately 1.5 times the estimated amount required to consume all of the oxygen in 60 mL of air and 60 mL of water. Concomitant with the disappearance of PCE was the appearance of ethane, which accounted for about 60% of the initial PCE. The lower ethane yield may be due to side reactions caused by the presence of oxygen. In a similar experiment using Pd-GAC, PCE sorbed to the carbon, and reacted only slightly to ethane upon later addition of H₂ (Figure 3b). Although ethane production in this case was initially rapid after the addition of H₂, production slowed greatly after about 10 minutes. The rapid increase was probably due to formation of ethane through the path in depicted Scheme II. The slower appearance may have been due to the slow conversion to ethane of some products of oxygen-induced side reactions. It is not clear whether the rate of ethane production also decreased in the Pd-alumina experiment because the experiment was terminated early. Additional work should be done to understand better the effects of oxygen and identify the remaining products.

Palladium on Activated Carbon Powder

Determination of kinetic parameters

In an effort to understand the mechanism of PCE transformation and the effects of some common anions on the reaction, experiments were conducted using Pd-PAC as the catalyst. Activated carbon powder rather than granular carbon was chosen in order to minimize potential intraparticle mass transfer effects and because the powder can easily be made into a slurry which was necessary for preparation of dilute solutions--determination of the PCE reaction order was achieved by using much less catalyst compared to the above experiments which slowed the rate of transformation. The observed pseudo-first order rate constants (k_{obs} in Eqn. 5), observed half-lives, and ethane yields are summarized in Table 1.

TABLE 1. Summary of data for Pd-PAC experiments. Unless otherwise noted, init. PCE=1.1 μmoles, Pd=0.055 μmole, H₂=200 μmoles; 60 mL Milli-Q water; 400 rpm shaking; room temperature.

Entry	Description		$k_{\text{obs}} \times 1000$ (min^{-1})*	$t_{1/2}$ (min)*	% Ethane**
1	Pre-reduced	A [†]	76±5	9.1±0.6	75
2		B	79±7	8.8±0.8	76
3	Pre-adsorbed		67±6	10.3±0.9	69
4	0.014μmole Pd	A	9±1	77±8	66
5		B	13±0	53±0	70
6	0.027μmole Pd	A	47±3	15±1	75
7		B	33±2	21±1	70
8	0.087μmole Pd		130±40	5.3±1.6	77
9	nitrite (8.4 mg/L)		39±6	18±3	63
10	nitrate (11 mg/L)		58±1	12±2	68
11	sulfate (18 mg/L)		66±12	11±2	69

* Errors are 95% confidence intervals.

** Percent yield after >99% PCE disappearance.

† A and B indicate duplicate bottles.

As shown in Figure 4a, the use of 9.7 mg/L of Pd-PAC (0.055 $\mu\text{mole Pd}/60\text{ mL solution}$) resulted in first order transformation of PCE. (See also Table 1, Entries 1-3.) The pseudo-first order rate constants were approximately the same regardless of whether the catalyst was pre-reduced (by mixing with H_2 before the addition of PCE) or whether PCE was first allowed to adsorb suggesting that H_2 transport to the surface is fast. (Note that k_{obs} was calculated using data $t \geq 10$ minutes because the pre-adsorbed case indicated that after this time, losses due to adsorption were insignificant.) The ethane yield (70-75%) was also similar in both cases (Figure 4b), suggesting that PCE was not irreversibly adsorbed to the carbon support. The yield was much

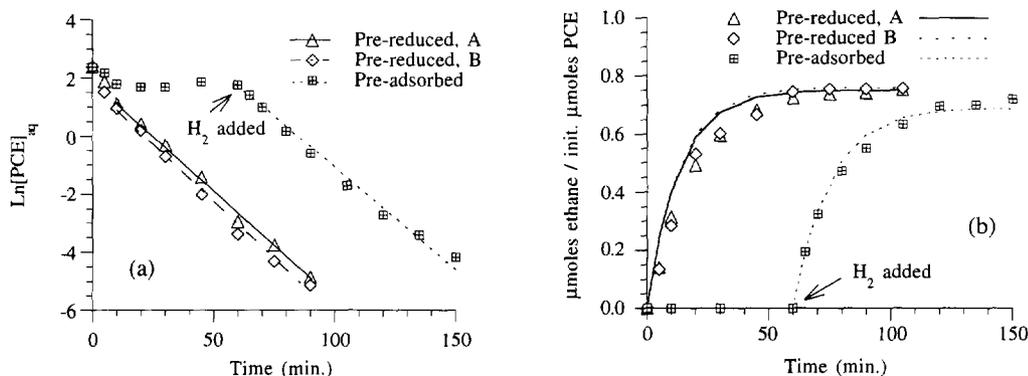


FIGURE 4. PCE transformation using 0.055 $\mu\text{mole Pd}$ (added as 1% Pd-PAC), 200 $\mu\text{moles H}_2$; 1.1 μmole initial PCE; 400 rpm shaking; room temperature. Pre-adsorbed = H_2 added after 60 minutes. a) First order disappearance of PCE; b) Appearance of ethane; symbols indicate measured data, lines indicate first-order model fits.

higher (70% versus 50%) than that obtained using Pd-granular carbon, however. The cause of this difference is unclear.

The appearance of ethane is depicted in Figure 4b. No lesser chlorinated ethylenes or ethanes (the most likely intermediates) were observed. Some ethene was produced, but it was a reactive intermediate whose maximum amount accounted for less than 2% of the initial PCE. Its presence does indicate, however, that at least some of the PCE was transformed via the upper pathway (k_a and k_b) in Scheme I. To determine whether ethane production was indeed first order as hypothesized, k_{obs} (obtained from $[\text{PCE}]_{\text{aq}}$ vs. time) and $k_1/(k_1+k_2)$ = observed ethane yield where substituted into Eqn. 6. The results are shown as the lines in Figure 4b. The rate of production is slightly lower than expected in the pre-reduced cases, but fits quite well in the pre-adsorbed case. The cause of the difference is unclear.

It should be noted that external mass transfer was apparently not rate limiting in these systems since an experiment conducted with shaking at 200 rpm instead of 400 rpm resulted in no significant difference in the rate constant (data not shown).

The equilibrium constant for adsorption of PCE onto carbon (K_{nrs}) can be calculated from the data in Figure 4a. According to the pre-adsorbed case, 0.5 μmoles of PCE was lost due to sorption. The aqueous phase concentration was 5.9 μM and the mass of the catalyst support was $5.8 \times 10^{-4}\text{ g}$. Thus, $K_{\text{nrs}} = 150\text{ L/g}$. Substituting this value into Eqn. 8 and using a Henry's constant of $H_c = 0.723$ (Gossett 1987) for PCE and $V_g = V_{\text{aq}} = 0.06\text{ L}$ yields $B = (0.10 + 150M_{\text{sup}})$.

A plot of $k_{\text{obs}}B$ versus amount of metal (Figure 5; see also Table 1, entries 1-2, 4-8) suggested a linear relationship as expected from Eqn. 7, indicating that in a first approximation, PCE transformation is first order with respect to the amount of metal. Additional experiments should be conducted, however, to determine

whether the relation holds if Pd is increased by increasing the metal loading (i.e. using 5% or 10% Pd-PAC) rather than by increasing the amount of catalyst.

The slope of the line in Figure 5 (obtained by forcing the regression through zero since no transformation is seen in the absence of catalyst) is $k_{\text{cat}} = 2900 \text{ L}/(\text{g min.})$. With this information, the amount of metal required to obtain a desired transformation rate can be estimated. Substituting Eqn. 8 into Eqn. 7 and noting that the $M_{\text{sup}} = M_{\text{met}}/x$ where x = the fractional metal loading of the catalyst, yields, upon rearrangement,

$$M_{\text{met}} = \frac{k_{\text{obs}}(H_c V_g + V_{\text{aq}})}{k_{\text{cat}} - (k_{\text{obs}} K_{\text{nrs}}) / x}$$

For example, if the desired half-life for PCE transformation is 5 minutes (that is, $k_{\text{obs}} = 0.14 \text{ min}^{-1}$), the reactor is devoid of headspace, and the catalyst will be 1% Pd-PAC, then

$$\left. \frac{M_{\text{met}}}{V_{\text{aq}}} \right|_{(t)_{1/2} = 5 \text{ min}} = \frac{0.14 \text{ min}^{-1}}{2900 (\text{L g}^{-1} \text{ min}^{-1}) - [0.14 \text{ min}^{-1} * 150 (\text{L g}^{-1}) / 0.01]} = 180 \mu\text{g Pd}$$

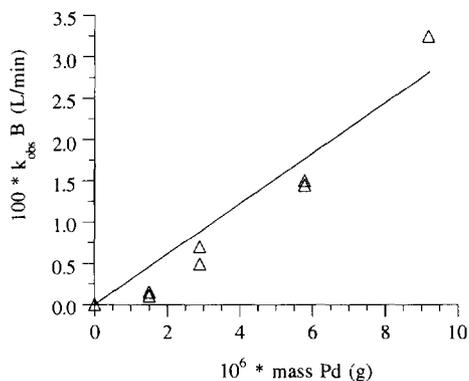


FIGURE 5. The effect of amount of Pd on transformation rate. 200 $\mu\text{moles H}_2$; 1.1 μmole initial PCE; 60 mL Milli-Q water; 400 rpm shaking; room temperature; Pd pre-reduced for 15 minutes before adding PCE.

Effect of nitrite, nitrate, sulfate, chloride and bisulfide

The effect of some ions often found in water, specifically nitrite, nitrate, and sulfate, was investigated. The results are shown in Figure 6 and in Table 1, Entries 9-11. The amount of each ion (supplied as the sodium salt) was 11 μmoles (approximately 10-25 mg/L) which was 10 times the amount of initial PCE and 200 times the amount of Pd. All three ions caused a decrease in PCE transformation rate, though the effect was greatest for nitrite which caused a 50% decrease in the rate constant. (Compare entries 1-2 and 9-11). The amount of ethane produced (Figure 6b; lines indicate models) was about 5-10% less than in the absence of these ions. The difference may have been due to an increase in side reactions (k_2 in Scheme II). Interestingly, of the three ions tested, only the concentration of nitrite decreased during the course of the reaction (Figure 7). The different catalyst used by us compared to Sell et al. (1983) probably explains why nitrate was removed from their system but not from ours.

The effects of chloride and sulfide were also tested since these are potential poisons. Addition of 10 mM sodium chloride to the aqueous phase had no detrimental effect on the rate of transformation or the yield of ethane (data not shown). This is consistent with the observation that transformation of 1 μmole of PCE is first order throughout the reaction (that is, no deactivation of the catalyst is evident) even though the number of chloride ions released is about 70 times the amount of Pd (0.055 μmoles) in the system. In contrast, addition of approximately 2 mM sodium bisulfide (in a 100 mM bicarbonate solution, pH 8) resulted in complete deactivation of the catalyst (data not shown). (The carbonate solution alone had no significant effect on the rate of PCE transformation.) The disappearance of some PCE disappearance in the first 10 minutes was attributed to adsorption onto the activated carbon. After this initial drop, the concentration remained constant. No ethene or ethane was observed. These results indicate that sulfide-containing water must be pre-treated, perhaps with aeration, before contacting the catalyst. No effort was made to regenerate the catalyst.

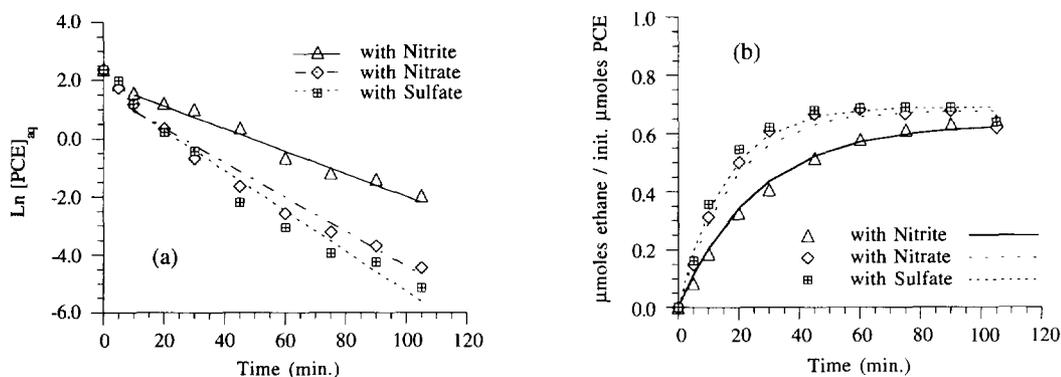


FIGURE 6. a) Disappearance of PCE. b) Appearance of ethane; symbol indicate measured data, lines indicate model fits. Conditions as in Figure 4 except that aqueous phase contains 11 μmoles (10-25mg/L) of stated ion.

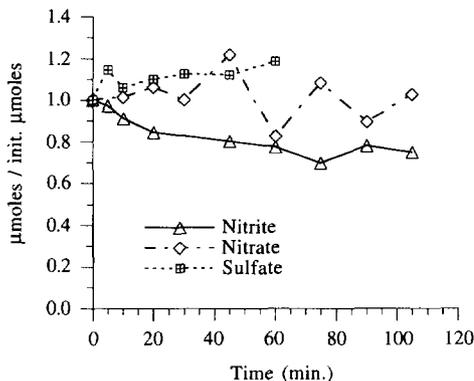


FIGURE 7. Change in concentration of ions with time. Same experiment as in Figure 6.

CONCLUSIONS

Catalytic hydrodehalogenation using supported Pd and H_2 appears to be a potentially viable method for the treatment of water contaminated with chlorinated hydrocarbons even in the presence of oxygen, nitrite,

nitrate, sulfate, and chloride. However, bisulfide poisoned the catalyst. Both alumina- and carbon-supported Pd readily transformed PCE to ethane and other unidentified products, though the ethane yield was greater for Pd-alumina. Pd on carbon may be better for water treatment, however, because PCE would still be removed (through adsorption rather than destruction) in the event of failure of the hydrogen supply, or in the presence of a large spike of a competing substrate. Transformation of sorbed PCE might then occur once optimal conditions are re-established. The lower ethane yields compared to Pd-alumina might be improved by increasing the hydrogen partial pressure, or by increasing the percentage of Pd on the carbon.

The amount of Pd-PAC needed to transform PCE at a specific rate (i.e., with a specified half-life) can be estimated for various reactor types. In particular, the effect of headspace and aqueous phase volume and the metal loading on the catalyst can be taken into account.

The presence of oxygen greatly decreased the amount of ethane produced regardless the type of catalyst used. Further work is needed to understand the effects of oxygen on PCE transformation, but practically, the effects can be avoided by deoxygenating the water prior to treatment.

The presence of some common ions, specifically nitrite, nitrate and sulfate, caused a relatively minor decrease in the rate of PCE transformation. The effect was greatest for nitrite which increased the half-life from about 9 minutes in the absence of ions to about 18 minutes. The mechanism of these effects (competition or catalyst poisoning) is not clear since of the three ions, only nitrite disappeared. This would be beneficial since water would not have to be pre-treated to remove the ions. The reduced rates of PCE transformation could probably be overcome by simply increasing the amount of catalyst employed.

Bisulfide completely deactivated the catalyst and would have to be removed from the water prior to contacting the catalyst.

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LITERATURE CITED

- Balko, E.N. Hoke, J.B., Gramiccioni, G.A. Hydrodehalogenation of Aromatic Compounds. United States Patent: 5,177,268, January 5, 1993.
- Gilham, R.W., O'Hannesin, S. F. Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron. Ground Water, 32, 958-967, 1994.
- Gossett, J. M. Measurement of Henry's Law Constants for C1 and C2 Chlorinated Hydrocarbons. Environ. Sci. Technol., 21, 202-208, 1987.
- Hughes, R. *Deactivation of Catalysts*, Academic Press, London, 1984.
- Kovenklioglu, S., Balko, E.N., Hoke, J.E., Farranto, R.J., Gramiccioi, A. Method of Hydrodehalogenating Halogenated Organic compounds in Aqueous Environmental Sources. United States Patent: 5,196,617, March 23, 1993.
- Kraus, M., Bazant, V. In *Catalysis*. Hightower, J. W., Ed., Am. Elsevier: New York, 1973, Vol. 2, p. 1073.
- Lipczynska-Kochany, E., Harms, S., Milburn, R., Sprah, G., Nadarajah, N. Degradation of Carbon Tetrachloride in the Presence of Iron and Sulfur Containing Compounds. Chemosphere, 29(7), 1477-1489, 1994.

- Matheson, L. J., Tratnyek, P.G. Reductive Dehalogenation of Chlorinated Methanes by Iron Metal. *Environ. Sci. Technol.*, 28, 2045-2053, **1994**.
- Marques, C.A., Selva, M., Tundo, P. Facile Hydrodehalogenation with H₂ and Pd/C Catalyst under Multiphase Conditions. *J. Org. Chem.*, 58, 5256-5260, **1993**.
- Marques, C.A., Selva, M., Tundo, P. Facile Hydrodehalogenation with H₂ and Pd/C Catalyst under Multiphase Conditions. 2. Selectivity and Kinetics. *J. Org. Chem.*, 59, 3830-3837, **1994**.
- Miyabe, K., Orita, N., Iwasaki, M., Tsurumaru, Y., Nakahara, T. A Method for Treatment of a Fluid Containing Volatile Organic Halogenated Compounds. *European Patent Office*: 0563669A1. October 6, 1993.
- Rylander, P.N. *Hydrogenation Methods*, Academic Press, New York, 1985.
- Rylander, P.N. *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, New York, 1979.
- Schreier, C.G., Reinhard, M. Transformation of Chlorinated Organic Compounds by Iron and Manganese Powders in Buffered Water and Landfill Leachate. *Chemosphere*, 29(8) 1743-1753, **1994**.
- Schreier, C.G., Reinhard, M. Catalytic Dehydrohalogenation and Hydrogenation using H₂ and Supported Palladium as a Method for the Removal of Tetrachloroethylene from Water. Preprint Extended Abstract, Division of Environmental Chemistry, 209th National Meeting of the American Chemical Society, Anaheim, CA, April 2-7, 1995.
- Siantar, D., Schreier, C.G., Reinhard, M. Transformation of the Pesticide 1,2-Dibromo-3-Chloropropane (DBCP) and Nitrate by Iron Powder and By H₂/Pd/Al₂O₃. Preprint Extended Abstract, Division of Environmental Chemistry, 209th National Meeting of the American Chemical Society, Anaheim, CA, April 2-7, 1995.
- Sell, M., Ross, B., Feist, H.R., Behling, R.-D., Kneifel, K., Peinemann, K.-V. *Proceedings of the Membrane Technology Conference, American Water Works Association*, Baltimore, MD, August 1-4, 1993.
- Smith, K., Editor. *Solid Supports and Catalysts in Organic Synthesis*, Ellis Horwood Ltd., 1992.