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Electrochemical reduction of terbuthylazine under acidic conditions and structural determination of post-electrolysis product with the aid of GC/MS, IR, and ^{1}H NMR spectroscopy

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ABSTRACT

Terbuthylazine (*N*-*t*-butyl-6-chloro-*N*′-ethyl-1,3,5-triazine-2,4-diamine) is an important chloro-*s*-triazine herbicide that is used to prevent the growth of weeds during the production of a variety of crops in several European nations. The compound is also used as an algaecide to inhibit the growth of algae in water-cooling ponds and towers in the United States. These compounds can undergo electrochemical reduction under acidic conditions. Reduction pathways for several chloro-*s*-triazine herbicides have been proposed based on a variety of electrochemical, chromatographic, and spectroscopic techniques. There was general agreement in the literature that protonated forms of these compounds undergo a 4-electron reduction. The proposed reactions were elimination of the chloro group, elimination of an alkyl or alkylamino group, and reduction of the *s*-triazine ring. The present paper describes an electrochemical study of terbuthylazine with subsequent analyses of the post-electrolysis product by means of GC/MS, IR, and ^{1}H NMR spectroscopy. This work provides evidence for a 4-electron reduction involving elimination of the chloro group and reduction of the *s*-triazine ring.

1. Introduction

Terbuthylazine (*N*-*t*-butyl-6-chloro-*N*′-ethyl-1,3,5-triazine-2,4-diamine) is an important herbicide that is used to prevent the growth of broad-leaf and grassy weeds during the production of a variety of crops including beans, peas, corn, and grapes in several European nations [1]. The compound is also used as an algaecide to inhibit the growth of green algae in water-cooling ponds and towers in the United States. Terbuthylazine is a member of the chloro-*s*-triazine family of herbicides. A possible mode of action for these compounds involves competition between the herbicide and a plastoquinone (PQ) group in the Photosystem II (PS II) protein complex in susceptible weeds [2]. Herbicide bonding to a PQ site appears to cause free-radical oxidative damage to the electron-transport chain of PS II. Refined x-ray crystallographic data indicated that herbicide bonding to the PQ site involved the formation of multiple hydrogen bonds [3].

These compounds can undergo electrochemical reduction under acidic conditions. Reduction pathways for several chloro-*s*-triazine herbicides have been proposed on the basis of a variety of electrochemical, chromatographic, and spectroscopic techniques [4–12]. There was general agreement in the scientific literature that protonated forms of these compounds undergo a 4-electron reduction. Proposed pathways involved elimination of the chloro group, elimination of an alkyl or alkylamino group, and reduction of the *s*-triazine ring. Experimental verification of these reactions is important because they can be used for environmental remediation procedures [13]. The present paper describes an electrochemical study of the chloro-*s*-triazine herbicide terbuthylazine with subsequent analyses of the post-electrolysis product by means of GC/MS, IR, and ^{1}H NMR spectroscopy. This work provides evidence for a 4-electron reduction involving elimination of the chloro group and reduction of the *s*-triazine ring.

2. Results

Cyclic voltammetry (CV) was used to determine the extent of reversibility and to obtain a measurement of the peak potential [14,15]. A 100 mL solution of 0.02 g terbuthylazine at pH 2.0 was prepared as described in detail elsewhere [11,12]. A 20 mL portion of this solution was pipetted into the electrochemical cell. CV experiments with scan rates of 50–2000 mV/s revealed a chemically irreversible system for terbuthylazine (Fig. 1). This indicated the cleavage of covalent bond(s) within the herbicide structure.

Controlled-potential electrolysis (CPE) was then used to determine the number of electrons in the reduction process and to produce a sample of the final product for subsequent analyses [14,15]. A fresh 100 mL solution of terbuthylazine at pH 2.0 was prepared as above. The

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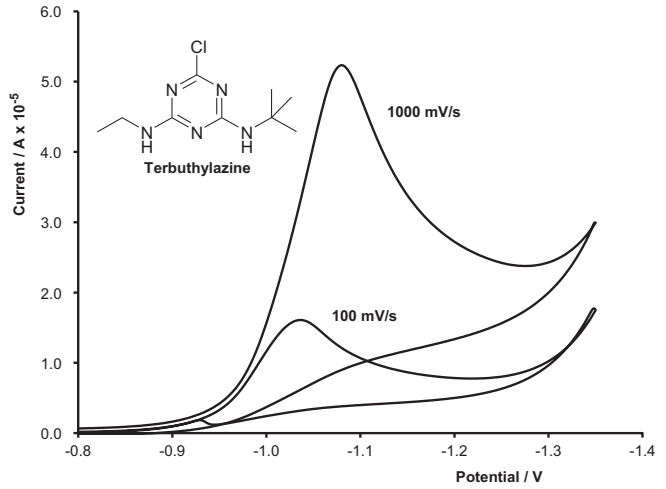

Fig. 1. Cyclic voltammograms of terbuthylazine at pH 2.0 with scan rates of 100 and 1000 mV/s.

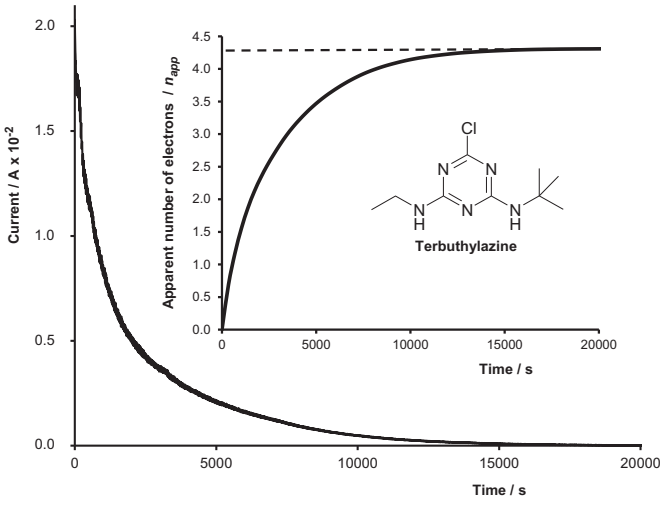

Fig. 2. Controlled-potential electrolysis of terbuthylazine at pH 2.0 and an applied potential of − 1.21 V (vs. Ag/AgCl/3 M NaCl).

entire solution was poured into the bulk electrolysis cell. A CPE experiment was then conducted with an applied potential of − 1.21 V (vs. Ag/AgCl/3 M NaCl). The selection of an appropriate applied potential is described in detail elsewhere [11,12]. The applied potential was roughly − 0.17 V negative of the peak potential from the CV work (Fig. 1; 100 mV/s). The baseline of the CPE curve was set to zero to remove the continuous faradaic current (Fig. 2) [16].

The CPE curve was integrated to obtain the accumulated charge [17]. Faraday's law of electrolysis was then used to calculate the apparent number of electrons in the reduction process (Eq. (1)):

$$n_{app} = q_{acc}/FN \quad (1)$$

where n_{app} is the apparent number of electrons per molecule, q_{acc} is the accumulated charge (C), F is Faraday's constant (96,485 C/eq), and N is the number of moles of reactant (mol). The apparent number of electrons increased over time to a maximum of 4.3 electrons/molecule (Fig. 2 inset). The average and standard deviation determined from the data of three exhaustive CPE reductions was 4.1 ± 0.2 electrons/molecule.

The post-electrolysis CPE sample was then poured into a 500 mL separatory funnel and made basic by addition of 100 mL of 10% (w/w) sodium carbonate saturated with sodium chloride. The sample was then extracted with chloroform as discussed elsewhere to yield a slightly yellow liquid residue [11,12]. The residue was dissolved in 1 mL of chloroform-*d* ($CDCl_3$). A 1 μL sample of the $CDCl_3$ solution was then injected into the GC/MS system. The chromatogram showed a single reduction product (Fig. S1). The corresponding mass spectrum had a molecular ion (M^+) peak at m/z = 197 (Fig. 3). The odd numerical value of the molecular ion peak m/z ratio indicated that the reduction product contained an odd number of nitrogen atoms [18,19].

Fragmentation analysis of the mass spectrum was used to identify the various groups in the reduction product. Loss of a hydrogen atom from the molecular ion (M^+) provides the peak at m/z = 196. The peak located at m/z = 182 is from the elimination of a methyl group. Loss of a hydrogen atom from the cation lacking a methyl group would give the peak at m/z = 181. Elimination of an ethylamino group provides the peak at m/z = 153. Loss of a *t*-butyl group would give the peak at m/z = 139. Elimination of a *t*-butylamino group provides the peak at m/z = 124. Loss of both a *t*-butylamino group and an ethyl methyl group would give the peak located at m/z = 111. Peaks located at the smaller m/z ratios could be the result of concerted cleavage mechanisms [18,19]. The reduction product likely contained methyl, ethyl, ethylamino, *t*-butyl, and *t*-butylamino group(s).

Two drops of the $CDCl_3$ solution were placed in the IR interferometer and dried under a nitrogen gas stream for 15 min. The resulting IR spectrum showed a small C−Cl stretching peak at 805 cm^{-1} (Fig. S2). This small peak was likely the result of a trace of unreacted terbuthylazine in the extracted reduction residue [4,5]. Careful inspection of the GC/MS data revealed a few trace impurities in the extracted residue which included unreacted terbuthylazine, the hydrolysis product hydroxyterbuthylazine, and a plasticizer leachate (diethylphthalate) from the bulk electrolysis cell [20]. The reduction product of terbuthylazine is probably a dechlorinated compound.

A ^{1}H NMR spectrum was then acquired by use of the remaining $CDCl_3$ solution of the reduction product (Fig. 4). Resonances from a ring methylene group (2H: *singlet*; δ 4.48), an ethyl methylene group (2H: *quartet*; δ 3.38), *t*-butyl methyl groups (9H: *singlet*; δ 1.41), and an ethyl methyl group (3H: *triplet*; δ 1.18) were observed in the ^{1}H NMR spectrum [21]. Coupling between the ethyl methyl and ethyl methylene protons ($^3J_{HH}$ = 7.18 Hz) was measured on the spectrum. A small impurity peak located at about δ 1.24 overlapped the ethyl methyl resonance and slightly increased the integrated area in the spectrum. The assignment of the ring methylene group was consistent with previous studies on atrazine and propazine [11,12]. Two broad peaks located at δ 8.01 and δ 7.30 in roughly a 1:2 area ratio were assigned to the cyclic and exocyclic NH protons, respectively. The broad NH resonances and overlap with the solvent peak resulted in inaccurate area integrations for these protons. Delocalization of the nitrogen lone-pair electrons could explain the deshielding of the NH protons observed in the ^{1}H NMR spectrum [22]. Efficient quadrupolar relaxation prevented the determination of coupling constants for the NH protons [21]. Nonetheless, the reduction product of terbuthylazine contained a ring methylene group, an ethyl group, a *t*-butyl group, one cyclic NH proton, and two exocyclic NH protons.

Given all the experimental evidence discussed above, the reduction product of terbuthylazine at pH 2.0 and an applied potential of − 1.21 V (vs. Ag/AgCl/3 M NaCl) is *N*-*t*-butyl-*N*′-ethyl-1,6-dihydro-1,3,5-triazine-2,4-diamine. This product arises by a 4-electron reduction that involves elimination of the chloro group and reduction of the *s*-triazine ring (Schemes 1–2).

3. Experimental

Terbuthylazine (Sigma-Aldrich; 99.9%) was used without further purification after analysis with GC/MS, IR, and ^{1}H NMR to confirm its structure and purity. A BioAnalytical Systems Inc. (BASi) Epsilon-2 potentiostat was used for this project. The electrochemical cells used in this study were described in detail elsewhere [11,12]. The CV static mercury drop working electrode had an average surface area of