

Interaction of Thiram with Glassy Carbon Electrode Surfaces under Applied Potentials Conditions

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Degradation of thiram is greatly facilitated by potential application, where the major oxidation appears at +0.75 V at glassy carbon electrodes in the aqueous KCl medium. Effects of repetitive scans, the magnitude of the scan rate and the bulk concentration on the peak current of the major oxidation reaction of thiram suggest that both adsorption and diffusion be responsible for the electrochemical process. Investigation of the reactivity of simple model compounds, such as amines, carbon disulfide and thiourea, as compared to that of thiram, indicates that the main oxidation is associated with the thioamide functionality.

Keywords: Thiram, Adsorption, Pesticides, Glassy carbon electrodes, Cyclic voltammetry

1. INTRODUCTION

Pesticides degrade in the environment due to physical, chemical or biological factors, giving rise to several residues, which may include the parent compound that forms the pesticide [1-4]. Some degradation products are reported to be even more hazardous than the pesticide that is degraded [5]. Hence, the investigation of the fate of pesticides, and pesticide residue analysis are important steps in monitoring pesticide pollution in the environment.

Detection of thiram and similar sulfur containing compounds has been advanced significantly in the recent past because of their usage in agriculture and industry [6-8]. However, the determination of the fate of a pesticide in the environment is a complex issue, because the fate depends on many factors such as kinetics of the degradation process, mechanism of each degradation step, stability of degraded products and adsorption equilibrium of the pesticide and/or its residues with different types of species found in the environment, such as solid particles present in channels where pesticides travel through [9, 10]. Such studies are cumbersome owing to the necessity of employing a multi-technique approach. Another issue is that the validity of the prediction of the fate of a pesticide, determined

based on simulation studies usually conducted in the laboratory scale within a considerable short time period, is often questionable.

It can be argued that accurately characterized oxidation/reduction processes of a pesticide under plausible extreme conditions (*i.e.*, potential application, extreme *pH*, high temperature, etc.) can be extrapolated within a reasonable accuracy to less aggressive, realistic conditions (*i.e.*, real environment) provided with a suitable model. Accuracy of this extrapolation process should meet the challenge of assuring public of environmental safety. Development of models for prediction of degradation patterns of pesticides under environmental conditions has not yet reached a satisfactory level. Nevertheless, model studies to investigate transport of some pesticides in soil and clay minerals, and sorption and degradation patterns in aquifers have been reported in recent years [11-14].

The study reported here is on electrochemical investigation of the reactivity of thiram $[(\text{CH}_3)_2\text{N-CS}_2\text{-CS}_2\text{-N}(\text{CH}_3)_2]$ (Figure 1), an organo-sulfur fungicide, at glassy carbon electrode surfaces, under aggressive conditions, in particular, different *pHs* and applied potentials. Special attention was given to investigate adsorption characteristics of thiram at glassy carbon surfaces. The detection aspects of this pesticide at glassy carbon electrodes have already been reported elsewhere [7]. Electrochemical activity of simple parent compounds and model compounds of thiram such as aliphatic amines, thiourea and carbondisulfide was also investigated in support of the interpretation of electrochemical responses of thiram.

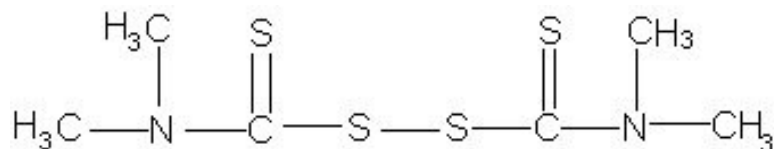


Figure 1. Structure of thiram.

2. EXPERIMENTAL PART

2.1. Instrumentation

All electrochemical experiments were carried out using a Bioanalytical Systems (BAS) CV-1B Cyclic Voltammograph and recorded on a BAS X-Y recorder. The three-electrode cell consisted of a glassy carbon (GC) or platinum working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). All potentials were reported with respect to SCE, and all experiments were conducted under N_2 saturated conditions. The volume of solution of the electrochemical cell was 25.0 cm^3 .

2.2. Materials

A commercial sample of Pormasol Fortae (80% w/w thiram) was gifted by Heychem (Cey.) Ltd, Sri Lanka, which was used throughout all experiments without further purification. The model

compounds: CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, $(\text{NH}_2)_2\text{CS}$ and CS_2 were of analytical grade. The electrolytes, KCl and NaCl, were purchased from BDH (UK). Each solution was freshly prepared in distilled, deionized water. Standard solutions were prepared daily.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltammetric Behavior of Thiram

Thiram is electroactive in aqueous medium at bare GC electrodes, giving rise to many oxidation and reduction processes (Figure 2). However, the electrochemistry of thiram at platinum surfaces is quite different from what is observed at GC surfaces, according to cyclic voltammetric studies conducted in aqueous medium under various experimental conditions. The characteristic features of platinum surfaces are significantly altered when small amounts of thiram are added. For instance, H-adsorption and H-desorption peaks are disappeared, and the formation of platinum oxide and subsequent reduction processes are greatly reduced. Further, many electrochemical features of thiram observed at GC electrodes are not apparent at Pt except that the appearance of the major oxidation peak at +0.92 V in 0.1 mol dm^{-3} KCl as compared to +0.75 V at bare GC electrodes under similar conditions. Previous reports on the oxidation of thiram at graphite-teflon composite electrodes and gold microelectrodes at similar potentials also support the suggestion that the oxidation peak (O_1) is associated with thiram [15, 16].

3.2. Adsorption Characteristics of Thiram at GC Surfaces

Repeated application of cyclic potential scans on thiram at GC electrodes under different experimental conditions leads to many important observations: The peaks, O_2 and R_2 , do not appear in the first scan, and appear only after a few scans; The main oxidation peak (O_1) is shifted towards more positive potential values, together with decrease in the peak current; When the voltammetric experiment was repeated after re-polishing the GC electrode, the main oxidation peak arose during the first scan at the same potential of + 0.75 V with the full peak height, while the O_2/R_2 couple reappeared only after a few scans. Furthermore, the plot of logarithmic current of peak O_1 vs. logarithmic scan rate results in a slope of 0.64 (Figure 3).

All the observations reported above and in the previous section support involvement of poisoning adsorption of thiram on the GC surface, and the peak at +0.75 V is in fact due to the oxidation of thiram molecules. Both diffusion and adsorption are responsible for this process according to the magnitude of the slope in Figure 3. Adsorption phenomena are very common with many organic molecules, in particular, polar organic molecules, on GC surfaces (17-19). In the case of thiram, repeated potential application would probably promote the build-up of adsorbed layers of thiram and its oxidation products, which would poison the electrode. Adsorption of thiram on mercury and gold surfaces has already been reported to support this observation [16, 20]. Consequently, the peak R_2 is probably due to the reduction of the adsorbed oxidation product.

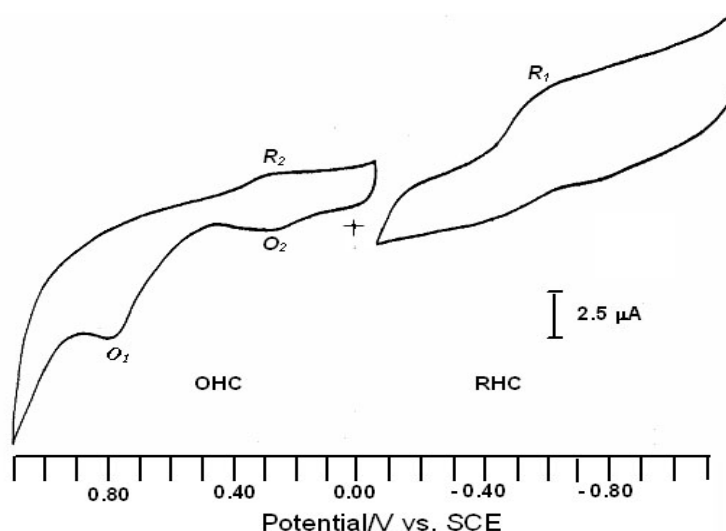


Figure 2. Cyclic voltammogram (10th scan) of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ thiram as two separate cycles at a potential scan rate of 50 mV s^{-1} in 0.1 mol dm^{-3} KCl under N_2 saturated; OHC= Oxidation half cycle, RHC= Reduction half cycle.

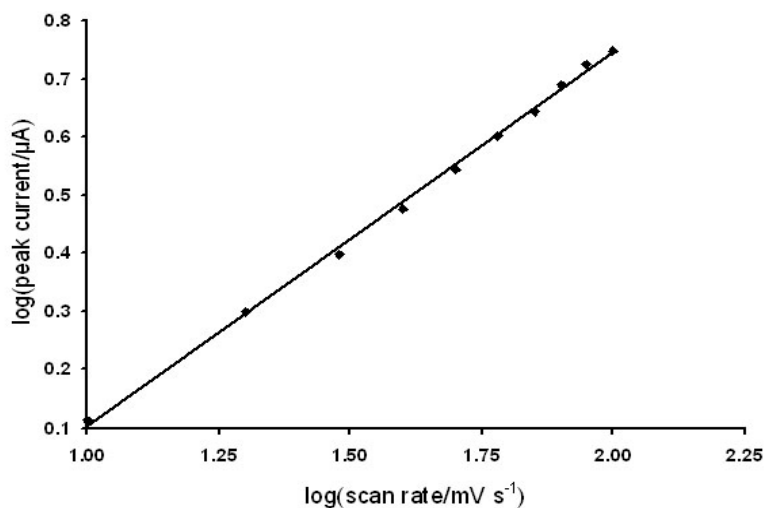


Figure 3. Plot of log (peak current) vs. log (scan rate) for peak O_1 , in 0.1 mol dm^{-3} KCl under N_2 saturated.

Adsorption characteristics of thiram at the GC surface can be further investigated by analyzing current - concentration relationships although it is not easy to rationalize adsorption effects. For this task, it is assumed that the deviation of the experimentally obtained current - concentration curve for Peak O_1 from the expected diffusion-control behavior¹ is mainly due to adsorption. It is also assumed

¹The theoretical diffusion limited current - concentration linear relationship

$$i = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C^*$$

where i is the peak current in A, n is the number of electrons involved in the reaction, A is the surface area of the electrode in cm^2 , D is the diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$, v is the potential scan rate in V s^{-1} and C^* is the bulk concentration in mol cm^{-3} [21].

that thiram is the principal adsorbed product, and that thiram does not undergo electroinactive degradation (*e.g.*, hydrolysis) to a significant extent within voltammetric time window. This assumption is supported by absorption spectroscopy, where the absorbance of a thiram solution in 0.1 mol dm^{-3} KCl at its characteristic wavelength does not change with time for a period of several hours. The experimental peak current (i) - bulk concentration (C) relationship (Figure 4) should thus be analyzed to investigate adsorption effects. This curve can be mathematically approximated to the following second order fit.

$$i = -1.294 + 4.134 C - 0.503 C^2 \quad (\text{Regression coefficient, } R^2 = 0.998) \quad (1)$$

where i is in μA and C is on the $10^{-5} \text{ mol dm}^{-3}$ scale. The slope of the curve is given by the derivative of Equation (1), as shown in Equation (2).

$$di/dC = 4.134 - 1.006 C \quad (2)$$

The slope of the tangent drawn at the lowest concentration of $9.10 \times 10^{-6} \text{ mol dm}^{-3}$ is calculated to be 3.219 according to Equation (2). As diffusion is the predominant mode of mass transfer at low concentrations, this tangent could be used to represent the diffusion-controlled behavior. The current-concentration relationship for the tangent can be obtained using the peak current of $2.00 \mu\text{A}$ for the concentration of $9.10 \times 10^{-6} \text{ mol dm}^{-3}$ [Equation (3)].

$$i = -0.929 + 3.219 C \quad (3)$$

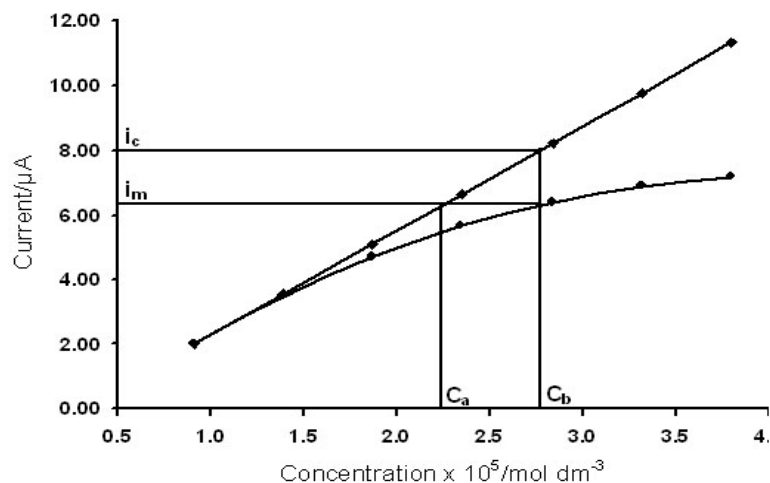


Figure 4. Experimental current-bulk concentration relationship for the main oxidation reaction of thiram (\bullet), and the corresponding simulated diffusion-controlled characteristics (\blacklozenge).

This situation is clearly illustrated in Figure 4, where i_c is the current calculated for the bulk concentration, C_b , in the absence of any adsorption effects. The measured current, i_m , is always less than i_c . The value, C_a , is the concentration of thiram corresponding to the measured current, i_m , if there

is no adsorption. Hence, the deviation of current due to adsorption for the bulk concentration, C_b , is given by $(i_c - i_m)$. This is a measure of the amount of thiram adsorbed according to the assumption stated earlier. This current difference is directly proportional to the corresponding concentration difference, $(C_b - C_a)$. Table 1 summarizes the data necessary for adsorption analysis, assuming that thiram is adsorbed at the GC surface in its molecular form. The amount of thiram adsorbed per unit area of the surface (θ) at the bulk concentration of C_b is determined using Equation (4).

$$\theta = (C_b - C_a) VM/A \quad (4)$$

where V is the volume of the electrolyte solution in the cell in dm^3 (0.0250 dm^3), M is the molecular weight of thiram in g mol^{-1} and A is the surface area of the GC electrode in m^2 ($d = 3\text{mm}$). The plot of θ vs. bulk concentration, C_b , (Figure 5) shows that the amount of thiram adsorbed under applied potentials conditions is steadily increasing with the amount of thiram in solution within the concentration range of $9.10 \times 10^{-6} \text{ mol dm}^{-3}$ and $3.80 \times 10^{-5} \text{ mol dm}^{-3}$. Further, it is noteworthy to state that adsorption of thiram may be accompanied with small amounts of degraded products formed during hydrolysis although this process is not significant in neutral media [22].

Table 1. Determination of the amount of thiram adsorbed at different bulk concentrations.

| $C_b \times 10^5, \text{ mol dm}^{-3}$ | $i_m, \mu\text{A}$ | $i_c, \mu\text{A}$ | $(i_c - i_m), \mu\text{A}$ | $(C_b - C_a) \times 10^5, \text{ mol dm}^{-3}$ | Amount adsorbed, g m^{-2} |
|--|--------------------|--------------------|----------------------------|--|------------------------------------|
| 0.910 | 2.000 | 2.000 | 0.000 | 0.00000 | 0.000 |
| 1.390 | 3.482 | 3.545 | 0.063 | 0.0196 | 0.167 |
| 1.870 | 4.680 | 5.091 | 0.411 | 0.128 | 1.09 |
| 2.350 | 5.646 | 6.636 | 0.990 | 0.308 | 2.62 |
| 2.840 | 6.393 | 8.213 | 1.820 | 0.565 | 4.80 |
| 3.320 | 6.891 | 9.758 | 2.867 | 0.891 | 7.57 |
| 3.800 | 7.158 | 11.303 | 4.145 | 1.288 | 11.0 |

Note: $(C_b - C_a) \times 10^5 / (i_c - i_m) = \text{slope} = 3.219$; $VM/A = 8.50 \text{ g mol}^{-1} \text{ dm}^3 \text{ m}^{-2}$

Electrochemical reactions coupled with a poisoning adsorption step are often slow and deviated from reversibility, and consequently, peak potentials of such reactions highly depend on the potential scan rate. This nature was observed for thiram electrochemistry as shown in Figure 6.

3.3. Electrochemical Behavior of Model Substances

In addition to adsorption studies, electrochemical behavior of simpler model compounds, containing individual functionalities of thiram, such as CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, $\text{CS}(\text{NH}_2)_2$ and

CS_2 , was investigated in an attempt to obtain a better understanding of the electrochemistry of thiram. Oxidation and reduction potentials of these substances, recorded in the same electrolyte medium, are given in Table 2. All the three aliphatic amines and thiourea show oxidation potentials similar to that of the major oxidation peak (O_1) of thiram. However, carbon disulfide is electroinactive within the conditions employed.

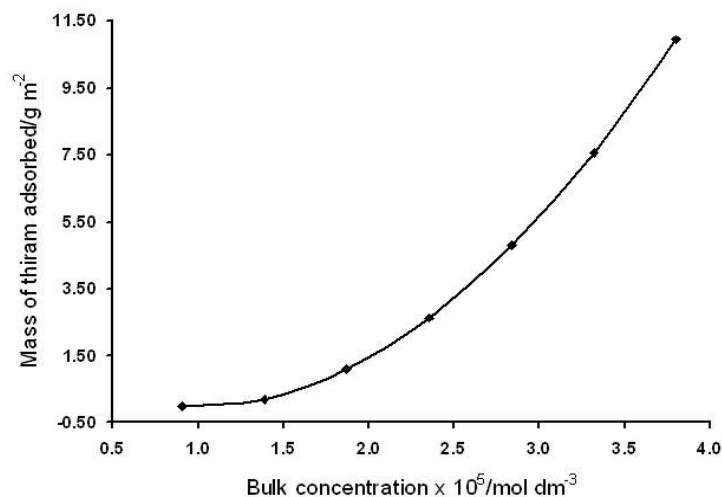


Figure 5. Variation of the amount of thiram adsorbed with bulk concentration of thiram.

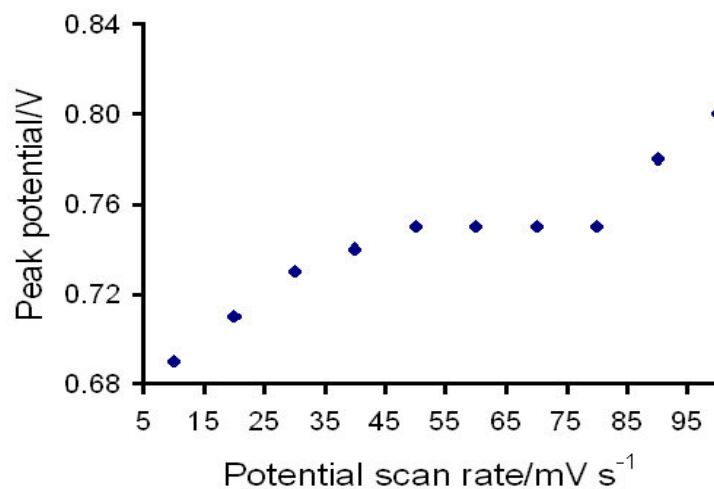


Figure 6. Dependence of the potential of peak O_1 of thiram on the potential scan rate, observed in $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ solution of thiram in 0.1 mol dm^{-3} KCl under N_2 saturated.

Further, the oxidation of amines is observed to be irreversible even after a large number of scans in contrast to the electrochemical features of thiram. Therefore, the amine functionality does not fully explain the electroactivity of thiram. However, electrochemical activity of dimethylamine and

thiram was further investigated at $pH = 1$ and $pH = 10$ as thiram has the secondary amine functionality. At $pH = 1$, the oxidation peak of dimethylamine, that was observed in 0.1 mol dm^{-3} KCl, completely disappears. In the case of thiram, both O_1 and R_1 become less intense although they do not disappear. In contrast, at $pH = 10$, both thiram and dimethylamine show enhanced peak currents. Figure 7 shows the voltammetric behavior of dimethyl amine at $pH = 10$.

Table 2. Oxidation and reduction potentials of model compounds, recorded in 0.1 mol dm^{-3} KCl at a potential scan rate of 50 mV s^{-1} under N_2 saturated.

| Compound | Oxidation potential/V | Reduction potential/V |
|------------------|-----------------------|-----------------------|
| Methylamine | + 0.87 | Not observed |
| Dimethylamine | + 0.76 | Not observed |
| Trimethylamine | + 0.82 | Not observed |
| Thiram | + 0.75 | - 0.47 |
| Thiourea | + 0.72 | - 0.17 |
| Carbon disulfide | Not observed | Not observed |

The significant decrease of the electro-oxidation ability of amines and thiram in acidic medium can be explained by considering their protonation reactions. The protonated form is electron deficient over the neutral form, decreasing their ability towards oxidation.

Electroactivity of thiourea was also further investigated at $pH = 1$ and 10 (Figure 8). Thiourea gives rise to a redox couple where oxidation and reduction appear at $+0.45 \text{ V}$ (O) and at -0.30 V (R), respectively at $pH = 10$ (Table 3). However, the peaks were broadened with a wider separation at $pH = 1$, having the two peaks at $+0.65 \text{ V}$ (O) and -0.55 V (R). The peaks, O_1 and R_1 , of thiram also exhibit a similar behavior. Further, at $pH = 1$, the reduction peaks of both thiram and thiourea (R_1 and R) become less intense, as protons disfavor the reduction as in amines.

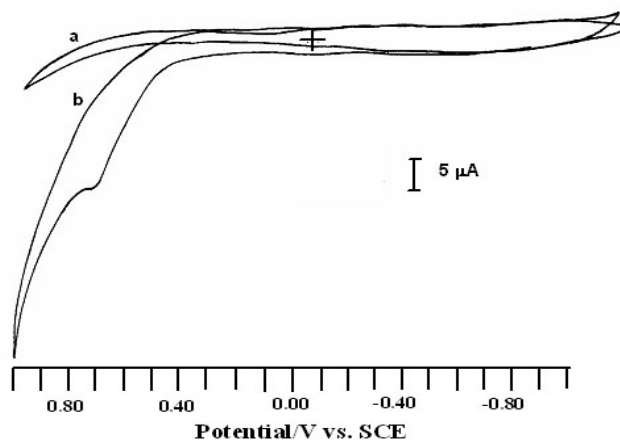
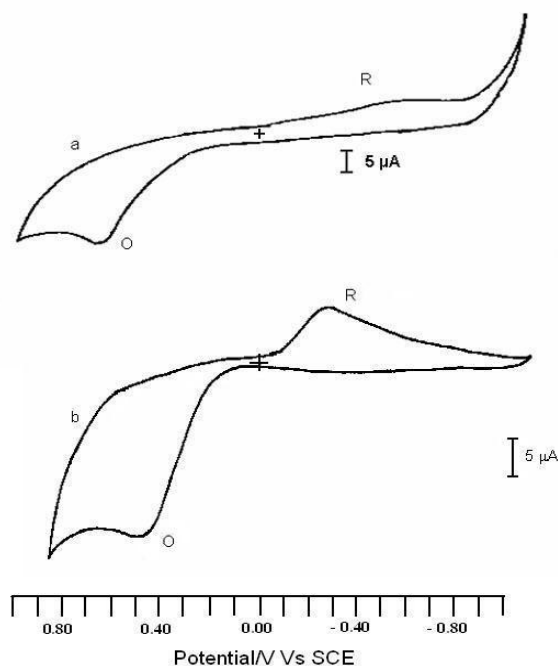


Figure 7. Cyclic voltammogram of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ N, N-dimethylamine in $pH = 10$ buffer at a potential scan rate of 50 mV s^{-1} under N_2 saturated, (a) electrolyte response (b) analyte response.

Table 3. Comparative electroactivity of thiram, dimethylamine and thiourea at pH = 1 and 10 electrolytes, under N₂ saturated conditions.

| Compound | Oxidation (O)/Reduction (R) Potential/V at pH = 1 | Oxidation(O)/Reduction (R) at Potential/V at pH = 10 |
|---------------|---|--|
| Thiram | + 0.71 (O), -0.58 (R) | +0.50 (O), -0.40 (R) |
| Dimethylamine | Not observed | +0.75 (O) |
| Thiourea | + 0.65 (O), -0.55 (R) | +0.45 (O), -0.30 (R) |

**Figure 8.** Cyclic voltammogram of 1.0×10^{-3} mol dm⁻³ thiourea in (a) pH = 1 (b) pH = 10 buffer at a potential scan rate of 50 mV s⁻¹ under N₂ saturated.

These electrochemical studies suggest that thiourea and thiram exhibit very close electrochemical relation, whose electroactivity considerably depends on solution pH. It is therefore logical to consider that the thioamide functionality of thiram is responsible for its electroactivity at +0.75 V in 0.1 mol dm⁻³ KCl. As in the electrochemical degradation of thiram, many products are reported to form during electroinactive degradation of thiram under different environmental conditions [22]. Electroactivity of the functionalities of degraded products can be used to detect the residues of this fungicide in the environment. In one reported residue analysis method, thiram is hydrolyzed to dimethylamine, which is determined by titration with standard HCl solution [5]. This less sensitive classical titration method may be replaced by cyclic voltammetric analysis as dimethylamine is electroactive.

4. CONCLUSIONS

Cyclic voltammetric investigation of thiram under laboratory conditions indicates that it is electroactive and that the transfer of thiram molecules from the bulk solution to the electrode surface is controlled by both diffusion and adsorption. The adsorptive behavior of thiram in the presence of aggressive conditions such as applied potentials within the laboratory time scale can be extended to less aggressive real environmental conditions so that the fate of thiram in the environment can be predicted. Furthermore, information from such studies would be useful in designing detoxification procedures of pesticides containing similar structural features. More experimental investigation is however necessary for accurate extrapolation of the experimental data to real situation.

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