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

HUI-MING HUNG, FRANK H. LING, AND MICHAEL R. HOFFMANN\* W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125

Sonolysis, reduction by elemental iron (Fe<sup>0</sup>), and a combination of the two processes were used to facilitate the degradation of nitrobenzene (NB) and aniline (AN) in water. The rates of reduction of nitrobenzene by Fe<sup>0</sup> are enhanced in the presence of ultrasound. The first-order rate constant,  $k_{US}$ , for nitrobenzene degradation by ultrasound is  $1.8 \times 10^{-3}$  min<sup>-1</sup>, while in the presence of Fe<sup>0</sup>, the rate was found to be substantially faster. The observation of similar degradation rates for aniline in each system suggests that the sonication process was not affected by the presence of Fe<sup>0</sup>. The observed rate enhancements for the degradation of nitrobenzene can be attributed primarily to the continuous cleaning and chemical activation of the Fe<sup>0</sup> surfaces by acoustic cavitation and to accelerated mass transport rates of reactants, intermediates, and products between the solution phase and the Fe<sup>0</sup> surface. The relative concentrations of nitrosobenzene and aniline, the principal reaction intermediates generated by Fe<sup>0</sup> reduction, are altered substantially in the presence of ultrasound.

## Introduction

Ultrasonic irradiation has been applied as an advanced oxidation technology for water treatment (1, 2). The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation (3-5). Temperatures inside of the cavitation bubble are on the order of 5000 K (4), and pressures of the order of 1000 bar have been calculated (4). In homogeneous reactions, the destruction of organic compounds occurs inside the caviation bubbles by a pyrolysis reaction or in the nearby interfacial region by hydroxylation (3, 5). In heterogeneous reactions, the primary mode of action by sonication is erosion involving the removal of oxide layers and impurities together with pitting of metal surfaces. It is thought that sonication serves to sweep reactive intermediates or products from metal surfaces thereby reactivating and cleaning the surfaces for subsequent reactions (3, 5).

Elemental iron (Fe<sup>0</sup>) has been proposed as a suitable source of electrons for the in situ remediation of contaminated groundwater (6-14). Tratnyek and co-workers (7-10) have used Fe<sup>0</sup> to reduce chlorinated hydrocarbons to nonchlorinated products and to reduce nitroaromatic compounds (NACs) to anilines (13, 14). A linear correlation between the observed rate constants for the reduction of

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nitrobenzene and the square-root of mixing rate (rpm) indicated that the observed reaction rates were controlled by mass transfer of the substrates to the  $Fe^0$  surfaces (14).

Since acoustic cavitation is known to increase the surface area of reactive solids by causing particles to rupture, Reinhart et al. (15) investigated the dechlorination of trichloroethylene by Fe<sup>0</sup> in the presence of ultrasound. In our previous paper (16), the kinetics and mechanism of carbon tetracholoride degradation by Fe<sup>0</sup> in the presence of ultrasound was reported, and it was noted that the rate of CCl<sub>4</sub> degradation was enhanced by a factor of 40 compared to the same reaction system in the absence of ultrasound.

In this study, we investigate the combination of ultrasound and  $Fe^0$  for the reduction of nitrobenzene and aniline, the byproduct from the nitrobenzene reduction by  $Fe^0$ . The influence of ultrasonic power density is also discussed.

## **Technical Background**

**Mechanism of Nitrobenzene Sonolysis**. The sonolytic degradation of nitrobenzene has been studied by Weavers et al. (17). Pyrolysis and hydroxylation are the main pathways for the sonolytic degradation of nitrobenzene as follows where ')))' refers to the application of ultrasound and [O] refers to the •OH radical or other oxidants (e.g.,  $H_2O_2$ ) produced by ultrasound:



$$NO_2 + \bullet OH \longrightarrow HNO_3$$

(3)



The formation of *m*-nitrophenol (MNP), *p*-nitrophenol (PNP), and 4-nitrocatechol (4-NC) was observed during sonolysis of nitrobenzene in water at 20 kHz (*17*). However, at 500 kHz, *o*-nitrophenol (ONP) was also observed as an intermediate. With continuous irradiation these intermediates are further degraded to inorganic products, e.g., HNO<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O.

**Mechanism of Nitrobenzene Reduction by Fe**<sup>0</sup>. According to Agrawal and Tratnyek (*14*), the pathway for nitrobenzene reduction by elemental iron can be described by the following

<sup>\*</sup> Corresponding author phone: (626)395-4391; fax: (626)395-3170; e-mail: mrh@its.caltech.edu.



where the overall stoichiometry is given by

$$\begin{array}{c} \text{NO}_2 \\ & \\ \end{array} + 3 \text{ Fe}^0 + 6 \text{ H}^+ \longrightarrow \\ \end{array} + 3 \text{ Fe}^{2+} + 2 \text{ H}_2 \text{O} \qquad (9)$$

Based on the overall reaction depicted in eq 9, the primary product observed after several hours of reaction is aniline with nitrosobenzene found as the only intermediate (eq 6).

#### **Experimental Procedures**

High-purity reagents, nitrobenzene (Aldrich, 99%), nitrosobenzene (Fluka, 99%), and aniline (Fluka) were used without further purification. Standard solutions of nitrobenzene and aniline were made with water purified by a Millipore Milli-Q UV Plus system (18.2 MΩ-cm resistivity). For nitrosobenzene, the stock solution was prepared with 50% acetonitrile (EM Science, GR). The initial reaction volume was 0.285 L, and the initial nitrobenzene concentration was 25  $\mu$ M. Solutions were not buffered.

Zerovalent iron particles (Fluka) were prepared by sieving raw particles through a 20-mesh screen (1.0 mm opening size). The elemental iron was not pretreated with acid prior to use. The degradation reactions with Fe<sup>0</sup> were carried out in tightly closed systems with reaction volumes of 300 mL. Sample aliquots were obtained by syringe through a Teflon septum. The reaction vessels were wrapped in aluminum to limit exposure to light. Reaction solutions were preequilibrated at 15 °C in a circulating water bath.

Kinetic runs were initiated by adding a measured amount of Fe<sup>0</sup> to the reactor system which was placed on a variablespeed rotary shaker. The entire shaker was kept in an aircooled refrigeration unit at a constant temperature of 15 °C.

Sonolyses were performed with a VCX-400 Vibracell (Sonics and Materials, Inc., Danbury, CT) operating at 20 kHz. The temperature was maintained at 15  $\pm$  2 °C with a Haake A80 Refrigerated Bath and Circulator. Replaceable titanium tips with diameter of 1.27 cm on the 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 with air equilibrium. The physical dimensions and fundamental characteristics of the transducer and the reactor configuration have been presented (16). 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

# TABLE 1. HPLC Retention Times and Specific Topic Data for Nitrobenzene (NB) and Its Sonolysis Reaction Intermediates $^{a}$

	$\lambda$ , nm	av retention time, min	$\epsilon$ , $M^{-1}$ cm <sup>-1</sup>
NB	267	$\sim$ 4.5	$6.36 \times 10^{6}$
NSB	307	${\sim}5.5$	$6.60  imes 10^{6}$
AN	224	$\sim$ 2.0	$4.85 \times 10^{6}$
ONP	224	$\sim 1.5$	$4.56 \times 10^{6}$
MNP	224	$\sim$ 2.4	$7.37 \times 10^{6}$
PNP	318	~2.2	$8.53 \times 10^{6}$
4-NC	224	~3.7	$5.71 \times 10^{6}$

<sup>*a*</sup> NB = nitrobenzene; NSB = nitrosobenzene; AN = aniline; ONP = *o*-nitrophenol; MNP = *m*-nitrophenol; PNP = *p*-nitrophenol; and 4-NC = 4-nitrocatechol.

solution. The reactor was made gastight with two O-ring seals in a threaded Teflon 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. The ultrasonic power output was measured by calorimetry.

**Chemical Analyses.** Sample aliquots of 0.5 mL were collected at designated times and filtered through Teflon syringe filters (Gelman Acrodisc) into amber colored liquid chromatography vials. Quantification of nitrobenzene and its intermediates was performed on a Hewlett-Packard Series II 1090 Liquid Chromatograph with a 3  $\mu$ m 100 × 4 mm Hypersil BDS-C18 column (Hewlett-Packard). The method called for a 1 mL min<sup>-1</sup> flow rate, 40 °C temperature, and a 25  $\mu$ L injection volume. The runs were 6 min long with an isocratic mixture (70:30) of water to acetonitrile (EM Science, HPLC grade). The postrun time was 1 min.

### **Results and Discussion**

Experiments were performed at an initial nitrobenzene concentration of 25  $\mu$ M and an initial pH of 6 without an added buffer. The loss of nitrobenzene was found to be less than 5% in control experiments in the absence of ultrasound and iron. After completion of each kinetic run with ultrasound alone, the final observed pH was close to 5.5. With Fe<sup>0</sup> alone the final observed pH was close to 7, and with the combination of ultrasound and Fe<sup>0</sup>, the observed pH was near 8. In the reactions involving Fe<sup>0</sup>, a rise in pH is consistent with the following stoichiometries:

$$Fe^{0} + 2H_{2}O \Rightarrow Fe^{2+} + H_{2} + OH^{-}$$
 (10)

$$2Fe^{0} + O_{2} + 2H_{2}O \Rightarrow 2Fe^{2+} + 4OH^{-}$$
 (11)

The observed higher pH with the combined US/Fe<sup>0</sup> systems indicates that more Fe<sup>0</sup> is involved in the degradation of nitrobenzene or oxidized by water and oxygen in the presence of ultrasound.

Nitrosobenzene (NSB) and aniline (AN) were the major products observed in the reduction of nitrobenzene by Fe<sup>0</sup>. However, during sonication the principal observed intermediates were *o*-nitrophenol (ONP), *m*-nitrophenol (MNP), *p*-nitrophenol (PNP), and 4-nitrocatechol (4-NC). The key UV-vis spectroscopic and chromatographic data for nitrobenzene and its intermediates are presented in Table 1.

First-order plots of ln{[NB]/[NB]<sub>0</sub>} vs time during sonolysis at 20 kHz and during reduction by Fe<sup>0</sup> are shown in Figure 1. The slopes obtained from linear regression of the data yield the observed first-order rate constants for nitrobenzene degradation. The corresponding reaction rate for nitrobenzene degradation by ultrasound in the presence of iron was also found to be first-order at lower Fe<sup>0</sup> loadings, [Fe<sup>0</sup>]. At higher [Fe<sup>0</sup>], the second-order polynomial function (dashed line) gives a better experimental fit than a simple first-order



FIGURE 1. The degradation of nitrobenzene by ultrasound ( $\bullet$ ), 10 rpm/70 g L<sup>-1</sup> Fe<sup>0</sup> ( $\blacktriangle$ ), and US/70 g L<sup>-1</sup> Fe<sup>0</sup> ( $\blacksquare$ ); the solid lines are the fitted results from the first-order analysis, and the dashed line is the second-order fitting from eq 18 for US/70 g L<sup>-1</sup> Fe<sup>0</sup>.

TABLE 2: Comparison of *k* Values for Nitrobenzene Degradation in the Combined US/Fe<sup>0</sup> System (Ultrasound Power Amplitude: 35%) and on the Rotary Shaker System

[Fe <sup>0</sup> ], g L <sup>-1</sup>	$k_{US}+k_{Fe^0}$ , min $^{-1}\cdot$ 10 $^3$	<i>k<sub>Fe<sup>0</sup></sub></i> , min <sup>-1</sup> · 10 <sup>3</sup>	$k_{ m sec}k_{p_l}$ min <sup>-2</sup> · 10 <sup>5</sup>	$k_{10rpm/Fe^0}$ , min <sup>-1</sup> · 10 <sup>3</sup>
0	1.8 (± 0.1)	0	0	0
18	2.9 (± 0.1)	1.1	0	0.8
35	5.9 (± 0.2)	4.1	$\sim$ 0	1.5
53	6.9 (± 0.4)	5.1	$2.8\pm0.5$	3.5
70	7.8 (± 0.4)	6.0	$\textbf{9.8}\pm\textbf{0.5}$	4.8
88	12.4 (± 1.5)	10.6	$21.0 \pm 2.4$	9.9

relationship (solid line) as shown in Figure 1. The average deviation for nitrobenzene reductions determined in replicate experiments was < 10%.

**Reduction by Elemental Iron Surfaces.** Agrawal and Tratnyek (*14*) reported that the nitrobenzene reduction rate constants exhibited a linear relationship with respect to the square root of the stirring rate (i.e., rate  $\propto \omega^{0.5}$ ), which indicated that the apparent reaction rate was limited by mass transport. In this study, we mixed the suspension with a 360° rotary shaker at  $\omega = 10$  rpm. The rate of reduction of nitrobenzene by Fe<sup>0</sup> is observed to be first-order. The observed reaction rate constants,  $k_{10rpm/Te0}$ , as a function of [Fe<sup>0</sup>] are listed in Table 2. As expected,  $k_{10rpm/Te0}$  increases with [Fe<sup>0</sup>].

In the combined US/Fe<sup>0</sup> systems, the overall rate of nitrobenzene disappearance can be described by a linear combination of first-order terms (17)

$$-\frac{d[NB]}{dt} = k_{US}[NB] + k_{Fe^0}[NB] + k'[NB] = (k_{US} + k_{Fe^0} + k') [NB]$$
(12)

where  $k_{US}$ ,  $k_{Fe^0}$ , and k' are, respectively, the first-order degradation rate constants for sonolysis, reduction by Fe<sup>0</sup>, and the synergistic kinetic effect achieved by combining the two systems. k' may be related to the generation of increased surface area or reactive intermediates, which are capable of degrading nitrobenzene. The k' should be dependent on the newly created reactive surface sites and on the concentration of the reactive intermediates. k' can be expressed by the following generalized equation

$$k' = k_{\text{sec}}[X_{i,j}] \tag{13}$$

where  $k_{\text{sec}}$  is the average second-order rate constant for the reaction between the Fe<sup>0</sup> surface sites or the reactive



FIGURE 2. The fitted results from eq 18 in the combined US/Fe<sup>0</sup> systems as a function of [Fe<sup>0</sup>].

intermediates and nitrobenzene, and  $[X_{i,j}]$  is effective concentration of the newly generated Fe<sup>0</sup> surface sites (*i*) and the reactive intermediates (*j*). Since the reactive intermediates will be consumed very fast with any reactants in the solution, the contribution in  $[X_{i,j}]$  from the reactive intermediates can be ignored. If we assume that  $[X_{i,j}]$  is mainly contributed from the newly generated Fe<sup>0</sup> surface by ultrasound, the total activated Fe<sup>0</sup> surface (*x*) increasing rate is proportional to *x* with a rate constant,  $k_{a}$ , as follows:

$$\frac{dx}{dt} = k_a x \tag{14}$$

x as a function of time can be solved as follows

$$x = x_0 + [X_{i,i}] = x_0 \ e^{k_a t} \tag{15}$$

where  $x_0$  is the initial activated Fe<sup>0</sup> surface before ultrasound is applied. Since the influence of ultrasound at low [Fe<sup>0</sup>] can be ignored, the exponential term in eq 15 could be expanded into polynomial terms. Without consideration of the high order terms, [ $X_{i,j}$ ] can be expressed as follows

$$[X_{i,j}] = x_0 k_a t = k_p t \tag{16}$$

where  $k_p = x_0 k_a$  is a zero-order rate constant that increases with added [Fe<sup>0</sup>]. Substitution of eqs 13 and 16 into eq 12, yields the following time-implicit equations:

$$-\frac{d[NB]}{dt} = (k_{US} + k_{Fe^0} + k_{sec}k_p t)[NB]$$
(17)

The integration of eq 17 gives

$$-\ln\left[\frac{[NB]}{[NB]_{0}}\right] = (k_{US} + k_{Fe^{0}})t + \frac{1}{2}k_{sec}k_{p}t^{2}$$
(18)

Values of  $k_{US}$  were determined from the separate sonicationonly experiments. Figure 2 shows the fitted results from eq 18 for various [Fe<sup>0</sup>]. The individual rate constants are listed in Table 2.

The values of  $k_{Fe^0}$  in the combined US/Fe<sup>0</sup> system are slightly higher than  $k_{10rpm/Fe^0}$  values in part because of the higher relative mixing rates achieved during sonication. The new surface area and species created by ultrasound are reflected in ' $k_{sec}k_p$ ', which increases with Fe<sup>0</sup> loading at higher [Fe<sup>0</sup>]. The higher values of ' $k_{sec}k_p$ ' obtained with increasing [Fe<sup>0</sup>] are due primarily to the effects related to the direct reactions with elemental iron. Since  $k_{sec}$  is a rate constant quantifying the impact of the secondary effects on nitrobenzene, it is independent of [Fe<sup>0</sup>]. On the other hand,  $k_p$  should increase with [Fe<sup>0</sup>] as mentioned above.

The higher degradation rates observed in the combined US/Fe<sup>0</sup> systems can be attributed to the indirect chemical effects associated with the continuous ultrasonic cleaning and activation of the Fe<sup>0</sup> surface, the enhanced rate of mass transport resulting from the turbulent effects of cavitation, and the H<sup>+</sup> released to solution from the HNO<sub>3</sub> produced during the sonolysis of nitrobenzene and water (eq 3). The shock wave and microjets formed during cavitational bubble collapse are primarily responsible for the surficial 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 reduction of the nitro group to an amine group via eq 9.

It has long been recognized that air-saturated water, which is exposed to the action of ultrasound, leads to the formation of  $NO_2^-$  and to a lesser extent  $NO_3^-$  as well as  $H_2O_2$  (18–21). The observed pH decrease during sonication should result in a faster rate of reduction of Fe<sup>0</sup> (eq 6). Since the sonolytic degradation of nitrobenzene produces HNO<sub>3</sub> according to eqs 1–3, we expect to see a faster reduction rate in the combined reaction system, but this contribution can be ignored because of higher pH observed at US/Fe<sup>0</sup> systems. The H<sup>+</sup> produced during sonolysis should be consumed by Fe<sup>0</sup> oxidation or nitrobenzene reduction according to the following stoichiometry:

$$\begin{array}{c} NO_2 \\ + 3 Fe^0 + 6 H^+ \\ \end{array} + 3 Fe^{2+} + 2 H_2O \quad (19) \end{array}$$

Aqueous-phase  $Fe^{2+}$  (i.e.,  $Fe(H_2O)_6^{2+}$ ) and the  $Fe^{2+}$  sorbed on the surface of  $Fe^0$  can also react with  $H_2O_2$ , which is produced from the sonication of  $H_2O$  (*20*) as follows:

$$Fe(H_2O)_6^{2+} + H_2O_2 \rightarrow Fe(H_2O)_6^{3+} + OH^- + \cdot OH$$
 (20)

$$\{\operatorname{Fe}\cdot\operatorname{Fe}^{2^+}\} + \operatorname{H}_2\operatorname{O}_2 \to \{\operatorname{Fe}\cdot\operatorname{Fe}^{3^+}\} + \operatorname{OH}^- + \cdot\operatorname{OH} (21)$$

The •OH radical will be available for further reactions such as the degradation of nitrobenzene and aniline. Since high concentrations of  $Fe^{2+}$  are produced from oxidation of  $Fe^{0}$ , the subsequent Fenton's Reagent reaction should be independent of  $[Fe^{0}]$ . The contribution of the Fenton's reaction in the combined US/Fe<sup>0</sup> systems should be relatively constant and thus reflected in the second term of eq 18. Since a similar degradation rate for aniline is observed in both the US and combined US/Fe<sup>0</sup> systems, the secondary Fenton's reaction appears to be negligible compared to other secondary effects. Ultrasound also enhances the mass transfer of the product, aniline, away from the Fe<sup>0</sup> surface.

The observed nitrobenzene reduction rates in our study are somewhat lower than those reported by Agrawal and Tratnyek (14). These differences may be due to the specific nature of the buffers and the elemental iron used in each case. In our study, the elemental iron was used without pretreatment, and therefore the initial reactive surface areas may have been somewhat different than those used by Agrawal and Tratnyek (14).

**Aniline Sonolysis.** The final observed product of nitrobenzene reduction by Fe<sup>0</sup> is aniline, which is a well-known corrosion inhibitor. The mechanism of inhibition is believed to involve an interference with mass transport of the primary oxidant to the metal surface, which in turn is strongly influenced by the orientation of the sorbed aniline. The sonolytic degradation of aniline is a first-order reaction with an apparent rate constant of  $2.4 \times 10^{-3} \text{ min}^{-1}$  at 20 kHz with

an input power density of 139 W L<sup>-1</sup>. In this case, there is no enhancement due to the presence of Fe<sup>0</sup> surfaces because aniline cannot be reduced by Fe<sup>0</sup>. The observed rate enhancements in the reduction of nitrobenzene in the combined US/Fe<sup>0</sup> system could also due to the degradation of aniline by sonolytic cavitation. The degradation of aniline with US or the combined US/Fe<sup>0</sup> (35 g L<sup>-1</sup>) system has the same observed rate constants. This result indicates that the sonolyses are not affected by Fe<sup>0</sup> and the enhancement of nitrobenzene degradation by US/Fe<sup>0</sup> is mainly due to a faster rate of nitrobenzene reduction by Fe<sup>0</sup> in the presence of ultrasound.

The rate constants for the sonolytic degradations of nitrobenzene and aniline are smaller than those observed for  $CCl_4$  (*16*). This may be due to the lower tendency for the substituted benzenes to partition into the vapor phase of the cavitation bubbles due to their lower Henry's Law constants (*17*). The principal observed intermediate during aniline sonolysis is benzoquinone. The possible mechanism for the degradation of aniline by sonication is as follows.



**Identification of Byproducts and Reaction Intermedi** ates. The intermediates observed at relatively high concentrations during nitrobenzene sonication at 20 kHz are *m*-nitrophenol, *p*-nitrophenol, and 4-nitrocatechol (17). These intermediates are eventually decomposed sonochemically to CO<sub>2</sub> and HNO<sub>3</sub>. In this study, nitrosobenzene and aniline were observed as the main intermediates in the presence of Fe<sup>0</sup>. Other reaction intermediates such as 4-nitrocatechol and benzoquinone have concentrations less than 1  $\mu$ M in the combined US/Fe<sup>0</sup> systems and are ignored in Figure 3 (a). The nitrophenols (eq 4) were not observed. This may be due to a fast transformation rate to 4-nitrocatechol such that the nitrophenols concentrations were kept below the detection limits under current experimental conditions. The relative effects of sonication on the observed intermediates and the total mass balance around nitrobenzene are shown in Figure 3. After 3 h of reaction, the total mass of aromatic compounds does not change in the mechanically agitated Fe<sup>0</sup> system but is decreased by 12% in US system and by 40% in the combined US/Fe<sup>0</sup> system. The



FIGURE 3. The concentrations of the reactant, intermediates, and products as a function of time: (a) in the US/70 g  $L^{-1}$  Fe<sup>0</sup> system and (b) in the 10 rpm/70 g  $L^{-1}$  Fe<sup>0</sup> system.

principal intermediate, aniline, which is not degraded by  $Fe^0$ , is eventually destroyed by ultrasound. The array of aromatic compounds observed during nitrobenzene degradation should be more efficiently decomposed in the combined US/Fe<sup>0</sup> systems. The higher concentration of aniline in US/Fe<sup>0</sup> systems suggests that the nitrobenzene degradation rate is apparently enhanced from the reduction of nitrobenzene by Fe<sup>0</sup>.

**Effects of Ultrasonic Power Density.** The reduction of nitrobenzene by Fe<sup>0</sup> occurs at the Fe<sup>0</sup>/H<sub>2</sub>O interface. The heterogeneous reactions involves five steps (*3*, *22*): (i) mass transfer of the reactant to the Fe<sup>0</sup> surface from the bulk solution; (ii) adsorption of the reactant on the surface; (iii) chemical reaction at the surface; (iv) desorption of the products from the surface; and (v) mass transfer of the products into the bulk solution. Any one of these steps may be rate limiting and, therefore, be reflected in the values of  $k_{obs}$  reported in this study. To properly interpret trends in the observed reaction rates, it is important to distinguish between mass transport and reaction-limited kinetics.

A common criterion for detecting mass transfer-limited kinetics is a variation in the reaction rate with the intensity of mixing. An increase in ultrasonic power will increase the mixing intensity due to the turbulence generated by cavitational bubble collapse. The ultrasonic power levels adjusted by changing the ultrasound power amplitude and the corresponding calorimetry results are given in Table 3. The reactions taking place at an Fe<sup>0</sup> loading of 35 g L<sup>-1</sup> are pseudo-first-order. Under these conditions, the relative enhancement in the nitrobenzene reduction rate increases with increasing sonication power. For example, when the applied power density is increased from 39 to 73 W L<sup>-1</sup>, the reaction rate is approximately doubled. However, when the power density is increased further to 139 W L<sup>-1</sup>, the reaction rate is only

## TABLE 3: Ultrasonic Power Amplitudes and the Corresponding Absorbed Power as Determined by Calorimetry

applied power (W)	140	80	40
absorbed power (W)	40	21	11
power density, W L <sup>-1</sup>	139	73	39
$k_{US}$ , min <sup>-1</sup>	$1.8  imes 10^{-3}$	$1.4 \times 10^{-3}$	$0.7 \times 10^{-3}$
$k_{US+35gL^{-1}Fe^0}$ , min <sup>-1</sup>	$6.1 \times 10^{-3}$	$4.8  imes 10^{-3}$	$2.4 \times 10^{-3}$

increased another 50%. As reported previously (*16*), the efficiency of energy transfer to solution decreases with higher power densities due to a greater loss of input energy as heat. The observed rate constants are directly proportional to the power density at low power inputs; however, at high input powers the relationship becomes nonlinear. Furthermore, at higher sonication intensities, the Fe<sup>0</sup>-corrosion pathways (eqs 10 and 11) are enhanced, and thus the net degradation rate of nitrobenzene is no longer directly proportional to the sonication power.

In this study, we demonstrated that the rate of nitrobenzene reduction by Fe<sup>0</sup> could be enhanced in the presence of ultrasound. The higher apparent rates of reaction in the combined US/Fe<sup>0</sup> systems compared to Fe<sup>0</sup> reaction alone can be attributed primarily to the continuous cleaning and activation of the Fe<sup>0</sup> surface by the chemical and physical effects of ultrasound. Furthermore, the rates of mass transport rates of nitrobenzene, nitrosobenzene, and aniline to and from the Fe<sup>0</sup> surface are enhanced by hydrodynamic cavitation. Oxidation of the reaction intermediates during sonication also contributes to the observed rate enhancements. The relative concentrations of the principal reaction intermediates in US/Fe<sup>0</sup> systems, nitrosobenzene, and aniline appear to be influenced significantly by total available surface area of Fe<sup>0</sup>. In conclusion, the combination of ultrasound and Fe<sup>0</sup> appears to have a positive synergistic effect on the reduction of nitro aromatic compounds.

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