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Rapid reductive dechlorination of atrazine by zero-valent iron under acidic conditions

T. Dombek, E. Dolan, J. Schultz, D. Klarup *

Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, USA

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"Capsule": *The effect of pH on atrazine dechlorination via metallic iron may be due to triazine ring protonation.*

Abstract

The dechlorination of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) via reaction with metallic iron under low-oxygen conditions was studied using reaction mixture pH values of 2.0, 3.0, and 3.8. The pH control was achieved through addition of sulfuric acid throughout the duration of the reaction. The lower the pH of the reaction mixture, the faster the degradation of atrazine. The surface area of the sulfuric acid-treated iron particles was 0.31 (±0.01) $m^2\ g^{-1}$ and the surface area normalized initial pseudo-first order rate constants (k_{SA}, where rate $= k_{SA} \times$(surface area/l)$\times$[Atrazine]) at pH values of 2.0, 3.0, and 3.8 were equal to, respectively, 3.0 (±0.4)$\times 10^{-3}\ min^{-1}\ m^{-2}$ l, 5 (±3)$\times 10^{-4}\ min^{-1}\ m^{-2}$ l, and 1 (±1)$\times 10^{-4}\ min^{-1}\ m^{-2}$ l. The observed products of the degradation reaction were dechlorinated atrazine (2-ethylamino-4-isopropylamino-1,3,5-triazine) and possibly hydroxyatrazine (2-ethylamino-4-isopropylamino-6-hydroxy-*s*-triazine). Triazine ring protonation may account, at least in part, for the observed effect of pH on atrazine dechlorination via metallic iron. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Atrazine; Iron; Dechlorination; Herbicide; Degradation

1. Introduction

The herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) has been used extensively in corn, sorghum, and sugarcane fields for the last 30 years (Bridges, 1998). Although atrazine usage per acre has dropped in recent years, 80 million pounds of atrazine still are applied annually in the USA alone. This heavy usage, combined with atrazine's relatively long half-life in the environment (up to 1 year) (Wackett, 1999) means that agricultural fields remain as significant sources of atrazine to surface and groundwater systems. Concerns over drinking water contamination by atrazine, combined with the uncertainty of atrazine's carcinogenic and toxicological effects (and that of its metabolites), have spurred interest in techniques that might more rapidly degrade atrazine and its metabolites.

One method to degrade atrazine is via its reaction with metallic iron. This was first reported by Sweeny (1979), who also noted the dechlorination of many other compounds, including chlorinated solvents. Solvent reductive dechlorination using zero valent metals has been studied extensively in recent years (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Johnson et al., 1996; Orth and Gillham, 1996; Roberts et al., 1996; Allen-King et al., 1997). Although the mechanisms of these reactions are not well elucidated, it appears that, generally, a two-electron transfer occurs either directly at the iron surface or through some intermediary (Weber, 1996), oxidizing the iron to iron(II) ions:

$$R\text{–Cl} + \text{Fe}^{\circ}(\text{s}) + \text{H}^{+} \rightarrow \text{Fe}^{2+} + R - \text{H} + \text{Cl}^{-} \qquad (1)$$

The pH of the reaction solution is important in these reactions, probably because a low pH allows more of the iron surface to remain available for reaction with the halogenated molecule via:

$$\text{Fe(s)} + 2\text{H}^{+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \qquad (2)$$

or at least assists in the corrosion of the iron by the halogenated molecule [Eq. (1)]. At higher pH values oxide and hydroxide coatings undoubtedly develop which hinder access to the Fe° surface. Pretreatment of

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* Corresponding author. Tel.: +1-217-581-6227; fax: +1-217-581-6613.

E-mail address: cfdgk@eiu.edu (D. Klarup).

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iron with mineral acids, or increasing the available iron surface area, generally increases the rate of metal–solvent dechlorination reactions (Johnson et al., 1996; Su and Puls, 1999), confirming the importance of iron surface availability.

Solution pH has also been found to be important in the dechlorination of atrazine. Pulgarin et al. (1996) found a low pH to greatly assist atrazine dechlorination under photo-oxidizing conditions, attributing the effect to enhanced corrosion of the iron and Fenton-like reactions. Balmer and Sulzberger (1999) also found photo-Fenton atrazine degradation in the presence of oxalate to depend on solution pH. In this case the pH controlled the iron speciation in the solution which in turn controlled the photolysis efficiency. These aerobic mechanisms, however, are quite different from the abiotic, anaerobic, reductive dechlorination mechanism. Light and O_2 are central to the photo-oxidizing process where an hydroxide radical is responsible for the degradation.

Although no studies have been reported on the effect of solution pH on the reductive dechlorination of atrazine with iron, investigators have found that under ambient (environmentally relevant) pH conditions atrazine either degrades only slightly or sorbs onto the iron surface. Monson et al. (1998), found dechlorination of 30% of introduced atrazine in the dark, although the time span of their experiments was very long (25 days), and they used a very high iron to atrazine ratio (10 g to 30 ml of 1000 $\mu g\ l^{-1}$ atrazine). The pH of their solution rose to approximately 10 during the reaction due to water dissociation and H_2 generation. Davenport (1996) concluded that atrazine had adsorbed to the surface of the iron, not dechlorinated, although dechlorination of alachlor and metolachlor proceeded quite readily in non-acidified media (Eykholt and Davenport, 1998). Similarly, sorption of atrazine onto iron was observed, using an initial pH of 6.1, by Singh et al. (1998). These reported results indicate that at ambient pH values the dechlorination of atrazine with iron is relatively difficult to achieve compared to other pesticides and chlorinated solvents. Davenport (1996) suggested that the reduction potential for the dechlorination of atrazine might be too high for iron to be effective.

The objective of the study reported here was to determine how acidified media affects the reductive dechlorination of atrazine with metallic iron. To accomplish this we measured the rate of the reaction as a function of pH.

2. Materials and methods

2.1. Reaction conditions

The reaction of atrazine (Pfaltz & Bauer INC, Waterbury, CT, USA) with iron powder (100-mesh, Fisher Scientific Company, St. Louis, MO, USA) was studied at pH 2.00 (±0.3), pH 3.00 (±0.3) and pH 3.8 (±0.3) in a 500 ml round bottom three-neck flask under N_2. One port was covered with a septum, the middle port was used with a ground glass adapter and glass stirring rod, and a pH electrode was clamped in the third port and the opening sealed with Parafilm®.

The iron was prepared by stirring 10 g in 50 ml of 0.5 M H_2SO_4 for 10 min at 250 rpm, removing the wash solution and repeating with a second wash. After removal of the second wash solution, 200 ml of degassed 45.9 ppm atrazine solution was added to the reaction flask and the pH adjusted with 3 M H_2SO_4. For the pH comparative experiments, the reaction was conducted at a stir rate of 750 rpm and the solution pH continually adjusted by adding 3 M H_2SO_4 acid with a syringe through the septum.

The duration of each reaction was approximately 2 h during which 20.00-ml aliquots of the atrazine solution periodically were removed from the reaction flask (with a syringe) for analysis. The reaction also was conducted using deuterium oxide (Cambridge Isotope Laboratories, Andover, MA, USA) at a measured pH of 2.0 (adjusted with H_2SO_4) to confirm reactant origins via comparative gas chromatography–mass spectrometry (GC–MS).

2.2. Aliquot treatment

For the pH comparative studies, solid phase extraction cartridges (3 ml AccuBond®, 40-μm particle size, 60 Å pore size, J&W Scientific, Folsom, CA, USA) were used to concentrate and purify the reaction mixture species for analysis. The cartridges were prepared by pulling 20 ml of deionized (DI) water, 20 ml of methanol, and 5 ml of DI water through the cartridges by vacuum filtration. Then the 20.00-ml reaction aliquot was pulled through the cartridge followed by 5 ml of DI water. A standard sample was prepared by extracting a 20.00-ml aliquot of 45.9 ppm atrazine solution in the same manner. Two milliliters of methanol [high performance liquid chromotography (HPLC) grade, Mallinckrodt, St. Louis, MO, USA] were added to the cartridge and allowed to gravitate through the cartridge. The methanol solutions were then filtered using Millex® — GV_{13} 0.22 μm, 13 mm millipore filter units and stored over 3A molecular sieve until analysis with GC, GC–MS, or HPLC.

For quantitative GC analysis of the samples, 1 ml of each sample was combined with 0.25 ml of 780 ppm 3-nitro-*o*-xylene (Chem Service, West Chester, PA, USA) which served as an internal standard. The system used for analysis was a Hewlett Packard 5890 GC equipped with manual injection, flame ionization detection, and a DB1 30 m×0.53 mm ID, 1.5-μm film thickness capillary column (J&W Scientific). Injector and detector temperatures were held at 250°C and the oven programmed to start at 50°C for 3 min, then ramped at 20°/min up to 250° and held at this temperature for 2 min.

GC–MS was conducted with a Hewlett Packard 5890 GC equipped with a HP-5 M.S. (Crosslinked 5% Ph Me Silicone), 30 M×0.25 mm×0.25 μm film thickness column and a Hewlett Packard Model 5971 Mass Selective Detector. A similar temperature program was used as with GC alone.

HPLC was conducted on the final reaction solution of the pH 2.00 run. This apparatus consisted of a Beckman model 112 HPLC pump equipped with a 20-μl sample loop (Beckman Coulter Inc., Fullerton, CA, USA), a Waters Model 450 variable wavelength detector (Waters Corp., Milford, MA, USA) (set to 222 nm) and a Shimadzu Chromatopac C-RIB Data Processor (Shimadzu Scientific Instruments Inc., Columbia, MD, USA). The column used was a 4.6×250 mm reverse-phase Whatman PARTISPHERE® C-18 column equipped with a removable guard cartridge assembly (Whatman Inc., Clifton, NJ, USA). The mobile phase used was degassed HPLC grade 40:30:30 methanol–acetonitrile–water, buffered to pH 7 with 0.01 M ammonium acetate.

2.3. Surface area determination

The Brunaver-Emmett-Teller (BET) surface areas of the iron particles both before and after H_2SO_4 treatment were determined using a Quantasorb Sorption System (Quantachrome Corp., Boynton Beach, FL, USA). In order to minimize exposure to oxygen, H_2SO_4 treatments were carried out directly within the BET analysis cell and degassed under N_2.

3. Results and discussion

3.1. Surface area

The sulfuric acid treatment of the iron particles did not drastically alter the measured BET surface area of the iron. Prior to acid treatment, the measured surface area was 0.30 (±0.01) $m^2\ g^{-1}$. After treatment, the measured surface area was 0.31 (±0.01) $m^2\ g^{-1}$. This value is in good agreement with the surface area reported by Su and Puls (1999) for hydrochloric acid-treated Fisher 100-mesh iron.

3.2. Atrazine degradation rates

Fig. 1 shows how the rate of atrazine degradation varied with pH. No evidence of atrazine sorption to the iron (by analysis of metal wash solutions) was observed under these acidic conditions, and the absence of light did not affect our results. At a pH of 2.0 the atrazine

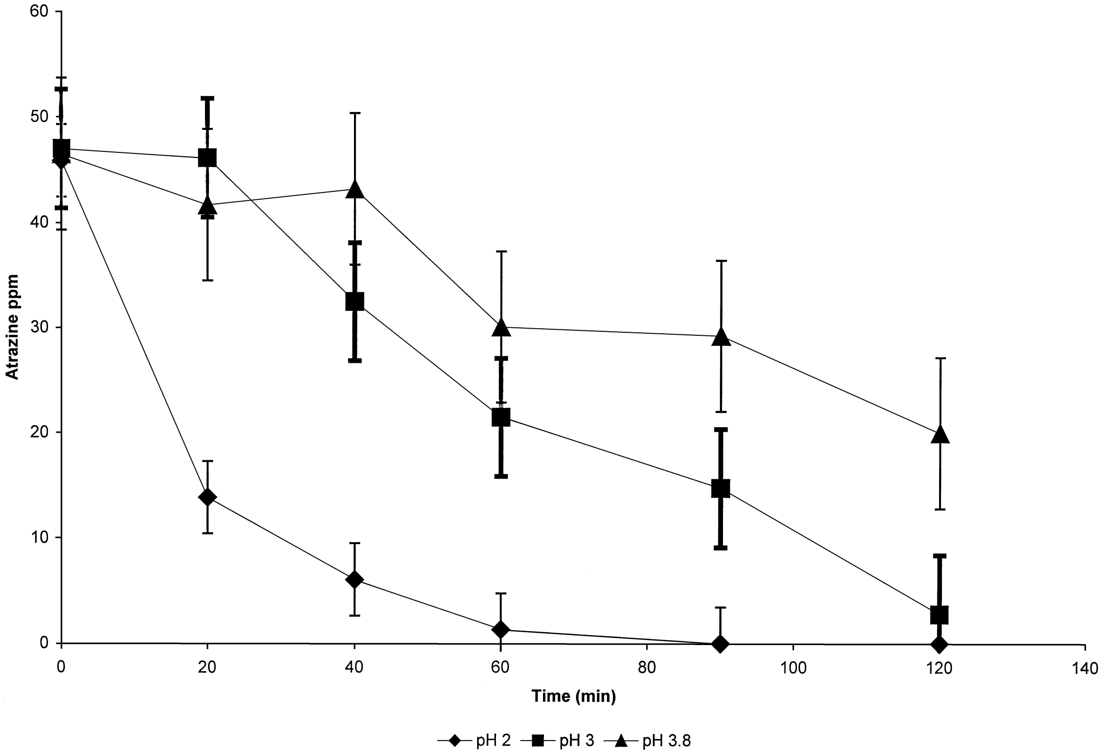

Fig. 1. Representative runs of the degradation of atrazine via reaction with metallic iron as a function of pH. pH control (to within ±0.3 pH units) was achieved by continual monitoring and addition of 3 M sulfuric acid as required. Uncertainty estimates (error bars) reflect standard error of exponentially fitted results of multiple runs using identical starting conditions at pH 3.0 (±.3). The surface area normalized initial pseudo-first order rate constants (k_{SA}, where rate $= k_{SA} \times$(surface area/l)×[Atrazine]) at pH solution values of 2.0, 3.0, and 3.8 were equal to, respectively, 3.0 (±0.4)×10^{-3} $min^{-1}\ m^{-2}$ l, 5 (±3)×10^{-4} $min^{-1}\ m^{-2}$ l, and 1 (±1)×10^{-4} $min^{-1}\ m^{-2}$ l.

essentially was completely degraded by 100 min. In contrast, only about 50% of the atrazine was degraded within this time span at a pH of 3.8. The surface area normalized initial pseudo-first order rate constants (k_{SA}, where rate = $k_{SA} \times$(surface area/l)$\times$[Atrazine]) at pH values of 2.0, 3.0, and 3.8 were equal to, respectively, 3.0 ($\pm$0.4)$\times 10^{-3}$ min^{-1} m^{-2} l, 5 ($\pm$3)$\times 10^{-4}$ min^{-1} m^{-2} l, and 1 ($\pm$1)$\times 10^{-4}$ min^{-1} m^{-2} l. Although these values essentially are the same as the overall pseudo first-order rate constants, it is the initial rates which best reflect known experimental conditions. As the reaction proceeds, the solution:iron ratio changes due to sample removal and the available active iron surface is likely to change due to solution conditions.

Within the relatively short time-span of these experiments, the only product identified via GC, and confirmed with GC–MS, was dechlorinated atrazine (DCA, 2-ethylamino-4-isopropylamino-1,3,5-triazine). Fig. 2 shows the gas chromatograms of samples collected during a pH 2.0 degradation reaction. With this instrumentation the retention time of atrazine was 11.6 min and that of DCA was 10.3 min. The concentration of DCA did, at all pH values, initially grow as the atrazine concentration decreased. However, after its initial growth, the concentration of DCA often began to decrease and/or show concentration fluctuations. Clearly the DCA can react further. HPLC analysis of the final (pH 2.0) reaction solution (which contained no atrazine) showed the presence of what was possibly hydroxyatrazine (HA) (based on retention time comparison). Because of the inability of GC to detect this compound, our quantitative data do not show if the degraded atrazine first formed DCA, then HA, or if HA was an additional product of atrazine degradation. Neither of the major microbial metabolites of atrazine, de-ethylatrazine and de-isopropylatrazine, was detected.

Fig. 3A shows the GC–MS chromatogram of a sample collected from a pH 2.0 solution at 90 min. The mass spectrum of the peak at 10.7 min, shown in Fig. 3B, is DCA. The parent ion of this molecule has a mass/charge ratio of 181, corresponding to the replacement of the chlorine of atrazine with hydrogen (215−35+1= 181). The lack of an appropriate isotopic ratio of the parent ion confirms that this molecule does not contain chlorine. Fig. 4A shows the GC–MS chromatogram of a sample collected during a run using D_2O as the solvent. The mass spectrum of the DCA produced during this reaction (Fig. 4B) proves that the proton replacing the chlorine of atrazine came from the solvent. The parent ion in this mass spectrum has a mass/charge ratio of 182, one more than when the reaction is conducted in water.

3.3. The role of solution pH

It is clear from these results that pH plays a role in the rate of reductive dechlorination of atrazine via metallic iron. The rate of the process increases as the solution pH decreases. Enhanced corrosion of the iron at lower pH values is probably one of the reasons for the observed pH dependence, but the general success of iron-mediated reductive dechlorination reactions at ambient (environmental) pH values reported by other

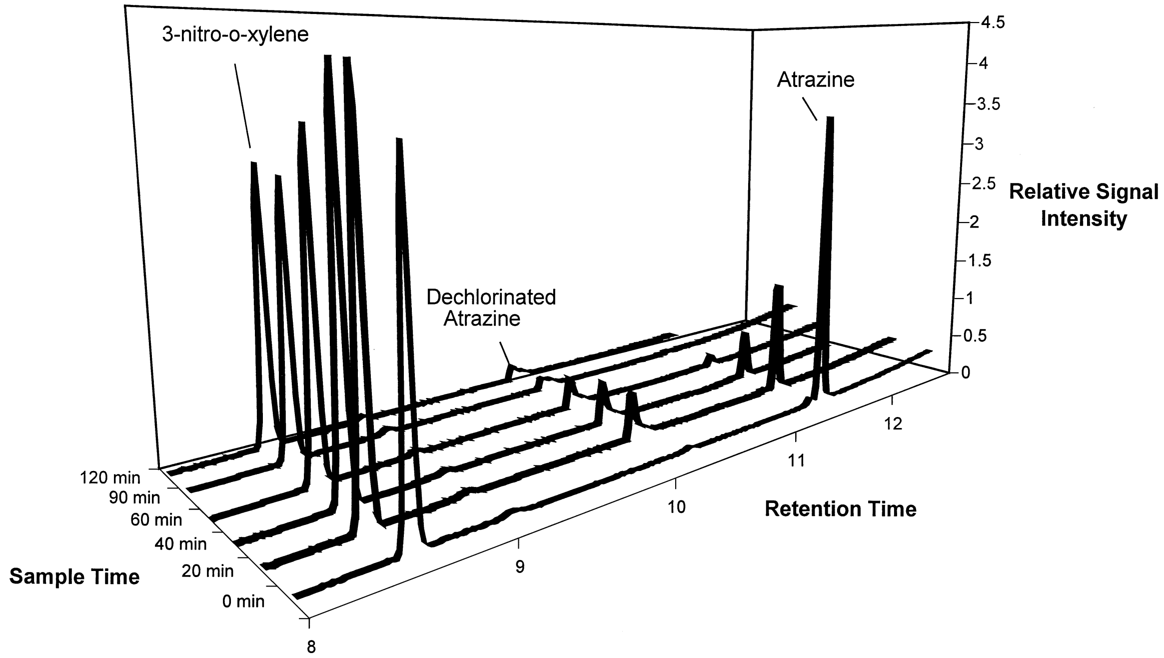

Fig. 2. Gas chromatograms of aliquots withdrawn from a pH 2.0 experimental run at various times. The 3-nitro-*o*-xylene was used as an internal standard. Note the initial formation and the degradation of the dechlorinated atrazine as the reaction proceeded.

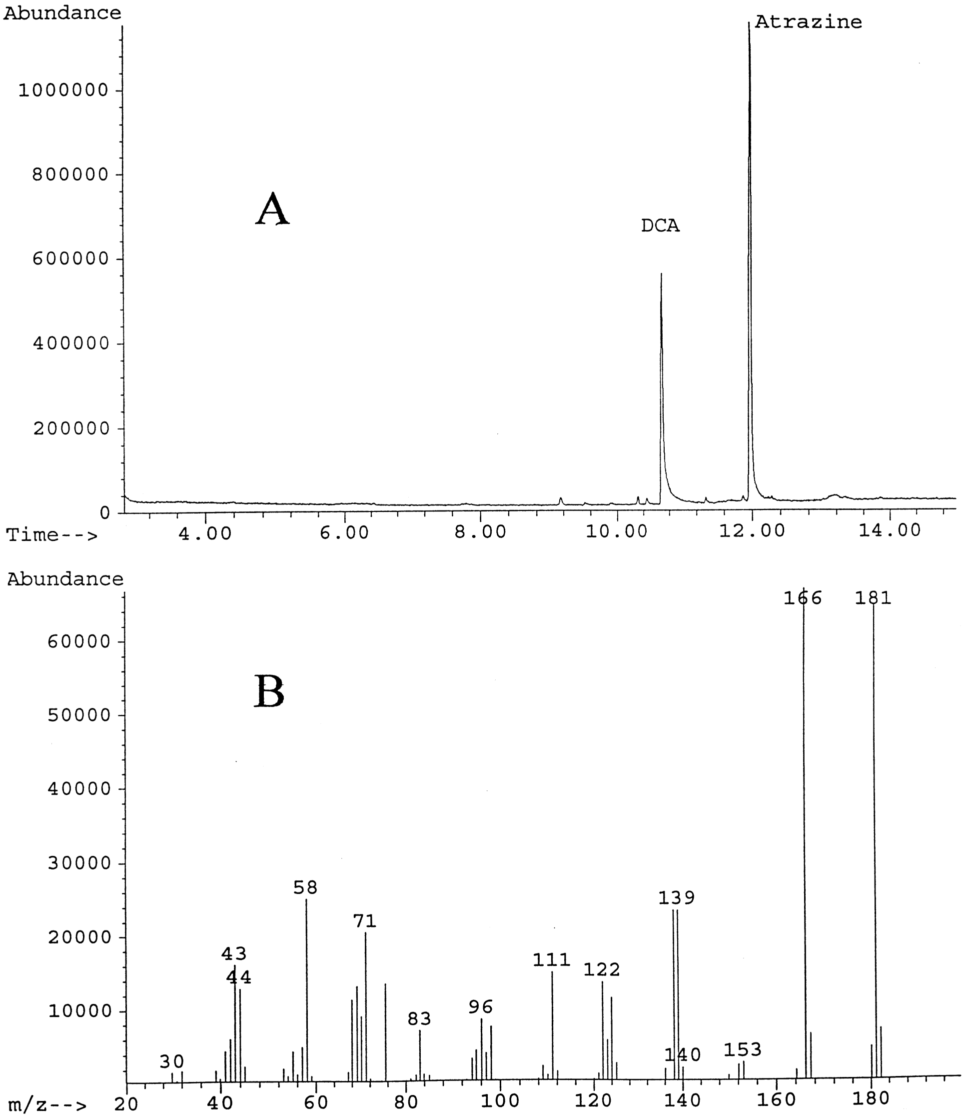

Fig. 3. (A) The total ion current gas chromatogram from a typical 90-min sample of a pH 2 reaction. The peak at 12.0 min is atrazine and that at 10.7 min is dechlorinated atrazine (DCA). (B) The mass spectrum associated with the chromatographic peak at 10.7 min, clearly identifying this peak as DCA.

investigators suggests reactive iron sites are available even at near neutral pH values. Given the fact we did not observe atrazine dechlorination at ambient pH values (although the time span of our experiments was relatively short), it seems reasonable to suspect that there are factors other than surface corrosion which account for the pH effects presented here.

The pKa of (protonated) atrazine is 1.7, so approximately 33% of the atrazine is protonated at a pH of 2, 5% at a pH of 3, and 1% at a pH of 4. The correlation between the rate of degradation and the degree of atrazine protonation certainly is suggestive. The protonation of the triazine ring would draw electron density from the C–Cl bond, weakening the bond and better allowing the dechlorination reaction to proceed. In effect, reducing the magnitude of the reduction potential to a point where dechlorination can occur readily. Pospisil et al. (1995) determined that electrochemical reductive dechlorination of atrazine at a mercury electrode required acidic media, and they concluded the reactive species was the protonated atrazine. It seems probable that protonated atrazine also is the actual species which undergoes reductive dechlorination via metallic iron:

$$[\mathrm{H-Atr-Cl}]^{+} + \mathrm{Fe(s)} \rightarrow \mathrm{Atr-H} + \mathrm{Fe}^{2+} + \mathrm{Cl}^{-} \quad (3)$$

where $[\mathrm{H-Atr-Cl}]^{+}$ represents the protonated atrazine and Atr–H the dechlorinated product. The lower the pH, the higher the equilibrium concentration of the protonated atrazine and the faster the reaction rate.

3.4. Atrazine hydrolysis

Solution pH also plays a significant role in the acid-catalyzed hydrolysis of atrazine. Plust et al. (1981)

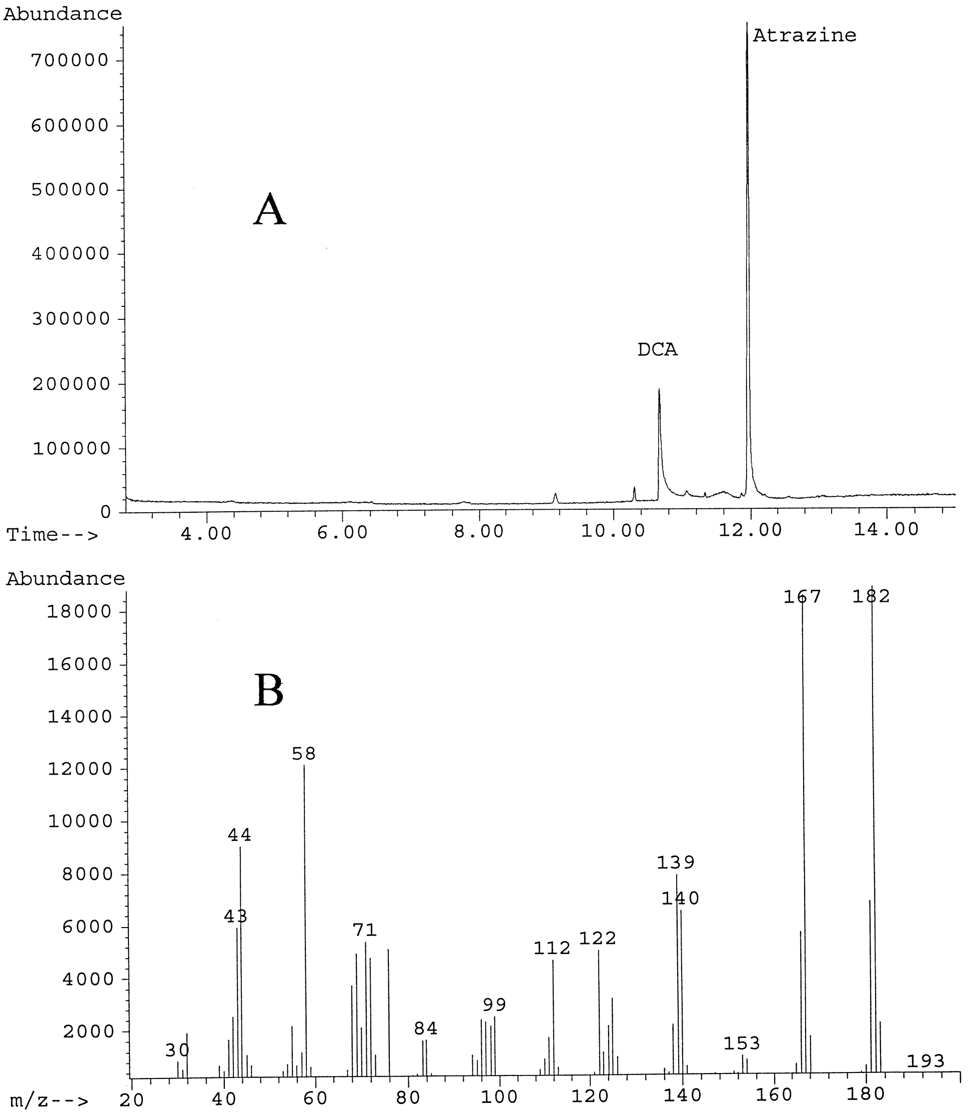

Fig. 4. (A) The total ion current gas chromatogram obtained when carrying out the reaction in D_2O. (B) The mass spectrum associated with the dechlorinated atrazine (DCA) which elutes at 10.7 min. The parent ion and fragmentation pattern confirm that the substituted deuterium atom comes from the solvent.

found that although atrazine was quite stable in water at neutral pH, it does undergo acid hydrolysis at lower pH values. The hydrolysis reaction occurs with the protonated atrazine species. Although this confirms the reactivity of the protonated species versus the neutral species (which is a general observation for triazines; see Joule et al., 1995) the hydrolysis reaction, even at a pH of 2.0, is not rapid enough to account for the degradation of atrazine we observed. Indeed, we saw no measurable atrazine degradation (within the time-span of our experiments) in the absence of iron.

3.5. Influence of buffers and acidic species

The pH control of the reaction solutions was difficult. Phosphoric, formic, sulfurous, and acetic acid buffering systems were employed in an attempt to control pH. Only the pH 2 phosphoric acid buffer held promise for pH control, although even here the results were not consistent with the non-buffered pH 2 experiments and were difficult to interpret (data not shown). When the other buffer systems were attempted for pH control, either the reaction did not occur, or the atrazine was degraded while in solution, perhaps via a specific-acid–general-base sequence (Plust et al., 1981).

In addition to sulfuric acid, nitric and hydrochloric acid were tested in carrying out the reaction. Preliminary results show that although degradation occurs with all of these acids, the rates vary: $\text{Rate}_{H_2SO_4} > \text{Rate}_{HCl} > \text{Rate}_{HNO_3}$ (data not shown). Further experiments to determine the reasons behind the rate dependence on acid species are required. It is possible for sulfate to act as an oxidant under our reaction conditions, although atrazine oxidation usually results in initial products which are dealkylated or oxidized (Larson et al., 1991), none of which was observed in our experiments.

4. Conclusions

Compared to other chlorinated compounds which have been reductively dechlorinated via reaction with metallic iron under anaerobic conditions, atrazine dechlorination at environmental pH occurs very slowly and with great difficulty. At low pH, however, the reaction proceeds readily, producing dechlorinated atrazine and possibly hydroxyatrazine. The influence of pH on the degradation rate is probably the result of both maintaining the available iron surface area for reaction and protonation of the triazine ring.

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References

Allen-King, R.M., Halket, R.M., Burris, D.R., 1997. Reductive transformation and sorption of cis- and trans-1,2-dichloroethene in a metallic iron–water system. Environmental Toxicology and Chemistry 16 (3), 424–429.

Balmer, M.E., Sulzberger, B., 1999. Atrazine degradation in irradiated iron/oxalate systems: effects of pH and oxalate. Environmental Science and Technology 33 (14), 2418–2424.

Bridges, D.C., 1998. A simulation analysis of the use and benefits of triazine herbicides. In: Ballantine, L.G., McFarland, J.E., Hackett, D. (Eds.), ACS Symposium Series 683: Triazine Herbicides: Risk Assessment. American Chemical Society, Washington, DC, p. 24.

Davenport, D.T., 1996. Degradation and sorption of select triazine, analide and carboxylic acid herbicides using zero-valent iron. M.S. thesis, Civil and Environmental Engineering, The University of Wisconsin — Madison.

Eykholt, G.R., Davenport, D.T., 1998. Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. Environmental Science and Technology 3, 1482–1487.

Gillham, R.W., O'Hannesin, S.F., 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. Ground Water 32 (6), 958–967.

Johnson, T.L., Scherer, M.M., Tratnyek, P.G., 1996. Kinetics of halogenated organic compound degradation by iron metal. Environmental Science and Technology 30, 2634–2640.

Joule, J.A., Mills, K., Smith, G.F., 1995. Heterocyclic Chemistry, 3rd Edition. Chapman & Hall, New York.

Larson, R.A., Schlauch, M.B., Marley, K.A., 1991. Ferric ion promoted photodecomposition of triazines. Journal of Agricultural and Food Chemistry 39, 2057–2062.

Matheson, L.J., Tratnyek, P.G., 1994. Reductive dehalogenation of chlorinated methanes by iron metal. Environmental Science and Technology 28 (12), 2045–2053.

Monson, S.J., Ma, Li., Cassada, D.A., Spalding, R.F., 1998. Confirmation and method development for dechlorinated atrazine from reductive dehalogenation of atrazine with Fe°. Analytica Chimica Acta 373, 153–160.

Orth, W.S., Gillham, R.W., 1996. Dechlorination of trichloroethene in aqueous solution using Fe°. Environmental Science and Technology 30, 66–71.

Plust, S.J., Loehe, J.R., Feher, F.J., Benedict, J.H., Herbrandson, H.F., 1981. Kinetics and mechanism of hydrolysis of chloro-1,3,5-triazines. Atrazine. Journal of Organic Chemistry 46 (18), 3661–3665.

Pospisil, L., Trskova, R., Fuoco, R., Colombini, M.P., 1995. Electrochemistry of s-triazine herbicides: reduction of atrazine and terbutylazine in aqueous solutions. Journal of Electroanalytical Chemistry 395, 189–193.

Pulgarin, C.O., Schwitzguebel, J.-P., Peringer, P.A., Pajonk, G.M., Bandara, J.S., Kiwi, J.T., 1996. Abiotic oxidative degradation of atrazine on zero-valent iron activated by visible light. J. Adv. Oxid. Technol. 1, 94–101.

Roberts, A.L., Totten, L.A., Arnold, W.A., Burris, D.R., Campbell, T.J., 1996. Reductive elimination of chlorinated ethylenes by zero-valent metals. Environmental Science and Technology 30 (8), 2654–2659.

Singh, J., Shea, P.J., Hundal, L.S., Comfort, S.D., Zhang, T.C., Hage, D.S., 1998. Iron — enhanced remediation of water and soil containing atrazine. Weed Science 46, 381–388.

Su, C., Puls, R.W., 1999. Kinetics of trichloroethene reduction by zerovalent iron and tin: pretreatment effect, apparent activation energy, and intermediate products. Environmental Science and Technology 33, 163–168.

Sweeny, K.H., 1979. Reductive degradation treatment of industrial and municipal wastewaters. In: Water Reuse Symposium Proceedings, Vol. 2, March 25–30, Washington, DC.

Wackett, L., 1999. Atrazine pathway map The University of Minnesota Biocatalysis/Biodegradation Database. Available on-line at: http://www.labmed.umn.edu/umbbd/

Weber, E.J., 1996. Iron-mediated reductive transformations: investigation of reaction mechanism. Environmental Science and Technology 30 (2), 716–719.