Study the Electrochemical Reduction of Some Triazines in N,N-Dimethylformamide at Glassy Carbon Electrode

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Received January 6, 2003

An electrochemical study related to the electroreduction of 4-amino-6-methyl-3-thio-1,2,4-triazin-5-one(I), 6-methyl-3-thio-1,2,4-triazin-5-one(II), and 2,4-dimetoxy-6-methyl-1,3,5-triazine(III) in dimethylformamide at glassy carbon electrode has been performed. A variety of electrochemical techniques, such as differential pulse voltammetry (DPV), cyclic voltammetry (CV), chronoamperometry, and coulometry were employed to clarify the mechanism of the electrode process. The compounds I and II with thiol group exhibited similar redox behavior. Both displayed two cathodic peaks, whereas the third compound, III, without thiol group showed only one cathodic peak in the same potential range of the second peak of I and II. The results of this study suggest that in the first step the one electron reduction of thiol produced a disulfide derivative and in the second reduction step the azomethane in the triazine ring was reduced in two electron processes. A reduction mechanism for all three compounds is proposed on this basis. In addition, some numerical constants, such as diffusion constant, transfer coefficient, and rate constant of coupled chemical reaction in the first reduction peak were also reported.

Key Words : Electrochemistry, Triazine, Disulfide, Coupled chemical reaction

Introduction

S-triazine compounds containing both -C=N- moiety and thiol group are of interest in agriculture and biological processes. From the agricultural point of view these compounds have proved to be useful as herbicides and pesticides. Owing to the NH-C=N- moiety they are able to compete with a molecule of the natural electronic acceptor at the same binding site in the protein of the photosynthetic reaction center.[1] From the biological importance, a variety of mercapto alkyl compounds have been studied with regard to their properties as radiation protective drugs for animals.[2]
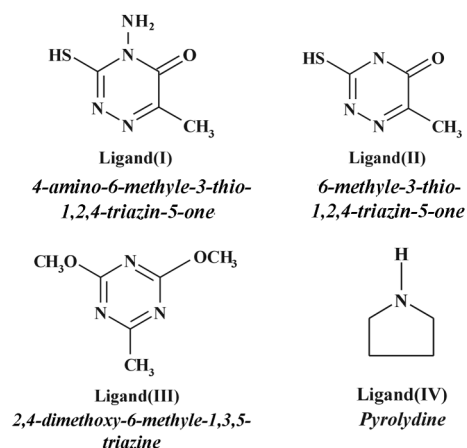
In spite of the importance of the electron transfer reaction of these compounds, there are some electroanalytical procedures for their determination and their protonation constants.[3-5] Up to now little attention has been given to the reduction mechanism of such compounds. In the continuation of our work in the electrochemistry of biologically active organic compounds,[6-8] we investigated the redox characteristics of such compounds, namely 4-amino-6-methyl-3-thio-1,2,4-triazin-5-one(I), 6-methyl-3-thio-1,2,4-triazin-5-one(II), and 2,4-dimetoxy-6-methyl-1,3,5-triazine(III).

A variety of electrochemical methods, such as cyclic voltammetry, chronoamperometry and coulometry, were used in dimethylformamide, DMF, at glassy carbon electrode. The reduction mechanism and some numerical parameters, such as diffusion coefficients and transfer coefficients, are also reported here.

Experimental Section

Reagents and Solutions. All the compounds were synthe-

Figure 1. The structure of compounds.

sized and characterized according to a published procedure[9] (Fig 1). Tetrabuthylammonium perchlorate (TBAP) and N,N-dimethylformamide, DMF, were obtained from Fluka and Merck, respectively. As supporting electrolyte, 0.10 M TBAP was used. Stock solutions of each compound were prepared at a constant concentration of 0.01 M in DMF. All other reagents were of analytical grade.

Electrodes and Instrumentation. All voltammetric experiments were performed at 25 ± 0.1 °C, using a Metrohm model 764 VA Trace Analyzer connected to a 747 VA stand. A 100 mL three-electrode measuring cell comprising a glassy carbon disk (GC) of 1 mm geometric radius as a working electrode, a platinum wire as a counter electrode, and a Ag/AgCl as a reference electrode were used for the measurements. Before use, the working electrode was sequentially polished with graded alumina powder 10 μm (Merck), rinsed with doubly distilled water, and repeatedly

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scan in the range of 1.40 to -1.40 V in 0.10 M NaHCO$_3$. This was followed by electrochemical treatment. The pulse height and scan rate at differential pulse voltammetry was 6 mV and 20 mVs^{-1}, respectively. The scan rate at cyclic voltammetry was 100 mVs^{-1}, with the evident exception of the experiments in which the influence of this variable was studied. Oxygen was removed from the solutions by passing a stream of pure argon.

Double-potential-step chronoamperometry measurements were conducted using 4 mM of each compound in 0.10 M TBAP in DMF at GC. The initial potential (E$_i$), where no electrolysis occurs, the step potential (E$_s$), where complete electrolysis occurs, and the final potential (E$_f$) after an internal time, $\tau = 5$ s, were obtained from each cyclic voltammogram. The potentials chosen were -1.0 V, -1.7 V, and -1.0 V, for first peak and -2.0 V, -2.6 V, and -2.0 V for second peak, respectively.
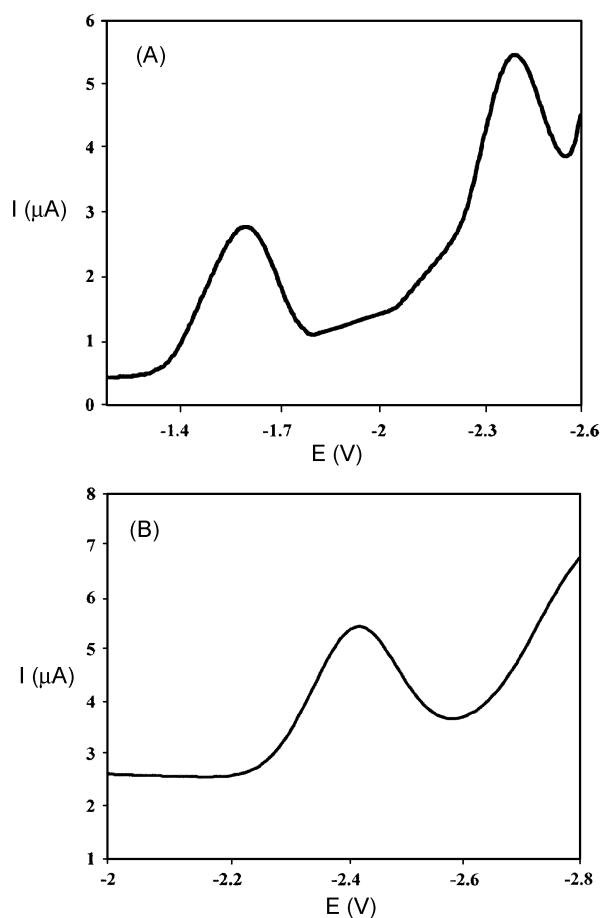
Potential controlled electrolysis was performed using an EG& G PAR model 173 potentiostat/galvanostat. A three-carbon rod (1 cm diameter and 5 cm length) was used as the working electrode. An argon stream and stirring were maintained in the solution during electrolysis. The electrolysis was terminated when the electrolytic current decreased to the residual current value measured in the supporting

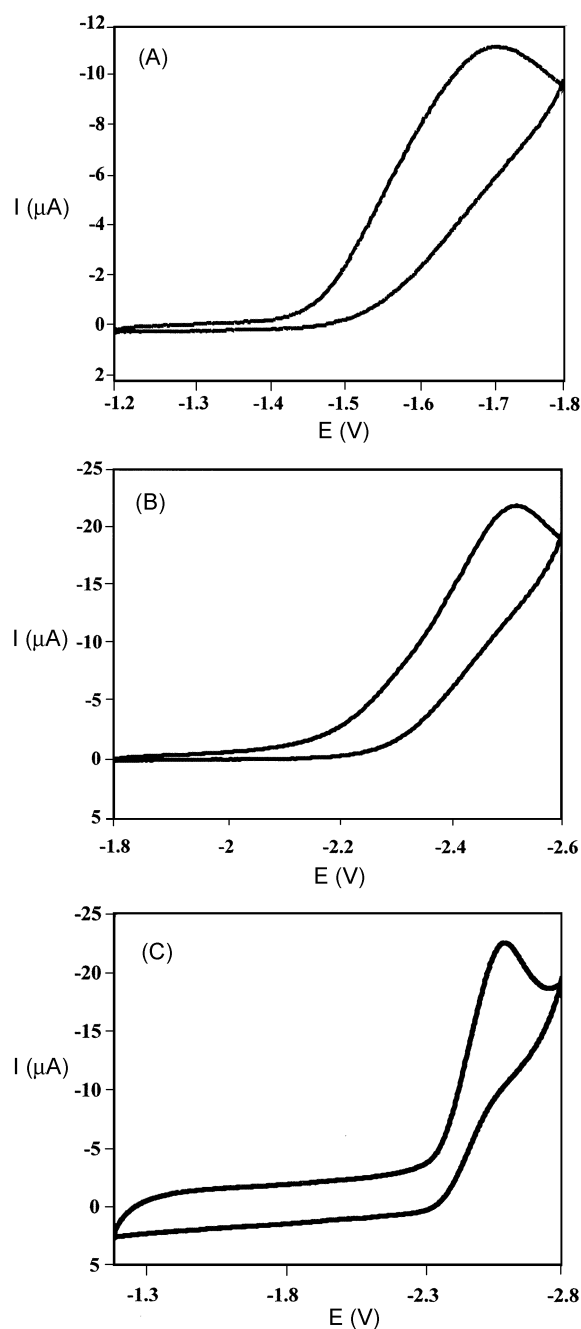electrolyte before the addition of the analyte.

Spectrophotometric measurements were carried out with a Unicam 8700 series Uv-vis spectrophotometer, using 1cm quartz cell.

Results and Discussion

Differential Pulse Voltammetry (DPV). Figure 2a shows a typical DP voltammogram for 4 mM of I at a glassy carbon (GC) electrode in 0.10 M TBAP in DMF. As illustrated in Figure 2a, I was reduced at two cathodic peaks, at -1.61 and

Figure 2. (A) Differential pulse voltammogram of 4 mM compound I. (B) Differential pulse voltammogram of 4 mM compound III. Supporting electrolyte: 0.10 M TBAP in DMF, pulse height 6 mV, and scan rate 20 mVs^{-1}.
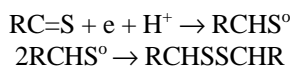

Figure 3. (A) Cyclic voltammogram of first cathodic peak of compound I. (B) Cyclic voltammogram of second cathodic peak of compound I. (C) Cyclic voltammogram of compound III. Supporting electrolyte: 0.10 M TBAP in DMF, scan rate 100 mVs^{-1}.

-2.40 V. The height of the cathodic peaks showed linear variation with concentration, which showed that the electron-transfer is diffusion-controlled. With increasing concentration, peak potential (E_p) was shifted to more negative potential due to the irreversibility of the process. Compound II shows a similar voltammogram with two cathodic peaks. The DP voltammogram of III is shown in Figure 2b, which shows only one cathodic peak in the same potential range of the second peak at I and II. It is also a diffusion-controlled process due to the linear dependence of its peak height with concentration. According to the molecular structure, both II and I have a thiol group, which is absent in compound III.
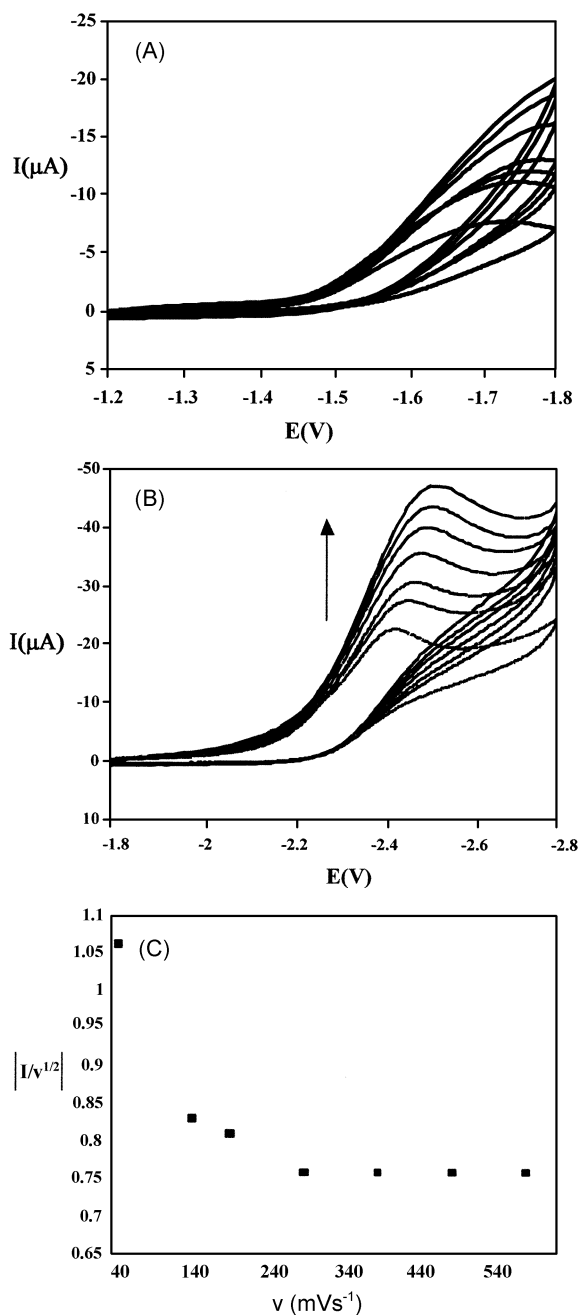
Considering that the triazine moiety has an important role in the structure of most biological molecules and in pesticides, we were interested in studying the effect of the presence of a thiol group on the structure of the molecules of triazine and on the mechanism of the redox behavior of such compounds.

Cyclic Voltammetry. The cyclic voltammograms of 5 mM of I in 0.10 M TBAP in DMF is shown in Figure 3a, b. The cyclic voltammograms of I exhibit two cathodic peaks at -1.70 and -2.50 V, without any anodic peak at reverse scan, indicating that both cathodic peaks were irreversible electron transfer processes. Compound II showed similar behavior. Figure 3c shows the cyclic voltammogram of III, which showed only one irreversible reduction wave. The peak potentials of three compounds are shown in the Table 1.

A general study of the electrochemical reduction of thiol compounds[10-12] proposes a reaction scheme in which after the uptake of one electron, the produced radical dimerize to a disulfide (EC mechanism). We have observed similar behavior in our compounds.

$$RC=S + e + H^+ \rightarrow RCHS^o$$
$$2RCHS^o \rightarrow RCHSSCHR$$

Due to the presence of the first cathodic peak only in the voltammogram of both I and II (compounds with a thiol group) and the absence of this peak in the voltammogram of III (compound without a thiol group), it can be concluded that the first cathodic peak could follow the above EC mechanism, which is well-defined in the most thiol compound.[10-12] On the other hand, there are some reports[13] on the electrochemical reduction of 1,3,5-triazine derivatives bearing reducible azomethine (C=N-) bonds. In all cases, the overall reaction involving 2e-reduction of azomethine in triazine ring is observed. Here, since the first cathodic peak appeared only in the voltammograms of both I, II, whereas

Figure 4. (A) Cyclic voltammograms of compound I at potential range -1.20 to -1.80 V at scan rates: 50, 150, 200, 300, 400, 500, and 600 mVs^{-1}. (B) Cyclic voltammograms of compound I at potential range -1.80 to -2.80 V at scan rate: 100, 150, 200, 300, 400, 500, and 600 mVs^{-1}. Supporting electrolyte: 0.10 M TBAP in DMF. (C) The current function ($i/v^{1/2}$) as function of scan rate of compound I.

the second cathodic peak appeared in the voltammograms of all three compounds, we supposed that the first peak may correspond to the formation of disulfide in an EC-mechanism, and the second peak is due to the reduction of azomethine bond.

To ascertain whether the reduction mechanism follows the above suggested pattern, the cyclic voltammograms of I at different scan rates (Fig. 4a, b) have been carried out in the
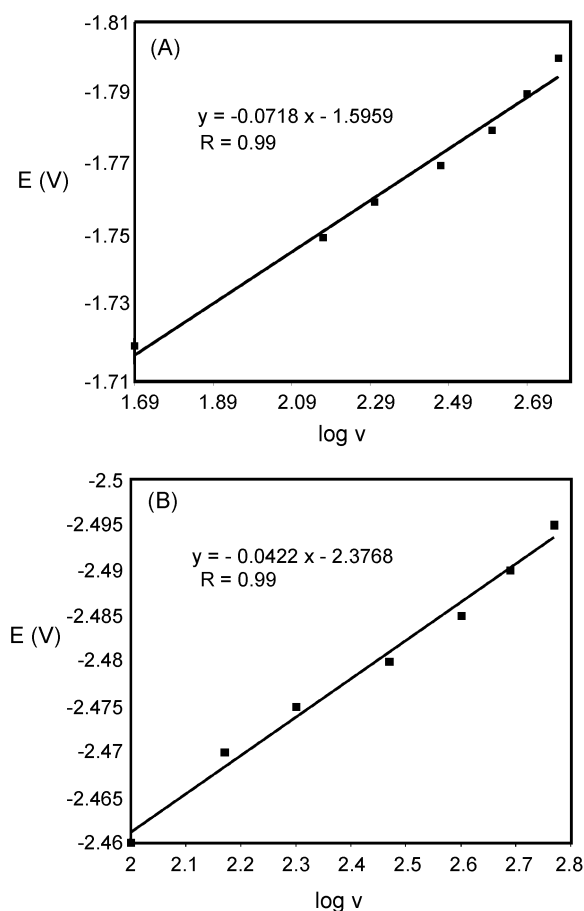
Table 1. The peak potentials of all three compounds

Ligand	E_p (DP)/V	E_p (CV)/V
I (1 st peak)	-1.61	-1.70
I (2 nd peak)	-2.40	-2.50
II (1 st peak)	-1.70	-1.62
II (2 nd peak)	-2.37	-2.43
III	-2.43	-2.48

potential range of first and second cathodic peaks. Figure 4c shows the current function ($i/v^{1/2}$) of the first cathodic peak *vs.* scan rate. As can be seen from this figure, the current function decreases with increasing scan rate, which confirms the presence of coupled chemical reaction following the electron transfer process, (EC mechanism). However, the current function of the more negative peak was constant for the range of the scan rate, which indicates that there was only an irreversible electron transfer without any coupled chemical reaction (E mechanism).[14,15]

The peak potentials of both peaks were shifted toward more negative values with an increase in the scan rate, indicating electrochemical irreversible processes ($\Delta E_p = 50$ mV for scan rate 50 to 600 mVs^{-1}). The extent of Ep shifts became greater with the increase in scan rate. This means that under these conditions the electrochemical processes are more irreversible.

For a totally irreversible electron transfer, the transfer coefficients (α) were calculated according to the following equation.[16]

$$E_p = (b/2) \log v + \text{const.}$$

Where, b is Tafel slope. The plot of E_p *vs.* logv is shown in Figure 5a, b. The slope of the linear plot is equal to $b/2 = 0.059/\alpha n$. So, $b = 2(0.059/\alpha n)$ V. The calculated transfer
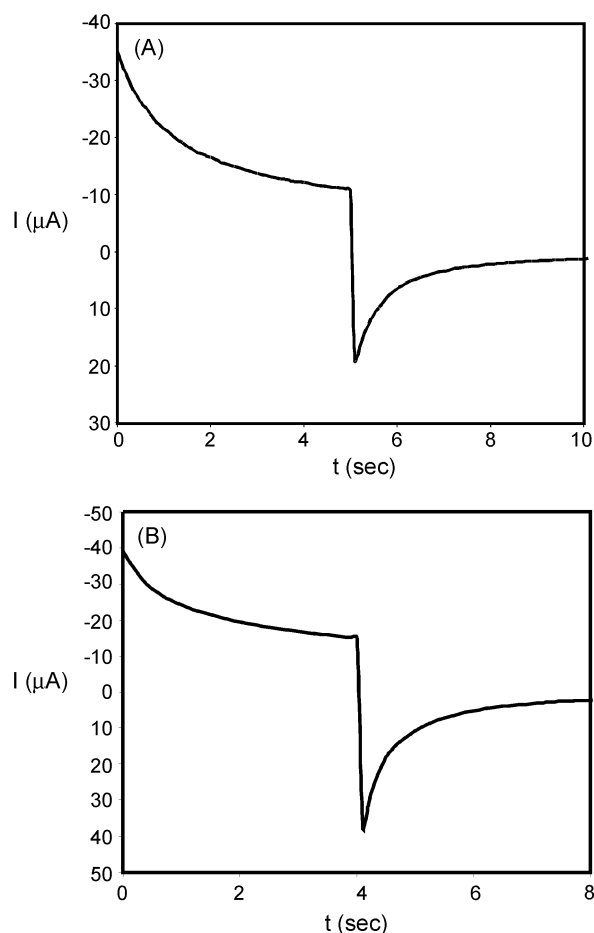
coefficients of the first peak of I and II are 0.41 and 0.44, and 0.35, 0.35, and 0.33 for the second peak in I, II, and III, respectively.

The transfer coefficients can also be obtained according to equation[15]:

$$\alpha = 1.857 \, RT/nF \, (E_p - E_{p/2})$$

Where $E_{p/2}$ is the half-peak potential. The observed values are 0.39, 0.56 for the first peak in I and II and 0.30, 0.30, and 0.59 for the second peak in I, II, and III, respectively.

Double-Potential Step Chronoamperometry. Double-potential step chronoamperometry has proven useful for investigating the EC mechanism. In the absence of a coupled chemical reaction the cathodic current, i_c, (after step potential, $E_s = -1.7$ V) and anodic current, i_a, (after final potential, $E_f = -1.0$ V, $\tau = 5$ s) are equal. However, the chronoamperograms of both I and II at first cathodic peak show that i_a/i_c decreases with increasing time due to the consumption of the product of electron transfer reaction in a following chemical reaction at long time (EC mechanism).[15] The chronoamperometry at the second cathodic peak of I and II and the only cathodic peak of III shows that the ratio

Figure 5. (A) The plot of E_p *vs.* logv for the first peak of compound I. (B) The plot of E_p *vs.* logv for the second peak of compound I.

Figure 6. (A) The double-potential step chronoamperogram of first cathodic peak of I. (B) The double-potential step chronoamperogram of the only cathodic peak of III. First cathodic peak of I: $E_i = -1.0$ V, $E_s = -1.7$ V and $E_f = -1.0$ V, $\tau = 5$ s. For compound III: $E_i = -2.0$ V, $E_s = -2.5$V and $E_f = -2.0$ V, $\tau = 4$ s.

i_a/i_c is equal to unit, which confirms the electron transfer process without coupled chemical reaction (E mechanism) for the second cathodic peak in all compounds. Figure 6 shows the chronoamperograms of I and III. The rate constant, k, can be obtained by employing the working curves, which show i_a/i_c as a function of $k\tau$ and t-τ/τ.[17] The rate constants of the formation of disulfide after one electron transfer in the first cathodic peak of I and II were found to be about 0.14 and 0.07 respectively, using the working curves.
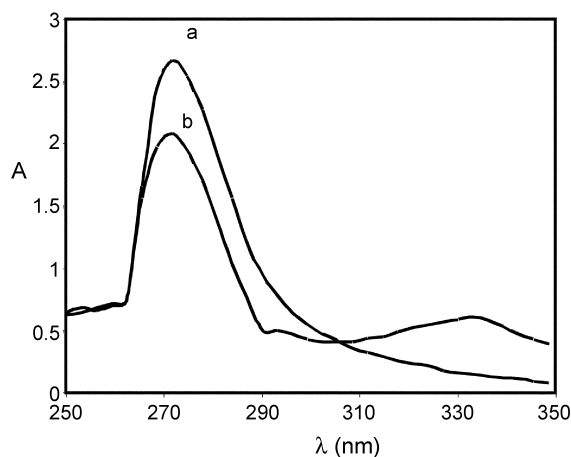
The diffusion coefficients can also be obtained by chrono-amperometry. An average value of $it^{1/2}$ over a range of time is determined at an electrode area that is accurately known and with a solution of known concentration by Cottrell equation.[15] The diffusion coefficients are 1.23×10^{-5}, 0.65×10^{-5}, 0.77×10^{-5}, 0.69×10^{-5} and 0.33×10^{-6} cm^{2}s^{-1} for I, II, and III, respectively.

Coulometry. The number of electron transfered in the two cathodic peaks were obtained by constant potential coulometry. The potential control was selected at -1.70 V, it was much more negative than the first peak in the voltammetric curves of I and II. Under this condition, the electrolysis proceeded completely and an overall number of 1 ± 0.1 mol of electrons per mol of molecule was obtained for both compounds of I and II. However, the overall electrons obtained on the second cathodic peak was 3 ± 0.1 mol electron per mol of I and II. By considering one electron in the first step the second peak involved a 2e-reduction process.

Coulometry at the controlled-potential of -2.55 V in compound III, showed the overall electron transfer of 2 ± 0.1 electron per molecule, which is in good agreement with the second peak in I and II.

UV Spectrophotometry. The UV-absorption spectrophotometric method was performed to prove more detailed information for the elucidation of the electrode processes.

Compounds I and II showed an absorption maxima situated at 270 and 273 nm, respectively, without any band in the range of 300-400 nm. The compounds, including -S-S-bond, showed a long-tail absorption band of about 310 nm,[18]
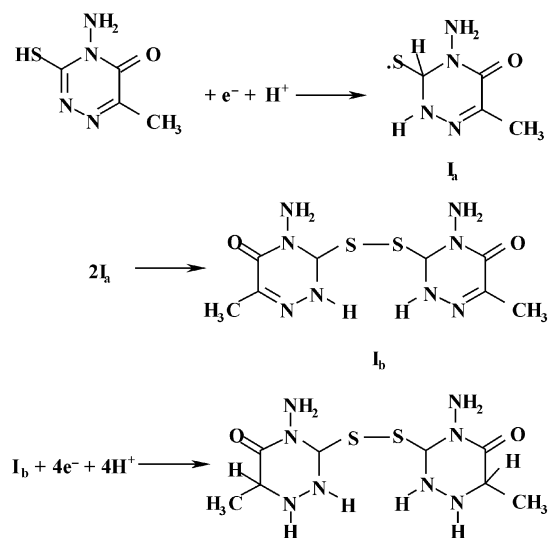
a good indication of the formation of disulfide during the electrolysis at a potential more negative to the first cathodic peak of I and II. The UV spectra of I before and after coulometry at -1.70 V are shown in Figure 7. With electrolysis beginning at -1.70 V, the absorption peak at 270 nm decreased and its location shifted toward longer wave-length near 330 nm, which is consistent with the formation of disulfide bond.[19] Compound II also showed similar behavior.

The UV spectra of solutions of III before and after electrolysis did not show an absorption peak at 330 nm, because there was no thiol group in its structure.

Mechanism. As shown previously in cyclic voltammetry, two cathodic peaks were demonstrated by both compounds I and II (with thiol group). The current function in the first diffusion-controlled peak decreased with increasing scan rate. On the other hand, the ratio of i_a/i_c in the chronoamperometry of the first peak was less than one, which indicates an EC mechanism. From the above results we have concluded that the reduction in the first cathodic peak followed the well-defined EC mechanism in thiol compounds[10-12] (Scheme 1).

According to the proposed mechanism one cathodic peak (due to the formation of dimer, I_b) would be expected to appear in the voltammograms of I and II due to the thiol group. Formation of I_b would consume one mol of electron per mol of I_a, which agrees with the experimental n value of 1 ± 0.1. The identification of disulfide in the first reduction was based on UV-experiments. In UV-spectra, electrolytic reduction caused the appearance of a long-tail absorption peak at 330 nm, which is characteristic of the -S-S- bond.[18,19] At the second peak of I and II, the azomethine in each monomer of dimer was reduced in 2e process (4 electrons per mol of dimer, I_c, or two electrons per mol of monomer), whereas the azomethine in compound III was reduced in only one reduction step (Scheme 1).

The E mechanism in the second peak was confirmed by cyclic voltammetry (constant $i/v^{1/2}$ *vs* scan rate) and chronoamperometry (the ratio $i_a/i_c = 1$). To prove that the 2e-

Figure 7. The Uv-absorption spectra of I (a) before electrolysis at E = -1.70 V, (b)After electrolysis.

Scheme 1

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reduction step is due to azomethine bond in the triazine ring, the cyclic voltammogram of a similar compound without any azomethine (compound IV) was recorded, showing no reduction peak at potential range -1.20 to -2.80 V.

The peak height of the second peak is twice that of the peak height of the first peak in I and II. At the first peak, $n_1 = 1$ with the concentration of C_1, whereas in the second peak each monomer in the resulting dimer in the first step, was reduced in 2e, with $n_2 = 4$ for the concentration of $C_2 = C_1/2$. Thus, $i_2/i_1 = n_2 C_2/n_1 C_1 = 4 (C_1/2)/1 C_1 = 2$.

Conclusion

The electroreduction of I and II follows a well-defined mechanism in thiol compound. At the potential of the first peak, the uptake of one electron gives a radical that dimerizes to disulfide. The azomethine in each monomer of dimer reduces in 2e process. Compound III shows only one reduction peak due to an azomethine moiety. The diffusion constants, transfer coefficients, and the rate constants of coupled chemical reaction in EC mechanism were also obtained.

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