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Electrochemical Behavior of Some Thioheterocyclic Compounds in Aqueous-Methanolic Media at Mercury Electrodes

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This paper presents the electrochemical behavior of 4-amino-3-thio-1,2,4-triazole (I), 4-amino-3-thio-5-methyl-1,2,4-triazole (II) and 4-amino-6-methyl-3-thio-1,2,4-triazin-5-one (III) at mercury electrodes. The study is performed in aqueous-methanolic solutions by differential pulse polarography (DPP), cyclic voltammetry (CV), chronoamperometry, coulometry and spectrophotometry. All three compounds exhibited one reversible oxidation peak, accompanied by a prepeak, due to the adsorption of these compounds on the electrode. The main peak in each case was found to be diffusion controlled. Their polarographic responses were similar to those of common thiol compounds and involved a one electron oxidation of mercury followed by a disproportionation step to form the mercury(II) salt and Hg, (EC mechanism). The protonation constants (pK), diffusion constants, the rate constants of coupled chemical reaction and transfer coefficients were also obtained.

Key words: oxidation, triazole, triazine, polarography, cyclic voltammetry

The importance of thioheterocyclic compounds [1,2] in pharmaceutical and agricultural industries demands much intention in this field. Among these the thiotriazines and thiotriazoles have received especial attention, because they can mimic sulfur protein compound [3] and also because of their antifungal activities [4].

To best of our knowledge, there are only some reports on electrochemical behavior of triazines and there is no report concerning polarography of these compounds. The electroreduction of 1,2,4-triazine was investigated by Zuman [5]. The reduction of benzimidazole-2-thion was also reported [6].

The compounds that are object of our study are 4-amino-3-thio-1,2,4-triazole (I), 4-amino-3-thio-5-methyl-1,2,4-triazole (II), and 4-amino-6-methyl-3-thio-1,2,4-triazin-5-one (III) (Fig. 1), that exhibit very similar chemical structure and properties. These compounds are well known as antifungal and have the basic structure of many natural products with interesting physiological activities. Because of these aspects and the continuing interest of our laboratory in the electrochemistry of biologically active organic compounds [7–9], it is worthwhile to continue with the redox characteristics of such compounds. Thus, the electrochemical behavior of these compounds in

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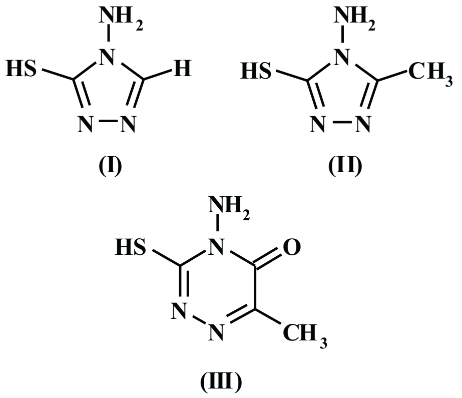
*Corresponding author; E-mail: lfotouhi@alzahra.ac.ir acetate buffer (pH 4.6, 10% V/V methanol) at the mercury electrode was investigated by differential pulse polarography, cyclic voltammetry, chronoamperometry and coulometry.



(I) (II) (III)

Figure 1. The structure of compounds.

EXPERIMENTAL

Chemicals and reagents: All three compounds I, II, and III were prepared and purified by well established method [10]. Stock solutions were prepared by dissolving the appropriate amount of these compounds in acetate buffer, 0.1 M (pH 4.6). Due to the low solubility of these compounds in aqueous media, 10% V/V methanol solutions were used. A stock Britton-Robinson buffer solution, which was 0.04 M with respect to boric, orthophosphoric and acetic acid was prepared from analytical- reagent grade. From this stock solution of buffer, solutions of various pHs were prepared by the addition of 0.2 M sodium hydroxide solution. All other chemicals were of analytical-reagent grade.

Instrumentation: Electrochemical measurements were carried out with a Metrohm model 746 VA Trace Analyzer connected to a 747 VA Stand. The working electrode was a multimode mercury drop electrode, Metrohm 6.1246.020. A platinum-wire electrode and a commercial saturated Ag/AgCl from Metrohm were used as an auxiliary and a reference electrode, respectively. For DP polarography the pulse amplitude was 50 mV. In cyclic voltammetry the scan rate was 100 mVs^{-1}, with the evident exception of the experiments, in which the influence of this variable was studied.

Controlled-potential coulometry was performed using EG & G model 173 potentiostat and galvanostat on the mercury pool as working electrode. Solutions were purged with purified argon. The pH values were measured with pH meter Metrohm model 744. The UV-vis absorption spectra were recorded on a Unicam 8700 series UV-vis spectrophotometer.

RESULTS AND DISCUSSION

The polarographic oxidation of each compound was investigated in acetate buffer at pH 4.6 and with a 10% V/V methanol to ensure the solubility. At concentration below 8.6×10^{-4} M of I, one peak (i_a) was observed at –0.037 V. At higher concentration than 8.6×10^{-4} M another peak (i_d) has appeared at 0.051 V. The height of less positive peak (i_a) at first increased with concentration and then became constant, but height of second peak (i_d) was a linear function of concentration (Fig. 2). From the above results we can conclude that the first peak (i_a) is an adsorption peak and second one (i_d) is a diffusion-controlled peak.

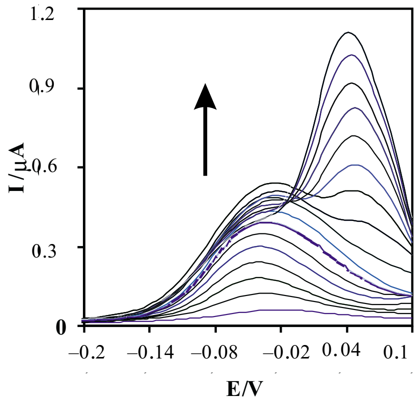


Figure 2. The differential pulse polarograms of 0.10, 0.20, 0.29, 0.39, 0.48, 0.58, 0.67, 0.77, 0.86, 0.95, 1.04, 1.13, 1.22, 1.31, 1.40, 1.48 and 1.57 (mM) of compound I in 10% V/V methanol-acetate buffer pH 4.6, pulse height 50 mV, scan rate 20 mVs^{-1}.

DP voltammetry of I on glassy carbon electrode did not show any oxidation peak in the potential range observed in the case of mercury electrode. The peak due to oxidation of the I itself occurs at much more positive potential (more than +0.800 V) [11]. This confirms that the anodic peaks obtained with mercury electrode are due to mercury compound formation.

Similarly to I, both compounds II and III show a main anodic peak complicated by adsorption phenomena as a prepeak. The half-wave potential and peak potentials for all three compounds are shown in Table 1.

Table 1. The peak potentials of all compounds.

Compound	E_p(DP)/V	E_p(CV)/V
I	0.051 (±0.001)	0.071 (±0.001)
II	0.033 (±0.001)	0.066 (±0.001)
III	0.132 (±0.002)	0.152 (±0.002)

The cyclic voltammograms of each compound at different concentrations also exhibited two peaks, one reversible peak accompanied by one prepeak. The cyclic voltammograms of I at different scan rates in the low and high concentration are shown in Fig. 3a and 3b, respectively. There are two pairs of oxidation peaks; the first pair is $i_{a,O}$ ($E_{a,O} = -0.016$ V) and $i_{a,R}$ ($E_{a,R} = -0.018$ V) and the second pair is $i_{d,O}$ ($E_{d,O}$ = 0.055 V) and $i_{d,R}$ ($E_{d,R} = 0.013$ V), in which a and b are adsorption and diffusion peaks, while O and R are oxidation and reduction peaks, respectively. When the concentration of I was lower than 3.9×10^{-4} M, only prepeak ($i_{a,O}$ and $i_{a,R}$) was observed which exhibits the behavior of adsorbed species. Its peak height increased with concentration and then became constant. Moreover, the peak current was proportional to ν ($i = 0.0004\nu + 0.0058$) and at lower concentration it was increased when the pre-equilibration (pre-accumulation) was implemented. This behaviors is characteristic for reactants adsorbed on the electrode [12]. At higher concentration the main peaks ($i_{d,O}$ and $i_{d,R}$) were also observed. Their peak currents were proportional to the concentration and to the square-root of the scan rate, $\nu^{1/2}$ ($i = 0.0881\nu^{1/2} + 0.0545$). The peak height did not change upon extending the pre-equilibration time. These facts show that the main peak corresponds to a diffusion-controlled process. Two other compounds II and III showed a similar behavior.

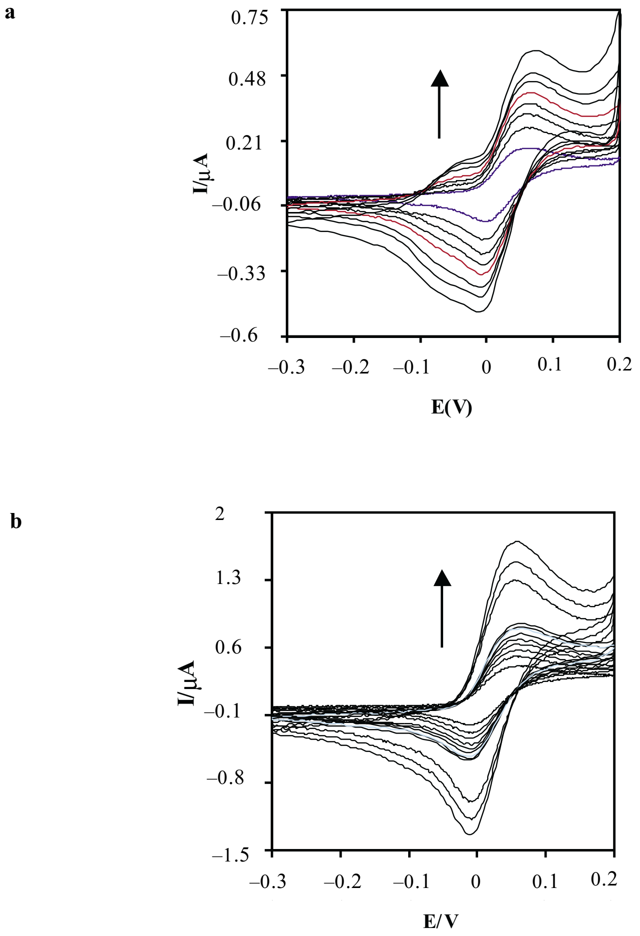


Figure 3. a) Cyclic voltammograms of 8.6×10^{-4} M of I, scan rates: 25, 75, 100, 150, 200, 300, 400 and 500 mVs^{-1}. b) Cyclic voltammograms of 2×10^{-3} M of compound I, scan rates: 10, 20, 30, 40, 50, 70, 90, 100, 200, 300 and 400 mVs^{-1}.

In order to investigate the mechanism of electro-oxidation of these compounds, the i_{pc}/i_{pa} ratio (Fig. 4a) and current function, $i_{pa}/\nu^{1/2}$, for the main peak of I (Fig. 4b) were plotted against the scan rate. As can be seen from Fig. 4, the ratio i_{pc}/i_{pa} was approximately one at scan rate exceeding 90 mVs^{-1}, but it was less than one for the scan rates lower than 90 mVs^{-1}, and decreased as the scan rate decreased. Moreover, the current function ($i_{pa}/\nu^{1/2}$) for I decreased with scan rate (Fig. 4). These results show that a coupled chemical reaction follows the electron transfer step (EC mechanism) [13]. ΔE_p for main peaks was about 60 mV, indicating a reversible behavior. These results are in good agreement with those obtained for thiol compounds and show that the anodic oxidation of mercury is followed by a disproportionation step to form mercury(II) salt and Hg [14–17].

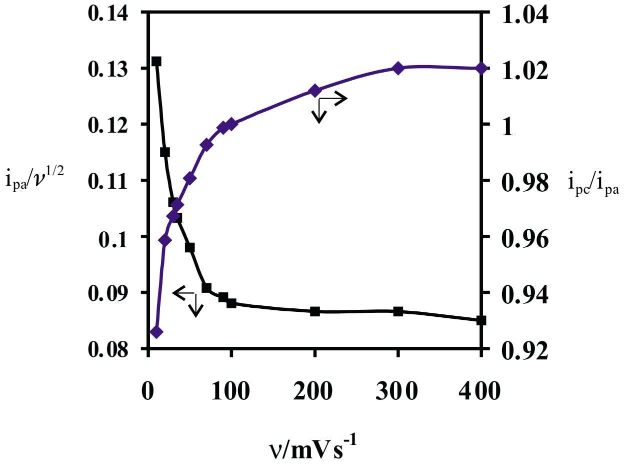


Figure 4. Variation peak current function ($i_{pa}/\nu^{1/2}$) (left) and peak current ratio (i_{pc}/i_{pa}) (right) as a function of scan rate.

Because the basic structure of these compounds, we anticipate that the electrooxidation process would be pH dependent. In order to ascertain this, polarographic responses of three compounds as a function of the pH solution were studied. The pH dependence and the effect of pH on the E_{pa} and i_{pa} of I by cyclic voltammetry are shown in Fig. 5.

The plot of E_p on pH shows a linear decrease of 59 mV per pH unit up to pH about 8. E_p becomes independent of pH above 8 (the pK_a values about 7– 8). The i_p – pH relationship is "V"-shaped (Fig. 5, inset) indicating the disappearance of the electroactive protonated form and the appearance of the unprotonated form, also electroactive at a potential slightly less positive, as indicated by the value at pH 7. The polarographic pK_a values for I, II, and III are 7.26, 8.18, and 7.26, respectively. The slope of linear part of E_p – pH plot ($E_p = -0.0543pH + 0.2967$, $r = 0.99$) is close to the Nernstian value of 59 mV, which indicates that the oxidation process takes place through a me-

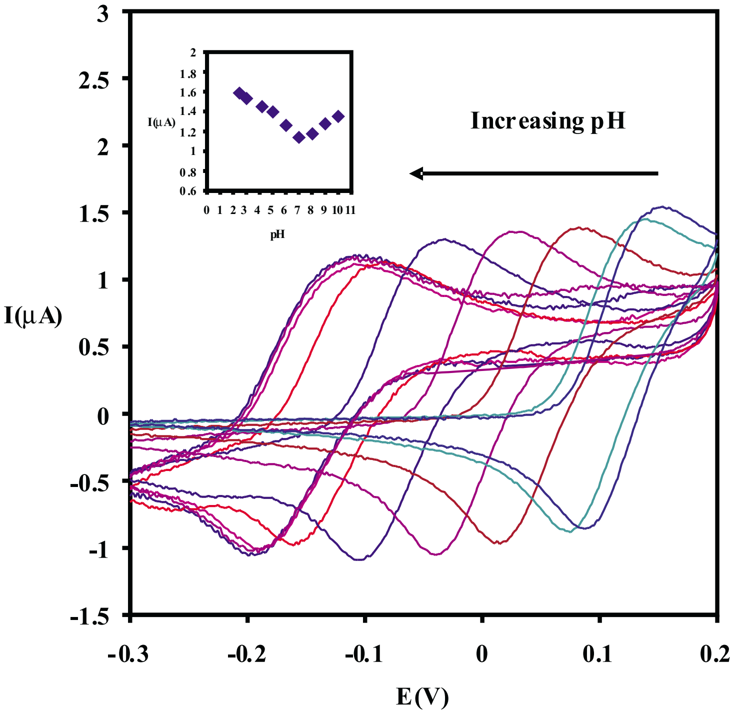


Figure 5. Cyclic voltammograms of 3×10^{-3} M of compound I in Britton-Robinson buffer with pH values: 2.5, 3.0, 4.2, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0, scan rate 100 mVs^{-1}. Inset: dependence of I *vs* pH.

chanism involving H^+: e^- ratio of one. This behavior is exactly the same as that observed for thiol compounds [14–17].

In order to investigate the mechanism of electrooxidation, the double potential chronoamperometry (initial potential, $E_i = -0.10$ V; step potential, $E_s = 0.15$ V; final potential, $E_f = -0.10$ V and interval time, $\tau = 5$ s) was used. The chronoamperogram of I was shown in Fig. 6a. The ratio of cathodic current (i_c) to anodic current (i_a) less than one indicates an EC mechanism, due to consuming the product of electron transfer reaction in a following coupled chemical reaction at long time.

The diffusion coefficient can be calculated using the Cottrell equation [13]. The plot of I *vs*. $t^{-1/2}$ is shown in Fig. 6b. The diffusion coefficients for all three compounds I, II, and III are 3.02×10^{-6}, 3.27×10^{-6}, and 4.43×10^{-6} cm^2 s^{-1}, respectively.

Constant potential coulometric analysis with 4×10^{-4} M solution of each compound at the plateau of their polarograms gave $n = 1\pm0.1$ per molecule of the compound. UV-vis absorption technique was performed to provide more detailed information about the electrode process. All three compounds showed an absorption maxima situated at 270 nm in 10% V/V methanol-acetate buffer (pH 4.6). Spectrophotometric monitoring of the electrolysis product (Fig. 7) shows the disappearance of the peak at $\lambda = 270$ nm and the appearance of another peak at $\lambda = 225$ nm, which is due to the for-

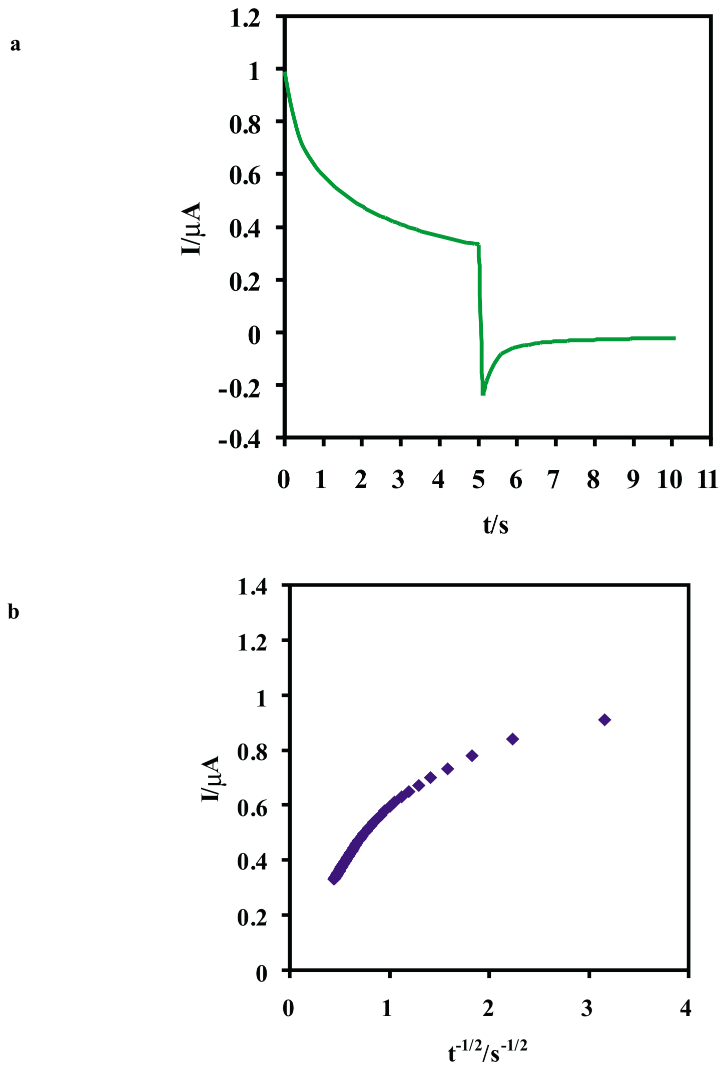


Figure 6. a) The double-potential step chronoamperogram of 2×10^{-3} M of compound I, acetate buffer pH 4.6, τ =5 s. b) The plot of I *vs* $t^{-1/2}$ for I. E_i = –0.1 V, E_s = 0.15 V, and E_f = –0.1 V.

mation $Hg^{(II)}$ L_2. The chemically prepared solution of $Hg^{(II)}$ L_2 shows a similar absorption peak at 225 nm, which is a good indication of formation of $Hg^{(II)}$ L_2 during electrolysis.

CONCLUSIONS

According to the experimental results reported above, for each compound I, II, and III, the overall electron reaction mechanism is the same as that previously pro-

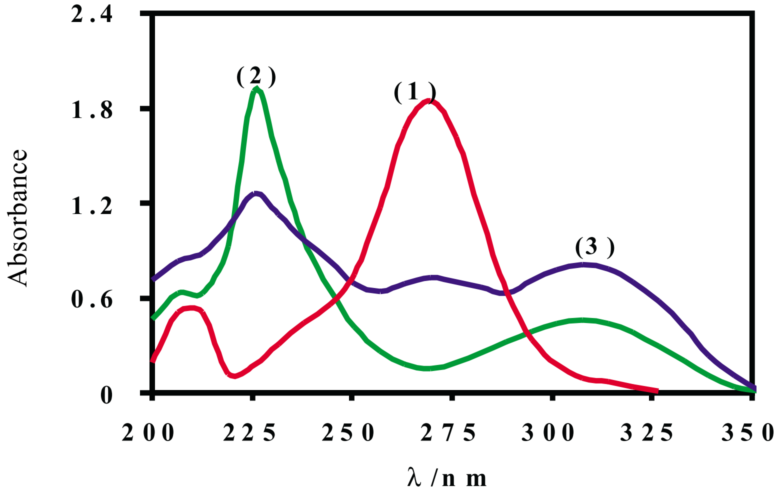


Figure 7. The absorption spectra of compound I: 1) Before electrolysis at E = 0.15 V; 2) After coulometry; 3) The chemically prepared solution of $Hg^{(II)} L_2$.

posed for thiol compounds [14–17]. Each compound shows two oxidation peaks. The first anodic peak is due to the adsorption process and the second one is a diffusion-controlled process. Both cyclic voltammetry (the ratio i_{pc}/i_{pa} less than one at lower scan rate) and chronoamperometry (the ratio i_c/i_a less than one) studies confirm the EC mechanism. Coulometry shows one electron per each molecule. Moreover, spectrophotometric results show the appearance of $Hg^{(II)} L_2$ during electrolysis. Thus, it can be concluded that the polarography of all compounds involves a one electron oxidation of mercury, followed by a rapid disproportionation step to form the mercury(II) salt. The following scheme is suggested.

$$Hg + L \rightleftarrows Hg^{(I)}L + e^-$$
$$2Hg^{(I)}L \longrightarrow Hg^{(II)}L_2 + Hg^{(0)}$$

This is the most probable mechanism for all the compounds studied, since the anodic peak observed in the case of each compound corresponded to a one electron oxidation of mercury, and the product of electrolysis was a mercury(II) compound.

Acknowledgments

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