



Mechanistic proposal for the electrochemical and sonoelectrochemical oxidation of thiram on a boron-doped diamond anode



Juliana R. Steter, Miriam H. Kossuga, Artur J. Motheo*

São Carlos Institute of Chemistry, University of São Paulo, Avenida Trabalhador Sancarlene, 400, São Carlos, SP 13566-590, Brazil

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ABSTRACT

A comparative study was carried out of sonochemical (Sch), electrochemical (ECh) and sonoelectrochemical (SECh) strategies for the degradation of the fungicide thiram in dilute aqueous solution. The Sch and SECh studies were performed using a sonicator equipped with an 11 mm titanium-alloy probe and operated at 20 kHz with a power intensity of 523 W cm^{-2} . In the ECh and SECh investigations, galvanostatic electrolyses were implemented using a single compartment electrochemical cell with a boron-doped diamond electrode as anode and applied current densities in the range $10\text{--}50 \text{ mA cm}^{-2}$. For these processes, the decrease in concentration of thiram was monitored by high performance liquid chromatographic (HPLC) analysis and values of current efficiency and energy consumption were determined. The results showed that the rate of degradation of thiram and the amount of energy consumed were directly proportional to the applied current density, while current efficiency was inversely related to current density. The kinetics of thiram degradation followed a pseudo first order model with apparent rate constants in the region of 10^{-3} min^{-1} . Thiram in aqueous solution was subjected to “exhaustive” degradation by ECh and SECh processes for 5 h at applied current densities of 35 mA cm^{-2} and the intermediates/byproducts so-formed were identified by HPLC–mass spectrometry. Mechanisms of the degradation reactions have been proposed on the basis of the results obtained.

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1. Introduction

The alkyldithiocarbamate thiram [tetramethylthiuram disulfide or bis-(dimethyldithiocarbamoyl) disulfide; Fig. 1] is a non-systemic fungicide employed in the protection of crops in the field and in the treatment of harvested seeds and fruits [1]. Following the banning of organochlorine-based compounds by many countries, the use of organophosphates and carbamates became more popular and these agents are now widely employed in agriculture throughout the world. Although these pesticides are undoubtedly effective, they cannot be generally classified as safe or less toxic since many inhibit acetylcholinesterase resulting in the accumulation of acetylcholine in nervous tissue.

Thiram is currently the second most popular fungicide after the traditionally used sulfur derivatives [2], and its fungicidal activity is mainly a consequence of its capacity to chelate physiologically important polyvalent cations [3,4]. Thiram exhibits neurotoxic activity and can also act as a developmental toxicant. According to the ecological risk assessment of the United States

Environmental Protection Agency [5], thiram shows risks to the reproductive cycle of birds and chronic effects on fish, aquatic invertebrates and mammals. However, available laboratory studies indicate that thiram is only slightly soluble in water and that it degrades more rapidly in acidic soils [6–8]. Reports are also available concerning the degradation of thiram in various segments of the ecosystem under diverse environmental conditions, in aqueous matrices and soil under controlled conditions, and in plants under field conditions [3,9].

A number of studies have focused on the degradation of several pollutants, including thiram, through ozonolysis in the presence or absence of UV radiation [10], oxidation by sodium hypochlorite [11,12], photolysis [2], photocatalytic processes using semiconductors such as TiO_2 [1,13–15], microbial catabolism [16,17] and electro-Fenton processes [18–21]. Among these approaches, strategies involving electrochemical reactions have been shown to be useful in the treatment/degradation of a wide variety of organic compounds [22–38]. Such processes tend to operate under mild conditions and offer a number of potential advantages including versatility, high-energy efficiency, ease of automation and security [18].

* Corresponding author.

E-mail address: artur@iqsc.usp.br (A.J. Motheo).

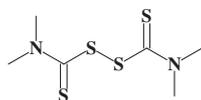


Fig. 1. Chemical structure of thiram (IUPAC name: tetramethylthiuram disulfide or bis-(dimethylthiocarbonyl) disulfide).

Ultrasonics has found application in a wide range of research fields including nanotechnology, chemical synthesis, food preservation, ultrasonic imaging and sonar detection among others [39]. The technique of coupling ultrasound power with an electrochemical process, a strategy known as sonoelectrochemistry, would appear to be extremely promising for the mineralization or degradation of toxic compounds and in the treatment of wastewater [40–44].

In consideration of the above, we have evaluated the electrochemical and sonoelectrochemical degradation of thiram and have identified the intermediate products formed using high performance liquid chromatography–mass spectrometry (HPLC–MS). Based on the results obtained, we have been able to propose distinct mechanisms for the two oxidative processes.

2. Materials and methods

2.1. Materials

Thiram ($C_6H_{12}N_2S_4$; 97% pure) was purchased from Sigma–Aldrich, potassium sulfate (K_2SO_4 ; analytical grade) was from Mallinckrodt, and chromatographically pure methanol (MeOH) and acetonitrile (CH_3CN) were from J T Baker. All chemicals were used as received. Solutions and electrolytes were prepared with ultrapure water (resistivity $> 18 M\Omega$) obtained from a Milli-Q (Millipore) water purification system.

2.2. Sonochemical, electrochemical and sonoelectrochemical setups

Sonochemical (SCh) studies were performed using a Misonix Sonicator model XL-2020 S Programmable Ultrasonic Liquid Processor[®] equipped with an 11 mm titanium-alloy probe. The Sonicator was operated at 20 kHz and the ultrasonic power was set to 30% corresponding to an intensity of $523 W cm^{-2}$. The SCh-induced degradation of thiram ($100 mg L^{-1}$) was performed in aqueous solution containing MeOH (30% v/v), with or without K_2SO_4 ($0.05 mol L^{-1}$), and was monitored over a 120 min period.

Electrochemical (ECh) studies were performed using a one-compartment Pyrex cell (400 mL) maintained at $25 \pm 1 ^\circ C$ and operated in the batch mode. The anode (geometric area $9.68 cm^2$) comprised a boron-doped diamond (BDD) thin-film deposited on a single-crystal p-type Si (100) wafer (Adamant Technologies, La-Chaux-de-Fonds, Switzerland), while a platinum net (apparent geometric area $10.24 cm^2$) formed the cathode and a saturated calomel electrode (SCE) acted as reference electrode. The BDD electrode was characterized in aqueous electrolyte containing thiram ($100 mg L^{-1}$) in K_2SO_4 ($0.05 mol L^{-1}$) and MeOH (30% v/v) by cyclic voltammetry in the potential range 0.0 to $+2.5 V$ vs. SCE at a scan rate of $50 mV s^{-1}$.

In order to monitor the degradation of thiram during the ECh process, the analyte was dissolved in aqueous electrolyte as described above and subjected to electrolysis at current densities of 10, 25, 35 or $50 mA cm^{-2}$ over a period of 120 min. All electrochemical investigations were performed using a Metrohm Autolab PGSTAT-30 potentiostat/galvanostat system and a model BSTR-10A current booster.

Sonoelectrochemical (SECh) degradations were conducted in a manner similar to those described for ECh but with the ultrasound system coupled to the electrochemical cell.

2.3. Sample collection and analysis

Aliquots (2 mL) of electrolyte solution were collected at the start of each reaction and at intervals of 20 min throughout the process. The amounts of thiram present were determined quantitatively by HPLC using a Shimadzu model LC-20AT instrument equipped with a SPD-20A UV module, a SPD-M20A diode array detector (DAD) and an Ascentis[®] (Sigma–Aldrich) C_{18} reverse phase column ($150 \times 4.6 mm$ i.d.; $3 \mu m$). Samples ($20 \mu L$) were eluted isocratically using a mobile phase comprising CH_3CN :water (45:55 v/v) supplied at a flow rate of $1.0 mL min^{-1}$ with UV detection set at 230 nm. Under these conditions, the retention time of thiram was 7.2 min.

In experiments designed to identify the byproducts of thiram degradation, aliquots (2 mL) of electrolyte solutions were collected every 30 min during “exhaustive” ECh and SCh processes performed over periods of 5 h with applied current densities of $35 mA cm^{-2}$. Samples were filtered through 0.45 mm Millipore membranes and analyzed by HPLC–MS using a Shimadzu 20A series chromatograph equipped with an Ascentis[®] (Sigma–Aldrich) C_{18} reverse phase column ($150 \times 4.6 mm$ i.d.; $3 \mu m$) coupled to a Brüker Daltonics Q-TOF micro II spectrometer. Samples ($20 \mu L$) were eluted with a mobile phase comprising a CH_3CN /water mixture containing 0.1% formic acid supplied at a flow rate of $1.0 mL min^{-1}$. Elution was isocratic with CH_3CN :water at 10:90 (v/v) for 5 min, followed by a linear gradient of CH_3CN from 10% to 100% over 50 min, and terminating in isocratic elution with CH_3CN at 100% for 3 min. MS analyses in the positive and negative ionization modes were conducted using the following conditions: capillary voltage 4500 V, helium gas flow rate $8.0 L min^{-1}$, gas drying temperature $200 ^\circ C$, nebulizer gas pressure 4 bar, and acquisition rate 2 Hz.

The mineralization of thiram was monitored by measuring chemical oxygen demand (COD) using a Hach DRB 200 reactor in conjunction with a Hach DR/890 calorimeter. Owing to the low solubility of thiram in water ($16.5 mg L^{-1}$ at $20 ^\circ C$), it was necessary to incorporate around 30% of organic solvent into the aqueous medium in order to prepare the electrolyte solution containing 100 pm of fungicide employed in the study. However, the presence of organic solvent precluded the possibility of monitoring mineralization of the fungicide through the determination of total organic carbon (TOC).

3. Results and discussion

3.1. Cyclic voltammetry

Prior to characterization by cyclic voltammetry, the BDD anode was subjected to electrochemical conditioning whereby the electrode was polarized at a constant current of $50 mA cm^{-2}$ for 30 min in aqueous K_2SO_4 ($0.05 mol L^{-1}$) in order to remove any surface impurities. With the aim of understanding the redox behavior of thiram on a BDD anode, cyclic voltammograms were recorded in the potential range 0.0 to $+2.5 V$ vs. SCE at a scan rate of $50 mV s^{-1}$ with: (1) fixed K_2SO_4 electrolyte solution ($0.05 mol L^{-1}$), (2) fixed K_2SO_4 electrolyte solution ($0.05 mol L^{-1}$) containing MeOH (30% v/v), and (3) K_2SO_4 electrolyte solution ($0.05 mol L^{-1}$) containing MeOH (30% v/v) and thiram ($100 mg L^{-1}$).

Analysis of the plots presented in Fig. 2 shows that the oxygen evolution potential in the supporting electrolyte was located at

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