Chapter 1

OXIDATIVE DEGRADATION OF CHLORINATED ETHYLENES BY POTASSIUM PERMANGANATE

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Introduction

Chemical approaches for the remediation of ground water contaminated by chlorinated solvents commonly utilize reduction or oxidation schemes to transform organic contaminants. To date, most work has concentrated on reductive dechlorination, which occurs with hydrolysis (Jeffers *et al.*, 1989) and surface reactions involving pyrite, sulfide, biotite or vermiculite (Kriegman-King and Reinhard, 1992 and 1994) and zero-valent iron (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994). In particular, remedial schemes developed around zero-valent iron have shown considerable promise due to the relatively short half lives of the reactions.

There has been much less recent work on oxidation processes, even though experience has shown oxidative degradation to be fast with half lives of degradation for chlorinated organic compounds of the order of several minutes in a O_3/H_2O_2 system (Glaze and Kang, 1988). An apparent limitation with this reaction is that the key reactive intermediate hydroxyl radical, generated in this advanced oxidation process (AOP), strongly reacts with common inorganic species in ground water such as carbonate and bicarbonate (Hoign0 and Bader, 1983).

Not all oxidants suffer from this limitation. Permanganate, as a metal-oxo reagent (Gardner and Mayer, 1995), does not apparently rely on generating a hydroxyl radical to oxidize halogenated ethylenes as AOPs do. Experience spanning more than a century in laboratory-scale organic synthesis indicates that metal-oxo reagents can attack a double carbon-carbon bond (Stewart, 1964) powerfully through direct oxygen transfer (Wiberg and Saegebarth, 1957). This feature of metal-oxo reagents facilitates the degradation of chlorinated ethylenes with little scavenging of carbonate or bicarbonate.

Both laboratory and field experiments have demonstrated the ability of potassium permanganate to oxidize common chlorinated ethylenes like trichloroethylene (TCE) and tetrachloroethylene (PCE). In a series of batch experiments with both water (Vella and Veronda, 1992) and soil (Gates *et al.*, 1995), both TCE in water and TCE and PCE in soil were oxidized by permanganate. Compared to Fenton's reagent (a mixture of hydrogen peroxide and ferrous ion), permanganate was less dependent on pH and had a higher efficiency in water or soil treatment. Schnarr *et al.* (1998) observed in column tests that more than 90% of the TCE and PCE was degraded after flushing with several pore volumes of aqueous permanganate. Most of these experiments can be considered as a proof-of-concept that demonstrates the efficacy of the remedial concept with less emphasis on reaction pathways and kinetics.

Our investigations provide a detailed process-level understanding of the oxidative destruction of chlorinated ethylenes by permanganate. The specific objectives are (1) to examine reaction order, degradation rate and kinetic behavior of chlorinated ethylenes in reactions with permanganate, (2) to demonstrate the extent of dechlorination, and (3) to assess the effects of pH and other organic compounds in subsurface environment on the TCE degradation rate. Further work is underway to elucidate the detailed reaction pathways based on product analysis.

Chemical Background

There has been little direct process-oriented work on the oxidation of chlorinated ethylenes by permanganate. However, the body of work on alkene (C=C) oxidation in chemical synthesis provides a general understanding of the oxidation of chlorinated ethylenes. Figure 1.1 depicts a reaction scheme for the oxidation of ethylene in a neutral to weak acidic condition. The oxidation reaction begins with the formation of a cyclic hypomanganate ester (**1**) (Wiberg and Saegebarth, 1957; Wiberg *et al.*, 1973; Lee and Brownridge, 1973). The cyclic ester then undergoes oxidative decomposition in a neutral to weak acidic medium through hydrolysis, with fission of the Mn-O bonds to form a glycol aldehyde (Wiberg and Saegebarth, 1957). The glycol aldehyde could be further oxidized to glyoxylic acid and oxalic acid (**2**) (Arndt, 1981; Szammer and J▬ky, 1992). Another possible reaction pathway has the ester directly cleaved by permanganate to form two formic acids (**3**) (Wiberg and Saegebarth, 1957). All the carboxylic products could be further oxidized to carbon dioxide under certain conditions (Stewart, 1965).

The kinetics and mechanism of the reaction are affected when halogens substitute for hydrogen on ethylene. Burdon and Tatlow (1958) observed a faster oxidation reaction (a few seconds) with fluorinated alkene, as compared to hydrocarbon alkene, using permanganate in acetone during the synthesis of carboxylic acids. They thought that an electron-withdrawing group such as fluorine on the alkene facilitates the nucleophilic attack by permanganate ions. Lee (1982) also pointed out that the oxidation of hydrocarbons could sometimes be facilitated by prior halogenation of the oxidation site. However, Freeman (1975) considered the permanganate ion as an electrophile in the reaction. In his overview of activated complexes in addition reactions, he suggested that the attack of permanganate ion on carbon double bond, as an electrophilic addition, resulted in the formation of a five-member cyclic activated complex in the transition state. A chlorine as an electron-withdrawing substituent induces a deficiency of electrons at the carbon double bond of the substituted ethylene. Based on the concept

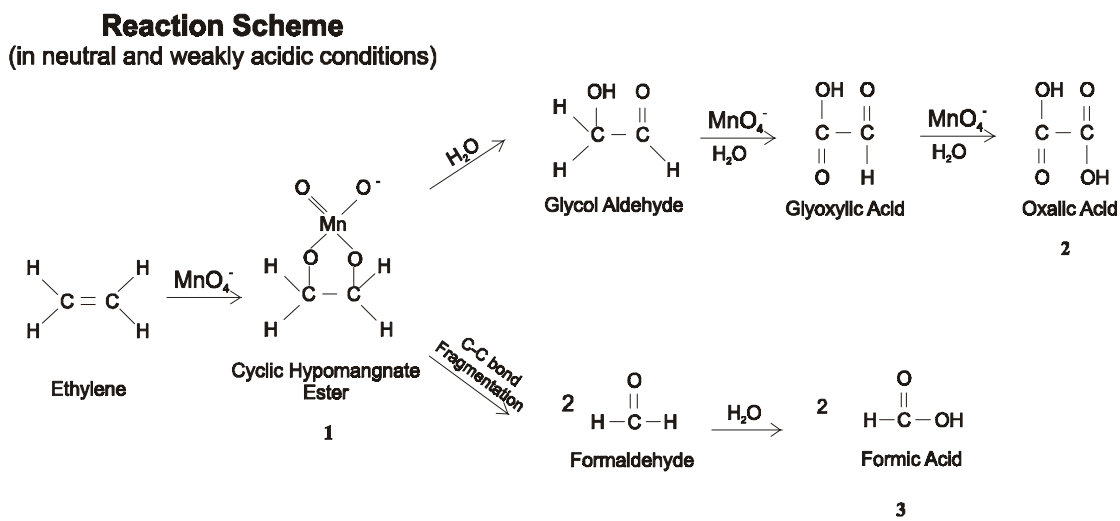

Figure 1.1. Reaction scheme. The oxidation of ethylene in a neutral to weak acidic condition.

of electrophilicity, a decrease of electron availability at the carbon double bond should decrease the rate of the electrophilic addition reaction.

Although only a few studies are available on the oxidation of halogenated ethylenes, we postulate the following reaction,

$$\alpha\, C_2Cl_nH_{4-n} + \beta\, MnO_4^- \rightarrow \gamma\, CA + \delta\, MnO_2 + \zeta\, Cl^- \qquad (1.1)$$

where α, β, γ, δ, and ζ are stoichiometric coefficients, $C_2Cl_nH_{4-n}$ represents various chlorinated ethylenes, including PCE, TCE and dichloroethylenes (DCEs), and CA is a group of intermediate products. These intermediate products could be either chlorinated or hydrocarbon carboxylic acids, which might be further oxidized to carbon dioxide under certain conditions as follows,

$$\gamma\, CA \xrightarrow{MnO_4^-} \eta\, CO_2 \qquad (1.2)$$

In oxidation by permanganate, pH is considered as a primary variable because it strongly influences the redox potential in a system. Table 1.1 lists the redox reactions, the corresponding potentials of various couples of manganese ions, and pH ranges in which each redox reaction predominates, based on Stewart's overview (1965) on oxidation by permanganate. Table 1.1 suggests that pH determines the number of electrons and couples of manganese ions involved in the over-all reaction. In general, the over-all redox potential of the system increases with decreasing pH. With organic substrates, however, mechanistic factors are of major importance, whereas the over-all free energy change of the oxidant, determined by its potential, is of minor importance. For the chlorinated ethylenes, a lack of knowledge about the reaction mechanism makes it unclear whether pH will affect the degradation rates of chlorinated ethylenes.

Materials and Methods

Materials

The chlorinated ethylenes, PCE (C_2Cl_4, 99+%), TCE (C_2HCl_3, 99.5+%), cis-DCE ($C_2H_2Cl_2$ 97%), trans-DCE ($C_2H_2Cl_2$ 97%), and 1, 1-DCE ($C_2H_2Cl_2$, 99%) were obtained from Aldrich Chemical Co.(Milwaukee, WI) and used as received. A high purity pentane of GC grade (Burdick & Jackson) from Baxter Diagnostics Inc. (McGaw Park, IL) was used as a liquid-liquid extraction solvent for analysis of chlorinated ethylenes. Potassium permanganate stock solution of 1-10 mg/mL was prepared by dissolving $KMnO_4$ crystals in Milli-Q water or phosphate-buffered Milli-Q water. The stock solution was stored in brown glass bottles and used freshly. The

Table 1.1. Redox reactions and their potentials of various couples of manganese ions.

Half-cell reactions (Mn)	E^0 (volts)	pH ranges in which the half-cell reaction predominates	
$MnO_4^- + e^- = MnO_4^{2-}$	+0.56	> 12	
$MnO_4^- + 3e^- + 2H_2O = MnO_2 + 4OH^-$	+0.59	3.5 – 12	pH high
$MnO_4^- + 3e^- + 4H^+ = MnO_2 + 2H_2O$	+1.70		pH low
$MnO_4^- + 5e^- + 8H^+ = Mn^{2+} + 4H_2O$	+1.51	<3.5	

reducing agents, thiosulfate and hydrazine hydrate (95+%), are both research grade and were prepared as a stock solution (6 mg/mL) for quenching the reaction in some kinetic experiments. A total organic carbon (TOC) stock solution (1000 mg C/L) for use in the TOC analysis was prepared by dissolving 0.2125 g of dried, reagent grade potassium hydrogen phthalate in 100 mL of Milli-Q water.

Experiments were performed using solutions prepared by dissolving the various chlorinated ethylenes in Milli-Q water (Millipore Corp., Bedford, MA), phosphate-buffered Milli-Q water, ground water, and contaminated ground water, respectively. Contaminated ground water was synthesized as a mixture of ground water and landfill leachate at various ratios. Ground water was collected from the uppermost perched aquifer below the CECOS/BFI landfill site in Cincinnati, Ohio, and landfill leachate was obtained from the same site. These waters were filtered by 0.2 µm filters to provide a homogeneous reaction solution but were not acidified. Apparently, most of metals in solution were oxidized when they were exposed to the atmosphere. For example, no ferrous iron was detected by phenanthroline colorimetric method. Thus, the effect of metal on oxidation of TCE by permanganate was not evaluated in this investigation.

Kinetic Experiments

Most of kinetic experiments were conducted in a sealed and water-jacketed spherical glass reaction vessel (Figure 1.2) where a zero headspace was maintained at all times. To test impact of subsurface environment on the reaction, experiment conditions were adjusted with pH ranging from four to eight. One experiment was run without a pH buffer to monitor the change in acidity of the solution. Other experiments were run with aqueous solutions prepared from phosphate-buffered Milli-Q water, ground water or contaminated ground water, and with initial concentrations of TCE ranging from two mg/L (1.52×10^{-5} M) to 10 mg/L (7.61×10^{-5} M). The test solution of contaminated ground water was a mixture of ground water with 2% or 20 % landfill leachate.

The rate at which the chlorinated-ethylene is degraded can be simply measured when the other reactant, permanganate, is held essentially constant through experiment. To maintain a constant concentration of $KMnO_4$, a more than ten-fold excess concentration of $KMnO_4$ was employed in each experiment. The activity of Cl^-, pH, temperature and the concentration of chlorinated ethylenes were monitored with time.

In addition to the above experiments, a set of experiments was designed to examine the consumption rate of $KMnO_4$ by organic compounds other than the chlorinated ethylenes. The organic compounds in ground water and contaminated ground water were characterized by TOC. In this set of experiments, $KMnO_4$ (20 mg/L) was isolated by using solutions containing various percentages of landfill leachate with excess concentration of TOC varying from 302 to 506 mg/L. The concentration of $KMnO_4$ was monitored through the experiment.

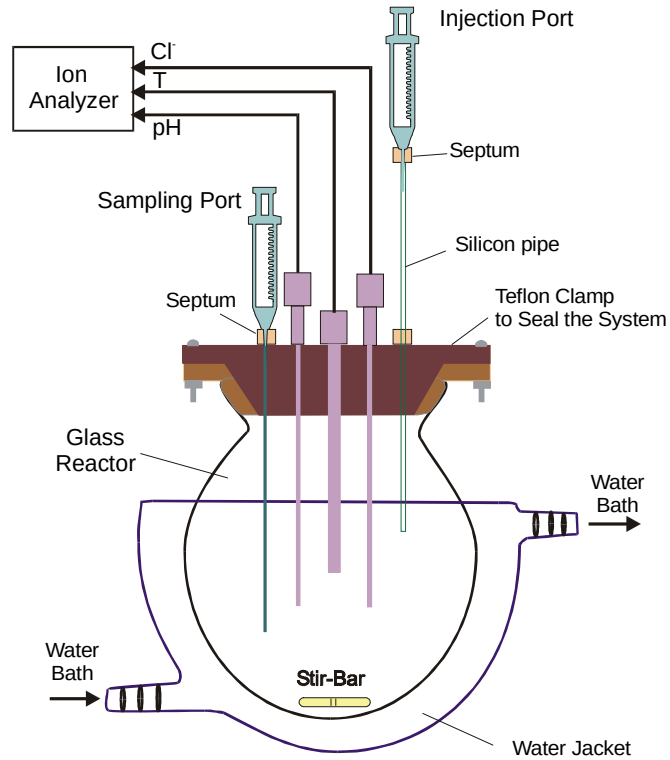

Figure 1.2. Schematic diagram of a reactor. In kinetic experiments, each sample aliquot was withdrawn from the sampling port by a syringe when the same volume of solution as the aliquot was injected via the injection port. Zero headspace was maintained at all times.

Chemical Analyses

(a) Analysis of chlorinated ethylenes. A sample ranging from 20-:L to 2-mL was collected at a fixed time interval from the reaction vessel using a syringe. The sample was diluted as necessary with Milli-Q water in 10-mL to 1-L volumetric glass flasks, depending on the concentration of the chlorinated ethylenes. A 10-mL sample after dilution was transferred to an extraction vial containing 4 mL of pentane. The vial was shaken for one minute and then equilibrated for 10 minutes. The extractant was analyzed for the particular chlorinated ethylene using a Fisons Instruments 8060 gas chromatograph equipped with a Ni^{63} electron capture detector and a DB-5 capillary column (J&W Scientific, Rancho Cordova, CA), 30 m H 0.32 mm I.D, with a film thickness of 1.0 µm. Helium was used as the carrier gas and nitrogen as the make-up gas. The gas chromatograph was calibrated daily with a minimum four calibration standards, and duplicate measurements were made for each sample or standard. If the standard deviation of measurements was greater than 10 %, another measurement

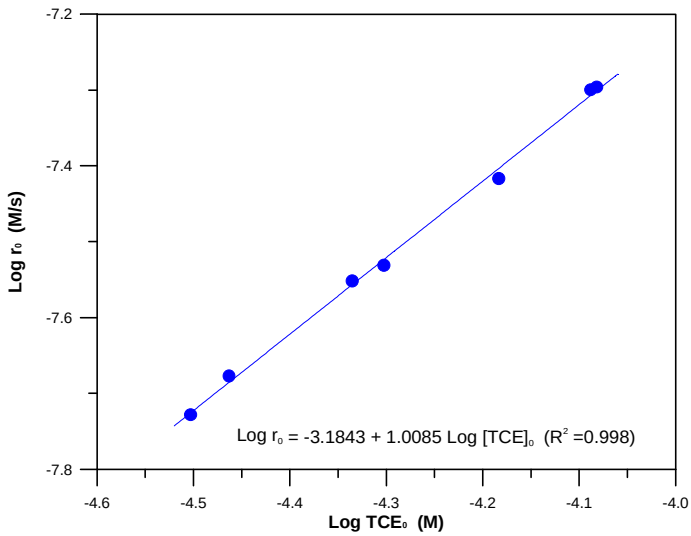

Figure 1.3. Plot of initial rates versus initial concentration for eight kinetic experiments. TCE ranging from 0.031 to 0.083 mM was oxidized by 1 mM MnO_4^- at pH 7.1. A slope $\alpha = 1.01 \pm 0.02$ confirms a first order reaction with respect to TCE.

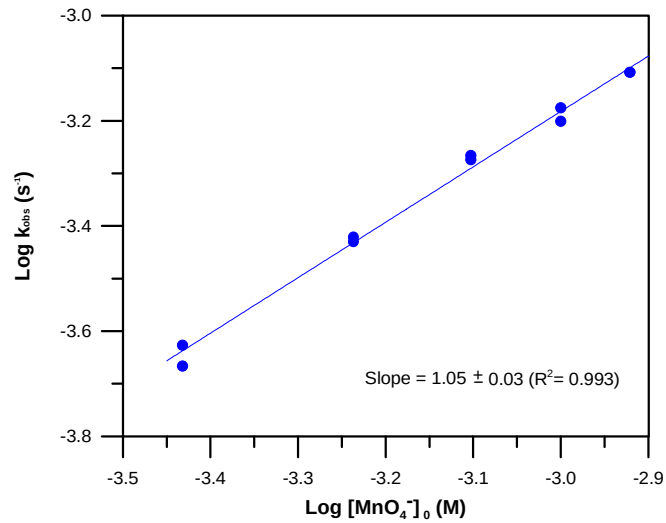

Figure 1.4. Plot of pseudo-order rate constant k_{obs} versus initial concentration of permanganate. TCE at 0.078 mM was oxidized by MnO_4^- concentration varying from 0.37 to 1.2 mM at pH 7.1. A slope $\beta = 1.05 \pm 0.03$ confirm a first order reaction with respect to MnO_4^-.

would be made.

(b) Analysis of $KMnO_4$ and its product. A 1.5-mL sample was collected and transferred into a quartz cuvette with 1 cm pathline and analyzed using a Varian Cary 1 UV-visible spectrophotometer at wavelengths ranging from 400 to 700 nm. In this range of wavelength, permanganate (MnO_4^-) and hypomanganate (MnO_4^{3-}) ions have a maximum of absorbance at 525/546 nm and 667 nm, respectively, while manganate (MnO_4^{2-}) has two absorbance peaks at 439 and 606 nm (Stewart, 1965). These species are almost transparent to radiation at 418 nm. The absorbance at 418 nm is a measure of either a cyclic hypomanganate ester (Wiberg *et al.*, 1973; Lee and Brownridge, 1973) or a soluble form of colloidal MnO_2 (Simandi and Jaky, 1976; Mata-Perez and Perez-Benito, 1985). These interpretations have been controversial for a long time.

(c) Measurement of Cl^-. Initially, the activity of Cl^- in the reaction vessel was measured using an Orion ion selective electrode (ISE) with a glass body (Model 9617). The ISE was calibrated using a standard solution of NaCl in the range from 0.1 to 10^{-5} M. Because of low sensitivity of the ISE to the trace amount of Cl^-, ranging from 10^{-4} - 10^{-5} M, additional samples were measured by a Buchler Digital Chloridometer, using a coulometric titration of chloride ions (Cotlove, 1958). Before the titration, a 0.1-mL aliquot of reducing reagent stock solution (6 mg/mL), hydrazine hydrate, was added to a 0.9-mL sample taken from the reaction vessel to quench the reaction in the sample solution. To prepare for the titration, the total 1-mL sample aliquot was added to a test vial containing 3-mL of an acid reagent comprised of 0.4 N HNO_3 and 40% glacial acetic acid. Finally, four drops of gelatin reagent were added to the test vial. The samples in the test vials were titrated at either the LOW or HIGH switch position in order to provide the proper concentration range from 3.3×10^{-3} to 33.3 mM.

(d) TOC analysis. TOC was analyzed using a Shimadzu TOC-5000 TOC Analyzer. The four standards for calibration were prepared by diluting the TOC stock solution to a concentration in the range of 10 - 60 mg C/L. All standards and samples were acidified with concentrated HCl and sparged with CO_2 free air. Samples of contaminated ground water and landfill leachate with high TOC concentration were diluted as needed in order for concentrations to fall within the calibrated range of the TOC analyzer. Standards and samples were analyzed in triplicate and the values of TOC were accepted when the standard deviation was less than 2%.

Results and Discussions

Reaction Order

Based on the Eq. 1.1, the degradation of chlorinated ethylenes can be described with the following general rate equation;

$$r = -\frac{1}{\alpha}\frac{d[C_2Cl_nH_{4-n}]}{dt} = k[C_2Cl_nH_{4-n}]^{\alpha}[MnO_4^-]^{\beta} \qquad (1.3)$$

When the concentration of $[MnO_4^-]$ is in excess, Eq. 1.3 can be simplified as Eqs.1.4 and 1.5.

$$r = k_{obs}[C_2Cl_nH_{4-n}]^{\alpha} \quad (1.4)$$

$$k_{obs} = k[MnO_4^-]^{\beta} \quad (1.5)$$

where r is a reaction rate, k is a rate constant, and k_{obs} is a pseudo-order rate constant because $[MnO_4^-]$ is effectively constant during the course of the experiment. By varying the values of $[C_2Cl_nH_{4-n}]$ and measuring reaction rate, the order α with respect to $[C_2Cl_nH_{4-n}]$ can be simply determined by a log-log form of Eq. 1.4:

$$\log r = \log k_{obs} + \alpha \log[C_2Cl_nH_{4-n}] \quad (1.6)$$

In a similar way but varying initial concentration of $[MnO_4^-]_0$ and measuring k_{obs}, the order β with respect to $[MnO_4^-]$ can be obtained by a log-log form of Eq. 1.5:

$$\log k_{obs} = \log k + \beta \log[MnO_4^-]_0 \quad (1.7)$$

To avoid complications from subsequent reactions or catalysis, an initial rate method (Casado *et al.*1986) was used here and Eq. 1.6 can be expressed as:

$$\log r_0 = \log k_{obs} + \alpha \log[C_2Cl_nH_{4-n}]_0 \quad (1.8)$$

The two sets of kinetic experiments were designed to estimate α and β values for TCE oxidation. The first set of eight experiments was conducted with initial TCE concentrations varying from 0.031 to 0.083 mM. The initial permanganate concentration was fixed at 1 mM for all experiments. The initial reaction rates were estimated as the tangent to the TCE concentration-time curve. As shown in Figure 1.3, the slope $\alpha = 1.01 \pm 0.02$ was calculated (based on Eq. 1.8) through a linear regression of the logarithm of initial rates versus the logarithm of initial TCE concentration (r^2=0.998). The reaction order with respect to TCE is unity and k_{obs} is a pseudo-first-order rate constant.

In the second set of five duplicate experiments, the initial concentration of TCE was fixed at 0.078 mM and TCE was reacted with excess MnO_4^- ranging from 0.37 to 1.2 mM. The pseudo-first-order rate constant k_{obs} for each experiment was obtained based on an integrated form of equation 1.4 at $\alpha = 1$. Thus, a slope of $\beta = 1.05 \pm 0.03$ was determined from a plot of the logarithm of k_{obs} versus the logarithm of MnO_4^- at initial concentration (Figure 1.4). The reaction order with respect to MnO_4^- is also unity.

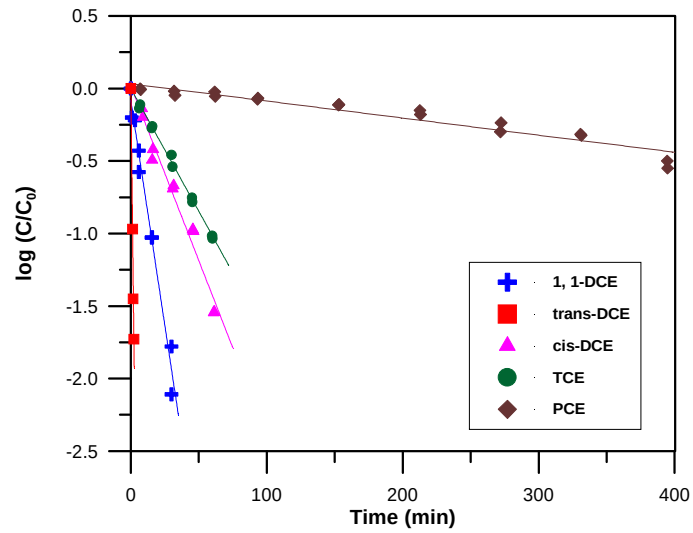

Figure 1.5. Degradation of chlorinated ethylenes by MnO_4^- (1 mM), at pH 7.1. Lines represent best fits using a pseudo-first-order kinetic model.

Hence, the results from both Figures 1.3 and 1.4 demonstrate that the initial reaction between TCE and MnO_4^- is a second-order reaction with α=1 and β=1. The second-order rate constant k of $0.66 \pm 0.01 M^{-1}s^{-1}$ can be estimated as shown in Figure 1.4.

Degradation of chlorinated ethylenes

Five chlorinated ethylenes were investigated through kinetic experiments using 1 mM MnO_4^-. As before, to maintain MnO_4^- in excess, the concentration of chlorinated ethylenes was at least 10 times less than MnO_4^-. Figure 1.5 depicts the degradation behavior of the chlorinated ethylenes. Apparently, the disappearance of chlorinated ethylenes can be simply characterized by a pseudo-first-order model. The pseudo-first-order rate constants were calculated from the results in Figure 1.5. Values range from 0.45 to 300×10^{-4} s^{-1} and are listed in Table 1.2. The degradation is rapid for most of compounds with half-lives generally less than 20 minutes. PCE is the exception with a half-life of 257 minutes or about four hours.

Figure 1.5 illustrates that the degradation rate is inversely

Table 1.2. Rate constants and half lives for the oxidative degradation of chlorinated ethylenes by permanganate (1 mM).

Chlorinated Ethylenes	k_{obs} (10^{-4} s^{-1})	Determination coef. of regression (r^2)	$T_{1/2}$ (min)
PCE	0.45±0.03	0.924	256.7
TCE	6.5±0.1	0.997	17.8
cis-DCE	9.2±0.5	0.976	12.6
trans-DCE	300±20	0.991	0.4
1,1-DCE	23.8±1.3	0.980	4.9

proportional to the number of chlorines as substituents on ethylenes. The fact that chlorine as a substituent slows down the reaction is consistent with the idea of electrophilic addition proposed by Freeman (1975). The high deficiency of electrons in the carbon double bond, induced by four chlorine substituents in PCE, reduces the rate of electrophilic attack. Therefore, PCE degradation is slow and its rate constant is small compared to the others.

Trans isomers are generally more stable than the corresponding cis isomers in alkenes. However, Figure 1.5 shows a higher reactivity of trans-DCE as compared to the degradation rate for cis-DCE. The ratio of k_{cis} to k_{trans} is only 0.03. It indicates that a significant steric effect was evident in the reaction. The steric interaction of cis substituents is caused by the change in bond angles in the addition reaction involving the large cyclic activated complexes, such as five- and six-membered cyclic complexes (Freeman, 1975). Apparently, a significant steric effect involving cis-DCE is consistent with the formation of the five-membered cyclic hypomanganate ester, which was originally proposed by Wagner (1895) and later supported by Wiberg and Saegebarth's (1957) experimental data.

Dechlorination

The oxidation of chlorinated ethylenes likely starts with a MnO_4^- attack on the C=C double bond to form a cyclic complex, similar to the oxidation of ethylenes. However, it is unclear whether dechlorination proceeds by hydrolysis or further oxidation during the decomposition of the cyclic complex. If chlorines remain in intermediate products after the cleavage of C=C bond, the most likely compounds would be chlorinated organic acids such as formyl chloride, oxalyl chloride and phosgene. Otherwise, all chloride ions would be released to the solution.

It is known that most of chlorinated organic compounds are much more toxic than the corresponding hydrocarbon compounds due to the existence of chlorine substituents. In treating chlorinated ethylenes, the ideal by-products and final products in the reaction are carboxylic acids and CO_2 without any chlorine substituent. To evaluate the extent of dechlorination of chlorinated ethylenes in more detail, the degradation of TCE was examined by monitoring Cl^- ions through a kinetic experiment. Stoichiometry indicates that the dechlorination of 1 M TCE (C_2HCl_3) releases 3 M Cl^- ions, or

$$C_2HCl_3 \rightarrow \gamma\, CA + 3Cl^- \qquad (1.9)$$

where CA is a group of carboxylic acids without chlorine substituents and γ is a group of stoichiometric coefficients, γ_1, γ_2, ,γ_n, for n potential carboxylic acids, respectively. When excess MnO_4^- is used for the oxidation of TCE, the degradation of TCE and the formation of chloride ions can be described by

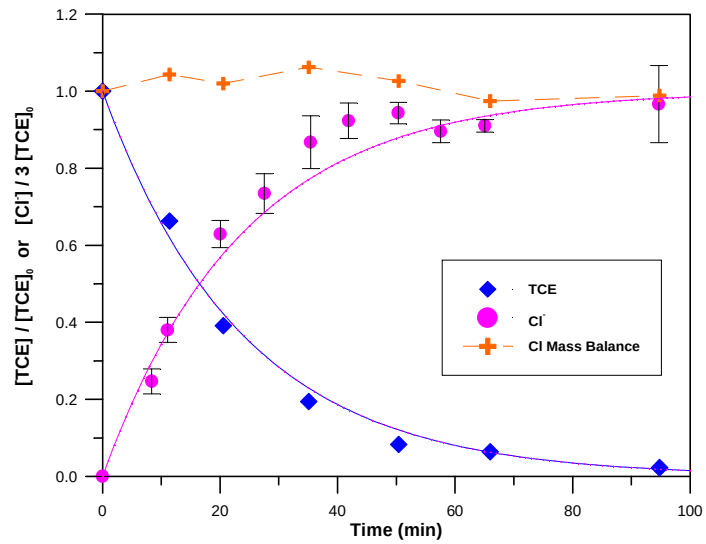

Figure 1.6. Liberation of Cl^- ions in the TCE oxidative transformation by 1 mM MnO_4^- at pH 7.1. The error bars for Cl^- ions are the standard deviation of triplicate samples. The solid lines were calculated from Eq. 10 with k_{obs} obtained from a best fit to TCE observations using Eq. 10(a).

$$\frac{[C_2HCl_3]}{[C_2HCl_3]_0} = e^{-k_{obs}t} \text{ (a)} \qquad \frac{[Cl^-]}{3[C_2HCl_3]_0} = 1 - e^{-k_{obs}t} \text{ (b)} \qquad (1.10)$$

where k_{obs} is the pseudo-first-order rate constant confirmed previously.

A kinetic experiment was conducted using 0.06 mM TCE with more than 15 fold excess of MnO_4^- (1 mM). The measurement of chloride concentration in the experiment was triplicated and the standard deviation is shown by error bars in Figure 1.6. About three times the concentration of Cl^- ions as compared to transformed TCE was observed over time (Figure 1.6). As shown in Figure 1.6, the total chlorine mass is accounted as both chlorine substituents in untransformed TCE and chlorides liberated from transformed TCE. This result indicates that the amount of chlorine substituents remaining in intermediate products is negligible.

The pseudo-first-order rate constant k_{obs}=7.0±0.5 $\times 10^{-4}$ s^{-1} was obtained from a best fit to the data points of TCE concentrations using Eq. 1.10(a). Based on a k_{obs} of 7.0×10^{-4} s^{-1}, both the degradation of TCE and the formation of Cl^- with time, as predicted from Eq. 1.10 (see lines in Figure 1.6), coincided very well with the observations. The kinetic results from this experiment suggest that the complete dechlorination be achieved rapidly during the decomposition of the cyclic complex after TCE is transformed.

Change in Acidity and pH dependence

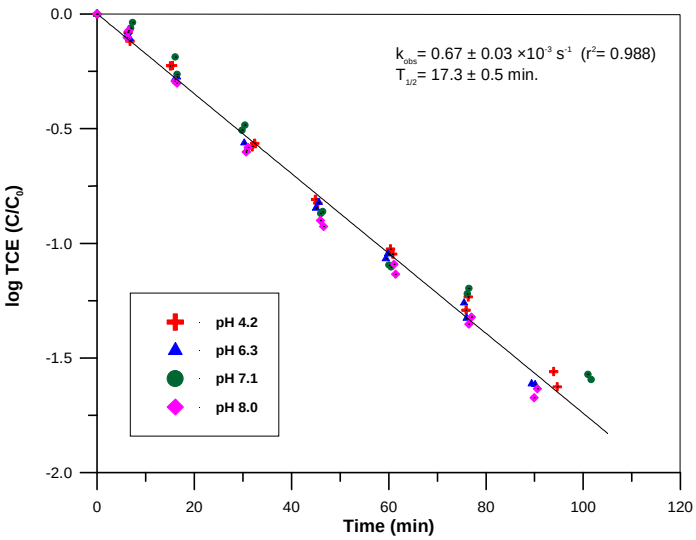

Figure 1.7. Pseudo-first-order plot of TCE transformation in 1 mM MnO_4^- over the pH range of 4-8. Rate constant k_{obs} = 0.67 ± 0.03 × 10^{-3} s^{-1} and half life $T_{1/2}$ = 17.3 ± 0.5 minutes.

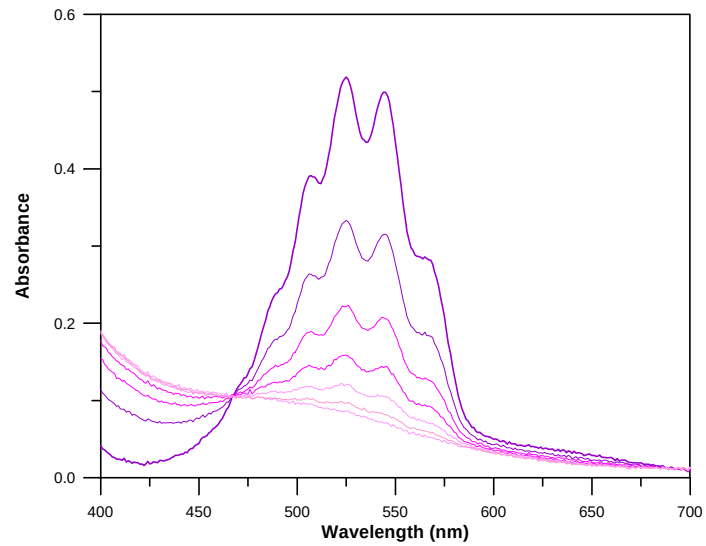

Figure 1.8. Overlay of UV-vis spectra at time intervals of 10 minutes during TCE (3.81 mM) oxidation by MnO_4^- (0.23 mM) at pH 7.1. The solid bold line is the initial MnO_4^- spectrum and the dashed line is the final spectrum due to a product from the decomposition of MnO_4^-.

The formation of carboxylic acids has been proposed to accompany the rapid decomposition of the cyclic complex. To examine the change in acidity of the solution due to the production of carboxylic acids, an experiment with a high concentration of TCE (0.76 mM) reacting with 3.8 mM MnO_4^- was conducted without the pH buffer. A drop in pH to 2-3 was observed within several minutes. Stewart (1965) pointed out that pH of the solution would be close to the pK of an acid produced in the reaction using permanganate. The carboxylic acids that likely formed would be oxalic acids, formic acids and so on. Oxalic acid has a pK_1=1.23 and a pK_2=4.19, and formic acid has a pK=3.75. A more detailed analysis of these carboxylic acids is now underway.

The effect of pH on the TCE degradation rate was studied over the pH range of 4-8 at constant concentration of MnO_4^- (1 mM). The pseudo-first-order rate constants (k_{obs}) obtained from four duplicate experiments are within 0.63-0.69× 10^{-3} s^{-1} with standard deviation up to ± 0.04× 10^{-3} s^{-1}. Apparently, they do not show strong pH dependence in the pH range 4-8. A TCE degradation rate, independent of pH, is in agreement with the suggestion that neither hydrogen nor hydroxyl ions significantly facilitate the attack by permanganate on C=C in TCE in an initial transformation step, where a cyclic complex forms. It is possible that pH affects the reaction afterwards. In a later step, when hydrolysis and further oxidation proceed, it is well known that the decomposition of the complex is highly pH dependent and that both permanganate and hydroxyl ions compete for reaction with a common cyclic intermediate (Wiberg and Saegebarth, 1957). A typical example is diol formation in a basic solution and ketol formation in a neutral solution.

To obtain the TCE disappearance rate over the pH range 4-8, log [TCE]/[TCE]$_o$ is plotted versus time for all data points from eight kinetic experiments at four pH levels with 1 mM MnO_4^-(Figure 1.7). A linear regression with a determination coefficient of 0.988 gives a rate constant k_{obs}=0.67±0.03 × 10^{-3} s^{-1}. A second-order rate constant, thus, can be simply estimated as k=0.67±0.03 M^{-1} s^{-1} by dividing 1 mM MnO_4^-. TCE degradation by permanganate is rapid with a half-life about 17 minutes.

Permanganate Decomposition and Products

Figure 1.9 shows the spectra of the reacting solution over time. The absorbance at both 525 and 546 nm at the beginning of the reaction (see a solid bold line in Figure 1.8) is representative of the initial concentration of MnO_4^- (0.23 mM). The reduction in absorbance with time in a first-order fashion indicates a decreasing concentration of MnO_4^-. A slight decrease in absorbances at 606 and 667 nm suggests that MnO_4^{2-} and MnO_4^{3-} apparently do not form as reaction products. At a wavelength 418 nm, the spectrum of the initial solution has the lowest absorbance and MnO_4^- is almost transparent to the source light. The increase of absorbance at 418 nm with time indicates the formation of a decomposition product of MnO_4^-. Based on independent observations when crotonic and cinnamic acid were oxidized by MnO_4^- , respectively, both Wiberg *et al.* (1973) and Lee and Brownridge (1973) interpreted a similar spectrum (a dashed line in Figure 1.8) as indicative of cyclic hypomanganate ester. However, Simandi and Jaky (1976) and Freeman *et al.* (1981) using an iodometric technique believed that it was a manganate (IV) with the +4 oxidation state.

In our spectrophotometric examination, all final spectra

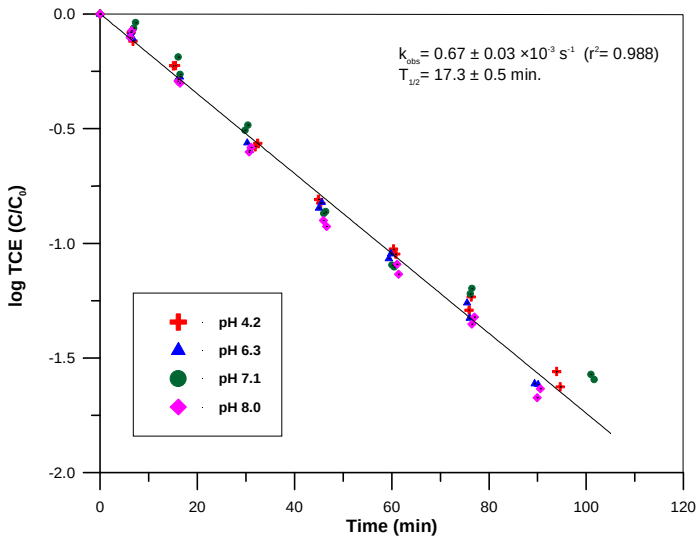

Figure 1.9. Log A versus log λ for the spectrum recorded at 80 minutes after the reaction between MnO_4^- (0.23 mM) and TCE (6.85 mM) at pH 8.2. The linear relationship with a slope =-4.22±0.05 obeys Rayleigh's law.

representing a decomposition product of MnO_4^- in TCE oxidation show a linear relationship between the logarithm of the absorbance and the logarithm of the wavelength. A typical plot of log A versus log λ has been reproduced in Figure 1.9. The linear relationship with the slope of -4.22±0.05 appears to be a reflection of Rayleigh's law, which can be written as in Eq. 1.11,

$$A = \frac{C}{\lambda^4} \quad (a) \qquad \log A = \log C - 4 \log \lambda \quad (b) \qquad (1.11)$$

where A is the absorbance, λ the wavelength, and C a constant depending on the polarizability, cell path length, mass and concentration of the colloidal particles. As a consequence of Rayleigh's law, the lost energy is due to light scattering by a product present in the form of colloidal particles. Figure 1.9, thus, confirms the suggestion that the product is actually soluble colloidal manganese dioxide.

Permanganate Consumption in Contaminated Ground Water

Permanganate is a powerful and reactive oxidant that would likely oxidize other organic compounds existing in ground water or contaminated ground water. The presence of these compounds would reduce the rate of TCE oxidation because of competition for the permanganate. To compare TCE loss rate in various solutions containing different quantities of other compounds, experiments were designed using 2 mg/L (0.015mM) TCE reacting with 20 mg/L (0.13 mM) MnO_4^- in the Milli-Q water, ground water (TOC < 2 mg/L), and contaminated

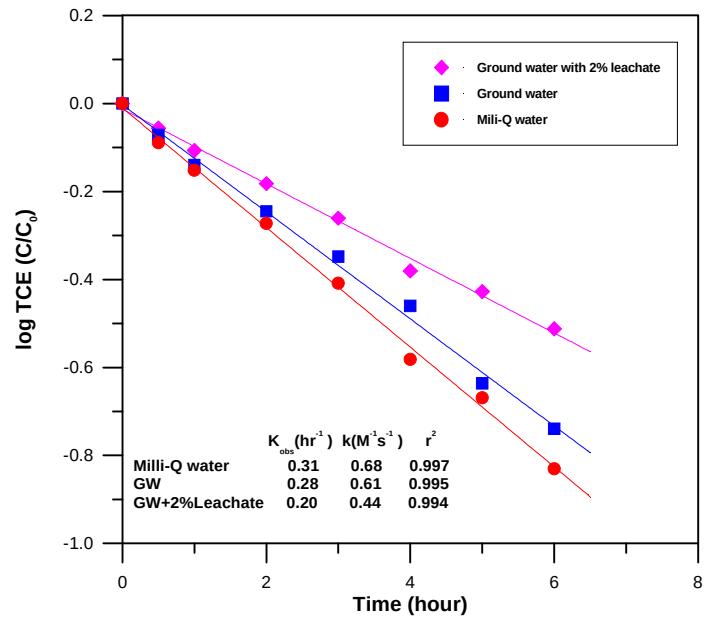

Figure 1.10. Comparison of TCE degradation by 0.13 mM (20 mg/L) MnO_4^- in Milli-Q water, ground water, and contaminated ground water (2% leachate). Lines represent best fits using a pseudo-first-order kinetic equation.

ground water (TOC = 10 mg/L), respectively. The contaminated ground water was synthesized by mixing ground water with 2% landfill leachate. Figure 1.10 depicts the reduction of TCE degradation rate due to the consumption of permanganate by other compounds in the solution. Based on the ratio of second-order rate constant in ground water (k_{GW}=0.61 M^{-1} s^{-1}) to that in Milli-Q water (k_{MQ}=0.68 M^{-1} s^{-1}), the TCE degradation rate in ground water was slightly decreased by 10%, compared to that in Milli-Q water. In the ground water contaminated by 2% landfill leachate, the second-order rate constant (k_{CGW}) is 0.44 M^{-1} s^{-1}. The rate was reduced to 65 % of that observed in Milli-Q water.

Although chlorinated ethylenes are the most frequently detected ground-water contaminants at hazardous waste sites, they are often found with other organic compounds. Accounting for the effects of competition in multi-contaminant solutions is complicated by the fact that many different organic compounds could be involved and many of which may not be identifiable. As a first-step in dealing with the issue of complex aqueous solutions, we provide results of several experiments involving ground water and contaminated ground water, where the relative abundance of these other organic compounds is represented by total organic carbon (TOC).

Clearly, using TOC to represent other reactive compounds assumes that all compounds present in solution would react with permanganate, which is able to oxidize most organic contaminants characterized by carbon-carbon double bonds (e.g. most alcohol, ketones, organic acids, phenolic compounds, and

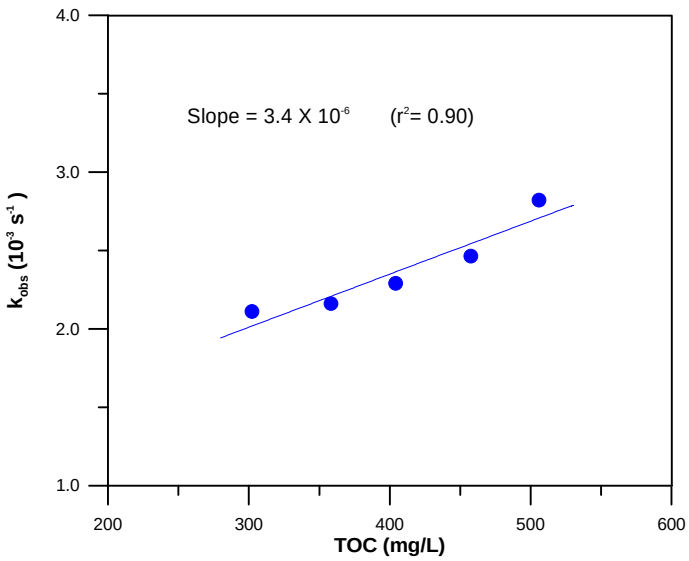

Figure 1.11. Plot of the maximum pseudo-first-order rate constant (k_{obs}) versus TOC concentration.

humic substances). Apparently, the competition of TOC for permanganate varies from site to site. However, the simplified kinetic-reaction model, which accounts for the general effect of other organic compounds in the reaction, would be a quick approach to evaluate the site-specific consumption of permanganate by TOC for a field application.

Here, we describe a simple and quick evaluation method for estimating site-specific consumption of permanganate and for predicting TCE degradation in a multi-organic compounds system. The approach is based on a series of experiments in an aqueous reaction system contaminated by landfill leachate from a sanitary landfill at age less than 10 years. The majority of organic compounds in this type of leachate is short chain volatile fatty acids (Lu *et al.*, 1985) and level of TOC mainly reflects the quantity of short chain organic acids present in the system

Experiments were designed using 20 mg/L (0.13 mM) MnO_4^- reacting with excess TOC prepared from landfill leachate at five different concentrations from 302 to 506 mg/L. MnO_4^-, as a monitoring species, was measured over time. The MnO_4^- disappearance rate is the greatest at the beginning of the 30-minute reaction period. A simple pseudo-first-order kinetic equation fits the initial 6 data points well during the first 10% of reaction time in a plot of logarithm of MnO_4^- versus time, which provides a slope indicating a maximum rate constant for permanganate decomposition. Figure 1.11 is a plot of the derived decomposition rate constant against TOC concentration. The rate constant (k_{obs}) depends almost linearly on TOC concentration. The over-all kinetic behavior of TOC reacting with MnO_4^- for this specific site is close to second-order. It indicates that the majority of organic compounds represented by TOC at this site react with MnO_4^- in second-order kinetics, which is reasonable for most reactions involving short chain organic acids based on previous studies in organic chemistry (Aendt, 1981 and Freeman, 1975). To simplify the evaluation of MnO_4^- decomposition by TOC, a second order kinetic equation was used and the second order rate constant $k_{TOC\text{-}MnVII}$ = 3.40×10^{-6} L/mg s^{-1} was obtained from the slope of a linear fitting line in Figure 1.11. Assuming that a single compound is utilizing MnO_4^- at the same reaction rate as all reacting organic compounds, reflected by TOC, the effective molecular weight of the compound will be equivalent to a composite molecular weight for all reacting compounds. This assumption provides a way of assessing the general impact on MnO_4^- utilization and of estimating an effective consumption rate of MnO_4^- by a broad spectrum of organic compounds. In this case, if the composite weight is between 50 and 300 g, the maximum rate constant for MnO_4^- decomposition by TOC is in the range from 0.17 to1.02 M^{-1} s^{-1}. This rate constant is similar to that observed for TCE.

To predict the TCE degradation in the system involving TOC, TCE and MnO_4^-, the rate equations are simplified based on the over-all kinetic behavior of TOC in the contaminated ground water we tested,

$$\frac{d[TCE]}{dt} = -k_{TCE-MnVII}[TCE][MnO_4^-],\quad [TCE](t=0) = [TCE]_0 \tag{1.12}$$
$$\frac{d[TOC]}{dt} = -k_{TOC-MnVII}[TOC][MnO_4^-],\quad [TOC](t=0) = [TOC]_0$$
$$\frac{d[MnO_4^-]}{dt} = -(k_{TCE-MnVII}[TCE] + k_{TOC-MnVII}[TOC])[MnO_4^-],$$
$$[MnO_4^-](t=0) = [MnO_4^-]_0$$

The equations can be generalized as follows

$$\frac{dy_i}{dt} = f_i(t, y_1, y_2, y_3),\quad y_i(t=0) = y_{i0},\qquad i = 1, 2, \text{and } 3. \tag{1.13}$$

where y_1, y_2, and y_3 represent TCE, TOC and MnO_4^-, respectively. Second order rate constants derived from previous experiments were used ($k_{TCE\text{-}MnVII}$ = 0.67 $M^{-1}s^{-1}$ and $k_{TOC\text{-}MnVII}$ = 3.40×10^{-6} L/mg s^{-1}). Equation 1.13 was solved numerically using the Runge-Kutta method with adaptive step-size control. In this case, the molar concentration of TOC is unknown without a composite molecular weight for TOC. However, it can be find from experimental data by solving an inverse problem.

Three experiments were conducted in a highly contaminated ground water containing 101 mg/L TOC. TCE at a fixed initial concentration of 2 mg/L reacted with three different concentrations of MnO_4^- (20, 80, and 120 mg/L). The data points in Figure 1.12 illustrate the TCE degradation at various concentrations of MnO_4^-. To model the experimental data using Eq. 1.13, an initial composite weight of 50 g was assigned to compute TCE degradation with time and the residual between predicted TCE and observed TCE. The automatic adjustment of the composite weight with a fixed step was made until a minimum residual was calculated. A composite molecular weight, 176 g, for TOC was obtained based on the

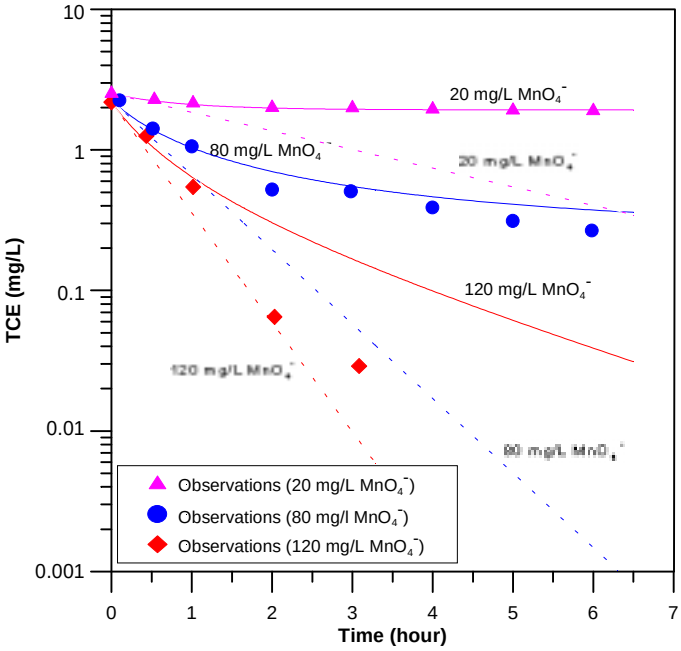

Figure 1.12. TCE degradation by MnO_4^- at various concentrations in a synthesized contaminated ground water containing 101 mg/L TOC. The solid lines were calculated using $k_{TCE\text{-}MnVII}$ = 0.67 M^{-1} s^{-1} and $k_{TOC\text{-}MnVII}$ = 0.60 M^{-1} s^{-1}at composite weight of 176 g for TOC. The dashed lines were calculated for TCE degradation in Milli-Q water without TOC.

first experimental data (20 mg/L MnO_4^-). The simulated results with a composite weight of 176 g match the observed rate of TCE degradation very well. In the second experiment, where 80 mg/L MnO_4^- was used, the simulated TCE-time curve is consistent with that observed in the first hour but deviates at later time. The same behavior was evident in the third experiment in which a relatively high concentration of MnO_4^- (120 mg/L) was used. However, the later-time deviation in the third experiment is much larger than that in the second. The observed TCE loss with time in the third experiment is close to the calculated result for Milli-Q water without TOC (the dashed line in Figure 1.12). Apparently, reduction in the TCE degradation rate due to the presence of other organic compounds was much less than expected with a high concentration of MnO_4^-. These results do not necessarily imply that some of the MnO_4^- was not being used in competing reactions with TOC. We believe that there was an actual increase in the TCE degradation rate. In effect, the increase in TCE degradation rate masked the effect of competition with TOC. The increased TCE loss rate could be caused by the large amount of colloidal MnO_2 produced in the reaction with the high concentrations of TOC and MnO_4^-. In the third experiment, the calculations indicate that 91 mg/L (0.58 mM) MnO_4^- was lost and converted to MnO_2. Meanwhile, 2.15 mg/L (0.016 mM) TCE and 99 mg/L of the other organic compounds represented by TOC were transformed. The MnO_2 has been reported to catalyze reactions between MnO_4^- and many organic compounds (Perez-Benito *et al.*, 1987; Perez-Benito and Arias, 1991).

The approach used in this study provides a way for estimating site-specific permanganate consumption by other organic compounds in field applications. This same procedure can be extended to evaluate permanganate removal by organic matter, mainly humic and fulvic acids, after being transported away from the treatment zone. To predict the TCE degradation rate in the system involving multiple matrixes, the rate constant $k_{TOC\text{-}MnVII}$ in equation 1.12 can be expanded to a sum of rate constants of permanganate utilization by TOC from various matrixes. In a system with high concentrations of MnO_4^- and TOC, an additional component need to be added into the modeling to account for the autocatalysis of MnO_2. A further study is now underway to examine autocatalysis of MnO_2 on TCE degradation rates.

Conclusions

This study shows that chlorinated ethylenes can be rapidly degraded by permanganate in aqueous solution. The half lives of TCE, cis-1, 2-DCE, trans-1,2-DCE and 1,1-DCE with 1 mM MnO_4^- range from 0.4-18 minutes. The half-life of PCE, however, is much longer, about four hours. In PCE degradation, the attack of permanganate ion, as an electrophile, is slowed by the deficiency of electrons in the carbon-carbon double bond induced by four chlorines in PCE. The ratio of k_{cis} to k_{trans} (0.03) represents a much higher reactivity of trans-DCE than that of cis-DCE. The significant steric effect of cis substituents on reaction rate supports the postulate that a five-membered cyclic complex is formed during the transition state and leads to an intermediate product, the cyclic hypomanganate ester.

Extensive kinetic studies of TCE oxidation by permanganate suggest that TCE degradation is a second-order reaction. The reaction can be reasonably described through major known reactants and products:

$$C_2HCl_3 + MnO_4^- \xrightarrow{k_1} I \xrightarrow{k_2} \gamma CA + MnO_2 + 3Cl^- \qquad (1.14)$$

where I is a cyclic complex, CA is carboxylic acids, and γ is their stoichiometric coefficients. In the first reaction step, the permanganate attack, as an electrophilic addition, on the C=C bond in TCE, leads to the formation of a cyclic complex. k_1 at this step is a second-order rate constant. The fact that the rate constant k_1 is independent of pH over the range 4-8 indicates that this attack is not affected by either hydrogen or hydroxyl ions. In the second step, however, the decomposition of I may involve hydrogen or hydroxyl ions as suggested by numerous studies on the oxidation of other organic compounds by permanganate in chemical synthesis. The reaction in the second step proceeds rapidly and k_2 is an unknown-order rate constant. A dechlorination of the complex (I) over time was observed in the kinetic experiments. The results show that Cl^- ions are

completely liberated from I immediately after its formation. Because the rate constant k_2 is much greater than k_1, the liberation of Cl^- ions in the kinetic experiment is in excellent agreement with the calculation based on a second-order reaction model using k_1. Therefore, the reaction rate in Eq. 1.14 can be approximated by the rate-limiting step (the first step) using the second-order rate constant k_1. Over the pH range 4-8, a k_1 value of 0.67 ± 0.03 M^{-1} s^{-1} at 21° C was calculated based on eight experiments.

The essentially complete dechlorination and possible formation of organic acids suggest that the degradation products of chlorinated ethylenes are much less harmful than parent compounds and miscible with water. In an in situ scheme-based permanganate flushing, those products would be readily removed from ground water as flushing proceeds. Research is continuing to identify the carboxylic acids and to elucidate the pathways of formation and further oxidation of acids.

In TCE oxidation, spectrophotometric evidence shows that permanganate is reduced to form soluble colloidal manganese dioxide. The consumption of permanganate in ground water with low TOC is limited. Ground water contaminated by landfill leachates, however, will consume permanganate depending on the TOC level. A simple and quick approach was used to estimate permanganate consumption by TOC. TCE degradation in a system involving TCE, TOC, and MnO_4^- was modeled with a system of ordinary deferential equations (Eq. 1.13) and solved using the Runge-Kutta method. The simulated results are consistent with the observations at early time but deviate from those at later time, especially in the experiment with a relatively high concentration of permanganate. A greater TCE degradation rate than expected at later time might be caused by autocatalysis on the surface of colloidal MnO_2 produced in the reaction. Competition of TOC for permanganate would be offset by the presence of a large quantity of MnO_2, which promotes the reaction between TCE and permanganate.

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