Aqueous Oxidation of Trichloroethene (TCE): A Kinetic and Thermodynamic Analysis


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AQUEOUS OXIDATION OF TRICHLOROETHENE (TCE): A KINETIC AND THERMODYNAMIC ANALYSIS

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An empirical kinetic rate law was determined for the aqueous oxidation of trichloroethene (TCE). By measuring both the rate of disappearance of TCE and the rate of appearance of carbon dioxide and chloride ion, mass balances were monitored to confirm that “mineralization” was the ultimate reaction. Dilute buffer solutions were used to fix pH and stoichiometrically sufficient amounts of dissolved oxygen were used to make the reactions zero-order in oxygen. Using standard chemical kinetic methods, two orders of magnitude were spanned in initial TCE concentration and used in the resulting double-log plot vs. initial rate (regressed using both linear and polynomial fits) to determine the rate constant and “true” reaction order (i.e., with respect to concentration, not time). By determining rate constants over the temperature interval 343-373K, an Arrhenius activation energy was determined for the reaction.

A study was made of the potential effect of buffer ligand concentration and type (phosphate, borate, acetate, carbonate, sulfate), ionic strength, specific electrolytes, and pH on the rate of TCE aqueous oxidation. The aqueous oxidation reaction rate was found to be pH dependent over the pH range pH 2 to pH 10 and strongly inhibited by high dissolved bromide concentration.

The equilibrium aqueous solubilities of TCE was determined by making reversed measurements from 294-390K. Together with the kinetic rate law, the thermodynamic data are required to develop in situ thermal remedial techniques for TCE and to model the reactive transport behavior of TCE in the subsurface.

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ABSTRACT: An empirical kinetic rate law was determined for the aqueous oxidation of trichloroethene (TCE). By measuring both the rate of disappearance of TCE and the rate of appearance of carbon dioxide and chloride ion, mass balance was monitored to confirm that “mineralization” was the ultimate reaction. Dilute buffer solutions were used to fix pH and stoichiometrically sufficient amounts of dissolved oxygen to make the reactions zero-order in oxygen. Using standard chemical kinetic methods, two orders of magnitude were spanned in initial TCE concentration and used in the resulting double-log plot vs. initial rate (regressed using both linear and polynomial fits) to determine the rate constant and “true” reaction order (i.e., with respect to concentration, not time). By determining rate constants over the temperature interval 343-373 K, an Arrhenius activation energy was determined for the reaction. The potential effects of buffer ligand concentration and type (phosphate, borate, acetate, carbonate, sulfate), ionic strength, specific electrolytes, and pH on the rate of TCE aqueous oxidation were studied. The aqueous oxidation reaction rate was found to be pH dependent over the pH range pH 2 to pH 10 and strongly inhibited by high bromide concentration. The equilibrium aqueous solubility of TCE was determined by making reversed measurements from 294-390 K.

INTRODUCTION:

Under oxidizing conditions, DNAPL components are thermodynamically unstable. Both ex situ and in situ methods, collectively known as “wet oxidation” using powerful oxidants like hydrogen peroxide, potassium permanganate, peroxydisulfate and ozone, have been developed capitalizing on this fact. However, when applied in situ these methods involve injection of fluids that, due to the very nature of plug flow, displace the contaminant. Efficient mixing can be problematic.

Another approach to in situ aqueous oxidation (Knauss et al., 1995) involves acceleration of rates using heat and is referred to as HPO (Hydrous Pyrolysis/Oxidation). The oxidant may include the dissolved oxygen already present in groundwater, the oxide minerals (e.g., MnO₂) already present in soils, or additional O₂ gas injected with steam into the subsurface. Benefits of the heated groundwater environment include enhancement of contaminant aqueous solubility and mobility by the in situ heating. Desorption and mobilization of DNAPLs from less permeable sediments will also be enhanced to achieve DNAPL destruction in areas which were commonly the source of problems for traditional pump and treat technologies.

Unfortunately, there is a lack of knowledge regarding the basic chemical mechanisms and rates of the aqueous/organic oxidation reactions for heated groundwater conditions. Basic thermodynamic data as a function of temperature required for transport modeling (e.g., solubilities, Henry’s Law constants, etc.) are also scarce. This work will begin to address the chemical kinetic and thermodynamic data information needs.

MATERIALS AND METHODS

The laboratory experiments were performed in flexible pure Au bag reactors employing a reusable pure Ti closure contained in a water-filled steel pressure...
vessel heated inside a large tube furnace. This hydrothermal system is ideal for studying the aqueous phase oxidation of pollutants because it allows repeated sampling of the reacting fluids while precisely controlling temperature and pressure for the duration of the experiment. In all experiments the gold bag was completely liquid filled; there was no headspace. A confining hydrostatic pressure of 1 MPa outside the gold bag was used for most runs, because this pressure was sufficiently high to keep the system single phase (liquid) within the gold bag at all temperatures studied.

Glass gas-tight syringes were used to collect separate samples for analysis of TCE (and any other hydrocarbons), pH, Cl\(^-\), CO\(_3\)\(^-\), and dissolved oxygen. Prior to collecting the TCE sample, the syringe was pre-loaded with an equal volume of HPLC grade methanol to act as a cosolvent. Analysis of samples for TCE (and other hydrocarbons) was made using GC and GC/MS. The aqueous samples were analyzed for inorganic anions (Cl\(^-\), Br\(^-\), SO\(_4\)\(^{-2}\), etc.) using HPLC/IC. Dissolved total CO\(_3\)\(^-\) (i.e., H\(_2\)CO\(_3\) + HCO\(_3\)\(^-\) + CO\(_3\)\(^{-2}\)) was determined using an IR CO\(_2\) analyzer. The sample pH was determined using glass electrodes calibrated following the NIST convention.

**RESULTS & DISCUSSION**

**Preliminary Experiments.** In order to identify alternate mechanisms to complete mineralization, a few runs were made with very high TCE concentrations (0.095 mmolal) and a stoichiometric excess of dissolved oxygen to make the reaction zero-order in O\(_2\). After approximately 16 days at 373K the concentration of TCE had dropped a thousand-fold and by 29 days was below the EPA maximum contaminant level of 0.000038 mmolal, representing a 2500-fold reduction. The analyses of total inorganic carbon and chloride ion indicated mass balance suggesting that complete mineralization had occurred.

With the initial TCE concentration set at 0.053 mmolal, initial dissolved oxygen concentrations were set at 0.094, 2.94 and 5.97 mmolal in experiments at 373K designed to investigate the reaction dependency on O\(_2\). Even at the lowest oxygen concentration, a stoichiometric excess of dissolved oxygen sufficient to completely oxidize the TCE was present. The results showed that no dependence on the dissolved oxygen concentration was apparent for the aqueous phase oxidation rates of TCE under these conditions. The results suggest that the only constraint at 373K for complete mineralization of TCE with respect to dissolved oxygen concentration is to have at least a stoichiometric amount of dissolved oxygen present to completely oxidize the TCE.

The molar ratio of H\(^+\) production to TCE destruction is 3 to 1, so in unbuffered systems where the pH of the solution is not fixed, a downward drift in the solution pH is observed as the reaction proceeds. Preliminary results suggest that the aqueous oxidation reaction rate is pH dependent (both acid and base catalyzed) over the pH range pH 2 to pH 10. For this reason the kinetic experiments were fixed to pH 7, the pH of normal ground water, using a dilute (1 mmolal) phosphate buffer. Results of kinetic runs made at the same pH using phosphate and carbonate buffers suggested that at these dilute concentrations there were no buffer effects.

In a series of runs to investigate ionic strength and other electrolyte effects, runs were made using Na salts of Cl\(^-\), Br\(^-\), SO\(_4\)\(^{-2}\), etc. No salt effects were noted, with the exception that high Br\(^-\) (≥ 10 mmolal) significantly inhibited aqueous oxidation of TCE.

**Kinetic Analysis.** The results of the preliminary screening experiments just
described suggest that in the presence of at least a stoichiometrically equivalent amount of dissolved oxygen ($O_2$(aq)), the rate of TCE aqueous oxidation is zero order in oxygen. The experimental matrix of kinetic runs was designed to take advantage of this so-called method of isolation, in which an unmeasured reactant is present in excess. In these runs, the $O_2$(aq) was actually measured periodically, but only to confirm that this reactant remained in excess throughout the entire run. As an experimental convenience, it was decided to fix initial $O_2$(aq) in all runs to the same value ($\approx 0.25$ mmolal) by equilibrating the fluids with the atmosphere before starting. This effectively meant that the experiments were limited to an initial TCE concentration below $\approx 0.18$ mmolal in order to maintain a stoichiometric abundance of oxygen. Because the reactant $H_2O$ is also the solvent, it is present in excess and the aqueous oxidation rate equation reduces to the form:

$$r_{TCE} = \frac{dC}{dt} = -kC_o^n$$

(1)

where $r_{TCE}$ is the rate, $k$ is the rate constant, $C$ is the concentration of TCE ($C_o$ being the initial concentration) and $n$ is the reaction order. This rate law may be linearized by taking the log of both sides to give:

$$\log r_{TCE} = n \log C_o + \log k$$

(2)

In the preferred differential method of kinetic analysis, separate runs are carried out at different initial concentrations, $C_o$. Initial rates are determined by measuring initial slopes. By using only concentration data collected at early time, potential catalysis or inhibition by reaction products is minimized. A double-log plot of log initial rate vs. log initial concentration has a slope of $n$, and an intercept equal to the rate constant, $k$. In order to span sufficient concentration space, it is desirable to vary initial TCE concentration by at least 2 orders of magnitude. These runs spanned the range 0.15 to 0.0015 mmolal TCE.

The influence of temperature on the rate of aqueous oxidation can be interpreted using the Arrhenius equation. This is commonly expressed in the form:

$$k = Ae^{E_a/RT}$$

(3)

where $k$ has been defined, $A$ is the pre-exponential factor (assumed to be independent of temperature), $E_a$ is the activation energy (assumed to be independent of temperature), while $R$ and $T$ have their usual meanings. By determining rate constants at a number of temperatures, one can use the linearized version of this equation:

$$\log k = \log A - \frac{E_a}{R}(1/T)$$

(4)

where a plot of rate constant, $k$, vs. $1/T$ will have slope $E_a/R$ and intercept $\log A$. These runs spanned the temperature range 343-373K.

**Rate Constant, Reaction Order & Activation Energy.** A regression analysis of the results at pH 7 and 90°C (Figure 1) yields the rate constant, $k$, and true reaction order with respect to TCE, $n_e$, for the aqueous oxidation of TCE. The results are $k = 5.77 \pm 1.06 \times 10^{-7}$ mols/kg-s and $n_e = 0.85 \pm 0.03$. The simplified rate expression for TCE aqueous oxidation under these conditions then becomes:

$$r_{TCE} = \frac{dC}{dt} = -(5.77 \pm 1.06 \times 10^{-7} \text{ mols/kg-s})C_o^{0.85 \pm 0.03}$$

(5)

at 90°C and pH 7 in the presence of stoichiometrically sufficient dissolved oxygen.

A regression analysis of the results over the temperature interval 343-373K
(Figure 2) yields the activation energy, $E_a = 108.0 \pm 4.5$ kJ/mol. Assuming that the 
pre-exponential factor is independent of temperature, the rate constant at any 
temperature may be calculated using:

$$\ln k_2 = \ln k_1 + \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where: the subscript 1 refers to the first temperature in K and subscript 2 refers to 
the second temperature in K and the other terms either have been defined or have 
their usual meaning. For example, the calculated rate at 25°C is about 2460 times 
slower than the 90°C rate of aqueous oxidation. At the average annual temperature 
of most ground waters contaminated with TCE, the rate would be significantly 
slower than at 25°C. This is why TCE degradation via aqueous oxidation is not a 
significant sink at normal temperature compared to other processes, except when 
microbially mediated.

\[\text{FIGURE 1. Double-log plot used to determine of log initial rate vs. log initial concentration having a slope of } n_e \text{ (true reaction order, i.e., with respect to concentration, not time) and an intercept equal to the rate constant, } k.\]
FIGURE 2. Arrhenius plot having a slope equal to $E_a/R$, where $E_a$ is the activation energy for the aqueous oxidation reaction.

**Solubility of TCE & PCE.** Equilibrium data (e.g., solubility data) measured over a wide temperature range allow calculation of the temperature dependency of thermodynamic quantities at constant pressure following the method of Clarke and Glew (1966). This method involves a linear multivariate regression analysis of the expression:

$$R \ln K = a_0 + a_1 \mu_1 + a_2 \mu_2 + a_3 \mu_3 + a_4 \mu_4 + a_5 \mu_5$$

$$- \sum_{i=0}^{n} a_i \mu_i \quad n \leq 5$$

where: $\mu_0 = 1$ and the $a_i$ are the partial regression coefficients of $R \ln K$ on the temperature variables $\mu_i$. The temperature variables $\mu_i$ are defined by:

$$\mu_i = x^i \sum_{n=1}^{\infty} \frac{n}{n+i+1} (-x)^{n-1} \quad 1 \leq i \leq 5$$

where: $x = (T-\theta)/\theta$, $T = 1(K)$ and $\theta$ is the reference temperature (= 298.15 K in this case). The relation of the first three regression coefficients to the thermodynamic parameters at $T = \theta$ are:
and by substituting Eqns. 6 and 7 into the expression $\Delta \bar{G} = \Delta \bar{H} - T\Delta \bar{S}$:

$$a_0 + a_1 = \Delta \bar{S} (\theta)$$

Applying the method of Clarke and Glew (1966) to the weighted (weighting factors proportional to the inverse of the measured variance - $\sigma^2$) $R \ln K$ data measured here, the following thermodynamic values are calculated at 298 K for TCE: $\Delta \bar{G}_{\text{soln}} = 11.282 (\pm 0.003)$ kJ/mol, $\Delta \bar{H}_{\text{soln}} = -3.35 (\pm 0.07)$ kJ/mol, $\Delta \bar{S}_{\text{soln}} = -49.07 (\pm 0.24)$ J/mol-K, and $\Delta \bar{C}_p \text{ soln} = 385.2 (\pm 3.4)$ J/mol-K.

FIGURE 3. Plot of $R \ln K$ for TCE vs. T (K), where: $K =$ equilibrium constant for the dissolution reaction: TCE$_{\text{aq}}$ = TCE$_{\text{aq}}$.

REFERENCES

