

Decrease of Chloroethyl in Metallic Iron-Water Systems

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Abstract: Batch experiments examining the kinetics and mechanism of vinyl Chloroethyl (VC) reduction by metallic iron in aqueous systems were performed. The effects of various iron loadings, VC concentrations, pH conditions, temperatures, and Fe-(II)/Fe(III) chelating agents (1,10-phenanthroline, 2,2'-bipyridyl, and nitri-lotriacetic acid) on reduction kinetics were examined. Ethylene was the major carbon-containing product of VC reduction under all conditions examined, indicating hydrogenolysis. The reaction was pseudo-firstorder with respect to aqueous VC concentration. The amount of VC adsorption on iron surfaces was estimated from the rapid initial loss of VC from solution, and the result adsorption isotherm was linear over the concentration range examined. The first-order kinetics and the linear adsorption for VC suggest that the portion of VC sorption to surface reactive sites relative to nonreactive sorption sites is constant, unlike the behavior observed for the higher chlorinated ethenes. The activation energy of the reaction was measured to be 41.6 (2.0 kJ/mol, sufficiently large to indicate that the chemical reaction at the surface, rather than aqueous phase diffusion to the surface, controls the overall rate of the reaction. Experiments with the chelating agents suggest that the effect of available Fe-(II) on VC reduction is not significant.

Keywords: Materials; Vinyl Chloride; Fe

1. Introduction

Vinyl chloride (VC) is a toxic and carcinogenic compound regulated by the U.S. EPA as a priority pollutant (1). Production of VC in the United States is estimated to be in excess of 7 million tons per year (2). Past incidental and intentional releases of VC into the environment may have led to groundwater and soil contamination. In particular, VC can be produced as an intermediate in the reductive transformation of other chlorinated ethylenes such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Remediation of groundwater contaminated with chlorinated ethylenes, including vinyl chloride, has been challenging. Traditional "pump-and-treat" treatment systems have proven to be costly and ineffective in many contamination sites with complex hydrogeological settings (3, 4). Extensive studies on biotransformations have shown that microorganisms can degrade VC and other chlorinated ethylenes in aerobic (5-8) and anaerobic (5, 9-11) systems. Biotransformations in anoxic groundwater can be very slow and sometimes take years to complete. Biodegradation of PCE and TCE can lead to an accumulation of less chlorinated but more toxic ethylenes such as VC (5, 9, 12).

It has recently been shown that chlorinated aliphatic compounds can be reduced by metallic iron (13-18). A reactive permeable barrier technology based upon using metallic iron as the source of electrons for reductive dechlorination has been proposed and successfully implemented for in situ groundwater remediation (16, 19).

Experiments in both batch and column systems have shown that VC is generally degraded more slowly by metallic iron than

are the other chlorinated ethylenes (16, 20). As a result, VC has been observed as a reaction intermediate during reduction of PCE (21), TCE (16, 22-24), and cis- and trans-1,2-dichloroethylenes (25, 26) in metallic iron-water systems. Even in a highly reactive palladized iron system, low levels of VC are still produced (23). The high toxicity of VC means that permeable reactive barriers must be engineered to

provide sufficient residence time for contaminated groundwater to degrade VC to below its maximum contamination level. The rate of VC degradation has been considered to be a primary parameter in calculating the required iron wall thickness for in situ groundwater remediation systems (27).

The kinetics and mechanism of VC reduction by metallic iron are not fully understood, and the factors affecting the reduction process have not been thoroughly investigated. Previous studies (16, 28-31) focused on monitoring the disappearance of VC in the presence of metallic iron, and no detailed mass balances and reaction kinetics have been reported. The purpose of this study was to identify the parameters that may affect rates of VC reduction by metallic iron.

2. Materials and Methods

Chemicals. Distilled deionized Milli-Q water (18 M Ω cm resistivity) was used in all experiments in this study. The metallic iron used was 40-mesh cast iron filings from Fisher. The iron filings were pretreated by washing with Ar-sparged 1.0 N HCl for 30 min, rinsed 15 times with Ar-sparged water, and dried at 100 ° C in a stream of N₂. The specific surfaces area of the pretreated iron filings was 1.1 m²/g as measured by a N₂-BET method on a Micromeritics FlowSorb 2300. VC was obtained as a pure gas (Fluka, 99.5%), which was diluted with N₂ to obtain working gas stocks. Aqueous VC stock solutions were prepared by bubbling the VC gas stocks into Ar-sparged Milli-Q water. The solutions containing both VC and a pH buffer or a complexing agent were prepared by mixing the aqueous VC stock and appropriate buffer or complexing agent solutions. Other chemicals used were nitrilotriacetic acid trisodium salt monohydrate (NTA, Aldrich, 99+%), 1,10-phenanthroline (Fisher, ACS cert.), 2,2'-bipyridyl (Aldrich, 99+%), imidazole (Fisher, 99.7%), triethanolamine (Baker), sodium acetate (Fisher, ACS cert.), and ammonium hydroxide (Mallinckrodt, ACS grade). GC-FID response was calibrated using two-component gas mix standards (Scott Spec. Gases, in N₂) containing VC (1000 ppm) or ethylene (1.00 (0.05%)).

Experimental Systems. Time series experiments were performed using 15 mL clear borosilicate crimp-top serum vials (Wheaton). Each time point consisted of three or four vials: two Fe-containing reaction vials and one or two controls (no Fe). Reaction vials contained 5.00 (0.05 g of pretreated iron filings unless otherwise specified. The vials were filled with aqueous VC and slightly over-filled to eliminate headspace, then quickly crimp capped with a Teflon-lined rubber septum. This filling operation was carried out in an anaerobic glovebox (10% H₂ in N₂). Control vials contained 1.92 g of 3 mm glass beads (Fisher) so that the control and reactive vials contained the same volume of aqueous phase when filled. The vials were mixed on a roller drum at 8 rpm with the vials positioned horizontally. All experiments were conducted at 20 °C unless otherwise indicated.

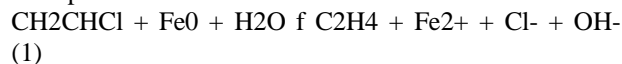
Analytical Methods. Aqueous concentrations of volatile organic compounds in the reaction and control vials were assayed by gas chromatography using the following procedure. An empty 10 mL crimp top serum vial was sealed with a Teflon-lined rubber septum. The septa of both the empty 10 mL assay vial and the reaction or control vial were punctured with either end of a 4" 1/8" stainless steel cannula, and an 18G needle was inserted through the 10 mL assay vial's septum as a vent. Then, 5.00 mL of air was pushed into the reaction or control vial by means of a 5.00 mL syringe, displacing 5.00 mL of aqueous sample through the cannula into the 10 mL assay vial. The cannula and the venting needle were then quickly removed and the assay vial inverted to minimize loss of volatile analytes. Then, 5.00 μ L of 1.00 mg pen-

tane/mL methanol internal standard was injected into the assay vial, and the vial was vortexed and placed in a 20 °C incubator for 10 min to equilibrate. A 100 μ L aliquot of headspace vapor from the assay bottle was analyzed using a HP 5890 GC with a 30 m 0.53 mm GSQ PLOT column (J&W Scientific). Oven temperature was programmed as follows: 50 °C initial with a 2 min hold, ramp at 30 °C/min to 200 °C, and then hold for 3 min. Injector and detector temperatures were 210 and 240 °C, respectively. Carrier gas was He at 30 cm/s (3.7 mL/min); detection was by FID. Quantification was by internal standard. Relative response factors were determined by spiking known volumes of gas standards into sealed 10 mL vials containing 5.00 mL of water and 5.00 μ L of pentane internal standard solution. For selected experiments, liquid samples were collected by filtration through 0.20 μ m membrane filters (Gelman Sciences). Dissolved iron in the filtrates was analyzed by atomic absorption spectroscopy with a graphite furnace, and chloride was analyzed by ion chromatography (Dionex).

3. Results and Discussion

Experiments performed under various conditions in this study indicated that VC reduction was always accompanied by the production of ethylene and inorganic chloride. Production of other hydrocarbons (e.g., methane, ethane, propene, and propane) was observed in all reactive bottles, but not exceeding the trace concentrations normally observed during corrosion of cast iron in such aqueous systems (32).

Results from a typical kinetic run are shown in Figure 1 (5 g Fe, 15 mL vial, no buffer, 20 °C). In the control bottles containing no iron, the aqueous vinyl chloride concentration ([VC]_{aq}) remains essentially constant with an average concentration of 2.69 μ M. In reaction bottles containing 5.00 g metallic iron, [VC]_{aq} drops to approximately 1.99 μ M within the first 2.0 h, followed by a much slower but gradual decrease. The gradual decrease in [VC]_{aq} is accompanied by a corresponding production of ethylene, the only observed carbon-containing product of VC reduction, indicating hydrogenolysis. Thus, the reaction stoichiometry under the anaerobic condition can be expressed as



The rapid initial drop of [VC]_{aq} observed in Figure 1 is most likely due primarily to adsorption to the iron surface rather than reductive transformation.

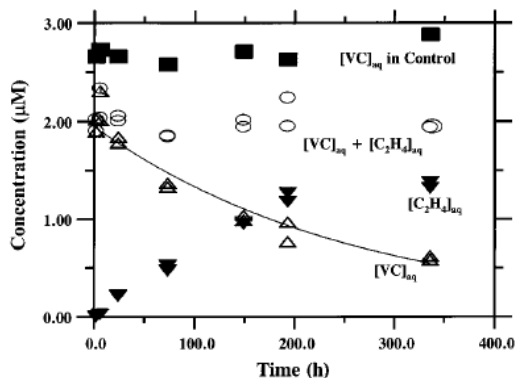


Figure 1. Reduction of vinyl chloride in aqueous suspension with 5.00 g Fe per 15.0 mL bottle at 20 ° C

This is supported by the fact that ethylene is produced gradually with no rapid initial concentration increase. Similar timecourses (i.e., quick initial drop followed by a more gradual decrease) have been observed in other surface-mediated processes where the quick initial drop is unambiguously shown to be from rapid initial adsorption (33, 34). Significant sorption of other chlorinated ethylenes (e.g., PCE, TCE, and DCEisomers) onto cast iron surfaces has been observed by determining both aqueous and sorbed concentrations (18, 25).

Direct measurement of vinyl chloride adsorption on the iron surfaces is difficult because the level of sorption is relatively low (especially compared to sorption of the higher chlorinated ethenes onto cast iron) and the reduction of vinyl chloride occurs at the same time. A method is developed here to estimate the amount of vinyl chloride adsorption based on the results of kinetic experiments such as those presented in Figure 1. The time course of [VC]aq in the presence of metallic iron is found to be best described by a first-order kinetic model:

$$-\frac{d[VC]_{aq}}{dt} = k_{obs}[VC]_{aq} \quad (2)$$

with its integrated form as

$$[VC]_{aq} = Be^{-k_{obs}t} \quad (3)$$

The observed first-order rate constant (k_{obs}) and the intercept at time zero (B) are fitting parameters. If the average concentration of VC in the controls is used as the initial VC concentration ($[VC]_0$), then the difference between $[VC]_0$ and the intercept at time zero can be used to calculate the amount of VC sorbed, thus leading to $[VC]_{ads}$. The estimated initial $[VC]_{ads}$ is 1.9 nmol/m² for the data set in Figure 1 using this approach.

Experiments with varying amounts of initial vinyl chloride (2.7-370 μ M) were performed with a constant iron loading of 5 g/vial. The changes in $[VC]_{aq}$ and $[ETH]_{aq}$ as a function of time were similar to the data presented in Figure 1 (e.g., initially $[VC]_{aq}$ drops off rapidly due to sorption followed by a gradual decrease due to reductive

dechlorination). The kinetic and initial sorption results based upon eq 2 are given in Table 1. The k_{obs} values are essentially constant with an average of $3.9 \times 10^{-3} \text{ h}^{-1}$ in the concentration range tested (Table 1). The constant k_{obs} under various VC concentrations indicates that VC reduction can be described by a first-order relationship with respect to $[VC]_{aq}$.

Figure 2 shows the adsorption isotherm constructed by plotting $[VC]_{ads}$ (see Table 1) versus $[VC]_{aq}$. The results show that a higher aqueous VC concentration results in a higher amount of VC adsorption. A least-squares fitting of the data generates a reasonably good linear relationship, $[VC]_{ads} = 0.338[VC]_{aq} + 2.58$ ($r^2 = 0.969$, $n = 8$).

Burris et al. (18) proposed that there are reactive sites and nonreactive sites on cast iron surfaces based on the non-linear adsorption behaviors observed for PCE and TCE. The adsorption onto the reactive sites results in their reduction. The adsorption on the nonreactive sites, most likely graphite inclusions in cast iron filings, sequesters PCE and TCE away from the reactive sites (35). The extent of VC adsorption onto cast iron is much less than that of PCE and TCE under comparable conditions (35) and can be characterized by a linear adsorption isotherm. The rate of VC reduction is directly proportional to the amount adsorbed. The probable explanation of the kinetics results with respect to the linear sorption behavior is that there is a constant proportion of VC sorbed to reactive relative to nonreactive sites. It is not possible to determine the proportion of reactive to nonreactive sites based upon the available data.

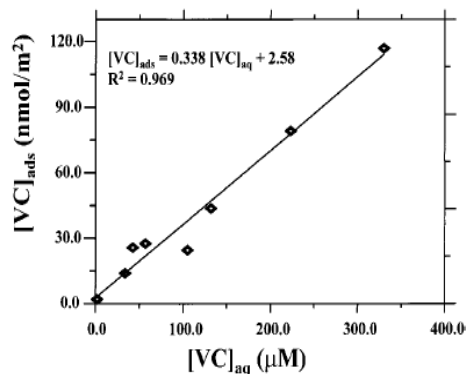


Figure 2. Vinyl chloride adsorption on metallic iron at 20 ° C, as calculated according to the experiments with constant iron loading (5.00 g Fe per 15.0 mL bottle) and various initial VC concentrations

The effect of different iron loadings was examined by conducting a series of runs with the same initial VC concentration of 52 μ M but with various amounts of iron. The results of these experiments are shown in Figure 3. A rapid initial drop in $[VC]_{aq}$ was observed for each iron loading, followed by a first-order decay. The extent of this initial drop increases with increased iron loading, but

there is no corresponding rapid initial increase in ethylene formation at any iron concentration. The rates of VC reduction and ethylene production increase with increasing iron loading. The observed rate constant (k_{obs}) increases in a linear fashion with increased iron loading as shown in Figure 4.

According to the reaction stoichiometry described by eq 1, VC reduction by metallic iron should increase solution pH. In addition, iron oxidation by H₂O also tends to increase pH (17). Thus, chemicals such as pyrite have been used to control pH in the kinetic studies of the dechlorination reaction (18). We compared VC reduction in the system containing 5.00 g Fe and 0.10 g pyrite and the system containing 5.0 g Fe only. The experiments, however, show that the pH conditions in the two systems were essentially the same (starting at 5.8 and ending at 6.2). The reaction kinetics is also not altered by the addition of pyrite.

To investigate the influence of pH on the VC reduction kinetics, experiments were conducted in the presence of various pH buffers including acetate, imidazole, triethanolamine, and ammonium, while keeping constant iron loading (5.0 g/bottle) and temperature (20 °C). The results are shown in Figure 5. The k_{obs} values are higher at low pHs (around 6) than those at high pHs. The system

buffered by imidazole (pH 7.1) has the lowest k_{obs}. The maximum variation of k_{obs} in the pH range examined is less than 10-fold. Considering the pH change of more than 4 orders of magnitude, the change in k_{obs} is small, indicating that protons may not be directly involved in the rate-limiting step of the reaction. This is comparable to the effect of pH on the reduction of carbon tetrachloride examined in the pH range 5.5-10.0 (17). The system buffered by imidazole (pH 7.1) has the lowest k_{obs}. The maximum variation of k_{obs} in the pH range examined is less than 10-fold. Considering the pH change of more than 4 orders of magnitude, the change in k_{obs} is small, indicating that protons may not be directly involved in the rate-limiting step of the reaction. This is comparable to the effect of pH on the reduction of carbon tetrachloride examined in the pH range 5.5-10.0 (17).

VC reduction was examined at 4, 20, 32, and 45 °C under constant iron loading (5.00 g/bottle) (see Figure 6). The reaction rate was found to increase as temperature was increased. The temperature effect adheres to the Arrhenius equation, $k = A \exp(-E_a/RT)$, as demonstrated by the linear $\ln k_{obs}$ versus $1/T$ plot. The activation energy (E_a) obtained in this temperature range is 42 (2 kJ/mol (95% confidence level)).

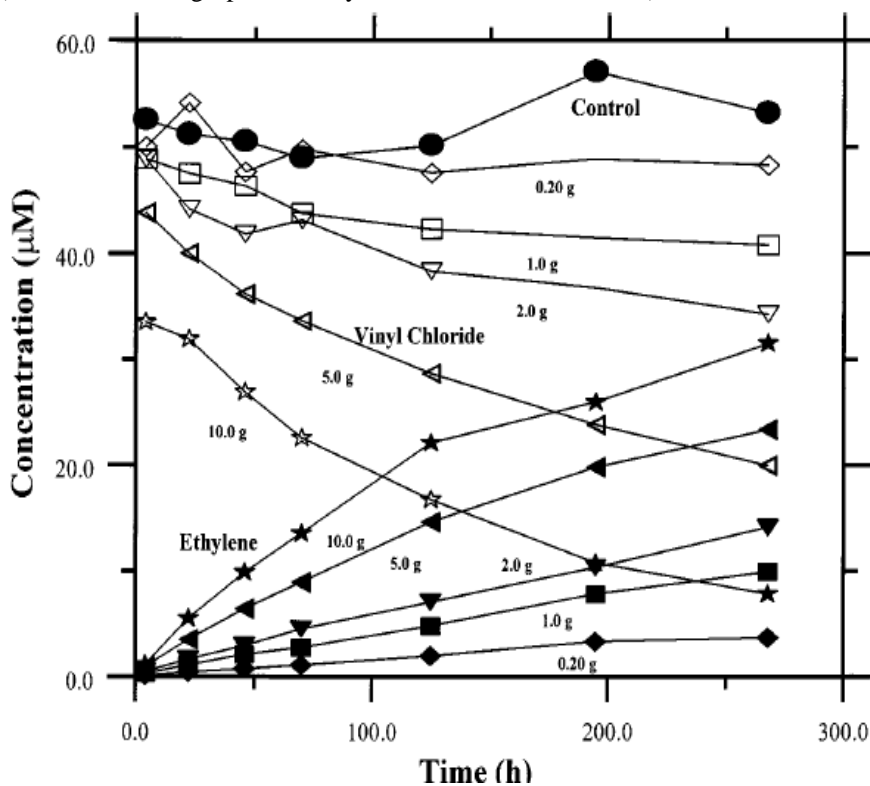


Figure 3. Vinyl chloride loss and ethylene production at various metallic iron loadings

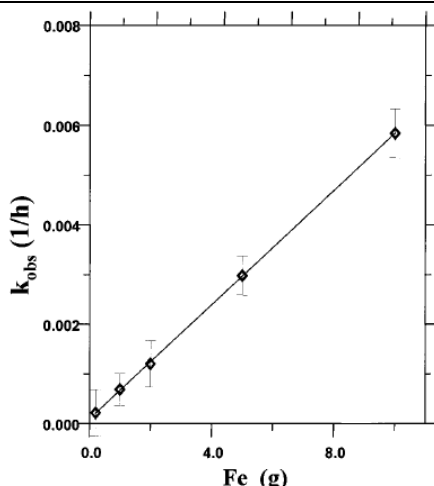


Figure 4. Observed rate constants (k_{obs}) for VC reduction by metallic iron using different iron loadings. (Error bars represent 95% confidence intervals.)

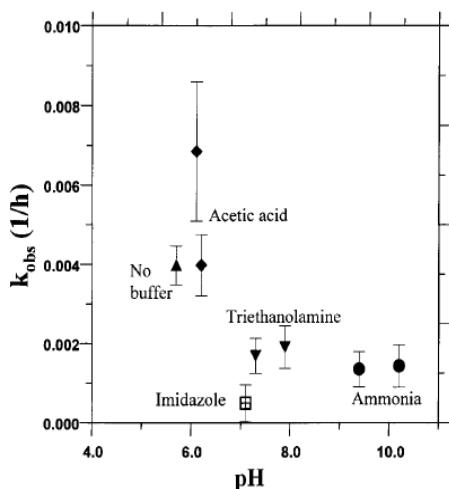


Figure 5. Effect of pH on the observed rate constant (k_{obs}) for VC reduction by metallic iron. (Error bars represent 95% confidence intervals.)

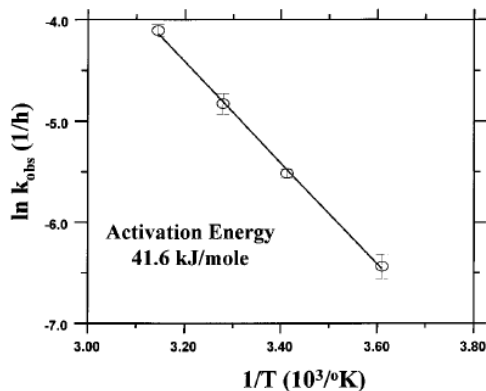


Figure 6. Observed rate constants (k_{obs}) for VC reduction by metallic iron as a function of temperature. (Error bars represent 95% confidence intervals.)

The experiments on the temperature effect not only provide necessary information for calculating the rate of VC reduction at different temperatures but may also give us insights regarding the reaction mechanism. For any surface mediated reaction, including VC reduction on metallic iron surfaces, a sequence of physical and chemical steps is involved: (1) movement of reactant molecules into the interfacial region by convection and diffusion; (2) diffusion of reactant molecules within the interfacial region; (3) surface chemical reaction such as ligand replacement and electron and group transfer reactions; (4) outward movement of product molecules from the interfacial region to bulk solution (37). The overall rates of the reactions depend on one or more of these steps. Reactions that are controlled by diffusion in aqueous media normally have activation energies less than 20 kJ/mol (38). An activation energy of 42 kJ/mol for the VC reduction suggests that the reaction is not controlled by diffusion in aqueous media but rather by the surface reactions. Vinyl chloride has higher activation energy than some other chlorinated compounds. For example, the reduction of carbon tetrachloride by metallic iron has a measured activation energy near zero, suggesting that that reaction might be diffusion controlled (17, 39).

In the examined iron-water systems, metallic iron is the primary reducing agent. Anaerobic iron corrosion can generate additional components such as Fe^{2+} and H_2 that may potentially reduce chlorinated compounds (17, 40). Iron- (III) oxide coatings that normally occur on iron filings may also influence the reduction kinetics. It has been postulated that chlorinated compounds may be reduced by surfacebound $Fe(II)$ species at the iron metal-water interface, and $Fe(II)$ on the passive iron oxide surface may serve as a mediator for the transfer of electrons from Fe^0 to adsorbed chlorinated hydrocarbons (41).

The observed rate constants of VC reduction in the presence and absence of the chelating agents 1,10-phenanthroline, 2,2'-dipyridyl, and nitrilotriacetic acid (NTA) are shown in Table 2. Experiments with different phenanthroline concentrations showed a significant drop in k_{obs} ; however, the addition of phenanthroline also produced an increase in pH which may have caused the reduced reactivity. To test this hypothesis, triethanolamine was used to control the pH near 7.5. Under those conditions, k_{obs} values reduced much less, only a 27% drop at 10 mM phenanthroline. Effects of dipyridyl and NTA were examined at the 1.0 mM concentration level. Dipyridyl slightly decreased the rate of VC reduction (17% decrease). NTA, however, slightly increased the rate by 15%. Dissolved iron concentrations ($[Fe^{II}]_{aq} + [Fe^{III}]_{aq}$) were measured by atomic absorption analysis. Dissolved

iron is from 0.18 to 1.64 mg/L in the absence of chelating agents. Dipyridyl slightly increases the dissolved iron concentration to the range 2.0-2.6 mg/L. NTA enhances the dissolved iron concentration significantly to the range 26.3-47.4 mg/L.

Phenanthroline and dipyridyl can form stronger complexes with Fe²⁺ than with Fe³⁺. If Fe²⁺ is a major reductant for vinyl chloride, it is expected that the presence of strong Fe²⁺-chelating agents may inhibit the reaction. Such inhibitive effects have been observed for chromate reduction by Fe²⁺ in soils, in which the presence of phenanthroline and dipyridyl totally blocked Cr(VI) reduction (42). Current experiments show that the VC reduction rate is decreased by phenanthroline, but the inhibitive effect is small at constant pH. Dipyridyl also decreases the rate of VC reduction slightly. Interpreting the effect of phenanthroline in the nonbuffered system is complicated by the fact that the solution pH is also significantly increased. The decrease in VC reduction in this case could be caused by high pH. In addition, more significant formation of iron oxide coating may occur at high pH if a trace amount of oxygen is present, since the rate of Fe(II) oxidation increases as pH is increased (43). It is thus concluded that Fe(II) may have participated in the process of VC reduction, but only to a small degree.

NTA forms stronger complexes with Fe³⁺ than with Fe²⁺, which is similar to ethylenediaminetetraacetic acid (EDTA) studied by other researchers (17, 44). It is interesting to note that the VC reduction rate is slightly increased in the presence of NTA, despite an accompanying pH increase. The dissolved iron concentration is also significantly increased. It is possible that NTA dissolves some surface oxide coating, leading to the higher VC reduction rate. Johnson et al. (44) reported that the reduction of carbon tetrachloride was inhibited by EDTA in HEPES buffer. The difference here could be attributed to many factors, including the nature of the substrate and complexing agents, buffer, pH, iron, and the concentration range of complexing agents used.

In summary, this study has established that VC reduction in metallic iron-water systems yields ethylene as the only major carbon-containing product. The reduction reaction was determined to be pseudo-first-order and appears to be controlled by the chemical reaction rate on the surface. A method has been developed to estimate VC adsorption based on its initial loss in the aqueous phase. The resultant sorption

isotherm was linear over the approximately 2 orders of magnitude concentration range examined. The first-order reaction kinetics and linear sorption behavior suggest a constant proportion of reactive to nonreactive sorption sites on the cast iron surface. Experiments with the chelating agents suggest that the effect of available Fe(II) on VC reduction is not significant.

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