Kinetics and Mechanism of the Enhanced Reductive Degradation of CCl₄ by Elemental Iron in the Presence of Ultrasound

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Enhanced rates of sonolytic degradation of CCl₄ in the presence of Fe⁰ are demonstrated. In Ar-saturated solutions, the first-order rate constant for CCI_4 degradation is k_{US} = 0.107 min⁻¹, whereas in the presence of Ar and Fe⁰, the apparent first-order rate constant is found to depend on the total surface area of elemental iron in the following fashion: $k_{obs} = (k_{US} + k_{Fe^0}A_{Fe^0}) \text{ min}^{-1}$, where $k_{US} = 0.107 \text{ min}^{-1}$, $k_{Fe^0} = 0.105 \text{ Lm}^{-2} \text{ min}^{-1}$, and $A_{Fe^0} = \text{reactive surface}$ area of Fe⁰ in units of m² L⁻¹. In the coupled ultrasound and iron system, the contribution to the overall degradation rate by direct reaction with Fe⁰ results in an overall rate enhancement by a factor of 40. These enhancements are attributed (1) to the continuous cleaning and chemical activation of the Fe⁰ surface by the combined chemical and physical effects of acoustic cavitation and (2) to accelerated mass transport rates of reactants to the Fe⁰ surfaces. Additional kinetic enhancements are due to the production of H⁺ during the course of the reaction. Furthermore, the concentrations of the principal reaction intermediates, C_2CI_6 and C_2CI_4 , are influenced substantially by the total available surface area of Fe⁰.

Introduction

Ultrasound is widely used for medical imaging, emulsification, plastic welding, and a wide variety of synthetic applications (1). In addition, ultrasonic irradiation has been applied as an advanced oxidation technology for water treatment (2, 3). Upon ultrasonic irradiation, organic compounds in water are degraded via several mechanisms. Three main pathways, which involve hydroxyl radical oxidation, pyrolytic degradation, and supercritical water reactions, have been proposed (3). In the case of an aqueous solution, water vapor present in the bubble is homolytically split to yield H• and •OH radicals. Chemical substrates present within the vapor phase or in the nearby liquid of the collapsing bubbles are subject to direct attack by 'OH radical (4, 5). Volatile compounds such as H₂S and CCl₄ partition into the gas phase (i.e., into the gaseous bubbles within the aqueous solution) and undergo direct pyrolysis (1, 5, 6). Furthermore, it has been found that hydrolysis reactions are accelerated by several orders of magnitude in the presence of ultrasound. These accelerated reaction rates have been attributed to the existence of transient supercritical water during ultrasonic irradiation (7).

The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation (1). Sound travels through a liquid as a wave consisting of alternating compression and rarefaction cycles. If the sound wave has a sufficiently high pressure amplitude, it can overcome the intermolecular forces bonding the fluid. As a result, the liquid will break down and voids will be created; that is, cavitation bubbles will be formed. In most liquids, cavitation is initiated with pre-existing microbubbles or weak spots, which are any type of inhomogeneity in the fluid. The inhomogeneity can be anything from particles to gas nuclei. These microbubbles grow sequentially during the compression and rarefaction cycles due to the phenomenon of rectified diffusion until they reach a critical size; in subsequent compression cycles, these cavities can collapse violently, releasing a large amount of energy. This rapid implosion is accompanied by an adiabatic heating of the vapor phase of the bubbles, which yields localized but transient high temperatures and pressures. Temperatures on the order of 5000 K have been obtained experimentally (8), and pressures of the order of 1000 bar have been calculated (9).

Elemental iron (Fe⁰) is a mild reductant with an $E_{\rm H^{\circ}} = -0.44$ V. It has been proposed as a suitable source of electrons for the in situ remediation of contaminated groundwater because of its low cost and nontoxicity (10). Fe⁰ barrier systems have the potential to replace the pump-and-treat systems for the remediation of contaminated groundwater to reduce the chlorinated compounds to nonchlorinated products (11, 12). The kinetics of carbon tetrachloride dechlorination in the presence of elemental Fe⁰ have been reported by Tratnyek and co-workers (10, 13–15). In addition to degrading chlorinated solvents, zero-valent metals may prove to be useful for the reduction of nitro aromatic compounds to anilines, which can be further degraded microbiologically (16–19).

Because acoustic cavitation can increase the surface area of the reactive solids by causing particles to rupture, sonication in the presence of Fe⁰ has been explored for the dechlorination of trichloroethylene (TCE) (*20*). In this study, we investigate the combination of ultrasound and Fe⁰ for CCl₄ degradation. Carbon tetrachloride is degraded by pyrolysis reaction inside the bubble, by reduction on the surface of Fe⁰, and synergistically on Fe⁰ surface sites created by ultrasonic effects. The combination of ultrasound and Fe⁰ is a heterogeneous reaction system involving solid/liquid, gas/solid, and gas/liquid interfaces.

There are two modes of cavitational bubble collapse that can affect the surface of solids (21). First, cavitational bubble collapse directly on a surface may cause direct damage by shock waves produced upon implosion. These bubbles are formed on nuclei such as surface defects, entrapped gases, or impurities on the surface of the material. Second, cavitational collapse near the solid surface in the liquid phase will cause microjets to hit the surface and produce a nonsymmetrical shock wave. This phenomenon results in the well-known cleaning action of ultrasound. As a consequence of these events, more reactant surface area is readily formed for further surface reactions.

In this paper, kinetics and mechanism of CCl_4 sonolysis in aqueous solution in the presence of two different Fe^0 samples are presented. In addition, the effect of Fe^0 on the fate and behavior of the primary reaction intermediates, tetrachloroethene (C₂Cl₄) and hexachloroethane (C₂Cl₆), is examined.

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Technical Background

Mechanism of CCl₄ Sonolysis. The sonolytic degradation of CCl₄ has been studied by several research groups (1, 3, 22-24). The overall reaction mechanism (3) can be written as

$$\operatorname{CCl}_{4} \xrightarrow{)))} \operatorname{Cl}^{\bullet} + \operatorname{^{\bullet}CCl}_{3} \tag{1}$$

$$\operatorname{CCl}_4 \xrightarrow{)))} \operatorname{Cl}_2 + :\operatorname{CCl}_2$$
 (2)

$$^{\bullet}\mathrm{CCl}_{3} \rightarrow ^{\bullet}\mathrm{Cl} + :\mathrm{CCl}_{2} \tag{3}$$

$$^{\bullet}CCl_{3} + ^{\bullet}CCl_{3} \rightarrow CCl_{4} + :CCl_{2}$$
(4)

$$^{\bullet}\mathrm{CCl}_{3} + ^{\bullet}\mathrm{CCl}_{3} \to \mathrm{C}_{2}\mathrm{Cl}_{6} \tag{5}$$

where))) indicates sonolysis. The trichloromethyl radical, produced via the pyrolysis of CCl_4 in eq 1, is an effective scavenger of the hydroxyl radical as follows:

$$^{\bullet}CCl_{3} + ^{\bullet}OH \rightarrow HOCCl_{3} \tag{6}$$

 $HOCCl_3$ reacts rapidly to yield phosgene, HCl, and CO_2 as follows:

$$HOCCl_3 \rightarrow HCl + COCl_2$$
 (7)

$$\text{COCl}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{HCl}$$
 (8)

Dichlorocarbene, which is produced via eq 2, can couple with itself to form tetrachloroethylene

$$:CCl_2 + :CCl_2 \rightarrow C_2Cl_4 \tag{9}$$

or it can react with water to form carbon monoxide and hydrochloric acid as follows:

$$:CCl_2 + H_2O \rightarrow 2HCl + CO \tag{10}$$

Chlorine atoms self-react to form molecular chlorine, which hydrolyzes to yield hypochlorous acid and chloride ion:

$$2Cl^{\bullet} \rightarrow Cl_2 \xrightarrow{+H_2O} HOCl + HCl$$
(11)

Mechanism of CCl₄ Reduction by Fe⁰. The following mechanism (eqs 12–16) for the reductive dehalogenation of CCl₄ by elemental iron has been proposed by Matheson and Tratnyek (*10*).

$$(Fe^{0})_{n} + CCl_{4} \iff Fe^{0}_{n-2} \xrightarrow{Fe^{0} \cdots Cl}_{Fe^{0} \cdots Cl}$$
(12)

$$Fe^{0}_{n-2} \xrightarrow{Fe^{0} \cdots Cl}_{Fe^{0} \cdots Cl} \xrightarrow{C_{n-2}} Fe^{0}_{n-2} \xrightarrow{Fe^{+}}_{Fe^{0}} + Cl^{-} + Cl_{3} \xrightarrow{(13)}$$

e

$$Fe^{\circ}_{n-2} \swarrow Fe^{+} + CCl_{3} + H_{2}O \longrightarrow$$

$$Fe^{\circ}_{n-2} + Fe^{2*} + HCCl_3 + OH^{-}$$
(1)

4)

TABLE 1. Physical Dimensions of the Different Frequency Transducers

frequency	emitting	emitting	sonication
	diam, cm	areas, cm ²	vol, mL
20 kHz + Fe ⁰ powder	1.27	1.27	245
20 kHz + Fe ⁰ turnings	1.27	1.27	285

 CCl_4 can also be degraded by H_2 produced from the reaction of H^+ with $Fe^0.$

$$\mathrm{Fe}^{0} + 2\mathrm{H}^{+} \rightarrow \mathrm{Fe}^{2+} + \mathrm{H}_{2}$$
(15)

$$\operatorname{CCl}_4 + \operatorname{H}_2 \to \operatorname{HCCl}_3 + \operatorname{Cl}^- + \operatorname{H}^+$$
(16)

The primary product observed after several hours of reaction is chloroform. Neither C_2Cl_4 nor C_2Cl_6 is observed as an intermediate. Matheson and Tratynek reported a pH increase during the course of the reaction that is consistent with the stoichiometry of eq 14. In addition, they observed that the rate of dehalogenation by Fe⁰ was faster at low pH (*10*).

Experimental Procedures

Commercially available organic high-purity reagents were used without further purification. They included carbon tetrachloride, CCl₄, 99.9% (J. T. Baker); chloroform, LC grade; hexachloroethane, C₂Cl₆, 98% (Aldrich); and tetrachloroethene, C₂Cl₄, 99.9% (Sigma-Aldrich). Pentane (Omnisolv grade, EM Science) was used as the carrier solvent for the GC. Aqueous solutions were made with water obtained from a MilliQ UV Plus water purification system (18.2 m Ω ·cm resistivity).

Two different sources of elemental iron were used in this study. Iron powder was obtained from J. T. Baker, and electrolytic iron turnings were obtained from Fluka. The Fe⁰ turnings were of a coarser grain size (mostly >40 mesh) and were cleaner and smoother than the Fe⁰ powder and had a high metallic luster. The nominal purity of the Fe⁰ turnings was 99.9%, with the remainder consisting primarily of iron oxides. Trace impurities were <0.02% by weight of C, <0.008% by weight of S, <0.003% by weight of Si, <0.02% by weight of P, <0.02% by weight of Mn, and <5 ppm of Mg (*19*). The desired concentrations of CCl₄ in Ar-saturated water were prepared by dilution of a saturated CCl₄ stock solution (5.1 mM), which was made by stirring excess CCl₄ with Ar-saturated water.

Sonolyses were performed with a Branson 200 sonifier operating at 20 kHz. The temperature was maintained at 15 °C with a Haake A80 refrigerated bath and circulator to compare the results with this study with those of Matheson and Tratnyek (*10*). Replaceable titanium tips on the 20 kHz transducer were polished and the transducer was tuned before each use to give a minimum power output when vibrating in air. The tuning process is a standard procedure to bring the transducer into resonance as part of the complete probe assembly. Sonolytic reactions at 20 kHz were performed in a 300 mL airtight reactor cell. The physical dimensions and fundamental characteristics of the transducer are given in Table 1; the reactor configuration is similar to the design shown in Hua and Hoffmann's paper (*3*).

In the kinetic experiments, $285 \text{ mL of } 0.1 \text{ mM CCl}_4$ solution was transferred into a water-jacketed glass cell, which was closed from the atmosphere. The bottom of the glass reactor was designed with a 1 cm indentation in the center for reflection of the sound waves and for an even distribution of the cavitation bubbles in the solution. The reactor was made gastight with two O-ring seals in the threaded Teflon



FIGURE 1. First-order plot for CCl₄ degradation: (\Box) by ultrasound alone; (\blacklozenge) by ultrasound + 2 g of Fe⁰ powder; the solid lines are the fitting results.



FIGURE 2. Effect of reactive surface area of Fe⁰ on the pseudofirst-order rate constant for CCI₄ degradation by (a) Fe⁰ powder and (b) Fe⁰ turnings [$\Delta k = k$ (ultrasound + Fe⁰) - k (ultrasound)].

collar that connects the glass cell to the stainless steel probe. In addition, sampling ports were sealed with Teflon valves and covered with rubber septa. Sample aliquots were withdrawn with a 1 mL Hamilton syringe, filtered through a 0.45 μ m nylon filter into a 2.5 mL glass vial with a PTFE/ silicone septum-lined threaded cap, and mixed with 0.5 mL of pentane. For quantification of the concentrations of CCl₄, C_2Cl_4 , and C_2Cl_6 , 0.5 μ L samples of the pentane extract were analyzed with an HP 5880A gas chromatograph with an electron capture detector (GC-ECD) operated in the splitless mode and equipped with an HP-5 column. The instrument was calibrated with commercial standards. Duplicate measurements were made for each sample. Time-sequenced samples were analyzed immediately by GC-ECD. The aqueous phase in the sample vial was analyzed by ionexchange chromatography (IC) for Cl⁻. The IC system was a Dionex Bio-LC system equipped with a conductivity detector and a Dionex OmniPac AS-II column. The ultrasonic power output was measured by conventional calorimetry (21). The measured output power employed in this study was 62 W.



FIGURE 3. Ratio of maximum concentration of C_2CI_4 and C_2CI_6 as functions of [Fe⁰] with respect to CCI₄ initial concentration: (a) for Fe⁰ powder; (b) for Fe⁰ turnings.



FIGURE 4. Fitting results for [CI⁻] concentration by eq 37: (a) ultrasound only; (b) ultrasound + 2 g of Fe⁰ powder.

Results and Discussion

Experiments were performed at an initial CCl₄ concentration of 1×10^{-4} M and an initial pH of 7. Degradation of CCl₄ was found to be >99% of its initial concentration after 90 min of exposure to ultrasound. Loss of CCl₄ was found to be <2% in the control experiments without ultrasound and iron. The pH at the completion of the reaction under ultrasound was 3.5; and with the combination of ultrasound and Fe⁰, the final pH was 6 (presumably due to the formation of OH⁻ from Fe⁰ reduction according to eq 14).

First-order plots of [CCl₄] versus time during sonolysis and Fe⁰ reduction of an Ar-saturated solution at 20 kHz are shown in Figure 1. The slopes from linear regression of the data yield the observed rate constants for CCl₄ degradation. The reaction rate for CCl₄ degradation by ultrasound in the presence of iron was also found to be first-order. In Figure 2, the results for enhanced rate constants $[\Delta k = k$ (ultrasound) + Fe⁰) – k (ultrasound)] for different sizes of the Fe⁰ particles (i.e., surface area) are shown. The iron powder had a higher reactive surface area than iron turnings; as a consequence, Δk was enhanced by a factor of 8 for Fe⁰ powder at the same Fe⁰ mass concentration. Figure 2 also shows that the rate constants for CCl₄ reduction increased linearly with increasing mass of Fe⁰ per unit reaction volume (gL⁻¹) until it reached a saturation value for mass concentrations larger than 30 g L⁻¹ (for iron turnings).

Assuming a constant specific surface area of $0.005 \text{ m}^2/\text{g}$ for Fe⁰ turnings (*19*), the following relationship for the reaction rates with the Fe⁰ surface area was obtained by linear regression:

$$\Delta k \text{ (min}^{-1}) = k_{\text{Fe}^0} A_{\text{Fe}^0} + 0.001 = 0.105 \text{ (L m}^{-2} \text{ min}^{-1}) \times A_{\text{Fe}^0} \text{ (m}^2 \text{ L}^{-1}) + 0.001 \text{ min}^{-1} \text{ (17)}$$

The differential rate constant (Δk) is in units of min⁻¹ and the surface area concentration, A_{Fe^0} , is in units of m² L⁻¹. These results (eq 17) can be compared directly to the results reported by Matheson and Tratnyek (*10*), who measured the rate of CCl₄ degradation by Fe⁰ without ultrasound as follows:

$$k = 0.0025A_{\rm Fe0} + 0.017 \tag{18}$$

This comparison confirms that ultrasonic irradiation enhances the rate of CCl_4 degradation due to Fe^0 by a factor of 40 compared to Fe^0 in the absence ultrasound.

The higher degradation rate contributed by Fe⁰ in our study can be attributed to the indirect chemical effects associated with the continuous ultrasonic cleaning and activation of the Fe⁰ surface, the enhanced rate of mass transport resulting from the turbulent effects of cavitation, and the lower pH caused by CCl4 sonolysis. The shock wave and microjets formed during cavitational bubble collapse are primarily responsible for the cleaning actions of ultrasound. Transient cavitation results in turbulent flow conditions within the reactor that enhance overall mass transport. The iron corrosion accelerated by ultrasound may also contribute to the reductive dehalogenation of CCl₄ via eq 16. The effect of a drop in pH during sonication is to produce a faster rate of reduction of Fe⁰. Since the sonolytic degradation of CCl₄ produces H⁺ according to eqs 10 and 11, we expect to see a faster rate in the combined system. The Fe⁰ reduction reaction involving H⁺ is as follows:

$$\operatorname{Fe} + \operatorname{CCl}_4 + \operatorname{H}^+ \to \operatorname{Fe}^{2+} + \operatorname{CHCl}_3 + \operatorname{Cl}^-$$
 (19)

 C_2Cl_4 and C_2Cl_6 were observed as intermediates during CCl₄ sonolysis discussed previously (3, 25). However, these intermediates were not measured by Matheson and Tratnyek (10). The principal products observed during CCl_4 reduction by Fe⁰ are CHCl₃ and CH₂Cl₂. During CCl₄ sonolysis, the concentrations of C2Cl4 and C2Cl6 increased with time and then decreased during continued sonication after reaching maximum concentrations. The maximum concentrations of C_2Cl_4 and C_2Cl_6 are shown as functions of the mass concentration of Fe⁰ in Figure 3. The measured C₂Cl₄ and C_2Cl_6 concentrations increase with increasing Fe^0 mass concentration up to 10 g/L. This effect can be explained by the production of higher levels of chloroform (CHCl₃) from the reductive dehalogenation of CCl₄ by Fe⁰. We have previously shown that CHCl₃ sonolysis produces more C₂Cl₄ than C_2Cl_6 (25). The overall reactions consistent with these observations are as follows:

$$\operatorname{CHCl}_3 \xrightarrow{)))} :\operatorname{CCl}_2 + \operatorname{HCl}$$
 (21)

$$:CCl_2 + :CCl_2 \rightarrow C_2Cl_4 \tag{22}$$

Another possible pathway involves CCl_4 sorption on the Fe⁰ surface, which subsequently reacts with $^{\circ}CCl_3$ produced during sonolysis as follows:

$$\operatorname{CCl}_4 \xrightarrow{)))} \operatorname{^{\circ}CCl}_3 + \operatorname{^{\circ}Cl}$$
 (23)

$$CCl_4 + {}^{1}\!/_{2}Fe \rightarrow {}^{\bullet}CCl_3 + {}^{1}\!/_{2}Fe^{2+} + Cl^{-}$$
 (24)

$$2^{\bullet}CCl_3 \rightarrow C_2Cl_6 \tag{25}$$

The reactions of eqs 20-25 help to explain the observed higher concentrations of C_2Cl_4 and C_2Cl_6 in the combination Fe⁰/CCl₄ system.

Kinetic Analysis. The final reaction product observed during CCl_4 sonolysis is Cl^- . The overall degradation mechanism can be simplified as follows:

$$\operatorname{CCl}_4 \xrightarrow{(1)) k_1} \operatorname{^{\circ}CCl}_3 + \operatorname{^{\circ}Cl}$$
 (26)

$$2^{\bullet} \text{CCl}_3 \xrightarrow{\kappa_2} C_2 \text{Cl}_6 \tag{27}$$

$$C_2 Cl_6 \xrightarrow{k_3} aCl^- + other products$$
 (28)

$$Cl + H_2O \xrightarrow{\kappa_4} HCl + OH$$
 (29)

with the corresponding kinetic equations

$$d[CCl_4]/dt = -k_1[CCl_4]$$
(30)

$$l[^{\circ}CCl_3]/dt = k_1[CCl_4] - 2k_2[^{\circ}CCl_3]^2$$
 (31)

$$d[C_2Cl_6]dt = k_2[{}^{\bullet}CCl_3]^2 - k_3[C_2Cl_6]$$
(32)

$$d[^{\circ}Cl]/dt = k_1[CCl_4] - k_4[^{\circ}Cl]$$
(33)

$$d[Cl-]/dt = k_4[°Cl] + ak_3[C_2Cl_6]$$
(34)

The solution to the coupled differential eqs 30-34 can be written as

$$[C_2Cl_6] = \frac{k_1}{2(k_1 - k_3)} [CCl_4]_0 (e^{-k_3 t} - e^{-k_1 t})$$
(35)

$$[Cl^{-}] = [CCl_4]_0 \left[1 - e^{-k_1 t} + \frac{ak_1}{2(k_1 - k_3)} (1 - e^{-k_3 t}) - \frac{ak_3}{2(k_1 - k_3)} (1 - e^{-k_1 t}) \right]$$
(36)

for C_2Cl_6 and Cl^- , respectively (25). On the basis of our previous measurements, we know that k_1 , which is the CCl_4 degradation rate constant for sonolysis alone, $\approx k_3$, the corresponding C_2Cl_6 degradation rate constant. Thus, eq 36 can be further simplified to

$$[\mathrm{Cl}^{-}] \approx [\mathrm{Cl}^{-}]_{\infty} \left(1 - \mathrm{e}^{-k_{\mathrm{Cl}}-t}\right) \tag{37}$$

The effect of Fe^0 can be treated as a simple step addition to the mechanism of eqs 26-29 as follows:

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$$\operatorname{CCl}_4 + {}^{1}/{}_{2}\operatorname{Fe} \xrightarrow{k} \operatorname{CCl}_3 + \operatorname{Cl}^- + {}^{1}/{}_{2}\operatorname{Fe}^{2+}$$
(38)

As a consequence, eq 30 can be rewritten as

$$[CCl_4] = [CCl_4]_0 e^{-(k_1 + k')t}$$
(39)

where k' ($k' = \Delta k$) is the enhanced CCl₄ degradation rate in the presence of Fe⁰. Because Fe⁰ has a negligible influence on the rate of C₂Cl₆ degradation (18), C₂Cl₆ degraded by Fe⁰ can be ignored relative to the C₂Cl₆ sonolysis. This allows the modification of eqs 35 and 36 to yield eqs 40 and 41 as follows:

$$[C_2 Cl_6] = \frac{(k_1 + k')}{2(k_1 + k' - k_3)} [CCl_4]_0 (e^{-k_3 t} - e^{-(k_1 + k')t})$$
(40)

$$[Cl^{-}] = [CCl_{4}]_{0} \left\{ 1 - e^{-(k_{1}+k')t} + \frac{a(k_{1}+k')}{2(k_{1}+k'-k_{3})}(1 - e^{-k_{3}t}) - \frac{ak_{3}}{2(k_{1}+k'-k_{3})}(1 - e^{-(k_{1}+k')t}) \right\}$$
(41)

The [Cl⁻] concentration versus time predicted by eq 37 is used to fit all of the kinetic data and obtain k_{Cl^-} values as a function of [Fe⁰]. In Figure 4, the fitted results for ultrasound alone and ultrasound +2 g of Fe⁰ powder systems are shown. Furthermore, the comparison of the rate constant, k_{Cl} , for [Cl⁻] production and the rate constant, k_{CCl_4} , for CCl₄ degradation as a function of [Fe⁰] is shown in Table 2. If we suppose that eq 41 can be simplified to eq 37, the k_{Cl} obtained from Figure 4b embodies the contribution of k', the enhanced CCl_4 degradation rate by Fe⁰. As mentioned above, k' is larger for Fe⁰ powder than Fe⁰ turnings. On the basis of the data summary in Table 2, we see that k' contributes more to k_{Cl} , which shows greater increases for Fe⁰ powder than for Fe⁰ turnings. From these comparisons, it is clear that k_{CI^-} increases with [Fe⁰] but the relative magnitude of the increase is less than that for k_{CCl_4} . This discrepancy could be due to the contribution of k' in eq 39; the difference between k_{CI} and $k_{\rm CCL}$ is consistent with increasing Fe⁰ mass concentration.

The degradation rate constant for ultrasound alone in this study is 0.107 min $^{-1}$ (=1.8 \times 10 $^{-3}$ s $^{-1}$) at 62 W in 285 mL; this is equivalent to a first-order rate constant of 4.3×10^{-3} s^{-1} adjusted to 50 W in 95 mL through power density normalization. This value is faster than that reported by Hua and Hoffmann (3) (i.e., $3.3 \times 10^{-3} \text{ s}^{-1}$ in 50 W and 95 mL). The relative enhancement may have been due to a power density effect in which increased power results in enhanced chemical effects instead of simply heating the solution due to relative inefficiencies in energy transfer (26). For the combination of ultrasound and Fe⁰, Reinhart et al. also observed similar rate enhancements for the reduction of trichloroethylene (TCE) by Fe⁰ (20). In addition, they reported an increase in the final pH of the mixture in the TCE-Fe⁰ system compared with the application of ultrasound alone.

In this study, we demonstrated that the rate of sonolytic degradation of CCl₄ can be enhanced by the presence of Fe⁰. The higher apparent rates of reaction in the coupled US/Fe⁰ system compared to Fe⁰ reaction alone can be attributed to the continuous cleaning and activation of the Fe⁰ surface by the chemical and physical effects of ultrasound. Furthermore, faster mass transport rates resulting from the hydrodynamic cavitation and production of H⁺ during the course of the reaction also contribute to the observed rate enhancements. The relative concentrations of the principal

TABLE 2. Comparison of k Values from CCl4 Degradation and Cl $^-$ Production: (a) Fe 0 Powder and (b) Fe 0 Turnings

	<i>k</i> _{CCI₄} , min ^{−1}	<i>k</i> _{Cl} −, min ^{−1}
(a) Fe ⁰ powder mass concn, g/L		
0	0.13	0.13
2.04	0.15	0.14
8.16	0.20	0.16
16.33	0.20	0.18
24.49	0.20	0.18
(b) Fe ⁰ turnings mass concn, g/L		
0	0.107	0.086
7.02	0.113	0.094
14.0	0.115	0.100
21.0	0.118	0.099
28.1	0.122	0.098
42.1	0.125	0.096

reaction intermediates, C_2Cl_4 and C_2Cl_6 , which are observed during the course of the reaction, appear to be influenced significantly by total available surface area of Fe⁰. In conclusion, the combination of ultrasound and Fe⁰ has a positive synergistic effect on the dehalogenation of chlorinated hydrocarbons.

Acknowledgments

We appreciate the contributions by Dr. Weavers about the details of the kinetics and mechanisms. Financial support from the Office of Naval Research (NAV5-N0001492J1901; NAV1-N47408-97-M-0771) and the Department of Energy (DOE 1 963472402) is gratefully acknowledged.

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Received for review March 17, 1998. Revised manuscript received June 1, 1998. Accepted June 15, 1998.

ES980273I