Degradation of Trazine Compounds via Metallic Iron Under Acidic Conditions

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Degradation of Triazine Compounds Via Metallic Iron Under Acidic Conditions
Abstract

The degradation of dissolved dimethoxyatrazine (2-chloro-4,6-dimethoxy-1,3,5-triazine), terbutylazine (2-chloro-4-ethylamino-6-terbutylamino-1,3,5-triazine) and deisopropylatrazine (2-amino-4-chloro-6-ethylamino-1,3,5-triazine) via metallic iron was studied as a function of solution pH. Generally, degradation was more rapid the lower the solution pH and higher the compound pKa. For dimethoxyatrazine $k_{SA} = k'(\text{min}^{-1}) * V(\text{L}) / M(\text{g}) / SA(\text{m}^2/\text{g})$ was found to be $1.33 (\pm 0.07) \text{E-4} \text{ min}^{-1} \text{ m}^2 \text{ L at pH 2, 6.1 (\pm 0.6) E-5 min}^{-1} \text{ m}^2 \text{ L at pH 3 and 4.4 (\pm 0.6) E-5 min}^{-1} \text{ m}^2 \text{ L at pH 4. For deisopropylatrazine k}_{SA}$ was found to be $7.2 (\pm 0.2) \text{E-4 min}^{-1} \text{ m}^2 \text{ L at pH 2 and 1.0 (\pm 0.4) E-4 min}^{-1} \text{ m}^2 \text{ L at pH 3. For terbutylazine k}_{SA}$ was found to be $2.41 (\pm 0.06) \text{E-3 min}^{-1} \text{ m}^2 \text{ L at pH 2, 6.9 (\pm 0.9) E-4 min}^{-1} \text{ m}^2 \text{ L at pH 3 and 2.4 (\pm 0.4) E-4 min}^{-1} \text{ m}^2 \text{ L at pH 4. Dechlorinated dimethoxyatrazine and terbutylazine products were detected in the reaction solutions.}$

The electrochemical reduction of these compounds on mercury electrodes was examined. Cyclic voltammetry and differential pulse polarography experiments with these triazines yielded a general pattern of two pH dependent irreversible reduction waves.

These results suggest the triazine degradation reaction via metallic iron begins with a 2-electron dechlorination reduction step and that the actual species undergoing reduction is the protonated triazine.
This is dedicated with all of my love to Christopher.
Acknowledgments

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Introduction

Triazine herbicides are used to control broadleaf and grassy weeds for a wide variety of crops including corn, sorghum, pineapples, sugarcane, wheat and lawn grasses (USEPA, 2000). Their versatility and cost effectiveness as weed control agents justifies their desirability in the agricultural industry. Atrazine and Terbutylazine are two commonly used triazine herbicides. They work primarily by inhibiting electron transport in photosynthesis. Binding occurs through the plant root to the reactive site for plastoquinone, thereby preventing its binding (Triazines, 2000).

The extensive use of triazines has raised concerns about their fate in the environment. Triazines are considered to be somewhat persistent in the water and mobile through the soil (USEPA, 2000). Mobility in the soil leads to their extended persistence and can result in contamination of ground water. Studies have shown that triazines are degraded in the environment (Plust et al., 1981; Comber, 1999).

Degradation in the environment occurs through hydrolysis (a chemical reaction with water).

Hydrolysis of atrazine to hydroxyatrazine

The hydrolysis of atrazine is an abiotic degradation pathway that occurs in soils and water leading to the formation of hydroxyatrazine. The reaction occurs very slowly in neutral solutions, but it has been found that it is both acid and base catalyzed. In addition,
the hydrolysis of atrazine has been found to proceed in the presence of humic and fulvic acid buffers. A detailed kinetic study of acid-catalyzed hydrolysis of atrazine by Plust et al., (1981), ascertained that the degree of protonation was significant and affected the rate of hydrolysis. In this study they compared rate constants for the hydrolysis of atrazine reported in earlier studies and established that the rate constants were much greater for the hydrolysis of atrazine when the diprotonated form of atrazine was present in solutions at extremely low pH levels. The rate constants reported decreased in solutions at higher pH levels.

In both soil and water, degradation by microorganisms leads to the formation of two primary metabolites of atrazine.

However these degradation processes occur slow and thus the persistence of these compounds in the environment is of concern.
Greater environmental awareness has led to changes and reductions in the use of herbicides. However, a recent study by Battaglin and Goolsby (1999), reported the average use of atrazine as a herbicide has only decreased by 2 percent. The continued use of triazines as weed killers necessitates studies that examine more aggressive degradation processes. It has been shown that advanced oxidation processes in which the addition of peroxide supplemented by UV light leads to triazine degradation (Comber, 1999). In a previous study, we observed the rapid dechlorination of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) with iron under acidic conditions (Dombek et al., 2001). It was found that pH is an important factor in the reduction of atrazine, but the pH dependence was not clearly understood.

The primary goal of this study was to develop an understanding of how pH influenced the reduction of triazines via metallic iron. The extent of reduction may likely depend upon the degree of protonation, therefore a compound with a lower pK$_a$ would be reduced at a slower rate compared to a compound with a higher pK$_a$. The triazines chosen for this study had different pK$_a$ values due to their different functional groups in the 4 and 6 positions on the triazine ring. Dimethoxyatrazine (2-chloro-4,6-dimethoxy-1,3,5-triazine) is a triazine used for chemical synthesis, terbutylazine (2-chloro-4-ethylamino-6-terbutylamino-1,3,5-triazine) a common herbicide, and deisopropylatrazine (2-amino-4-chloro-6-ethylamino-1,3,5-triazine) a primary dealkylated product resulting from biotic degradation of atrazine.

Structures of the compounds studied are shown below with their respective pKa values.
It has been shown that triazines are reduced on mercury electrodes and that pH influences their electrochemical reduction (Lippolis and Concialini, 1988; Pospisil et al., 1995; Skopalova and Kotoucek, 1995; Higuera et al., 1999). The number of electrons involved during the reduction process can be determined from electrochemical studies. So a second goal of this work was to determine if the number of electrons exchanged during the Fe reduction process for the triazines in this study is the same as reported in
Iron has been used as a reducing agent in organic synthesis for many years. Many studies have been conducted which examine the reduction of chlorinated compounds in the presence of metallic iron (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Burris et al., 1995; Helland et al., 1995; Gotpagar et al., 1997; Charlet et al., 1998; Johnson et al., 1998; Dombek et al., 2001). However none of these studies have clearly defined the mechanistic process of reduction with iron. Metallic iron is relatively inexpensive and quite effective in reducing harmful contaminants. The final goal of this study was to better understand the mechanism involved in the reduction process of triazine compounds via metallic iron.

Reductive dechlorination with Fe$^0$ – Literature review

In early studies of chlorinated methanes, ethanes, and ethenes, Gillham and O'Hannesin (1994), found that the reductions of some of these compounds appeared to be pseudo first order with respect to the organic compound with the rate constant being directly proportional to the surface area of the iron to solution volume ratio. The rate of dechlorination declined logarithmically and was dependent upon the degree of chlorination of the compound. In addition, an analysis of the degradation products showed that only the dechlorinated forms of the parent compounds were detected indicating that the process is reductive dechlorination, however, the mechanism for reduction was not clearly understood.
An extensive study done by Matheson and Tratnyek (1994), outlined 3 possible mechanisms through which the reduction process could be explained. One proposed pathway (Eq. 1) is that the reduction of the halogenated compound occurs through a direct electron transfer with the surface-bound compound serving as the oxidizing agent.

\[
Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \quad (Eq. 1)
\]

The second possible mechanism (Eq. 2) occurs with the reductant Fe\(^{2+}\), which results from the corrosion of solid iron by H\(_2\)O producing OH\(^-\) and H\(_2\) (g). The chlorinated compound then gets reduced while Fe\(^{2+}\) is oxidized to Fe\(^{3+}\).

\[
Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \\
2Fe^{2+} + RCl + H^+ \rightarrow 2Fe^{3+} + RH + Cl^- \quad (Eq. 2)
\]

The third possible mechanism may occur by dehalogenation with H\(_2\), but the reduction would require an effective catalyst or may occur through the surface bound H\(_2\).

This same study indicated that the surface of the iron is necessary for the reduction to occur. The addition of dissolved iron salt (FeCl\(_2\)) into controls that did not contain metallic iron resulted in no chemical change of the parent compound. This evidence is consistent with that found in a study by Burris et al., (1995), who also observed no degradation in the presence of FeCl\(_2\) and FeSO\(_4\). This evidence suggests that the pathway involving reaction 2 is unlikely. The control studies consisting of H\(_2\)-saturated water also produced no measurable dehalogenation showing that no uncatalyzed reduction by hydrogen gas is occurring. In addition, the study by Matheson and Tratnyek (1994), concluded that the iron surface area concentration was the most important
predictor in the rate of dechlorination. They found that pretreatment of the iron with HCl used in experiments was essential to both its effectiveness for dechlorination and the ability to achieve a reproducible surface. Burris et al., (1995), reported similar surface areas for both pretreated and untreated iron.

A study of the reductive dehalogenation of TCE by Gotpagar et al., (1997), found that the amount of TCE degraded at any given time was found to be directly proportional to the amount of dissolved iron in solution at that time. This result presents the possibility that (eq 1) is directly involved in the reduction process. For this particular study, pH was an important factor for the rate of Fe⁰ dissolution, but didn’t appear to enhance degradation of TCE.

Burris et al., (1995), studied the sorption of trichloroethylene (TCE) and tetrachloroethylene (PCE) in iron-water systems. In addition to findings that mass loss of the parent compound had occurred due to a reduction process they established that both compounds were sorbed to the iron surface with a greater amount of tetrachloroethylene sorbed relative to trichloroethylene. The distribution of PCE in solid phase compared to aqueous phase was fit to a generalized Langmuir isotherm fit. The fit is nonlinear showing a near-plateau region that corresponds to quasi-equilibrium sorption (it is termed quasi because degradation is occurring in addition to adsorption). The isotherm for PCE shows that a sorption-equilibrium is reached within 24 hours and this equilibrium is essentially the same at 456 hours (the time frame of reduction experiments), hence no further adsorption is occurring. This suggests that there are a finite number of available binding sites. They observed that no constant mass loss per unit time of the parent
compound in the near-plateau regions of the sorption isotherms thus suggesting that sorption may have occurred onto nonreactive sorption sites.

Sorption isotherms of both PCE and TCE together in solution showed that competitive binding occurred, however there was no evidence of competition in the degradation of either compound. This also supports the conclusion that binding may occur onto nonreactive sites. It was suggested that binding onto nonreactive sorption sites could sequester iron molecules from the reduction reaction. The rate of change in the aqueous phase with respect to time was evaluated. Accounting for losses due to degradation and sorption and a gain due to desorption, then combining this equation with a differentiation of the mass balance relationship with respect to time, they were able to show a first order reduction process existed for both compounds.

The role of oxygen in iron-mediated reduction processes was considered in a study by Helland et al., (1995). They noticed a decrease in the rate of dechlorination of carbon tetrachloride via metallic iron reduction in the presence of oxygen. The decrease in the rate of dechlorination due to oxygen might suggest that a mechanism that corresponds to eq. 1 is occurring. It seems likely that the decrease in the rate of reduction in the presence of oxygen would be more relevant for higher solution pH also. The formation of iron hydroxides would occur in neutral and basic solutions. The study by Helland et al., (1995), was conducted at a slightly higher than neutral pH and no increase in pH was observed during the course of their reactions. It would be expected that at low pH, the presence of oxygen would not severely interfere with the rate of reduction. If iron reduction were to occur via the formation of Fe^{2+}, then it might be that oxygen could
actually increase the rate of reduction, as more Fe$^{2+}$ would be produced by oxidation by oxygen.

The role of oxygen and Fe$^{2+}$ was investigated by Charlet et al., (1998). Their study concluded that the adsorption of Fe$^{2+}$ onto corrosion products, resulting from the corrosion of metallic iron by oxygen, coupled the reduction reactions of uranium and trichloroethane rather than the oxidation of solid iron to Fe$^{+2}$. They found that measurements of the redox potential during oxidation-reduction reactions correlated very strongly to the redox potential for the half reduction-oxidation eq. 3.

$$\frac{1}{2}α-Fe_2O_3(s) + e^- + 3H^+ \rightarrow Fe^{2+} + 3/2H_2O \quad (Eq. 3)$$

In a study by Johnson et al., (1998), the complexation effects on the oxide surface were explored. It was speculated that the oxide film already present on the iron surface influences the dissolution of Fe$^0$. The adsorption of some compounds may likely enhance the dissolution at the surface while the adsorption of other compounds may block the dissolution. This suggests that both oxidation-reduction reactions and coordination processes influence the rate of dissolution of the iron surface. The coordination of organic solvents that interact very weakly to the surface may be degraded as they facilitate the dissolution of iron through electron transfer. It was shown that coordination of compounds such as EDTA and borate decreased the rate of dechlorination of carbon tetrachloride in the study by Johnson et al. (1998). This supports that coordination of compounds at the surface by strongly interacting compounds can interfere with reductive dechlorination by blocking access to reactive surface sites.
Summary of Iron Reduction Literature review

The studies by (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Burris et al., 1995; Helland et al., 1995; Gotpagar et al., 1997; Charlet et al., 1998; Johnson et al., 1998; Dombek et al., 2001), of reductive processes by iron have been aimed at determining the mechanism of reductive dechlorination and how it is influenced by environmental factors. The identification of dechlorinated products by Gillham and O'Hannesin (1994), provided evidence of reductive dechlorination for chlorinated aliphatics. We (Dombek et al., 2001) identified dechlorinated atrazine as a product of degradation for atrazine providing evidence for triazine reductive dechlorination.

The rate of reduction of organic compounds by iron is dependent upon many different factors. The available surface area (Matheson and Tratnyek, 1994), affects the rate of reduction and it was determined by Burris et al. (1994), that adsorption without reduction also occurs. The available number of binding sites appear to be limited as shown by Burris et al. (1994). Johnson et al (1998), determined that degradation rates were effected by competitive binding. The competitive processes are significant especially in utilizing iron for remediation in the environment. It was shown that oxygen decreased the rate of reduction (Helland et al., 1995). Its affect would likely depend upon solution pH and the mechanism for reduction. As found in our previous study for atrazine reduction via metallic iron (Dombek et al., 2001), we observed slower reduction rates for higher pH reactions suggesting that the protonation of the compound was necessary to the reduction process.

Reductive dechlorination occurs via metallic iron. Evidence leading to the mechanism for reduction is quite substantial and many speculations exist yet the actual
mechanism has not been determined. This study aims to evaluate more closely the role of pH in the reduction of triazines via metallic iron in order to add to the evidence.

The role of pH is significant if the reduction were occurring via the hydroxide layer. At low pH the formation of iron hydroxides would be minimal. It seems reasonable that as the pH is increased more reduction of the compound could occur due to an increase in the hydroxide surface area, however if protonation of the compound is required for triazine reduction in metallic iron it will be difficult to evaluate this mechanism further. Perhaps reductive dechlorination occurs via multiple pathways.

*Electroanalytical Techniques*

The electrochemical reduction of triazines on the mercury electrode has been studied for the development of cost-effective analytical and detection methods. The general techniques applicable to this study and the literature review are presented below as described by Skoog and Leary (1992), and Strobel and Heineman (1989).

Electroanalytical techniques differ in how the excitation signal is produced. This is the signal that produces a characteristic current response based upon the waveform as a function of time. Another difference is the sensitivity of each technique to the bulk concentration of the solution.

DC polarography is an electrochemical technique in which a cell contains a dropping mercury working electrode, a reference electrode and an auxiliary electrode. The excitation signal is a linear scan of potential vs. time. This technique utilizes a mechanical knocker to continually renew the mercury drop at the surface of the capillary tube. The current is continually monitored while scanning a described potential range.
The current fluctuates with the frequency of the drop rate, resulting in the current falling to zero as the drop is dislodged.

Reduction of a compound commences at the surface of the mercury drop upon reaching its reduction potential. The current measured during the reduction of the compound increases until all of the compound present at the surface is reduced. When the current is limited by the diffusion of the compound to the surface of the drop, diffusion-limited current is reached. At this point, the current no longer increases, but reaches a constant level.

This allows for the diffusion-limited current to be calculated by subtracting the residual current that was measured prior to the beginning of the reduction of the compound being analyzed. The Ilkovic equation describes the diffusion-limited current ($i_d$):

$$i_d = knm^{2/3}D^{1/2}t_d^{1/6}C$$

Where $i_d$ = diffusion current (µA), $m$ = flow rate of the mercury from the electrode (mg/s), $t_d$ = drop time (s), $k$ = constant (706 for maximum current and 607 for average current), $C$ = concentration (mmol/L), $D$ is the diffusion coefficient of the compound, and $n$ is the number of electrons transferred. The sample concentrations as well as the number of electrons exchanged can be calculated.

Sampled dc polarography, sometimes called TAST polarography, is similar to this technique, but differs in how the current is sampled. Instead of sampling the current continually, the current is sampled for a short time interval just before the drop is dislodged. This reduces the current fluctuations present in classical polarography. Both
techniques have similar detection limits on the order of $10^2 - 10^4$ M with detection limits marginally better for sampled dc polarography.

Differential pulse polarography (dpp) is a polarography technique that like taste and sampled dc polarography utilizes a chemical cell containing a dropping mercury working electrode, a reference electrode and an auxiliary electrode. The excitation signal is a linear scan of the potential as a function of time. This technique involves superimposing a periodic pulse onto the linear scan. A pulse increases the potential by a small amplitude for a short duration of time, this is called stepping the potential forward. A second pulse steps the potential back by a smaller amplitude, so that the change in the potential is smaller than the change occurring with the first pulse. This stepping technique results in a linear increase of the potential in small increments over time.

The current is sampled twice, before and at the end of the first pulse, and the difference is plotted vs. the scanned potential. This technique offers the advantage that the current measurement contains just the faradaic current that is due to the reduction of the compound and subtracts off the charging current. This leads to greater sensitivity with detection limits on the order of $10^7 - 10^8$ M.

Adsorptive stripping voltammetry is an electrochemical technique that uses a cell typical to those for polarography techniques with a mercury drop electrode as the working electrode. The solution is stirred for several minutes in the cell to allow for deposition of the analyte onto the mercury drop. After a time period sufficient to allow for an accumulation of the compound, the stirring is ceased and a linear-scan method or pulsing method can be used to analyze the concentration of the compound. This method offers enhanced detection limits on the order of $10^{-10} - 10^{-11}$ M.
**Electrochemical reductive dechlorination on a mercury electrode – Literature review**

**pH effects**

Skopaloya and Kotoucek (1995), determined that the reduction of atrazine and terbutylazine on the mercury electrode depends upon the pH of the solution and the concentration. They conducted sampled dc experiments and observed two waves in the polarogram. Their experiments were conducted at various solution pH’s. At low pH the two waves were distinguishable but as solution pH was increased the two waves merged into one. Their data from sampled dc polarography experiments for atrazine and terbutylazine were conclusive that only the protonated form was reduced on the mercury electrode because they observed that no reduction of the compounds at pH > 4. These conclusions were also based on a shift in the slope of straight-line plots showing the dependence of peak potential as a function of pH. The intersection of the lines correlated very closely to the pKa values of the triazines studied.

These results are consistent with those reported in another study by Pospisil et al., (1995), in which they also concluded that the electrochemical reduction of atrazine occurred only in acidic conditions. In addition, earlier electrochemical studies by Lippolis and Concinalini (1988), were conclusive that the protonated form is reduced in acidic solutions for atrazine and simazine.

**Solution concentration**

Skopaloya and Kotoucek (1995), studied atrazine and terbutylazine with adsorptive stripping voltammetry at the hanging mercury drop electrode and concluded that the reduction of these compounds was also affected by the solution concentration. They noted that at very low concentrations two reduction waves could be observed, but
as the triazine concentration was increased the two waves merged into one. Concentration affected the electrochemical behavior of triazines because of adsorption onto the mercury drop. Ignjatovic et al. (1993), studied the reduction of atrazine and simazine using differential pulse polarography on a mercury electrode and concluded also that adsorption occurred. They compared calibration curves of the peak current vs. concentration for various triazine solutions and thus determined that curves were linear in solutions between 0.050 ppm and 5 ppm. This observation suggests that adsorption onto the mercury is occurring for solutions at concentrations higher than 5 ppm. The adsorption likely influences the total current measured during the reduction process interfering with quantitative measurements such as determining the total electrons transferred.

**Electrochemical Reduction Mechanisms**

In the electrochemical study of atrazine by Pospisil et al., (1995), it was determined that the differences in the electron densities of the 3 ring nitrogens were minimal. It is suspected that when nitrogen in the ring becomes protonated, it pulls electron density away from the carbon atom, weakening the carbon-chlorine bond. This leads to the reduction of the compound producing the dechlorinated product.

The product of electrochemical reduction has been isolated for the reduction of atrazine. Pospisil et al., (1995), isolated dechlorinated atrazine at low pH after exhaustive electrolysis at a constant potential. In the study by Skopaloya and Kotoucek (1995), they observed the formation of chloride ions in atrazine solutions from constant coulometry. Atrazine solutions subjected to constant coulometry were analyzed using dc polarography and the amount of chloride ions formed corresponded to the amount of reduced atrazine from constant coulometry measurements. This suggests that the electrochemical
reduction mechanism involves the dechlorination of atrazine. Skopaloya and Kotoucek (1995), determined that four electrons were exchanged during the reduction of atrazine on a mercury electrode through constant potential coulometry. There are two dc waves present for the reduction of atrazine, and by holding the potential constant at the limiting current corresponding to the first wave, they measured a 2-electron exchange for the first dc wave. They verified the number of electrons transferred by comparing the dc waves with that of a benzil dc wave.

Their proposed reduction scheme is shown below for atrazine:

Higurera et al., (1999) conducted a thorough investigation of simazine using differential pulse polarography. They deconvoluted the reduction wave for simazine from differential pulse polarography into 2 primary reduction waves from which they proposed their reduction scheme. The reduction process involved the exchange of 4
electrons consistent with the results of the other studies (Skopalova and Kotoucek, 1995; Higuera et al., 1999).

The reduction scheme that they proposed involves an ECE process which involves an electron transfer, a chemical step, then a second electron transfer, and a second irreversible 2-electron exchange follows the ECE process. The ECE process corresponding to the first reduction wave includes a chemical step in between the exchange of 2-electrons with the chemical step being the rate-determining step, for this scheme the addition of a proton is the chemical step. This ECE scheme leads to the formation of dechlorinated-simazine.
For the second observed reduction wave, they proposed that the dechlorinated-product is further reduced through an irreversible 2-electron process with the protonation step occurring concurrently with the first electron transfer and a 2nd protonation occurring after the transfer of the 2nd electron. Their proposed scheme for the 2nd wave is identical to the one proposed by Skopalova and Kotoucek (1995), shown earlier.

**Summary of electrochemistry literature review**

Reduction of triazines on a mercury electrode is dependent upon the protonation and the concentration of the compound. The reduction schemes for triazines have not been elucidated, but two reduction schemes proposed (Skopalova and Kotoucek, 1995; Higuera et al., 1999), are similar. All agree that reduction of triazines on mercury electrodes have the dechlorinated product as the first product of reduction.

It also was shown that concentration effects the electrochemical behavior of triazines (Lippolis and Concialini, 1988; Skopalova and Kotoucek, 1995; Higuera et al., 1999). It is reasonable that it may be possible to determine the number of electrons exchanged for triazines in our study by comparing dc waves of triazines for which the number of electrons exchanged are known. Concentration will be an important factor and it is expected that the triazines may adsorb differently onto the mercury electrode. In addition, the pKa of the molecules will be an important factor due to the pH dependence of the triazines in reducing conditions on the mercury electrode. It is speculated that the reduction occurring on mercury is similar to reductive dechlorination via metallic iron.

**Experimental**

*Fe Reactions*
Dimethoxyatrazine (CDMT).

The reaction of cdmt with iron was carried out at pH 2.00(±0.10), 3.00(±0.10) and 4.00(±0.01) under N$_2$(g) in a 1 L flask. The reaction was carried out in a 1 L flask that held 4 ports, the first port was fitted with a ground glass adapter through which a stirring rod was added with a Teflon stirrer. The pH electrode was fitted through a ground glass adapter in a second port. Rubber septa were placed on the remaining two ports which were used to add acid, supply nitrogen, remove samples with a syringe and for temperature monitoring.

A 500 mL solution of 40.0 ppm cdmt was degassed by purging with N$_2$ for 1 hour and was added to the reaction flask containing 20 g of pretreated iron. The iron was pretreated by washing 20 g of dry metallic iron powder (finer than 100 mesh, Fisher Scientific) twice with 50 mL portions of 0.5 M H$_2$SO$_4$. Twenty grams of iron were added to the dry 1 L reaction flask, then 50 mL of acid were added and the mixture was stirred at 300 rpm for 15 minutes. The acid wash was removed into a filter flask using a vacuum and the procedure was repeated with a second 50 mL portion of acid. After removing the second wash solution, the 40.0 ppm cdmt solution was added to the flask and the pH was adjusted to the necessary level with H$_2$SO$_4$. The contents were stirred at 300 rpm for 4 hours.

Terbutylazine and Deisopropylatrazine.

Terbutylazine and Deisopropylatrazine solutions of approximately 8 ppm and 40 ppm respectively were reacted with 10 g of iron in a 500 mL round bottom flask. The flask contained 3 ports, one containing a ground glass adapter through which a stirring rod with Teflon stirrer was placed. The second port contained a ground glass adapter
through which the pH electrode was placed and the third port contained a rubber septum used to add acid and supply nitrogen. Water-iron reactions were completed at pH 2, 3 and 4 for terbutylazine and at pH 2 and 3 for deisopropylatrazine. 250 mL solutions containing the dissolved triazine were degassed with N₂ for 1 hour. Upon removal of the acid wash, 235 mL of the degassed solution were placed in the flask and stirred at 300 rpm while maintaining the pH at the appropriate level.

Analytical Methods

Cdmt.

At time intervals of 2, 3 and 4 hours, samples were removed from the reaction flask using a 50 mL syringe. The volume of sample removed (ranging from 18-20 mL) was replaced by an equivalent amount of degassed deionized water.

Deisopropylatrazine and Terbutylazine.

At time intervals of 15, 30, 60 and 120 minutes, samples were removed from the reaction flask using a 15 mL pipette. The volume of sample removed was replaced by 15 mL of degassed deionized water.

The 15.00 mL aliquots of the removed aqueous samples for dimethoxyatrazine, terbutylazine and deisopropylatrazine were concentrated to 5 mL of acetonitrile (HPLC grade, Fisher Scientific) using solid phase extraction cartridges (3 mL AccuBond®, 40 micron particle size, 60 angstrom pore size, J&W Scientific). The cartridges were prepared by pulling through 20 mL of deionized water, 20 mL of acetonitrile, and 5 mL of deionized water utilizing vacuum filtration. The 15 mL aliquot was pulled through by vacuum filtration and followed by another 5 mL of deionized water. The sample was eluted with 2 mL of acetonitrile by allowing the solvent to gravitate through the cartridge.
into a 5 mL volumetric flask. The flask was diluted to mark with acetonitrile and the samples were dried over 3Å Molecular Sieve.

**Control samples.**

Control experiments were completed for each triazine studied to confirm that hydrolysis was not taking place. Solutions of analytes at concentrations similar to those used for iron experiments were adjusted to pH 2.00 with sulfuric acid and either stirred or allowed to sit for the duration of time equivalent to the reaction time with iron for each analyte. Analysis for the control experiments was identical to that for iron reactions in that the peak area of analyte was compared to the peak area of an external standard in order to determine the relative remaining concentration in solution.

**External standard.**

An external standard was prepared by removing a 15 mL aliquot from the degassed solution prior to placement of the solution with iron and extracting the sample in the same manner. The relative amount of remaining analyte was determined by comparing the relative area of that found in the aqueous phase to the area of the external standard.

**Solid iron extraction.**

For the purpose of determining the extent of adsorption onto the iron surface, solid iron extractions were performed. At the end of pH 2.00 reactions, the remaining solution was removed from the flask, and 25.00 mL of solvent were added to the flask. This was also completed for pH 2.00 reactions at the end of a 15 minute period to allow for a comparison of how much analyte was present on iron early in the reaction and at the end of the reaction. Terbutylazine and dimethoxyatrazine were both extracted from the
iron using dichloromethane. Deisopropylatrazine was extracted from the iron using acetonitrile.

**GC-MS analysis**

Product analysis was accomplished with a Hewlett Packard 5890 GC equipped with a HP-5 M.S. (Crosslinked 5% Ph Me Silicone), 30 m x 0.25 µm film thickness column and a Hewlett Packard Model 5971 Mass Selective Detector. The injector temperature was set at 125° C and the detector temperature was set at 250° C. The oven was programmed to start at 50° C for 3 minutes then ramped up to 250° C at 20º/min, and held here for 2 minutes.

**HPLC analysis**

Quantitative analysis was done with a Hitachi D-7000 High Performance Liquid Chromatograph equipped with L-7420 UV-VIS Detector and a Whatman® Partisphere C-18 column. For cdm/ and deisopropylatrazine analysis, a mixture of 75% water and 25% acetonitrile was used as the mobile phase with a flow rate of 1.000 mL/min. For atrazine and terbutylazine analysis, a mixture of 70 % methanol and 30 % water was used as the mobile phase with a flow rate of 1.000 mL/min. Samples were analyzed at 220 nm using a 20µL injection volume. The linearity of all compounds studied was determined at 220 nm using 5 point calibration curves.

**Error Analysis**

The relative concentration of analyte was determined for two or three consecutive reactions with iron. Error bars for the plots showing the disappearance of analyte over
time in the presence iron reflect the range of the data. The uncertainty values for the pseudo-first order rate constants were determined from the standard deviation of the slope from logarithmic analysis of the data. This uncertainty reflects the deviation of the data from linearity but does not account for the uncertainty in the range of the data.

**Determination of surface area**

The surface area of the iron was determined through (Brunauer-Emmett-Teller (BET) using a Quantasorb Sorption System.

**Electrochemical Analysis**

The electrochemical data was obtained using an EG&G Princeton Applied Research Model 264A Polarographic Analyzer/Stripping Voltammeter equipped with the EG&G Par Model 303A SMDE (Static Mercury Dropping Electrode). A three-electrode chemical cell was used with a Ag/AgCl reference electrode with 0.1 M NaCl as the electrolyte, the SMDE working electrode and a platinum auxiliary electrode.

For both differential pulse polarography and sampled dc polarography, the setup for the instrument was as follows: 2 mV/s scan rate, 10 µA current range, 25 mV pulse height, 8 minute purge time with N₂. The potential was scanned from -0.50 v - 1.40 V. The data collection software allowed for 15 pt averaging of the sampled current.

Differential pulse polarography was used to analyze the pH dependence of dimethoxatrazine. Samples were prepared by pipetting 1 mL of 1000 ppm dimethoxatrazine stock solutions in 95% ethanol into a 25 mL volumetric flask. 20 mL of 0.13M NaCl were pipetted into the flask followed by 1 mL of various concentrations of H₂SO₄ added to the flask using a pipette. The flask was diluted to mark with deionized water. Blank samples were prepared in the same manner as samples containing the
analyte. 1 mL aliquots of 95% ethanol were added into blank samples and pH measurements confirmed that pH of blank samples was identical to that of the analyte samples.

Sampled dc polarography was used to determine the number of electrons for dimethoxyatrazine and deisopropylatrazine and terbutylazine. Samples for dimethoxyatrazine, atrazine and deisopropylatrazine were prepared by pipetting 12.5 mL of 40.0 ppm analyte solutions into a 100 mL volumetric flask using a graduated pipette. Samples for terbutylazine analysis were prepared by pipetting 50 mL of a 10.0 ppm analyte solution into a 100 mL volumetric flask. 1 mL of 1M HCl was pipetted into each flask. The volumetric flasks containing dimethoxyatrazine, atrazine and deisopropylatrazine were diluted to mark with 0.11 M NaCl. The volumetric flask containing terbutylazine was diluted to mark with 0.2 M NaCl. Blank samples were prepared in the same manner as for the analytes, with an equivalent amount of deionized water replacing the addition of the analytes.

Results and Discussion

Iron/Triazine Reactions

The relative decreases in concentrations that were observed during iron-water reactions at a constant solution pH over time for dimethoxyatrazine, terbutylazine and deisopropylatrazine are shown in Figures 1, 2 and 3. The analysis of solutions that were allowed to sit for the duration of the experiments in acid at pH 2 showed no significant decrease in the concentration of the parent compound for terbutylazine and
dimethoxyatrazine. This evidence suggests that hydrolysis was not occurring during the time frame that the experiments were being conducted and that iron must be present in the solution in order to observe any decrease in the concentration of the parent compound. However, in the control experiments for deisopropylatrazine shown in figure 2, the relative percentage of remaining analyte was slightly lower than 100%. This suggests that some hydrolysis may have occurred, but since no other peaks were present during HPLC analysis it was not concluded positively that hydrolysis did occur. We are unsure if the hydrolysis product of deisopropylatrazine was eluted with acetonitrile during the solid phase extraction.

The degradation of triazines via metallic iron was pH dependent. Pseudo-first order rate constants were calculated and surface area normalized for a single pH using the equation shown below:

\[ k' \text{[analyte]} = -\frac{dc}{dt} \quad (eq. 4) \]

\[ \ln \frac{c}{c_0} = -k't \quad (eq. 5) \]

\[ k_{SA} = k' \text{ (min}^{-1}\text{)} \times \frac{V \text{ (L)}}{M \text{ (g)}} / \text{SA (m}^2\text{/g)} \quad (eq. 6) \]

The integration of eq. 4 gives eq. 5. From natural logarithmic plots (Figures 4, 5, and 6) of relative concentration analyte/initial concentration analyte vs. time, the slope values were obtained by regression analysis. The slope value from the natural log plots represents \((k')\), using eq. 6 the surface area normalized rate constants \((k_{SA})\) were calculated where \(V\) is the volume of the solution added to the reaction flasks, \(M\) is the amount of solid iron used for the reaction, and \(SA\) is the calculated surface area of the iron. The surface area of the iron was determined to be 0.22 m\(^2\)/g from BET.
measurements. The adjusted rate constants calculated for each analyte at each pH are shown in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Dimethoxy atrazine (L/m² min)</th>
<th>Deisopropylatrazine (L/m² min)</th>
<th>Terbutylazine (L/m² min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>1.33 (±0.07) E-4</td>
<td>7.2 (±2.0) E-4</td>
<td>2.41 (±0.06) E-3</td>
</tr>
<tr>
<td>pH 3</td>
<td>6.1 (±0.6) E-5</td>
<td>1.0 (±0.4) E-4</td>
<td>6.9 (±0.9) E-4</td>
</tr>
<tr>
<td>pH 4</td>
<td>4.4 (±0.6) E-5</td>
<td>No Reaction</td>
<td>2.7 (±0.4) E-4</td>
</tr>
</tbody>
</table>

TABLE 1

For all of the triazines studied, a similar pattern is seen in that as the pH of the solution is increased, the rate of degradation of analyte decreases in the presence of iron. This is consistent with results reported in our earlier study of atrazine (Dombek et al., 2001). The pH dependence may be due in part to the decrease in iron surface area since iron hydroxides could form at higher pH levels thus decreasing the effective available surface area for reduction.

The dechlorinated product was the only product detected in HPLC and GC-MS analysis for dimethoxyatrazine/iron and terbutylazine/iron reactions. Figure 7 shows the GC-MS chromatogram of a typical analytical sample of dimethoxyatrazine obtained during the reaction time. A peak with a mass/charge ratio of 175 and a retention time of 9.35 minutes is the parent compound dimethoxyatrazine. This peak has an isotopic ratio peak with a mass/charge ratio of 177 present for the chlorine atom. The peak corresponding to the dechlorinated product has a mass/charge ratio of 141 with no presence of an isotopic ratio giving further evidence that the chlorine atom is not present.

Figure 8 shows a peak with a mass/charge ratio of 229 corresponds to the molecular mass of terbutylazine. This peak has an isotopic ratio peak with a mass/charge ratio of 231. Figure 9 shows the GC-MS chromatogram of terbutylazine after 30 minutes
with iron The isotopic ratio is not present for the mass/charge ratio of 195 clearly showing the absence of the chlorine atom. The small peak with a retention time of 11.20 minutes has a mass/charge ratio of 195. This mass peak is the dechlorinated-product resulting from the reduction of terbutylazine by iron.

There were no products detected for the deisopropylatrazine/iron reactions. Further analytical work must be done to resolve what other products might be forming, but are not detected using our current analytical methods.

In order to detect the dechlorinated product for the terbutylazine/iron reactions, it was necessary to really concentrate the samples prior to analysis with GC-MS. In our dimethoxyatrazine/iron reactions, the dechlorinated product appeared and seemed to increase throughout the course of the reaction. Figure 10 is a gas chromatogram of a series of samples analyzed during the course of a reaction for dimethoxyatrazine in the presence of iron at pH 2. This data as well as other data obtained using HPLC indicates that the amount of dechlorinated product appears to increase throughout the duration of the reaction.

Comparison of Triazine/Iron reactions with different pKa values.

Figure 11 compares the relative amounts reduced via iron at pH 2 for all of the triazines studied. Error bars are not shown for atrazine, only 1 reaction for atrazine was completed in the presence of iron at pH 2.0 for this study in order to compare the triazines with reactions run under identical conditions. The error bars present for the other compounds represent the range of the relative concentrations from either 2 or 3 reactions with iron, the data points represent the average of the relative concentrations. The error bars are not visible for the deisopropylatrazine; this is because in the two
experiments completed for this compound at pH 2, the relative concentrations at the respective time intervals were almost identical.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pKa values</th>
<th>Rate constant (L/m^3 hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethoxy atrazine</td>
<td>&lt;1.0 (6)</td>
<td>1.04 E-4 (±.07)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>1.7 (6)</td>
<td>2.59 E-4 (±.09)</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>1.3 (10)</td>
<td>4.7 E-4 (±.2)</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>1.95 (9)</td>
<td>1.61 E-3 (±.06)</td>
</tr>
</tbody>
</table>

Table 2

The rate constants calculated for each analyte at pH 2 are shown in table 2. The results indicate that the reduction does not necessarily depend upon the pKa value of the compound. When comparing triazine compounds that have different pKa values, but are somewhat similar in their structures, it was predicted that the pKa values would dictate how easily the compounds may be reduced. There is a trend present in that dimethoxy atrazine with the lowest pKa value is reduced to a lesser extent than both atrazine and terbutylazine. In addition, atrazine with a lower pKa value than terbutylazine is reduced to a lesser extent than terbutylazine.

The observation that atrazine is reduced more slowly than deisopropylatrazine is inconsistent with the predicted outcome. The pKa values of atrazine and deisopropylatrazine differ by only .4 units. This small difference and the large variability that was seen in the reactions, are two factors that may have led to this inconsistency. A second concern was that we weren’t positive if hydrolysis of deisopropylatrazine was
occurring. The control samples showed less than 100% of deisopropylatrazine present after sitting for 2 hours at pH 2.0. This is a concern because hydrolysis would also enhance the apparent degradation rate.

Also the structure of deisopropylatrazine is different than the other triazines in that there is an amino group present attached to a carbon atom. It is possible that protonation of this amino group may account for the low pKa value whereas the protonation of the nitrogen atoms present in the ring occurs at a higher pH. In order to determine if there were two different protonation sites for the pH region of 1.00 – 6.00, a spectrophotometric titration was done for deisopropylatrazine utilizing the Shimazdu UV-VIS 3100. The spectra, shown in Figure 12, were analyzed at multiple pH values and show one clear isosbestic point. This would conclude that one form of the protonated species exists in this region. It may be that protonation of the amino group may occur at lower pH values than were investigated.

**Role of Iron**

The rate constants that were calculated were normalized for surface area of the iron. This assumes that the surface area from one reaction to the next was always the same. The validity of this assumption is questionable. The variability of the reactions was cause for concern, because it was impossible to duplicate the results from one reaction to the next. It is believed that the high ranges shown on Figures 1, 2, and 3 are somewhat due to the variability of the iron surface.

Previous BET measurements (Dombek et al., 2001), of the iron surface show that the measured surface area did not change when comparing the surface area found for pretreated iron to those found for iron without pretreatment. In the pretreatment of the
iron surface, acid is added to solid iron while stirring under nitrogen. This procedure results in dissolution of the iron and must change the surface of iron. This is certainly significant in light of the possible mechanisms discussed in the literature review. If the reduction of these compounds occurs either directly on the Fe$^0$ surface or adsorbed to hydroxides, then perhaps an alternative approach to measuring the actual surface area is needed. The effect that iron may have on the rate of degradation needs to be explored in more detail.

**Determination of [H$^+$] order**

The differential rate law for the reduction of triazines in the presence of metallic iron can be shown by the following equation.

$$\text{rate} = k[\text{Fe}]^a[\text{Triazine}][\text{H}^+]^b$$  \hspace{1cm} \text{Eq. (7)}

The pseudo first-order rate law at a certain pH simplifying this expression is shown below.

Define $k_{SA} = k[\text{H}^+]^b$ \hspace{1cm} \text{Eq. (8)}

Rate = $k_{SA}[\text{Fe}]^a[\text{Triazine}]$ \hspace{1cm} \text{Eq. (9)}

if $k' = k_{SA}[\text{Fe}]^a$ \hspace{1cm} \text{Eq. (10)}

Rate = $k'[\text{triazine}]$ \hspace{1cm} \text{Eq. (11)}

$k_{SA} = k'/[\text{Fe}]^a$ \hspace{1cm} \text{Eq. (12)}

It was assumed for equation 12 that "a" was equal to 1 and with this assumption, $k_{SA}$ was calculated for a certain pH. In addition, it was assumed that the specific surface area of iron determined in BET measurements was constant for each pH. The specific surface area was used to calculate the pseudo first-order rate constants with the slope of natural log plots (-k') of the rate of degradation of the triazine compound over time. The
experimental values of $k_{SA}$ obtained can be used to determine the order of $H^+$ by expressing equation 8 in the logarithmic form.

$$\log k_{SA} = \log k' + b \log [H^+] \quad \text{Eq. (13)}$$

The log of the calculated pseudo-first order surface area normalized rate constants were plotted as a function of pH for all three triazines in this study in order to determine the reaction order for $H^+$. The slope values representing the order for $H^+$ for each compound are shown in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Dimethoxyatrazine</th>
<th>Deisopropylatrazine</th>
<th>Terbutylazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order of $[H^+]$</td>
<td>.240</td>
<td>.857</td>
<td>.475</td>
</tr>
</tbody>
</table>

Table 3

It can be seen that the order of $H^+$ varies for each compound. This suggests that the order is specific for each triazine. This order was evaluated for dimethoxyatrazine and terbutylazine from pH 2-3, pH 3-4 and pH 2-4 using equation 14.

$$k_{SA} (\text{pH 2.0})/ k_{SA} (\text{pH 3.0}) = k[H^+]^b (\text{pH 2.0})/ k[H]^b (\text{pH 3.0}) \quad \text{Eq. (14)}$$

This was done assuming that the iron surface is constant and the triazine concentration is also constant.

The results are shown in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Dimethoxyatrazine</th>
<th>Terbutylazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH 2-3</td>
<td>.33</td>
<td>.54</td>
</tr>
<tr>
<td>PH 3-4</td>
<td>.14</td>
<td>.41</td>
</tr>
<tr>
<td>PH 2-4</td>
<td>.24</td>
<td>.48</td>
</tr>
</tbody>
</table>

Table 4
The order if it were specific for each compound should be the same when comparing the rate constants from one pH to the other. As can be seen from the results the order varies by (± 0.1) for both dimethoxyatrazine and terbutylazine. The large amount of uncertainty in the range of the data certainly contributes to these observed differences. This also gives additional evidence that the assumption that the iron surface is constant at all pH values is invalid.

*Adsorption onto the iron*

Adsorption of the dimethoxyatrazine, terbutylazine and deisopropylatrazine onto the iron was examined. A very small amount, less than 1 % of each compound was found on the iron. The amount found at 15 minutes was similar to the amount found at the end of the reaction. Although the adsorption of these compounds was not thoroughly investigated, it seems reasonable to assume that the decrease in concentration of these compounds over time is due to degradation.

*Electrochemical results*

The electrochemical reduction of dimethoxyatrazine was studied on the mercury electrode as a function of pH using differential pulse polarography. The DP polarogram at low pH contains two clearly separated peaks. It can be seen in Figure 13 that as the solution pH increases, the two peaks merge into one peak. In addition, the reduction potential shifts towards a more negative value. This observation provides evidence that protonation is required in order for the reduction of dimethoxyatrazine to occur. This can be explained using the Nernst equation and the half reaction for the reduction of dimethoxyatrazine.
It is believed that the first reduction peak corresponds to an irreversible 2-electron transfer (Skopalova and Kotoucek, 1995; Higuera et al., 1999). The reduction reaction is shown below.

![Chemical reaction](attachment://reaction.png)

The Nernst equation for this reduction is as follows:

\[
E = E^0 - 0.05916/2 \ln \left( \frac{C_R}{C_0} \cdot [H^+] \right)
\]

Eq. (11)

From the Nernst equation it can be seen that at higher pH, the reduction potential will become more negative because the natural log term decreases.

Figure 14 shows a comparison of the reduction waves for each of the compounds studied in pH 2 solutions at 5 ppm with differential pulse polarography. It is interesting that a clear separation of the reduction waves exists for dimethoxyatrazine compared to the other triazines studied. This study was done with solutions at 5 ppm in order to minimize adsorption. It is believed that the reduction waves may not be clearly separated due to some adsorption onto the mercury drop, but it seems reasonable that a dechlorinated, intermediate, product may be isolated more readily for dimethoxyatrazine. The reduction potential leading to the dechlorinated species is more positive than the reduction potential of the dechlorinated species making the intermediate appear more stable for dimethoxyatrazine compared to the other triazines studied.
The formation of dechlorinated-atrazine, dechlorinated-dimethoxyatrazine and dechlorinated-terbutylazine suggests that the reduction mechanism via metallic iron is similar to the reduction mechanism on the mercury electrode. It is believed that protonation is necessary in order to weaken the carbon-chlorine bond. The rate of degradation decreases as the solution pH is increased. Electrochemical studies on mercury electrodes have shown that triazines are more easily reduced in acidic solutions (Ignjatovic et al., 1993; Pospisil et al., 1995; Skopalova and Kotoucek, 1995). Their reduction potentials become more negative as the pH of the solution is increased. This suggests that protonation of the triazine aids in its reductive dechlorination. This supports the results of the iron reactions in that, a decrease in the amount of degradation occurs as the solution pH is increased.

**Determination of the number of electrons exchanged**

Sampled dc polarography was used to determine the number of electrons exchanged for the compounds studied. The limiting current was calculated from dc waves for dimethoxyatrazine, terbutylazine, and deisopropylatrazine and compared to the limiting current calculated from the dc wave for atrazine. The limiting current values are shown in Table 5 and the dc polarograms are shown in Figure 15.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Limiting current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethoxyatrazine</td>
<td>3.616</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>4.337</td>
</tr>
<tr>
<td>Deisopropylatrazine</td>
<td>4.738</td>
</tr>
<tr>
<td>Atrazine</td>
<td>3.245</td>
</tr>
</tbody>
</table>

Table 5
The results show that the limiting currents are not similar, so it would not be accurate to say that the number of electrons transferred are equivalent. However by examination of the Ilkovic equation shown below:

\[ i_d = \text{k}_{e}n_{d}m^{2/3}\text{D}^{1/2}t^{1/6}\text{C} \]

It would be reasonable to see that if the number of electrons transferred were to increase by just one then the limiting current would increase by a significant amount. The differences between the measured limiting current for each triazine were not large and may be explained by differences in other factors such as the diffusion coefficients and the sample concentrations. In addition the samples were prepared from water solutions assuming that the concentration was equivalent for each solution. Slight differences in the sample concentrations would certainly have an effect on the measured current.

Also adsorption may have been a factor, the samples were analyzed at 5 ppm in order to minimize adsorption. But studies for adsorption have been conducted on atrazine and terbutylazine while there have been no reported adsorption studies for dimethoxyatrazine and deisopropylatrazine. More work needs to be done examining adsorption of these compounds during the reduction process. Perhaps if they are adsorbing in 5 ppm solutions, this increased the total current measured during the reduction process. Determining the total number of electrons requires good reproducible quantitative results and adsorption would likely interfere with the reproducibility of the data.

Another factor is the pH dependence observed for triazines. It is believed that the protonated species is that which is being reduced at the mercury drop. Differences in pKa values would limit how much of each compound is present as the protonated species.
Although there are a number of remaining questions regarding the behavior of these triazines on the mercury electrode, it seems feasible that the total number of electrons transferred during the reduction process are identical.

**Method Development**

**Iron pretreatment**

The results were very difficult to duplicate. In order to examine how changes to the reaction procedure might effect the results, studies were completed with dimethoxyatrazine.

Table 6 shows results of two reactions at pH 2.00 (±.10). The first two columns of data are for samples that were analyzed from reaction in which the iron before the start of the reaction had been washed in sulfuric acid. The last two columns are from reactions in which no pretreatment of the iron preceded the reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH (w) 2.00 % cdmt</th>
<th>pH (w) 2.00 % cdmt</th>
<th>pH 2.00 % cdmt</th>
<th>pH 2.00 % cdmt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2 hrs</td>
<td>81.6</td>
<td>87.0</td>
<td>83</td>
<td>90.2</td>
</tr>
<tr>
<td>3 hrs</td>
<td>77.0</td>
<td>84.9</td>
<td>78.6</td>
<td>86.4</td>
</tr>
<tr>
<td>4 hrs</td>
<td>73.9</td>
<td>80.0</td>
<td>73.4</td>
<td>78.5</td>
</tr>
</tbody>
</table>

Table 6 (w) with pretreatment of iron.

Figure 16 depicts a graphical representation of the data. The iron pretreatment does not appear to affect the results. A comparison of the pH 2.00 reactions which were run with and without iron pretreatment show that the reproducibility of the results are not enhanced by the pretreatment of iron. It could be that the iron pretreatment does increase the available surface area, while increasing a chance for precipitate formation making it
less available for reduction of cdmt. Using a different acid for the pretreatment instead of H₂SO₄ could test this.

**Mass/Volume Ratio**

The effect of the ratio for the mass of iron/volume of solution was examined. Results were compared from reactions where the volume removed during the reaction time for analysis was replaced by an equivalent volume of deionized water to results from reactions where the solution volume was not maintained constant. Table 7 shows results obtained from earlier reactions at pH 2 and 3 without holding the volume constant denoted by "*" and from pH 2 and 3 reactions in which the volume was maintained constant. The data shown represents the average of duplicate reactions. Figure 17 depicts a graphic representation of the data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH 2.00</th>
<th>pH 2.00</th>
<th>pH 3.00</th>
<th>pH 3.00</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%cdmt</td>
<td>%cdmt *</td>
<td>%cdmt</td>
<td>%cdmt *</td>
</tr>
<tr>
<td>Blank</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>2 hrs</td>
<td>84.3</td>
<td>84</td>
<td>92.2</td>
<td>87</td>
</tr>
<tr>
<td>3 hrs</td>
<td>80.1</td>
<td>70</td>
<td>90.7</td>
<td>78</td>
</tr>
<tr>
<td>4 hrs</td>
<td>77.0</td>
<td>50</td>
<td>88.6</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 7

The mass/volume ratios for these reactions were 0.09 g/mL compared to 0.04 g/mL for the results shown in table 1. It can be seen in figure 17 that as the reaction time increases, the slope of the curves for the reactions in which the volume was not maintained constant increases. This clearly indicates that this ratio affects the rate degradation. This suggests
that mass transfer throughout the reaction time is an important concern. It is believed that
the iron mass if it were not held constant would also affect the rate of degradation. As a
result of increasing this ratio, the degradation is significantly increased.

Suggestions for improved methods

Analytical

The dechlorinated product was the only product we detected using GC-MS, although the formation of hydroxytriazine might have occurred. As part of this study, the
extraction of hydroxyatrazine was studied using our current extraction methods. The
samples were concentrated using C18 solid phase extraction cartridges and eluted with
acetonitrile. It was determined that hydroxyatrazine was not eluted from the cartridge
with our current solvent. This leaves inconclusive evidence whether or not the formation
of hydroxyatrazine occurs during the reduction of atrazine via metallic iron, but the
formation of the dechlorinated triazine does occur.

More analytical work is necessary in order to resolve what other products result
during the time frame of the reactions. It may be that we were not able to elute the
products from the C18 cartridges. It would be interesting to try different solvents for
elution of the analyte from the cartridges. Also it may be good to study the elution of the
analytes with other types of extraction cartridges. Another suggestion for improvement in
this area would be to find standards of the potential products in order to test their
solubilities in solvents and extraction efficiencies through the cartridges.

Reproducibility

40
Perhaps the reproducibility of the results may be explored more thoroughly by looking at the extraction efficiency of the parent compounds. It would be interesting to look at how different acids used for the pretreatment of the iron surface prior to the start of the reaction would affect the results. The time for the pretreatment of the iron should probably be extended.

An investigation of oxygen’s role in the reduction process should also be conducted. The reactions were conducted under anaerobic conditions for this study. It would be interesting to see if the results change under aerobic conditions and how this might effect what products are obtained.

It would be very interesting to examine the adsorption and possible reduction of these compounds in the presence of iron hydr(oxides) with or without the presence of metallic iron.

_Electrochemical Analysis_

The electrochemical reductive process seems similar to the reductive process via metallic iron in that the product of reduction of analogous compounds was similar. It would be interesting to try exhaustive analysis at a constant reduction potential corresponding to the first reduction wave for each of these compounds and look at the amount of product formed. Then try exhaustive analysis at a constant reduction potential corresponding to the second reduction wave for each compound and see if the amount of product forms corresponds to that obtained in the previous analysis.

In order to determine the number of electrons transferred, it would be better if the diffusion coefficients for each triazine were known. It also may be possible to analyze
each compound in a solution pH that matched its respective pKa value and compare the
de waves.

Conclusions

The reduction of triazines is pH dependent. This conclusion is supported by the
results of iron/triazine reactions in addition to electrochemical analysis of triazine
compounds on a mercury electrode. We were unable to clarify the order with respect to
the hydrogen ion concentration. The order was different for each triazine in this study and
at different pH values. This suggests that the order may be different for each triazine. It
also questions the validity of how constant is the iron surface from one pH to the next.

A mechanism of triazine reduction with metallic iron has not been suggested. The
mechanism for other chlorinated organic compounds has been suggested, but none have
been fully elucidated. Clearly more work needs to be done with iron/triazine reactions in
order to understand iron's role in the reductive process.

It seems likely that the reduction occurring via metallic iron is similar to that
occurring on a mercury drop. It is speculated that dechlorinated dimethoxyatrazine an
intermediate product of reduction on a mercury electrode. The presence of dechlorinated
dimethoxyatrazine in the iron systems combined with the suggestive evidence of its
formation in the electrochemical system lead to the conclusion that the general
mechanism for degradation of triazines via metallic iron is the same as the
electrochemical reduction. The mechanism for the 1st step in the reduction leading to the
dechlorinated species is shown below. The mechanism shows a 2-electron reduction of
the protonated species.
The occurrence of the dechlorinated product resulting from electrolysis reported for atrazine was identical to the product that we found resulting from iron reduction of atrazine. It was very difficult to isolate the dechlorinated species for terbutylazine and we were unable to isolate a product for the degradation of deisopropylatrazine. The dechlorinated product for dimethoxyatrazine was detected. In addition to its formation, it appeared to be rather stable in that it appeared to increase throughout the reaction time. The differential pulse waves support the relative stability of the dechlorinated dimethoxyatrazine. The differential pulse peaks for atrazine, terbutylazine and deisopropylatrazine were very similar in that the two peaks were overlapped significantly while the dp peaks for dimethoxyatrazine were well resolved. It may be concluded from
this evidence that a dechlorinated product for dimethoxyatrazine is easily detected because the reduction potential for its further reduction is shifted to a more negative potential.

Generally, low pKa values decreased the rate of degradation of triazines. This conclusion could be better stated with data that showed greater reproducibility. The large range of the data and perhaps the closeness of pKa values likely interfered and limited the ability to better resolve the rate of degradation of each compound studied.


Figure 1. Degradation of Dimethoxyatrazine over time in the presence of iron in acidic media. The data points represent the average of 2 or 3 reactions and the error bars represent the range of the data points.
Figure 2. Degradation of Deisopropylatrazine over time in the presence of iron in acidic media. The data points represent the average of 2 or 3 reactions and the error bars represent the range of the data.
Figure 3. Degradation of Terbutylazine over time in the presence of iron in acidic media. The data points represent the average of 2 or 3 reactions and the error bars represent the range of the data points.
Figure 4. Natural log plot of relative concentration vs. reaction time for dimethoxyatrazine.
Figure 5. Natural log plot of relative concentration vs. reaction time for deisopropylatrazine.
Figure 6. Natural log plot of relative concentration vs. reaction time for terbutylazine.
The mass spectrum of the product peak at 8.157 minutes. This peak is not present in control.

Note that the peak present at approximately 9.5 minutes is an artifact and not from the analyzed sample. Also the mass spectrum is shown for the dechlorinated species and not for the parent compound.
Figure 8. (A) Gas chromatogram/mass spectrum of terbutylazine. (B) The mass spectrum for terbutylazine.
Figure 9. (A) Gas chromatogram/mass spectrum, (the region of the product has been zoomed up) of terbutylazine after 30 minutes with iron. (B) The mass spectrum for dechlorinated terbutylazine, this peak is not present in control samples.
Figure 10 Gas Chromatogram of samples analyzed from a dimethoxyatrazine/iron reaction with the addition of biphenyl as an internal standard.
Figure 11. Relative concentration vs. reaction time comparing the degradation of triazines with different pKa values in the presence of iron at pH 2.0.
Figure 12. UV-VIS spectrum of spectrophotometric titration of deisopropylatrazine.
Figure 13. Differential pulse polarography of 40 ppm dimethoxyatrazine solutions as a function of pH. Solutions were prepared in 0.1M NaCl and various concentrations of sulfuric acid were added to adjust pH to the desired level.
Figure 14. Differential pulse polarography comparing triazines in pH 2.00 solution.
DC polarography of triazines at 5 ppm in pH 2.00 solutions

Figure 15. DC polarograms of triazines at pH 2.00 for determination of total electrons transferred.
Figure 16. Comparison of iron reactions at pH 2 for dimethoxytrazine. Data shown is the average data from duplicate reactions in which iron was pretreated with sulfuric acid and duplicate reactions in which no pretreatment of the iron was conducted.
Figure 17. Comparison of iron/dimethoxyatrazine reactions at pH 2 and pH 3 with and without maintaining a constant volume. * denotes reaction in which the volume was not maintained constant during the course of the reaction time.