

RESEARCH ARTICLE

Spectroscopic and electrochemical investigation of interactions between metal Cr(VI) and Thiram (Tetramethylthiuram disulfide)

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Abstract: Evidences for the presence of interactions between a widely used fungicide called thiram and Cr(VI) ions have been obtained by an electrochemical and spectroscopic approach. The highest absorbance (894 nm) and the peak current (Cyclic Voltammetry) have been detected when the equimolar-concentrated solutions of thiram and Cr(VI) were mixed in the ratio of 2:1. The interactions in the aforementioned mixture were further confirmed by FTIR studies.

Keywords: Fungicide, Dithiocarbamate, Cyclic voltammetry, Continuous variation method, Electrochemical.

INTRODUCTION

Thiram (tetramethylthiuram disulfide) is a thiocarbamate pesticide, which is mainly used as a fungicide to prevent crop damage in the field and to protect harvested crops from deterioration in storage or transport (Figure 1). It is also used to protect turf crops, vegetables, fruits and ornamental from a variety of fungal diseases. Thiram is an animal repellent too, so it protects fruit trees and ornamentals from damage by rabbits, rodents, and deer (Sharma *et al.*, 2003).

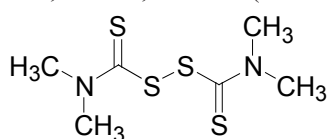


Figure 1: Structure of thiram.

Thiram usually gets into water, crops and soil when it is applied to the field. Thiram degrades more rapidly in soil high in organic matter (by microbial action) and in acidic soil (by hydrolysis) (Sharma *et al.*, 2003). The major metabolites of thiram in the soil are copper dimethyldithiocarbamate, dimethylamine and carbon disulfide (Howard, 1989). In water, thiram is rapidly broken down by hydrolysis (under acidic conditions) or photodegradation (Sharma *et al.*, 2003). In various research studies carried out around the world, thiram has been determined experimentally in a variety of plant bodies, mainly in fruits and vegetables (Malik *et al.*, 1998; Ekroth *et al.*, 1998). In the human body, carbon disulfide is formed from the breakdown of thiram

and this does contribute to the toxicity of thiram to the liver (Edwards *et al.*, 1991; Kidd and James, 1991). With the increased use of fungicides such as thiram, there is a potential for accumulation of them in soil and in aquatic environments too.

Thiram has the potential to act as a ligand and to form complexes with metals (Valle *et al.*, 2010). This ability has allowed the commercialization of a Zn enriched analogue of thiram which is known as Ziram (Borg and Tjaelve, 1988). Parham and co-workers have also determined thiram using Au nanoparticles with the aid of thiram-Au interactions (Parham *et al.*, 2015). It is known in literature that dithiocarbamates form lipophilic (water insoluble) complexes with di- and trivalent metallic cations by bonding through the sulphur atoms (Thorn and Ludwig, 1962) (Figure 2). The cleavage of S-S bond of Thiram has also been evidenced previously by surface-enhanced Raman spectroscopy (Sánchez-Cortés *et al.*, 1998) and this cleavage leads to two resonance structures (Kang *et al.*, 2002) as in Figure 2C below.

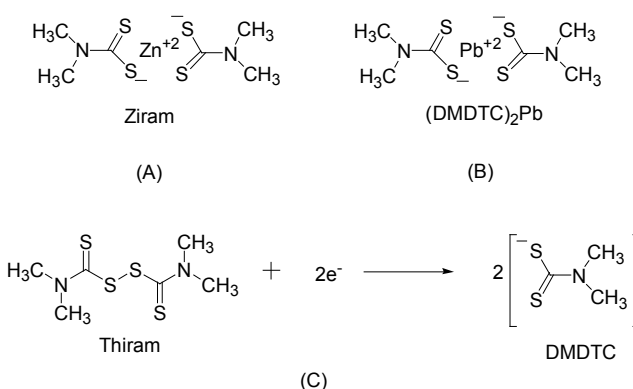



Figure 2: Schematic representation of (A) Ziram (Borg and Tjaelve, 1988); (B) The complex between Pb and Thiram (Valle *et al.*, 2010); (C) S-S bond cleavage of Thiram (Valle *et al.*, 2010; Sanchez-Cortes *et al.*, 1998; Kang *et al.*, 2002).

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Since heavy metal ions such as Pb, Cr can be present in the environment as an impurity of agro chemicals, metal complexes will be naturally formed in most soils where pesticides have been applied (Valle *et al.*, 2010). It has been known for many years that Cr(VI) is highly toxic and contributes to environmental pollution as well as plant toxicity vastly (Oliveira, 2012).

In the present study, the affinity of thiram for Cr(VI) ion has been studied by cyclic voltammetric and UV-Visible spectroscopic methods. With the help of such interactions, the degree of toxicity of both thiram and Cr(VI) towards the environment could be altered (Valle *et al.*, 2010). Such interactions could probably lead to utilize thiram (Valle *et al.*, 2010) as an entrapping agent for Cr(VI). Therefore, investigating interactions between thiram and Cr(VI) could be important as a solution to the increasing environmental pollution.

MATERIALS & METHODS

Materials

Thiram standard (98 %) was purchased from Sigma-Aldrich (Germany), so used without further purification. The solvents used to dissolve Thiram were ethanol (95 %) and deionized water. Ethanol was also distilled before using in the experiments. NaCl (Analytical grade, BDH) was used as the electrolyte in cyclic voltammetric experiments. K_2CrO_4 (Analytical grade, BDH) was used as the source of Cr(VI). KBr (IR grade, Sigma-Aldrich) was used as the material for pellet making in the Fourier-Transform Infrared (FTIR) spectroscopic experiments.

Apparatus

Cyclic voltammetric experiments were carried out with BAS (Bioanalytical System- USA) CV-1B cyclic voltammograph and recorded on BAS X-Y recorder. A Glassy carbon working electrode, saturated calomel reference electrode (SCE) and platinum wire counter electrode were used in the three-electrode system. All the cyclic voltammetric experiments were conducted with respect to SCE under N_2 saturated conditions. UV-Visible spectra were recorded on a Shimadzu 160 UV-Visible spectrophotometer. A 10 mm Quartz cell was used to measure both standard and unknown samples. FTIR spectra were recorded on a Shimadzu-IR Prestige-21 Fourier-transform infrared spectrometer.

Continuous Variation Method

Continuous variation method using UV-Visible spectroscopy was carried out to find out the stoichiometric

ratio between Cr(VI) and thiram. For that, a solution of thiram having a concentration of 10^{-4} mol L^{-1} (using thiram (98%) and Ethanol: H_2O (3:2) as the solvent system) and a solution of K_2CrO_4 having a concentration of 10^{-4} mol L^{-1} (using K_2CrO_4 and deionized H_2O) were prepared. UV absorbance for all the prepared compositions was recorded at a constant wavelength (λ_{max}) of 390 nm (Table 1).

Cyclic Voltammetric Experiments

Cyclic voltammograms were measured varying the volume ratio of thiram (10^{-4} mol dm^{-3}) and K_2CrO_4 (10^{-4} mol dm^{-3}) under N_2 saturated conditions. Thiram solution with the aforementioned concentration was prepared using thiram (98%) and ethanol: NaCl (3:2) solvent mixture. K_2CrO_4 solution having a concentration of 10^{-4} mol L^{-1} was prepared using K_2CrO_4 and NaCl solution. For all these preparations, a solution of 0.1 mol L^{-1} NaCl was used.

Fourier Transform Infrared (FTIR) Experiments

A 2:1 mixture of thiram: K_2CrO_4 was prepared using 10^{-4} mol L^{-1} thiram (using thiram (98%) and ethanol: H_2O (3:2) as the solvent system) and 10^{-4} mol L^{-1} K_2CrO_4 solutions. KBr of the respective grade (IR grade, Sigma-Aldrich) was used to prepare pellets for these experiments. A drop of the 2:1 mixture of thiram: K_2CrO_4 was added to the KBr pellet and then, the FTIR spectrum of the respective mixture was recorded. FTIR spectrum for 95% ethanol was also recorded in a similar manner. Another KBr pellet was made using thiram (98%) sample in order to obtain the FTIR spectrum for solid thiram.

RESULTS

Continuous variation method was carried out using UV-Visible spectroscopy. The measured absorbance values (at $\lambda_{max} = 390$ nm) for each volume composition prepared using thiram (10^{-4} mol L^{-1}) and K_2CrO_4 (10^{-4} mol L^{-1}) solutions are tabulated below (Table 1).

There, the highest absorbance has been observed when the molar ratio of thiram: Cr(VI) was 2:1 (Figure 3 below).

Furthermore, UV-Visible spectra of thiram (10^{-4} mol L^{-1}), K_2CrO_4 (10^{-4} mol L^{-1}) and the 2:1 mixture of thiram: Cr(VI) have been recorded and shown in Figure 4 below. There, appearance of a new peak was noted at 400 nm (in the dotted curve relevant to 2:1 mixture- Figure 4).

The recorded cyclic voltammograms of thiram (10^{-4} mol L^{-1}), K_2CrO_4 (10^{-4} mol L^{-1}), the solvent system (ethanol: NaCl= 3:2) and thiram: K_2CrO_4 (2:1) mixture are shown in Figure 5 below.

Table 1: Absorbance measurements of various volume compositions of thiram and K_2CrO_4 solutions.

Volume of thiram (mL)	Volume of K_2CrO_4 (mL)	Absorbance
1.00	5.00	0.539
2.00	4.00	0.681
3.00	3.00	0.752
4.00	2.00	0.894
5.00	1.00	0.858

Concentration of Thiram solution and K_2CrO_4 solution = 10^{-4} mol L^{-1} ; $\lambda_{max} = 390$ nm

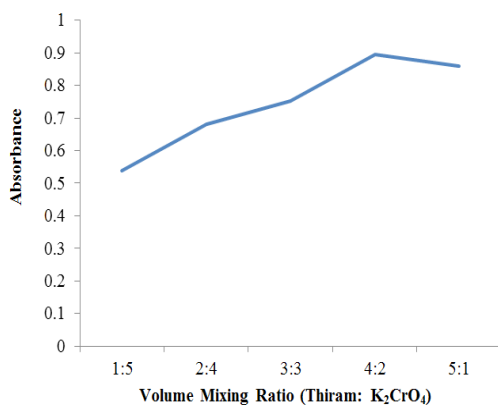


Figure 3: Continuous variation plot of absorbance vs volume mixing ratio of thiram: K₂CrO₄ (Concentration of thiram and K₂CrO₄ solutions = 10⁻⁴ mol L⁻¹).

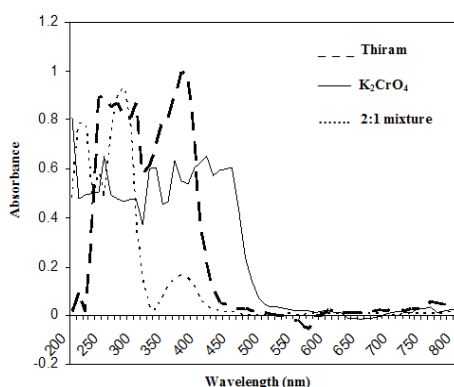


Figure 4: UV-Visible spectra of 10⁻⁴ mol L⁻¹ thiram (dashed line), 10⁻⁴ mol L⁻¹ K₂CrO₄ (continuous line) and 2:1 mixture of thiram: K₂CrO₄ (dotted line).

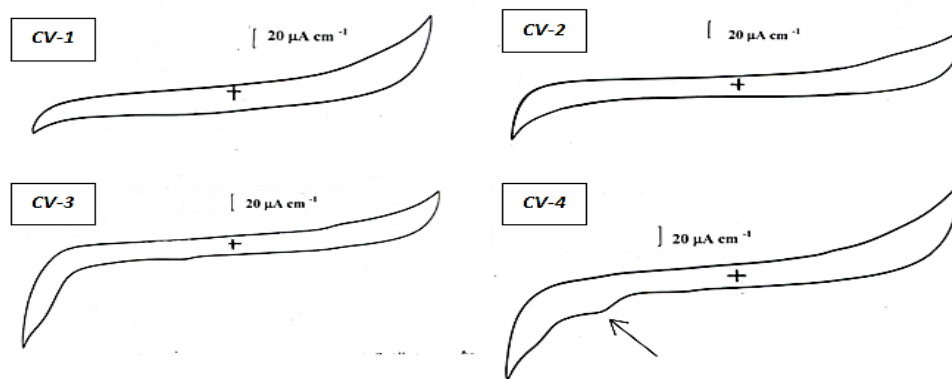


Figure 5: Cyclic Voltammograms obtained for 10⁻⁴ mol L⁻¹ of K₂CrO₄ (CV-1), Ethanol: NaCl=3:2 system (CV-2), 10⁻⁴ mol L⁻¹ of thiram solution (CV-3) and thiram: K₂CrO₄ = 2:1 mixture (CV-4); [X scale = 0.1 V cm⁻¹; Y scale = 20 μA cm⁻¹; Potential range = 1.000V to -1.000V; Scan rate = 100; Position of the new peak (indicated by the arrow) in CV-4 = 0.58 V; Height of the new peak in CV-4 = 30 μA].

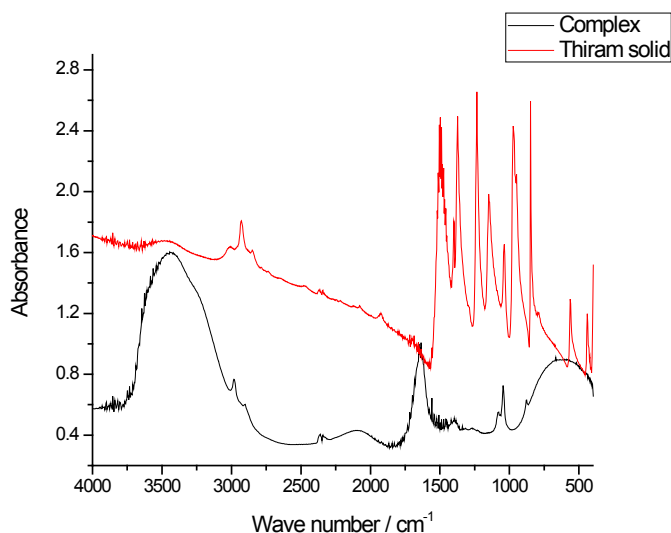


Figure 6: FT-IR spectra obtained for solid thiram (red line) and the 2:1 mixture of thiram: K_2CrO_4 (black line).

Subsequent FTIR measurements of solid thiram and the 2:1 mixture of thiram: K_2CrO_4 have also been recorded and shown in Figure 6 (above). The FTIR spectrum of the 2:1 mixture of thiram: K_2CrO_4 (black line) shows remarkable changes in the fingerprint region ($1500 - 500\text{ cm}^{-1}$) from that of the solid thiram (red line).

DISCUSSION

This study was mainly conducted in a nearly neutral environment as Cr(VI) could easily be reduced to Cr(III) in the soil due to the presence of Fe (II) ions, and then be precipitated under basic conditions. In acidic medium, S atoms of thiram could be protonated, so that it could affect the bonding of thiram to the metal cation (See Figure 2). Therefore, the study was mainly conducted in nearly neutral medium.

Since our main objective was to investigate the interactions between thiram and Cr(VI), it was initially decided to find out the stoichiometric ratio between thiram and Cr(VI). Therefore, continuous variation method was carried out as given in Table 1 using UV-Visible spectroscopy (Rana *et al.*, 2014). The highest absorbance was recorded (at $\lambda_{max} = 390\text{ nm}$) when the molar ratio of thiram: Cr(VI) was 2:1 (Figure 3). This confirms the stoichiometry of the reaction between thiram and Cr(VI). Furthermore, distinct differences had been observed when UV-Visible spectra of thiram, K_2CrO_4 and the 2:1 mixture of thiram: Cr(VI) were compared (Figure 4). The new peak observed at 400 nm (in the dotted curve relevant to 2:1 mixture- Figure 4) clearly indicated an interaction between thiram and Cr(VI).

The appearance of the aforementioned peak in the UV-Visible spectrum prompted us to analyze the thiram: K_2CrO_4 (2:1) mixture electrochemically. According to the subsequent cyclic voltammetric experiments carried out with thiram ($10^{-4}\text{ mol L}^{-1}$), K_2CrO_4 ($10^{-4}\text{ mol L}^{-1}$), solvent system (Ethanol: NaCl= 3:2) and thiram: K_2CrO_4 (2:1) mixture, it was possible to observe a new peak (as indicated by the arrow in *CV-4* of Figure 5) in the voltammogram

of thiram: K_2CrO_4 (2:1) mixture. This was followed by the analysis of a series of thiram: K_2CrO_4 mixtures (1:5, 2:4, 3:3, 4:2, 5:1) electrochemically. Among the five voltammograms obtained, the highest peak current was observed in the ratio of thiram: Cr(VI) is 4:2. This observation can be explained by the concept put forwarded by Rana *et al.* (Rana *et al.*, 2014). As the number of moles of the reactants (i.e. metal and the ligand) increases, the extent of reaction increases, so that more electrons are transferred subsequently resulting in increased peak current. These electrochemical findings also confirmed the (highest) interactions between thiram and Cr(VI) in the composition of 2:1 respectively.

Further attempts to confirm the interactions between thiram and Cr(VI) in the mixture of 2:1 using FTIR spectroscopy were also successful. Initially, FTIR spectrum of thiram was measured when thiram was in solution state. However, the presence of ethanol and H_2O in the thiram solution severely affected the detection of peaks in the FTIR spectrum. Hence, FTIR spectrum was measured using a solid thiram sample (Figure 6).

When the FTIR spectra (Figure 6) of solid thiram and the 2:1 mixture of thiram: Cr(VI) were compared, distinct differences in the fingerprint region ($1500 - 500\text{ cm}^{-1}$) of the 2:1 mixture have been noted from that of solid thiram. The broad peak that appears beyond 3000 cm^{-1} and the peak that appears between $1000 - 1250\text{ cm}^{-1}$ in the FTIR spectrum of the 2:1 mixture were mainly due to the peaks of ethanol, as it is a component in the solvent system. This was concluded by comparing the FTIR spectrum of ethanol with that of the 2:1 mixture. It is also possible that some of the peaks appeared in the region of $2750-3750\text{ cm}^{-1}$ (e.g.: C-H stretching) have been masked by the broad peak that covers the same region (Figure 6, Black line).

Another broad peak can be observed in the region of 1600 cm^{-1} to 1700 cm^{-1} in the FTIR spectrum of Figure 6 (Black line). There is also a broad peak between 1500 cm^{-1} and 1400 cm^{-1} in the FTIR spectrum of solid thiram (Figure 6, Red line) that appeared probably due to C-N stretching

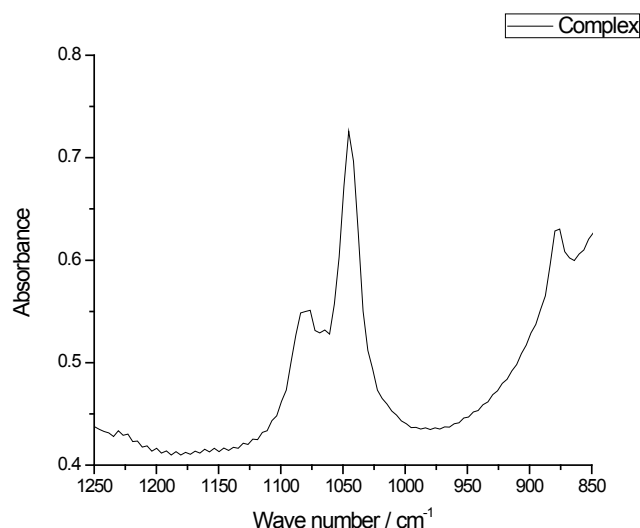


Figure 7: An enlarged region of the FTIR spectrum of the 2:1 mixture of thiram and K_2CrO_4 .

(Kang *et al.*, 2002). It is probable that the peak in the range of 1400-1500 cm^{-1} has been shifted to the range of 1600-1700 cm^{-1} due to the bonding of two S atoms of thiram to metal Cr(VI). It has been reported in literature that the C-N stretching mode (ν_{C-N}) is enhanced, if bonding to the metal substrate is through the S atom (Kang *et al.*, 2002). This speculation has also been governed by the literature known fact that the reduction of the intensity and the largest frequency shift of peaks indicative of the two S atoms of thiram bonded to the metal surfaces (Kang *et al.*, 2002).

According to the criterion of Bonati-Ugo (BU), the presence of a solitary band, without splitting, in the region of 950-970 cm^{-1} indicates a bidentate nature of the chelation of the dithiocarbamate ligands (Kellner *et al.*, 1984). The aforesaid region is, however slightly affected by the presence of H_2O in the 2:1 mixture of thiram and K_2CrO_4 . The feature described by Kellner *et al.* can be depicted in the FTIR spectrum of Figure 7 and also indicates the formation of a complex in the 2:1 mixture of thiram and K_2CrO_4 .

CONCLUSIONS

This study provides cyclic voltammetric, UV-Visible and FTIR spectroscopic evidences to support coordination between thiram and Cr(VI) with the molar ratio of 2:1.

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