

# Degradation of terbutylazine (2-chloro-4-ethylamino-6-terbutylamino-1,3,5-triazine), deisopropyl atrazine (2-amino-4-chloro-6-ethylamino-1,3,5-triazine), and chlorinated dimethoxy triazine (2-chloro-4,6-dimethoxy-1,3,5-triazine) by zero valent iron and electrochemical reduction

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Received 31 January 2003; accepted 13 October 2003

**“Capsule”:** *Reductive dechlorination via zero valent iron is dependent upon solution pH and the specific triazine.*

## Abstract

To help elucidate the mechanism of dechlorination of chlorinated triazines via metallic iron, terbutylazine (TBA: 2-chloro-4-ethylamino-6-terbutylamino-1,3,5-triazine), deisopropyl atrazine (DIA: 2-amino-4-chloro-6-ethylamino-1,3,5-triazine), and chlorinated dimethoxy triazine (CDMT: 2-chloro-4,6-dimethoxy-1,3,5-triazine) were degraded via zero valent iron under controlled pH conditions. The lower the solution pH the faster the degradation, with surface area normalized pseudo first order rate constants ranging from  $2 (\pm 1) \times 10^{-3} \text{ min}^{-1} \text{ m}^{-2}$  for TBA at pH 2.0 to  $4 (\pm 2) \times 10^{-5} \text{ min}^{-1} \text{ m}^{-2}$  for CDMT at pH 4.0. Hydrogenolysis (dechlorinated) products were observed for TBA and CDMT. Electrochemical reduction on mercury showed similar behavior for all of the triazines studied; the initial product of CDMT bulk electrolysis was the dechlorinated compound. The iron results are consistent with a mechanism involving the addition of surface hydrogen to the surface associated triazine.

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**Keywords:** Pesticide; Triazine; Reduction; Degradation; Iron

## 1. Introduction

Triazine herbicides have been used in agriculture for many years, particularly on corn and sugarcane fields. Their popularity stems from their effectiveness, affordability, and lack of viable and cost-effective alternatives (Bridges, 1998). The most heavily used of the triazine herbicides, atrazine, is relatively persistent in the environment and has been found in drinking water supplies. This is of significant concern because atrazine is a mammalian carcinogen (USEPA, 2002) and endocrine disrupter (Friedmann, 2002; Hayes, et al., 2002a and b; Tavera-Mendoza, et al., 2002).

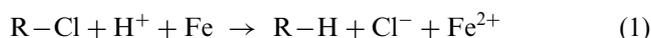
A number of techniques have been proposed and explored for the technological destruction of chlorinated

triazine herbicides, in particular atrazine. These methods have included photocatalytic degradation (Minero et al., 1996), advanced oxidation (Hapeman-Somich et al., 1992; Arántegui et al., 1995; Beltrán et al., 1993a and b), Fenton like reactions (Arnold et al., 1995; Larson et al., 1991), and electrocatalytic dechlorination (Stock and Bunce, 2002). An alternative method of atrazine chemical degradation that has the potential to be inexpensive and easy to implement is the use of zero-valent iron for the reductive degradation of chlorinated triazines (Dombek, 2001; Monson, 1998).

Over the past few years zero-valent iron has gained popularity as a treatment option to reductively dechlorinate solvents of environmental concern such as carbon tetrachloride, perchloroethylene and trichloroethylene (Matheson and Tratnyek, 1994; Campbell et al., 1997; Orth and Gillham, 1996; Burris et al, 1995; Roberts et al., 1996; Allen-King et al., 1997). The reaction results in the production of  $\text{Fe}^{2+}$ ,  $\text{Cl}^-$ , and the dechlorinated product:

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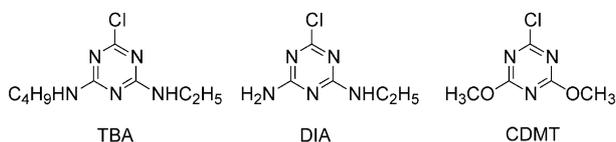
E-mail address: [cfdgk@eiu.edu](mailto:cfdgk@eiu.edu) (D. Klarup).



Despite extensive study, the mechanisms of many of these reactions remain unclear. Interpretation of zero valent rate data often is complicated by mass transfer limitations (Scherer et al., 2001) and the two-phase nature of the system. It is known that the iron surface is required for the reaction to proceed (Weber, 1996) and sorption does occur for at least some compounds on iron (Burris et al., 1995; Allen-King et al., 1997; Kim and Carraway, 2000) so direct adsorption and electron transfer is feasible. Electrochemical studies have been useful in elucidating possible reductive dechlorination mechanisms. Li and Farrell (2001) studied the reductive dechlorination of carbon tetrachloride and trichloroethylene with a rotating iron disc electrode. They concluded that carbon tetrachloride undergoes an outer sphere electron transfer process but that a chemical step is responsible for the reductive dechlorination of trichloroethylene—possibly a reaction between bound trichloroethylene and nascent hydrogen. Surface bound hydrogen may also be responsible for the electrocatalytic hydrogenolysis of atrazine on Pd (Stock and Bunce, 2002).

Triazine mechanistic electrochemical studies have been conducted primarily on mercury electrodes (Higuera et al., 1999; Pospisil et al., 1996; Skopalova and Kotoucek, 1995). In all cases the reductions appear to involve two 2-electron reduction steps, with the first step producing the dechlorinated triazine. Proposed electrochemical mechanisms have suggested that it is the protonated form of the triazine that undergoes reduction.

Here we report studies of zero-valent iron reductive dechlorination rates for three different chlorinated triazines: terbutylazine (TBA: 2-chloro-4-ethylamino-6-terbutylamino-1,3,5-triazine), deisopropyl atrazine (DIA: 2-amino-4-chloro-6-ethylamino-1,3,5-triazine), and chlorinated dimethoxy triazine (CDMT: 2-chloro-4,6-dimethoxy-1,3,5-triazine) under controlled pH conditions.



The results of electrochemical experiments, carried out to show general correlation between electrochemically produced and zero-valent iron produced products, also are presented.

## 2. Materials and methods

### 2.1. Zero Valent Iron Reactions

CDMT (Sigma-Alrich), DIA and TBA (Supelco) were used without further purification. Reactions were

conducted in either a 1.0 l, 4 port flask, or a 500 ml round-bottom 3 port flask using 10.0 g or 20.0 g of iron particles (finer than 100 mesh, Fisher Scientific, measured (Quantasorb Sorption System) Brunauer-Emmett-Teller (BET) surface area of 0.22 m<sup>2</sup>/g) and 500 or 235 ml of triazine solution. To ensure aqueous solution concentrations were well below saturation, initial concentrations of 40.0 ppm CDMT, 8.0 ppm TBA, and 40.0 ppm DIA were used. Runs of 40.0 ppm atrazine [ATR (Pfaltz and Bauer, Inc.)] also were conducted for comparison with earlier work. All solutions were initially degassed with N<sub>2</sub> and reactions were conducted under a N<sub>2</sub> atmosphere. The iron was pre-treated with two washings of 0.5 M H<sub>2</sub>SO<sub>4</sub> prior to combination with the triazine solutions. Solution pH was maintained by addition of small quantities of 3 M H<sub>2</sub>SO<sub>4</sub> throughout the course of the reaction.

Solution pH values of 2.0(±0.1), 3.0(±0.1), and 4.0(±0.1) for CDMT and TBA and 2.0(±0.1) and 3.0(±0.1) for DIA were used. Periodically aliquots of solution were removed for analysis. After aliquot withdrawal an equivalent volume of degassed, dionized water was introduced into the reaction vessel to maintain a constant solution volume. Blank (no iron) reactions were conducted at pH 2.0 to monitor hydrolysis. Triazine adsorption on iron was determined for pH 2.0 solutions after 15 min of reaction and at the end of the reaction by extraction of the iron with either dichloromethane or acetonitrile and subsequent analysis.

### 2.2. Analytical methodology

Triazine solution aliquots were concentrated via solid phase extraction cartridges (3 ml AccuBond<sup>®</sup>, 40 μm particle size, 60 Å pore size, J&W Scientific). The cartridges were prepared by first pulling (via vacuum) 20 ml dionized water, 20 ml acetonitrile (HPLC grade, Fisher Scientific), and 5 ml of deionized water through the cartridge. This was followed by aliquot (usually 15 ml) extraction and an additional 5.0 ml of deionized water. Acetonitrile was used to elute the cartridge. The acetonitrile triazine solutions were then subjected to either high performance liquid chromatography (HPLC), or gas chromatography-mass spectrometry (GC-MS) analysis.

### 2.3. HPLC analysis

Quantitative HPLC analysis was performed with a Hitachi D-7000 High Performance Liquid Chromatograph system equipped with a L-7420 UV-VIS detector and a 25 cm Whatman<sup>®</sup> Partisphere C-18 column. For CDMT and DIA analysis, a mobile phase of 75% water and 25% acetonitrile was employed at a flow rate of 1.00 ml/min. For TBA and ATR analysis, a mobile phase of 70% methanol and 30% water at 1.00 ml/min

was used. In all cases the analytical wavelength was 220 nm. The linear relationship between triazine concentration and detector response was determined via 5 point calibration curves.

#### 2.4. GC–MS analysis

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

#### 2.5. Electrochemical studies

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 cell was used with a Ag/AgCl reference electrode and platinum auxiliary electrode. Triazine solution concentrations of 5 ppm were used. The supporting electrolyte was 0.1 M NaCl and 3M H<sub>2</sub>SO<sub>4</sub> (aq) was used for pH adjustment.

For differential pulse polarography the instrumental parameters were as follows: 2 mV/s scan rate, 10 μA current range, 25 mV pulse height, and 8 minute N<sub>2</sub> purge. The potential was scanned (cathodically) from –0.50 V to –1.40 V. The data collection software allowed for 15 point averaging of the sampled current.

To determine the initial product of CDMT electrochemical reduction, bulk electrolysis was conducted with the EG&G Princeton Applied Research Model 264A Polarographic Analyzer/Stripping Voltammeter and a homemade electrolysis cell using a mercury pool cathode, Ag/AgCl reference electrode, and platinum wire counter electrode. Cathode potential was held at –1.00 V (vs. Ag/AgCl). Initial CDMT concentration was 40 ppm in 0.1 M NaCl and sufficient HCl to achieve a pH of 2.0. Product identification was carried out via solid phase extraction and GC-MS analysis.

### 3. Results and discussion

#### 3.1. Zero valent iron reactions

Fig. 1 shows the zero valent iron reaction concentrations of CDMT, DIA, and TBA as a function of time and pH. Under our experimental conditions, less than 1% of any triazine was found to have adsorbed to the iron surface, so these figures demonstrate triazine degradation. The only product detected via GC for

CDMT and TBA was the dechlorinated species, where a hydrogen atom replaced the chlorine atom. No product was detected via GC for DIA, but direct analysis (non-extracted) of the DIA reaction solution with HPLC revealed the growth of a product peak as the DIA peak decreased. Apparently the DIA reaction product was not efficiently extracted by the SPE cartridge or was otherwise unsuited to GC analysis. Table 1 lists the iron surface area normalized pseudo first order rate constants ( $k_{sa}$ ) for each triazine at each pH tested. Results for atrazine (ATR) using these experimental conditions at pH 2.00 are included for comparison.

As has been shown for atrazine, (Dombek et al., 2001), the degradation of the triazines is pH dependent: the lower the pH, the faster the rate of degradation. Fig. 2 shows the degradation rates of the triazines at pH 2.00. It is clear that TBA degrades quickly and CDMT degrades slowly. This is reasonable if it is the protonated form of the triazine that undergoes reduction. A much higher fraction of TBA, with a pKa of 1.95 (Coquart and Hennion, 1991), will be protonated at pH 2.00 than CDMT, with a pKa of less than 1 (Xing et al., 1996). This reasoning leads to the prediction that the rate of DIA [pKa = 1.3 (Loos and Niessner, 1999)] and ATR [pKa = 1.7 (Xing et al., 1996)] degradation should fall between those of CDMT and TBA, with ATR degrading faster than DIA. Fig. 2 shows that, indeed, the rates of DIA and ATR degradation fall between those of CDMT and TBA, but the rate of DIA is higher than that of ATR.

Perhaps the lack of an alkyl amino group allows better interaction with the iron surface for protonated DIA than protonated ATR—resulting in a larger reaction rate constant. Better (or different) interaction of the DIA with the iron also might explain the lack of GC-detectable product if a different mechanism, one which leads to polar products not amenable to solid phase extraction, is taking place.

The iron surface area normalized pseudo first order rate constant for atrazine found in Table 1 is significantly larger than we reported earlier (Dombek et al., 2001). The stir rates were different between the two experiments, but we were unable to establish any meaningful correlation between stir rate and degradation rate within the stir rate ranges used. The iron used in this work had been recently purchased, while the iron used in the earlier work had sat for many years with periodic openings of the container. It is not clear why the iron used earlier provided a faster degradation, though it is well known iron source and treatment greatly influence dechlorination reactions (Su and Puls, 1999).

#### 3.2. Electrochemical studies

Fig. 3 shows the differential pulse polarograms for ATR, TBA, DIA, and CDMT. Clearly each of the

triazines has similar electrochemical behavior on mercury, although the separation of the differential pulse polarogram peaks for CDMT is much greater. Note that the first reduction peak is at a similar voltage for each of the triazines studied. The electrochemical reduction of the chlorinated triazines is pH dependent, with little to no dechlorination occurring at solution pH values greater than approximately 4.5. These results closely follow those reported for atrazine (Skopalova and Kotoucek, 1995), propazine (2-chloro-4,6-di(isopropylamino)-1,3,5-triazine) and simazine (2-chloro-

4,6-di(ethylamino)-1,3,5-triazine) (Higuera et al., 1999; Marin Galvin et al., 2001). The two peaks exhibited by triazines reflect two 2-electron reduction steps. Higuera et al., (1999) proposed that the protonated triazine first undergoes a one electron reduction, resulting in a neutral radical. The neutral radical reacts with an additional proton to form a radical cation that undergoes another one electron reduction and subsequent product (dechlorinated triazine) production. The reaction between the neutral radical and proton constitute the rate determining step. The second 2-electron reduction

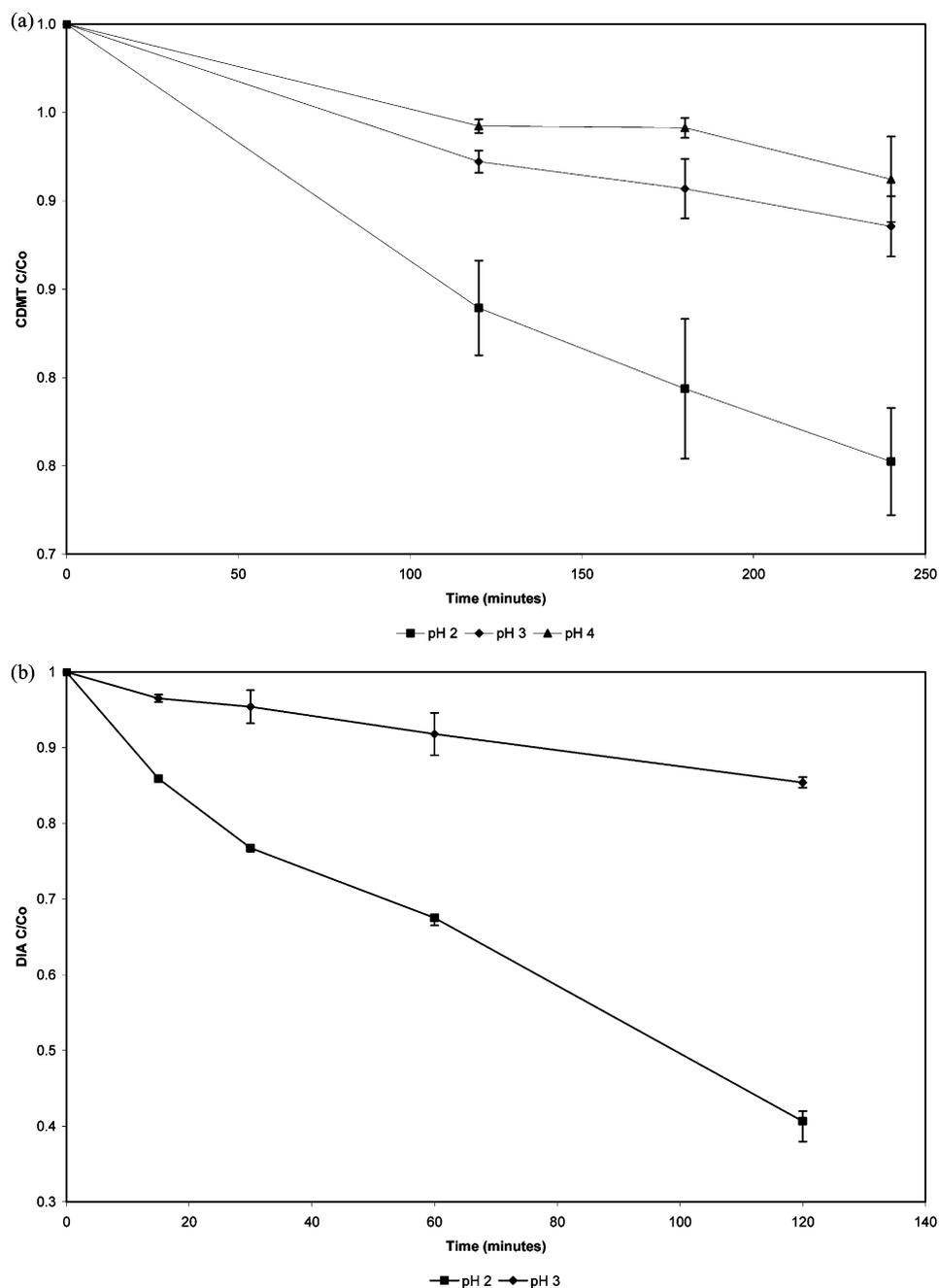


Fig. 1. Relative concentrations of (a) CDMT, (b) DIA and (c) TBA during reaction with zero valent iron. Corrected concentrations are shown in cases where detectable blank (no iron) reaction occurred (pH 2 solutions of CDMT and DIA). The error bars reflect the range of values measured.

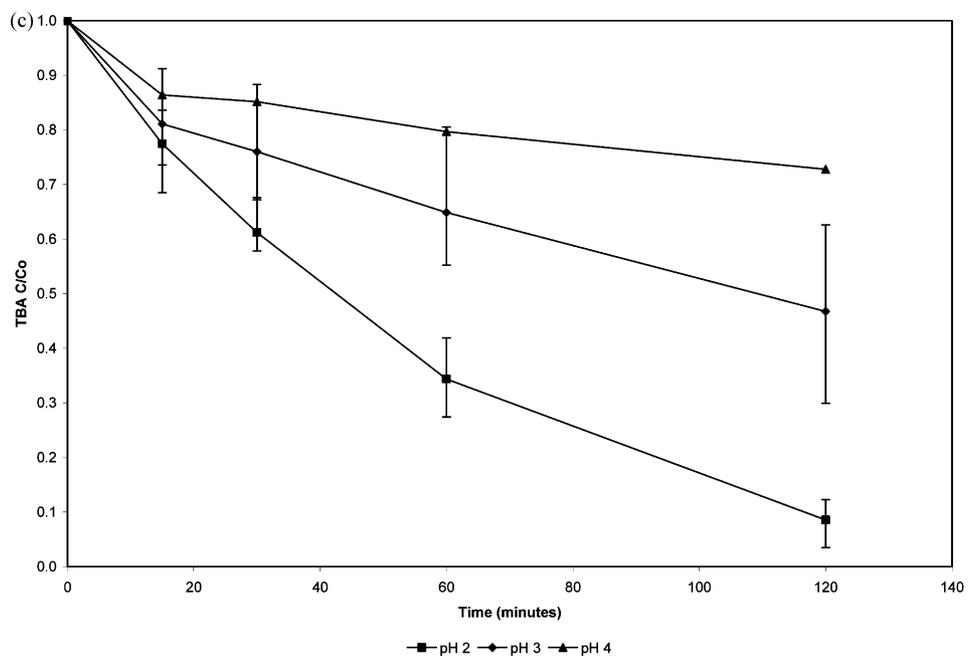


Fig. 1. (continued)

Table 1  
Surface area normalized pseudo first order rate constants,  $k_{sa}$  ( $\text{min}^{-1} \text{m}^{-2} \text{l}$ )

pH	CDMT	DIA	TBA	ATR
2	$1.4 (\pm 0.4) \times 10^{-4}$	$7.8 (\pm 0.4) \times 10^{-4}$	$2 (\pm 1) \times 10^{-3}$	$3.5 (\pm 0.1) \times 10^{-4}$
3	$6 (\pm 2) \times 10^{-5}$	$1.3 (\pm 0.2) \times 10^{-4}$	$7 (\pm 6) \times 10^{-4}$	
4	$4 (\pm 2) \times 10^{-5}$	NA	$2 (\pm 1) \times 10^{-4}$	

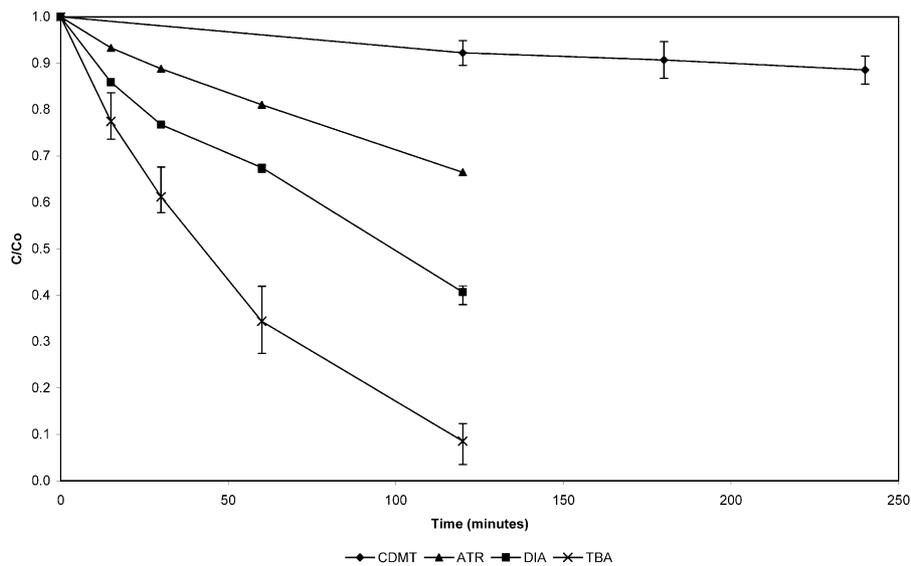


Fig. 2. Degradation of triazines via reaction with zero valent iron at pH 2.

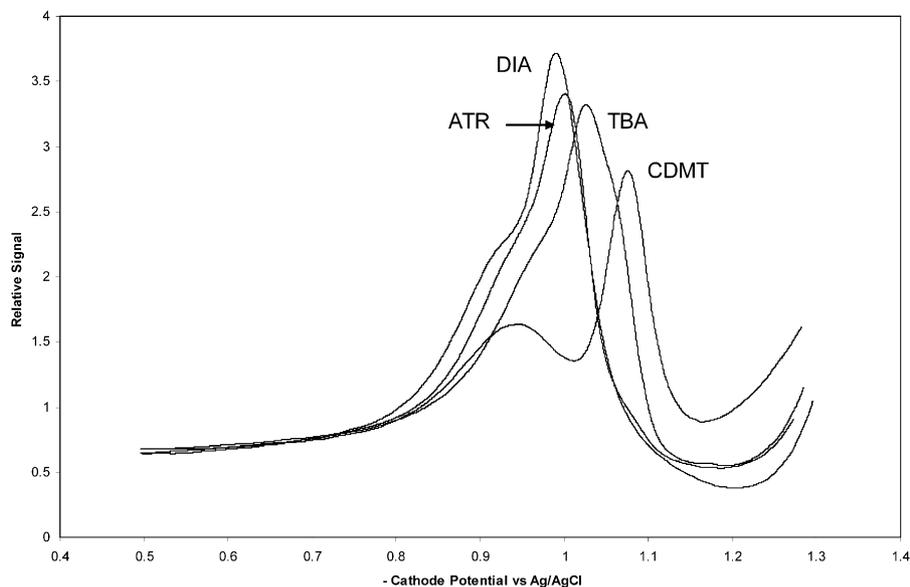


Fig. 3. Differential pulse polarograms of 5.0 ppm triazines in 0.1 M NaCl at pH 2.0 [adjusted with H<sub>2</sub>SO<sub>4</sub> (aq)].

is proposed to result in hydrogen addition to the triazine ring (Perez et al., 2002).

To confirm that the first electrochemical reduction step of CDMT results in the dechlorinated product, bulk electrolysis of CDMT was conducted. The initial product was, indeed, dechlorinated CDMT (see Fig. 4) but as the electrolysis continued multiple products formed. Tentative identification of some of these products (e.g., possibly CH<sub>3</sub>OCH<sub>2</sub>NHCH<sub>2</sub>Cl) suggest significant hydrogen addition and triazine ring breakage. Bubbles of hydrogen were visible on the mercury pool electrode, indicating that hydrogen reduction also was occurring, and it is possible that either nascent hydrogen or even molecular hydrogen contributed to multiple product formation.

### 3.3. Zero valent iron reaction mechanistic considerations

It seems probable that for the iron reaction the rate determining step (rds) involves the interaction between the protonated triazine and the iron surface (Scheme 1).



Scheme 1.

K<sub>a</sub> substitution into the rds rate expression leads to the corresponding rate expression for this scheme:

$$\text{Rate} = \frac{k_{\text{rds}}[\text{Fe}][\text{RCI}_m]}{\frac{K_a}{[\text{H}^+]} + 1} \quad (2)$$

At constant pH this rate expression is pseudo first order in triazine (assuming constant available iron surface area), with

$$k_{\text{sa}} = \frac{k_{\text{rds}}}{\frac{K_a}{[\text{H}^+]} + 1} \quad (3)$$

Since  $k_{\text{rds}}$  is unknown, direct comparison of model and experimental  $k_{\text{sa}}$  values is not possible. However, the ratio of  $k_{\text{sa}}$  values found with different pH conditions can be compared (Table 2).

The model shows too high a pH dependence, suggesting additional chemistry is occurring—probably pH dependent iron surface chemistry.

Table 2  
Surface area normalized pseudo first order rate constant ratios

Triazine	$k_{\text{sa}}(\text{pH } 2)/k_{\text{sa}}(\text{pH } 3)$		$k_{\text{sa}}(\text{pH } 3)/k_{\text{sa}}(\text{pH } 4)$	
	Model	Observed	Model	Observed
CDMT <sup>a</sup>	9.2	2±1	9.9	1.5±0.9
DIA	8.5	6±2	9.8	Na
TBA	5.8	3±3	9.3	3±3

<sup>a</sup> pK<sub>a</sub> = 1.0 assumed.

At the solution pH values studied hydrogen gas evolves via  $2\text{H}^+(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ . If this reaction occurs at the same iron surface sites as the triazine reductive dechlorination, or if the ensuing H<sub>2</sub> bubbles block iron reactive sites, H<sub>2</sub> generation would significantly limit the surface area available for triazine dechlorination. This could explain the rather complex dependence on pH for triazine dechlorination. As the pH of the acidic solution decreases, the proportion of protonated (reactive) triazine increases but surface site availability might actually be decreasing.

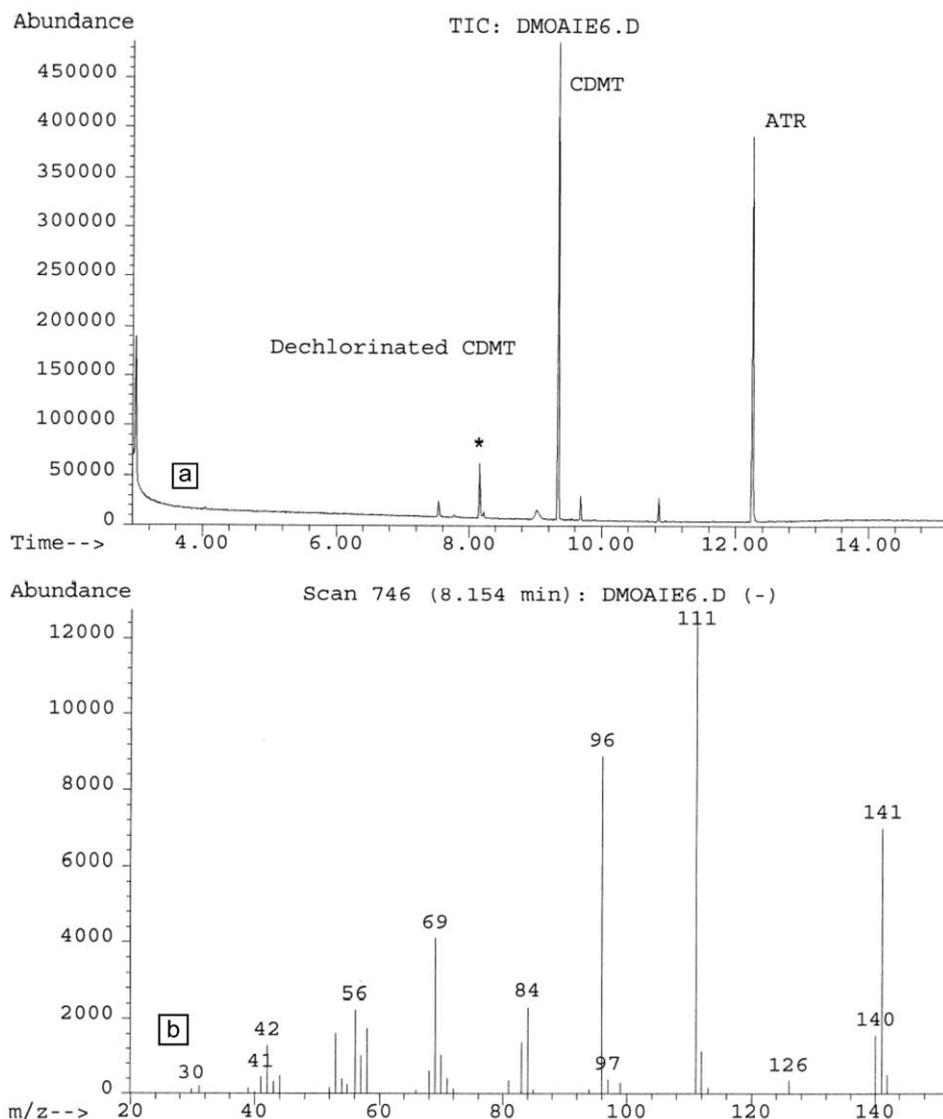
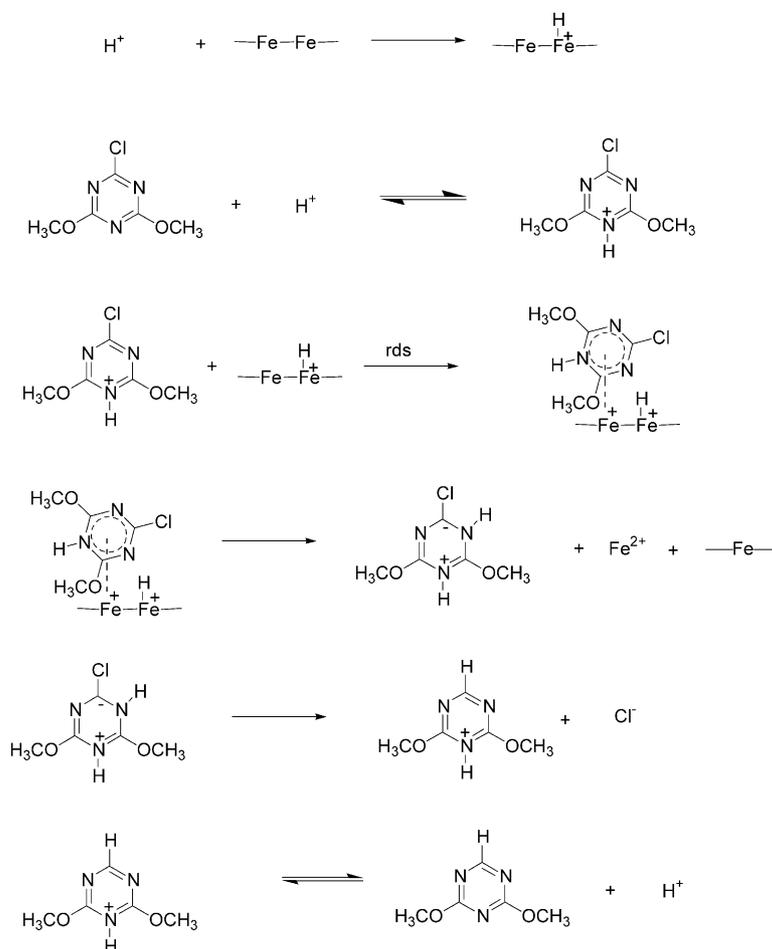


Fig. 4. (a) The gas chromatograph of a sample taken during the initial stages of bulk electrolysis of CDMT and (b) the mass spectrum confirming the presence of dechlorinated CDMT (b). Atrazine (ATR) was used as an internal standard. The small peaks at approximately 9.7 and 10.9 min are CDMT impurities.

It is possible that surface atomic hydrogen (nascent hydrogen) reacts with bound triazine on the iron surface. Such behavior has been suggested for dechlorination of gaseous chlorobenzene on iron coated char (Morlando et al., 1997) and for the electrochemical reduction of trichloroethylene on iron electrodes (Li and Farrell, 2001). Scheme 2 depicts such a mechanism for CDMT with  $-Fe-Fe-$  representing the iron surface. The exact nature of the triazine-iron surface interaction is unknown. Assuming that at constant pH the concentration of nascent hydrogen on the iron surface is constant the rate predicted from Scheme 2 would also be pseudo first order with the same apparent rate constant as that given in Eq. (3). An attractive feature of this mechanism is that it somewhat parallels

suggested electrochemical mechanisms (Higuera et al., 1999), with the major difference being the reaction occurs with surface bound hydrogen instead of solvated hydrogen ion. Modeling such a mechanism is quite complicated if, as suggested above, increased hydrogen gas evolution interferes with the triazine dechlorination process.

It should be pointed out that the rate results described here can be explained through a purely mass-transfer limited mechanism whereby the rate-determining step is actually diffusion of the protonated triazine to the iron surface. However, we found no clear correlation between stir rate and reaction rate, and the polarographic data showed no obvious difference between the diffusion coefficients for the triazines studied.



Scheme 2.

#### 4. Conclusions

Reductive dechlorination via zero-valent iron occurs for CDMT, DIA, and TBA but the rate of reduction is dependent upon solution pH and the specific triazine. The only detectable products of CDMT and TBA reduction were the corresponding dehalogenated triazine. Bulk electrolysis of CDMT also yields dehalogenated CDMT, in addition to other products.

For the iron reactions it is probable that the active species is the protonated triazine (as is the case in electrochemical reduction), but the exact mechanism of the reaction remains unclear. Rate comparisons suggest the rate determining step does not involve the reaction of a free hydronium ion, but instead reflects the adsorption of the protonated triazine onto the iron surface. Reaction of the bound, protonated triazine with surface bound hydrogen is consistent with the observed results. It is clear that all chlorinated triazines degrade more quickly as the pH is lowered, but not to the extent predicted by simple models. It is possible that  $\text{H}_2$  generation is a competing process on the iron surface that interferes with triazine dechlorination.

#### Acknowledgements

The authors would like to thank the Council for Faculty Research at Eastern Illinois University for financial support of this work.

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