Electrooxidation of carbo/thiocarbohydrazide and their hydrazone derivatives at a glassy carbon electrode

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Abstract. Electrochemical oxidation of thio/carbohydrazide and their hydrazone derivatives Benzaldehyde thiocarbohydrazone [BTCH] diacetylene thiocarbohydrazone [DATCH] have been studied in Britton Robinson buffer in aqueous and nonaqueous media at a glassy carbon electrode. The effects of pH, sweep rate, concentration, temperature and surfactants have been studied. The complex *bis* (carbo/thiocabohydrazide) Zn(II) chloride was also subjected to voltammetric analysis in order to understand the reactivity both in free and metal bound states. The reaction conditions were optimized for the determination of above compounds in micrograms quantities by differential pulse voltammetry, analytical utility of this investigation is also highlighted.

Keywords. Voltammetry; carbo/thiocarbohydrazide; glassy carbon electrode; electrooxidation.

1. Introduction

Thiocarbohydrazide[TCH] and Carbohydrazide [CH] are important analytical reagents of tremendous utility. For example, TCH posses anticarcinogenic and antibacterial properties.[1] It exhibits toxicity towards house-fly comparable to that of DDT.[2] The fungicidal properties[3] of thiocarbohydrazide have also been tested against different species. Thiocarbohydrazide is also used as an additive to prevent the excessive loss of cellulose during the alkaline work-up of wood pulp.[4]

Carbohydrazide acts as a denaturing agent both for bovine serum albumin[5] and for DNA.[6] The effect is attributed to stabilisation of the denatured DNA relative to native DNA by decrease in the ion solvation power and an increase in the hydrophobic character of the solvent. Carbohydrazide in the form of its cobalt complex produces hypertension without toxicity along with a simultaneous acute pyridoxine deficiency in dogs.[7] It also acts as a curing agent for epoxide-type resins.[8] Finally polymeric carbohydrazide prepared from phenylcarbamic acid esters are used as pharmaceuticals.[9]

The potentiometric and kinetic studies of these compounds were carried out a decade ago.[10–12] As a part of our continuing effort to understand the mechanism of electroreduction/oxidation of these molecules[13–17] we report here some recent results of electrochemical oxidation of TCH and CH and their hydrazone derivatives in aqueous solvents like DMF and DMSO at different pH on a glassy carbon electrode.

2. Experimental

2.1 *Reagents and chemicals*

All the above mentioned compounds were prepared in the laboratory in pure form by using standard procedures.[18,19] Purities were checked by TLC, MP and spectral studies.

Thicocarbohydrazide was prepared by adding CS_2 to a warm solution of hydrazine hydrate and water refluxing for 1 h.[18]

Monothiocarbohydrazone derivative such as BTCH, Cl-BTCH, CH_3-BTCH were prepared by refluxing equimolar mixture of respective aldehyde and TCH with ethanol as solvent Diacetylidene thiocarbohydrazone was prepared by[18] adding 50% excess of acetaldehyde in ethanol to a solution of thiocarbohydrazide in 1 mol/dm^3 acetic acid (2 : 1) and refluxing the resulting mixture for 1 h.

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The complex *bis*(thiocarbohydrazide) zinc(II) chloride was prepared[18] by mixing a warm solution of zinc chloride in dimethyl formamide water (5 : 1 v/v) and thiocarbohydrazide in dimethyl formamide, in an approximately 1 : 2 mole ratio.

Carbohydrazide was prepared by mixing diethyl carbonate and 85% hydrazine hydrate in 1 : 2·2 molar ratio[19] refluxing the reaction mixture for about 6 h.

The solvent used for the electrochemical study was water–DMSO (60 : 40) medium. All other reagents were of analytical grade. The solution was bubbled with nitrogen gas (99·99%) before electrochemical studies.

2.2 *Instrumentation*

The electrochemical experiments were carried out using a potentiostat coupled with a data acquisition PC interface card fabricated at the Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, compatible with an IBM personnel computer an linked to a printer. The electrochemical cell consisted of a glass container with a cap having holes for introducing electrodes and nitrogen. The cell was then maintained oxygen free by passing nitrogen over the solution. The reference electrode used was saturated calomel electrode (SCE). The auxillary and working electrodes were platinum foil and glassy carbon respectively, that were placed directly into the solution. Since the limiting (or peak) current in any type of voltammetry is temperature dependent, the cell was thermostated for the required temperature (295 K).

In a typical cyclic voltammetric experiment, the reaction mixture consisted of solution of substrate TCH/CH solution in DMSO, water and Britton Robinson buffer as supporting electrolyte. A stream of nitrogen was passed over them after keeping the reaction mixture in a thermostat. The three electrodes were connected to a computer controlled potentiostat and required potential scan rate, current sensitivity, initial potential and final potential were given and the resulting current was measured as a function of the applied potential.

2.3 *Pretreatment of glassy carbon electrode*

Before each measurement, the glassy carbon surface was polished with a fine emery sheet and then rinsed with purified water. The supporting electrolyte was placed in the cell and several potential sweeps were applied to obtain a low background. Effective area of GCE was 0·069 cm^2. The TCH/CH was added and the first potential sweep was registered.

3. Results and discussion

Cyclicvoltammetric oxidation of TCH (A) and CH (B) in DMSO : water medium was studied on a glassy carbon electrode surface using Britton Robinson buffer as a supporting electrolyte. The cyclic voltammogram showed a single irreversible anodic peak due to the oxidation of –NH$_2$ moiety presumably involving four electrons (figure 1).

3.1 *Effect of pH*

Effect of pH on the peak potential and peak current was studied using 2 mM TCH and CH respectively in Britton–Robinson buffer from pH 4·6 to11·25. The anodic peak potential E_{pa} decreases from 916 mV to 513 mV for TCH and from 1103 mV to 613 mV for CH respectively, suggesting that the oxidation becomes easier at higher pH for both these. More interestingly, above pH 6·5 the cyclic voltammogram showed two peaks indicating that oxidation take place in two steps involving three and one electrons. Peak width reflect this (figure 2).

3.2 *Effect of concentration*

The effect of concentration of TCH and CH were studied in DMSO-water media using a Britton-Robinson buffer as supporting electrolyte. As the concentration of TCH and CH were varied from
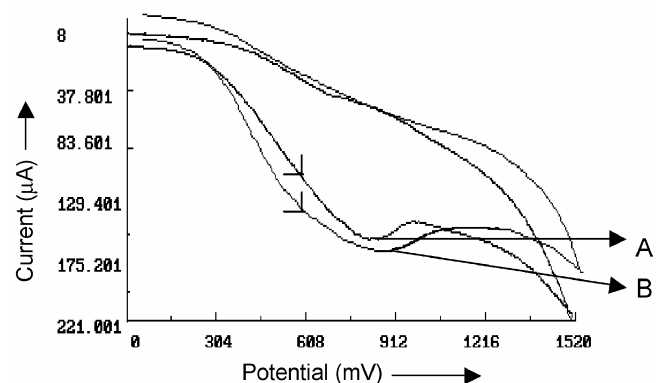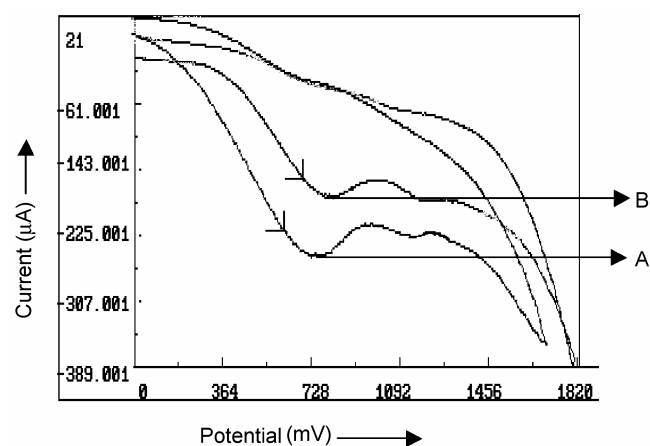

Figure 1. Cyclic voltammogram of TCH (A) and CH (B) at pH = 5·0 in Britton–Robinson buffer, scan rate = 50 mVs^{-1}, medium = DMSO : water (60 : 40) at GCE.

Table 1. Effect of concentration of TCH and CH on cyclic voltammetric parameters for the oxidation at GCE (electrode system : GCE/Pt/SCE medium = water : DMSO (60 : 40 v/v) Britton–Robinson buffer of pH = 7·50)

Conc. of TCH and CH (mM)	E_{pa} (mV)		i_{pa} (μA)		Diffusion coefficient ($D_0 \times 10^{-5}$ cm^2 s^{-1})		Standard heterogeneous rate constant ($k_0 \times 10^{-5}$ cm s^{-1})	
	TCH	CH	TCH	CH	TCH	CH	TCH	CH
0·5	498	731	51·90	34·50	27·02	20·73	1·71	1·14
1·0	506	841	88·20	62·20	23·41	20·66	1·45	1·02
1·5	603	862	121·20	78·70	21·78	19·32	1·33	0·87
2·0	690	1017	153·90	104·80	18·68	14·11	1·27	0·86
2·5	707	1042	170·70	125·20	16·44	13·85	1·29	0·74

Figure 2. Cyclic voltammogram of TCH (A) and CH (B) at pH = 6·5 in Britton–Robinson buffer, scan rate = 50 mVs^{-1}, medium = DMSO : water (60 : 40) at GCE.

0·5 mM to 2·5 mM, the anodic current i_{pa} values obtained were found to increase linearly with increase in concentration (table 1). The plot of i_{pa} verses concentration of TCH and CH show linearity further indicating electrode process was diffusion controlled.[20,21] It was also observed that the peak potential E_{pa} and half peak potential $E_{pa/2}$ were shifted towards more positive potential value with increase in concentration.

3.3 *Effect of scan rate*

The concentration of TCH and CH was kept constant at 2 mm in DMSO-water medium. The sweep rate was varied from 5 to 200 mVs^{-1}. The i_{pa} was found to increase linearly with the square root of the scan rate ($v^{1/2}$). These observations suggests that the process was diffusion controlled.[22] The peak poten-

tial was shifted towards the more positive values with an increase in the scan rate indicating that electrochemical process was irreversible. The cathodic charge transfer coefficients (n) were evaluated by measuring the $E_p - E_{p/2}$ using the expression.[22]

$$E_p - E_{p/2} = 47 \cdot 7 \text{ mV}/\alpha\, n,$$

where n is the number of electrons. The values found were $\alpha\, n = 0 \cdot 50 \pm 0 \cdot 05$.

3.4 *Effect of solvent composition*

The effect of solvent composition on the electrooxidation of TCH and CH were studied from 20% v/v to 70% v/v DMSO and water in Britton–Robinson buffer. It was observed that as the percentage of solvent increase, the oxidation potential value shifted towards more positive value (table 2). The shift may be due to the inhibition of the electrode process by the solvent molecules adsorbed on the electrode[23] and also due to dielectric effect.

3.5 *Effect of substituent*

In the presence of electron withdrawing and donating groups, oxidation occur at higher and lower potentials respectively. Accordingly benzaldehyde thiocarbohydrazone, *o*-chlorobenzaldehyde thiocarbohydrazone and methoxy benzaldehyde thiocarbohydrazone get oxidized at 849, 893 and 829 mV respectively.
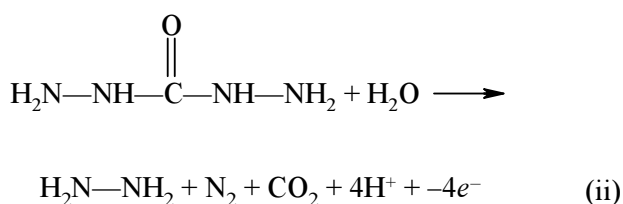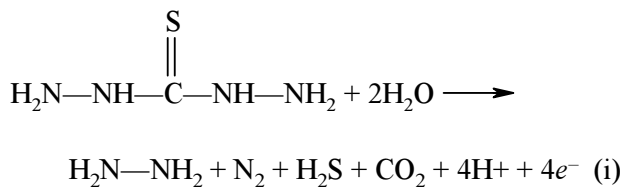
3.6 *Identification of product*

Electrochemical oxidation product of TCH and CH involving four electrons have been identified as $NH_2 \cdot NH_2$, H_2S for TCH and $NH_2 \cdot NH_2$, CO_2 for CH respectively by the following method.

Table 2. Cyclic voltammetry data of 2 mM TCH and CH at different composition of solvent in Britton-Robinson buffer (electrode system : GCE/Pt/SCE. media = DMSO : Water pH = 4·63)
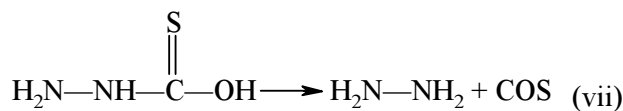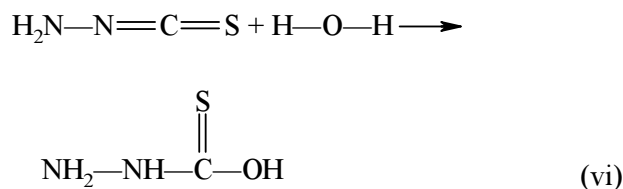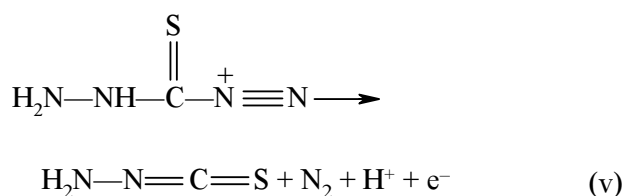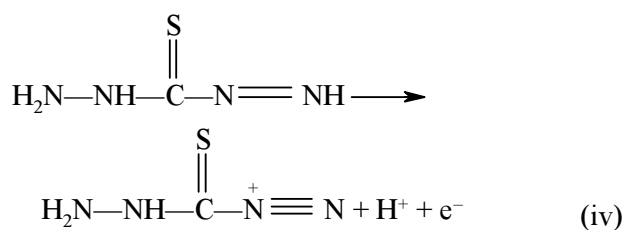
DMSO solvent (%)	TCH			CH		
	E_{pa} (mV)	$-i_{pa}$ (μA)	$D_0 \times 10^{-5}$ cm^2 s^{-1}	E_{pa} (mV)	$-i_{pa}$ (μA)	$D_0 \times 10^{-5}$ cm^2 s^{-1}
20	709	165·2	28·45	858	106·90	15·24
40	806	155·1	28·32	860	96·01	12·02
50	822	117·0	16·71	867	74·90	7·48
60	831	110·2	15·03	874	69·20	6·29
70	907	97·2	13·58	912	60·90	5·28

Five ml of 2×10^{-3} M TCH solution was taken in the cell. 8 ml of DMSO and 10 ml of Britton–Robinson buffer were added. With glassy carbon as a working electrode the solution was subjected to repeated oxidation with a scan rate of 50 mVs^{-1} at a potential range of 0–1500 mV. Later the solution was heated and the vapours were held to the lead acetate paper which turned black, thus confirming COS as the reaction product wherein, carbonyl sulphide combines with water forming CO_2 and H_2S. The product analysis agrees with the findings of potentiometric analysis of TCH and CH.[10–12]
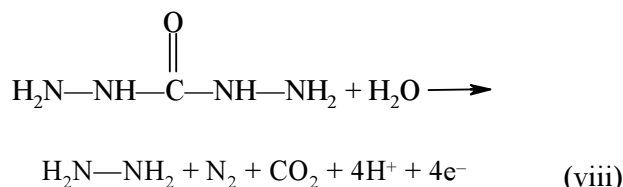
The overall oxidation process can be represented as follows.

$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-NH-NH_2 + 2H_2O \longrightarrow$$

$$H_2N-NH_2 + N_2 + H_2S + CO_2 + 4H+ + 4e^- \quad (i)$$

$$H_2N-NH-\overset{\overset{\textstyle O}{\|}}{C}-NH-NH_2 + H_2O \longrightarrow$$

$$H_2N-NH_2 + N_2 + CO_2 + 4H^+ + -4e^- \quad (ii)$$

On the basis of the above results the following mechanism involving four electrons is proposed for the electrochemical oxidation of TCH and CH

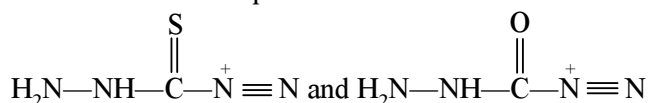$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-NH-NH_2 \longrightarrow$$

$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-N-NH + 2H^+ + 2e^- \quad (iii)$$

$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-N = NH \longrightarrow$$

$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-\overset{+}{N} \equiv N + H^+ + e^- \quad (iv)$$

$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-\overset{+}{N} \equiv N \longrightarrow$$

$$H_2N-N = C = S + N_2 + H^+ + e^- \quad (v)$$

$$H_2N-N = C = S + H-O-H \longrightarrow$$

$$NH_2-NH-\overset{\overset{\textstyle S}{\|}}{C}-OH \quad (vi)$$

$$H_2N-NH-\overset{\overset{\textstyle S}{\|}}{C}-OH \longrightarrow H_2N-NH_2 + COS \quad (vii)$$

$$COS + H_2O \longrightarrow H_2S + CO_2 \quad (viii)$$

For Carbohydrazide

$$H_2N-NH-\overset{\overset{\textstyle O}{\|}}{C}-NH-NH_2 + H_2O \longrightarrow$$

$$H_2N-NH_2 + N_2 + CO_2 + 4H^+ + 4e^- \quad (viii)$$
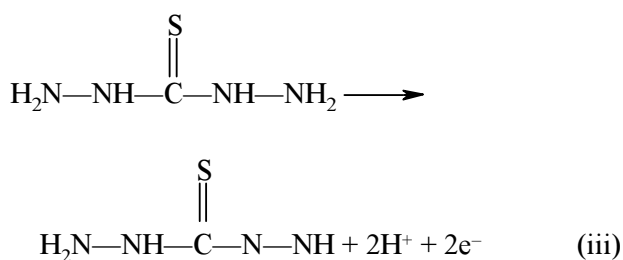
Above pH 6.5 the cyclic voltammogram showed two peaks I, II at 733 mV, 1050 mV for TCH and 806 mV, 1183 mV for CH respectively, indicating that oxidation takes place in two steps involving three and one electrons. A typical cyclic voltammogram of the
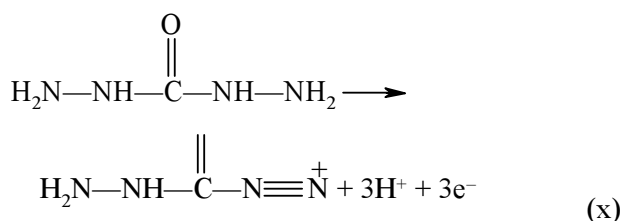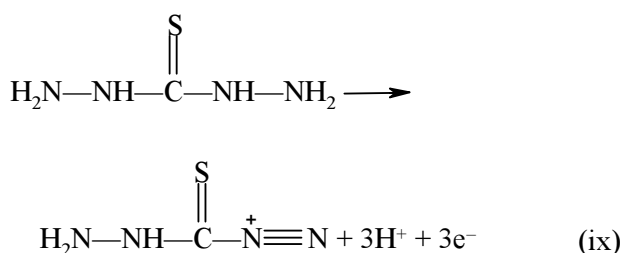
thiocarbohydrazide and carbohydrazide is shown in figure 2.

The intermediate product could be

$$H_2N—NH—\overset{\overset{\displaystyle S}{\|}}{C}—\overset{+}{N}\equiv N \quad \text{and} \quad H_2N—NH—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{+}{N}\equiv N$$
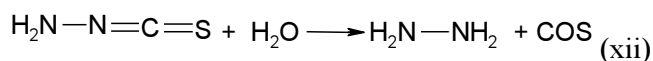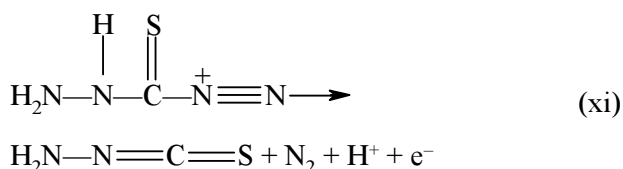
for TCH and CH respectively. The mechanism for the two step oxidation process involving three and one electrons can be represented by the following equations.
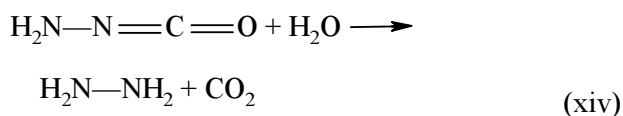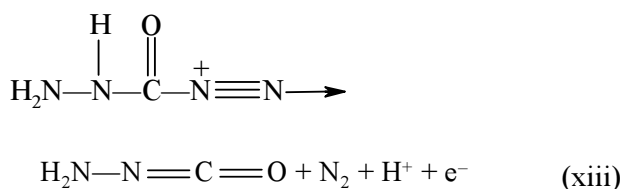
I step

$$H_2N—NH—\overset{\overset{\displaystyle S}{\|}}{C}—NH—NH_2 \longrightarrow$$

$$H_2N—NH—\overset{\overset{\displaystyle S}{\|}}{C}—\overset{+}{N}\equiv N + 3H^+ + 3e^- \qquad \text{(ix)}$$

$$H_2N—NH—\overset{\overset{\displaystyle O}{\|}}{C}—NH—NH_2 \longrightarrow$$

$$H_2N—NH—\overset{\overset{\displaystyle \|}{}}{C}—N\equiv \overset{+}{N} + 3H^+ + 3e^- \qquad \text{(x)}$$

II Step

$$H_2N—\overset{\overset{\displaystyle H}{|}}{N}—\overset{\overset{\displaystyle S}{\|}}{C}—\overset{+}{N}\equiv N \longrightarrow$$

$$H_2N—N\equiv C\equiv S + N_2 + H^+ + e^- \qquad \text{(xi)}$$

$$H_2N—N\equiv C\equiv S + H_2O \longrightarrow H_2N—NH_2 + COS \qquad \text{(xii)}$$

Similarly for carbohydrazide

$$H_2N—\overset{\overset{\displaystyle H}{|}}{N}—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{+}{N}\equiv N \longrightarrow$$

$$H_2N—N\equiv C\equiv O + N_2 + H^+ + e^- \qquad \text{(xiii)}$$

$$H_2N—N\equiv C\equiv O + H_2O \longrightarrow$$

$$H_2N—NH_2 + CO_2 \qquad \text{(xiv)}$$

In order to prove the $H_2N–NH_2$ is the end product, trial experiment have been conducted by taking hydra-

zine and found that it did not undergo oxidation at the working electrode under the conditions specified.

3.6 *In non-aqueous media*

TCH in dimethyl sulphoxide in 0.1 M tetra butyl ammonium hexa flurophosphate also showed two peaks (I) and (II) at 1000 mV and 1287 mV suggesting that the oxidation process take place in two steps involving three and one electrons respectively. A typical cyclic voltammogram of TCH is shown in figure 3.

3.7 *Effect of derivatization*

TCH and CH form corresponding monocarbohydrazones with benzaldehyde, ortho chlorobenzaldehyde, *p*-methoxy benzaldehyde respectively. The cv study showed both oxidation and reduction peaks. The reduction peak of the above carbazones could be due to the reduction of –CH=N– moiety. The oxidation peak was due to the oxidation of the free ends of thiocarbohydrazones.

3.7a. *Oxidation of benzaldehyde thiocarbohydrazone (BTCH):* Eectrochemical oxidation of BTCH was studied in DMSO-water media using Britton-Robinson buffer as supporting electrolyte in the potential range –2300 to 1500 mV. Single oxidation peak appeared at potential –779 mV due to the oxidation of BTCH to benzaldehyde hydrazone. On subsequent scan >CH=N moiety of benzaldehyde hydrazone further undergoes reduction at potential –1192 mV (figure 4).

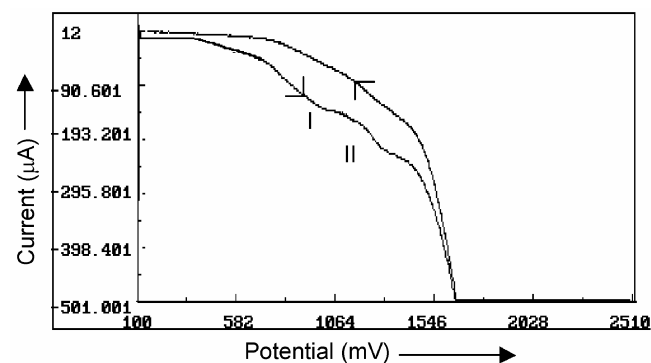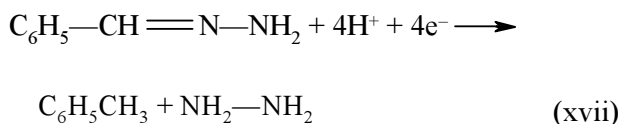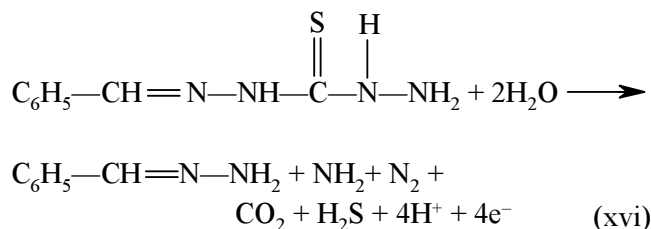**Figure 3.** Typical cyclic voltammogram of 2 mM of TCH in DMSO and 0.1 M TBAHFP, scan rate = 50 mVs^{-1} at GCE.

$$C_6H_5\text{—}CH = N\text{—}NH\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}\overset{\overset{\displaystyle H}{|}}{N}\text{—}NH_2 + 2H_2O \longrightarrow$$

$$C_6H_5\text{—}CH = N\text{—}NH_2 + NH_2 + N_2 +$$
$$CO_2 + H_2S + 4H^+ + 4e^- \qquad \text{(xvi)}$$

$$C_6H_5\text{—}CH = N\text{—}NH_2 + 4H^+ + 4e^- \longrightarrow$$

$$C_6H_5CH_3 + NH_2\text{—}NH_2 \qquad \text{(xvii)}$$

Separate trial experiments with benzaldehyde hydrazone could prove the point as described below.

Benzaldehyde hydrazone was prepared by refluxing benzaldehyde and hydrazine hydrate for 1 h in alcohol media. The pale yellow crystals separated out were recrystalised from alcohol.

Electrochemical reduction of Benzaldehyde hydrazone was carried in DMSO-water media using Britton–Robinson buffer in the potential range 0 to 1500 mV. Single reduction peak appearing at the potential –1254 mV (figure 5) agreed with the reduction
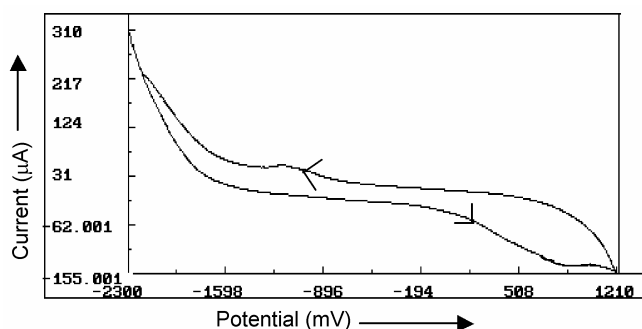
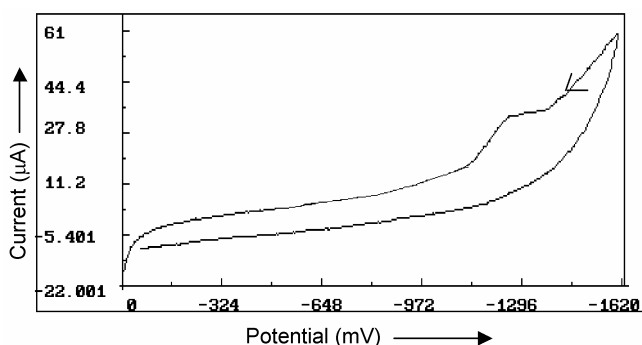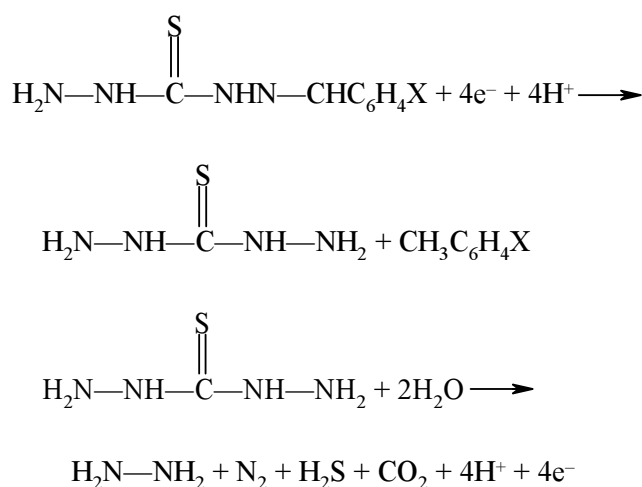**Figure 4.** Typical cyclic voltammogram of 2 mM BTCH in DMSO : water medium, scan rate = 50 mVs^{-1} at GCE.

Figure 5. Cyclic voltammogram of 2 mM benzaldehyde hydrazone in DMSO : water medium, scan rate = 50 mVs^{-1} at GCE.

of the oxidized product of benzaldehyde thiocarbohydrazone (equation xvi). No new peaks appearing from the multiple scans can be taken as a convincing justification for the formation of $C_6H_5CH_3$ and NH_2–NH_2 as reaction products.

3.7b. *Reduction of benzaldehyde thiocarbohydrazone*: Electrochemical reduction of BTCH was studied in DMSO–water media using Britton–Robinson buffer as supporting electrolyte in the potential range 1500 to 2000 mV. Single peak appeared at –1887 mV corresponding to the reduction of HC=N moiety with a subsequent oxidation peak at the reverse scan confirming quasireversible nature.

$$H_2N\text{—}NH\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}NHN = CHC_6H_4X + 4e^- + 4H^+ \longrightarrow$$

$$H_2N\text{—}NH\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}NH\text{—}NH_2 + CH_3C_6H_4X$$

$$H_2N\text{—}NH\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}NH\text{—}NH_2 + 2H_2O \longrightarrow$$

$$H_2N\text{—}NH_2 + N_2 + H_2S + CO_2 + 4H^+ + 4e^-$$

where, X = –Cl, –OCH$_3$.

The typical cyclic voltammogram of the benzaldehyde thiocarbohydrazone is shown in the figure 6.
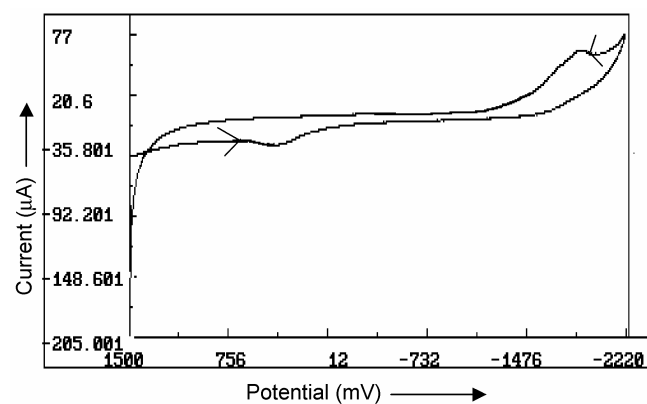
Figure 6. Cyclic voltammogram of 2 mM benzaldehyde thiocarbohydrazone in DMSO : water medium, scan rate = 50 mVs^{-1} at GCE.

3.7c. *Reduction of diacetelydene thiocarbohydrazone*: Diacetelydene thiocarbohydrazone was prepared and subjected to cv studies. Single reduction peak appeared at −1857 mV due to the reduction of two −HC=N− moieties, which undergoes oxidation in the subsequent scan indicating the quasireversible process (figure 7). However the oxidation scan in the range 0 to 1500 mV, it did not yield any oxidation peak at all. This shows that the molecule is protected against the oxidation due to the formation of hydrazones at both the ends.
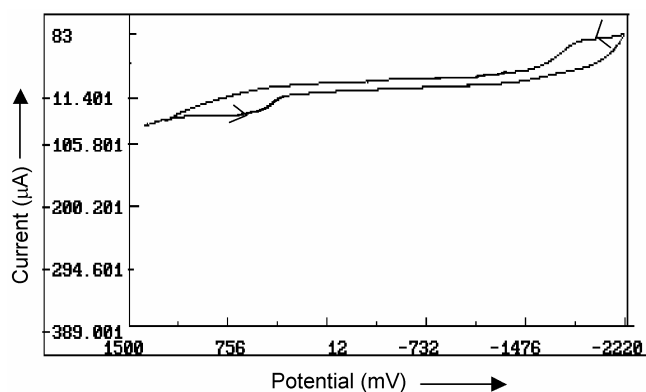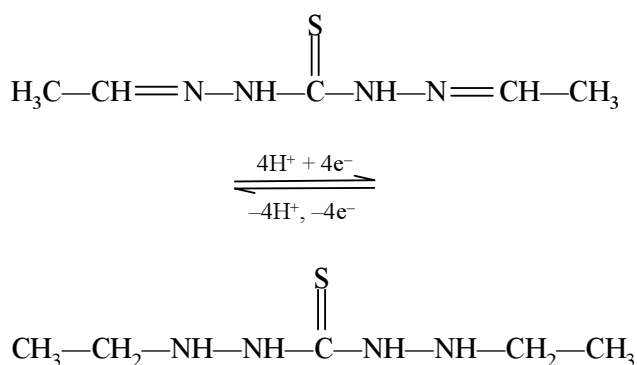
$$H_3C-CH{=}N-NH-\overset{\overset{\displaystyle S}{\|}}{C}-NH-N{=}CH-CH_3$$

$$\frac{\xrightarrow{4H^+ + 4e^-}}{\xleftarrow{-4H^+,\,-4e^-}}$$

$$CH_3-CH_2-NH-NH-\overset{\overset{\displaystyle S}{\|}}{C}-NH-NH-CH_2-CH_3$$

Figure 7. Cyclic voltammogram of 2 mM diacetelydene thiocarbohydrazone in DMSO : water medium, scan rate = 50 mVs^{-1} at GCE.

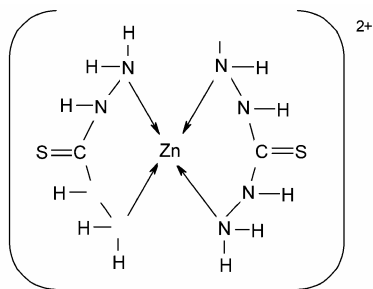**Figure 8.** Structure of a typical metal complex of thiocarbohydrazide, where M = Zn, the complex is *bis*(thiocarbohydrazide) zinc(II) ion.

3.8 *Effect of complexation*

Effect of complexation was studied by preparing the complex *bis*(thiocarbohydrazide) zinc(II) chloride. Structure of *bis*(thiocarbohydrazide) zinc(II) ion is shown in figure 8.

The Zn (II) complex of TCH in Britton Robinson buffer of pH 6·3 at GCE was subjected to CV studies at a potential range of 0 to 1500 mV. No oxidation peak was observed but in the potential range of 0 to −1110 mV although it showed a reduction peak at −869 mV. This indicated that the metal ion complex undergoes reduction and the ligand will not take part in the redox process.

On comparing the reduction potential of pure ZnCl$_2$ with that of Zn complex of TCH, it was observed that the pure ZnCl$_2$ got reduced at lower potential −743 mV. whereas, Zn complex was reduced only at a higher potential of −869 mV (figure 9).

This suggest that metal in the free state gets reduced at lower potential than in the metal bound formation.

3.9 *Differential pulse voltammetry at GCE*

Differential pulse voltammetry makes a still greater improvement in sensitivity. The current is measured twice- once before applying the pulse and again during the last 17 ms of the pulse. The first current is instrumentally subtracted from the second current. The differential pulse voltammetry is thus a plot of current difference versus applied potential. In order
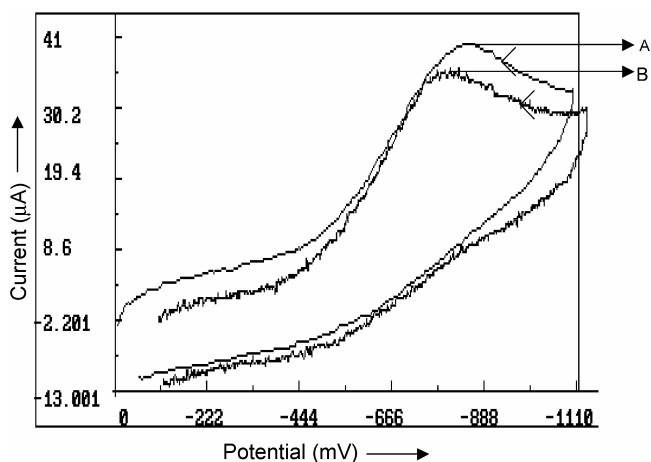

Figure 9. Cyclic voltammogram of 2 mM Zn(II) complex of TCH (**a**) and pure ZnCl$_2$ (**b**) in DMSO : water medium, scan rate = 50 mVs^{-1} at GCE.
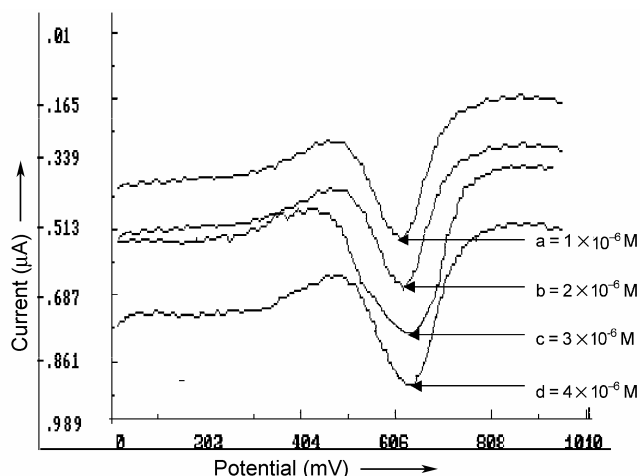
Figure 10. Differential pulse voltammograms for standard addition of 1×10^{-6} to 4×10^{-6} M of thiocarbahydrazide at GCE. Pulse amplitude = 50 mV, supporting electrolyte: Britton–Robinson buffer.

to know the concentration of TCH we compared the anodic peak obtained by differential pulse voltammetry. The best ratio of peak to background currents was obtained with differential pulse voltammetry for pulse amplitude of 50 mV and this was used in subsequent studies. The figure 10 shows the voltammogram of TCH on addition of 1 to 4 μM of TCH. The DPV curves are illustrated with *a*, *b*, *c* and *d* indicating their respective concentrations.

4. Conclusion

The anodic peak potentials for TCH and its derivatives are shifted to more positive values with increase in concentration of electroactive species. The electron withdrawing or electron donating group in the hydrazone derivative retard or accelerate the oxidation process.

The anodic peak current was found to increase linearly with square root of sweep rate and also with concentration of electroactive species, suggesting that the overall electrode process is diffusion controlled and irreversible.

At higher surfactant concentration (within critical micelle concentration) no oxidation peak was observed.

Bis(thiocarbohydrazide) zinc(II) complex shows reduction and not oxidation. Differential pulse voltammetry for the determination of microgram quantities of TCH yielded reproducible results.

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