Electrochemical Studies of Thiourea at Hanging Mercury Drop Electrode

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SEVERAL papers (1–4) on polarography of thiourea have been published, but non of the workers proposed a complete mechanism of the electrode reaction. Only recently (3) it has been agreed that the reaction mechanism involves mercury salt formation according to.

$$Hg \rightleftharpoons Hg^{+2} + 2e$$
$$Hg^{+2} + J\,(T.U) \rightleftharpoons Hg\,(T.U)_J^{2+}$$
where J = 2,3 or 4.

According to Nyman & Parry (2), the oxidation of T. U. in 1M HNO_3 is practically instantaneous. However, our present work employing cyclie voltammetry revealed that the oxidation of thiourea in 0.1M HNO_3 is negligible even after 48 hours.

In the present work we have studied the electrochemical behaviour of thiourea employing cyclic voltammetry, chronoamperometry and chronopotentiometry at HMDE in different supporting electrolytes, in order to elucidate the electrode mechanism.

EXPERIMENTAL

Electroscan 30 (Backman) was used in all the experiments. A tridentate cell, constructed for this work, has three compartments which was made by fusing GI frit in the two side arms. A paste of agar-agar in saturated KNO_3 was poured in two arms. On the top of the paste, saturated KNO_3 solution was poured. The auxiliary Pt electrode and reference SCE were connected with U tube filled with KNO_3 agar bridge to prevent chloride contamination. The sample solution was taken in middle compartment and deaerated with purified nitrogen gas before each experiment. AnalaR grade chemicals were used.

Thiourea was recrystallized from water and dried at room temperature in a vacuum descicator, Stock solutions were prepared from this, by weighing out appropriate amounts and diluting to desired volumes.

RESULTS AND DISCUSSION

Cyclic Voltammetry and Chronoamperometry : Cyclic voltammograms of thiourea (0.4 mM to 1.6 mM) in 0.1M $HClO_4$, 0.1M H_2SO_4, 0.1 M HNO_3 and 0.1 M KNO_3 were recorded at various scan rates, ν (Fig. 1a). The plot of i_p, $\nu^{\frac{1}{2}}$ vs $\nu^{\frac{1}{2}}$ was a

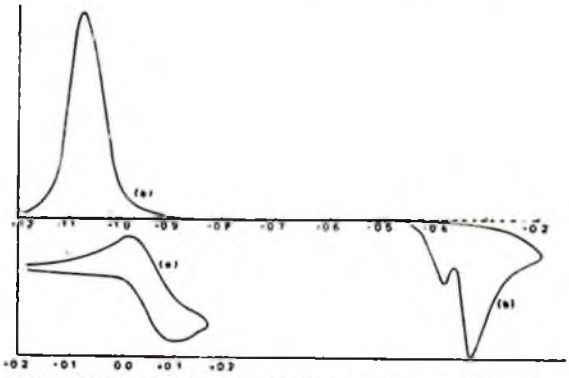


FIG 1 CYCLIC VOLTAMMOGRAM OF 0.4mM THIOUREA IN (a) 0.1M HNO_3 (b) 0.1M NaOH
SCAN RATE = 20 mV/sec SENSITIVITY = 14 μA

straight line parallel to $\nu^{\frac{1}{2}}$ axis. This showed that the electrode reaction is diffusion controlled in all the suppofting electrolytes.

The ratio of cathodic to anodic peak currents was 1.1 ±0.02 and $(E_p - E_{p^{\frac{1}{2}}})$ was about 45 mV which showed that the reaction was of the second order (5) and reversible. The proportionality between i_p and concentration in all the supporting electrolytes was found to be satisfactory.

Cyclic voltammetric and chronoamperometric experiments were performed successively using the same solution. The slope of i_c vs $\frac{1}{t^{\frac{1}{2}}}$ during the constant potential experiments and slope of i_p vs $\nu^{\frac{1}{2}}$ values from the linear scan experiments were confirmed and equivalent of $\sqrt{\pi \times (at)}$ was calculated without having to determine independently and accurately the individual values of concentrations, diffusion coefficient or electrode area. The

Value of $\sqrt{\pi}\chi$ (at) thus obtained was 0.35 ± 0.01 where χ (at) is a dimansionless parameter [5] and related to the current by

$$i_l = nFA\ Co\ \sqrt{\pi D_a a}\ \chi\ (at)$$

The value of $\sqrt{\pi}\chi$ (at) = 0.35 proved that the stoichiometric number of thiourea taking part in the electrode reaction is two with the formation of $Hg\ (T.U.)_2^{2+}$ complex as

$$Hg + 2\ (T.U.) \rightleftharpoons Hg\ (T.U.)_2^{2+} + 2e$$

The maximum value of $\sqrt{\pi}\chi$ (at), 0.3533, has been derived by Shuman [5] for a reversible electrode reaction of second order.

The constancy of anodic and cathodic peak potentials is supporting electrolytes such as 0.1M HNO_3, 0.1M $HClO_4$, 0.1M, H_2SO_4 and 0.1M KNO_3 showed that the electrode process is independent of pH upto 7.

In 0.1M NaOH, two anodic peaks were obtained at —0.4 and —0.33 V *vs* SCE for 0.4 mM T.U. at the scan rate of 0.01 V/sec. Only one cathodic peak, however, was obtained at ~ —1.05V [Fig. 1(b)]. The i_p for the prepeak (—0.04 V) was found to be propotional to, ν, scan rate, while that for the second peak was found to be proportional to the $\sqrt{\nu}$ which shows that the prepeak may be due to the adsoprtion of thiourea and the second peak is due to the diffusion process. ΔE_p, the difference between anodic and cathodic peak potentials was about 600 mV indicating irreversibility of electrode process. The cathodic peak current is more that the anodic peak current indicating the formation of insoluble compound at the electrode surface. This was coroborated by the chronopotentiometric data. The insoluble compound might be HgS formed by the following reaction.

$$S : C(NH_2)_2 + 2H_2O \xrightarrow{NaOH} CO_2 + H_2S + 2NH_3$$

$$Hg + HS^- + OH^- \longrightarrow HgS + H_2O + 2e$$

The T.U. solution in 0.1M NaOH was electrolysed at —0.1V for about 15 minutes. The surface of the mercury drop turned black. Further, mercury and thoiurea solutions were mixed in alkaline medium, a black ppt. was formed which showed the presence of sulphide. This shows that the insoluble compound was HgS.

Chronopotentiometry: Chronopotentiograms and current reversal chronopotentiograms of thiourea (0.4 mM to 1.6 mM) were recorded in 0.1 M HNO_3 0.1 M H_2SO_4, 0.1 M $HClO_4$ and 0,1 M KNO_3 (Fig. 2(a), The $E\tau/_4(_a)$ and $E\tau/_4(_c)$

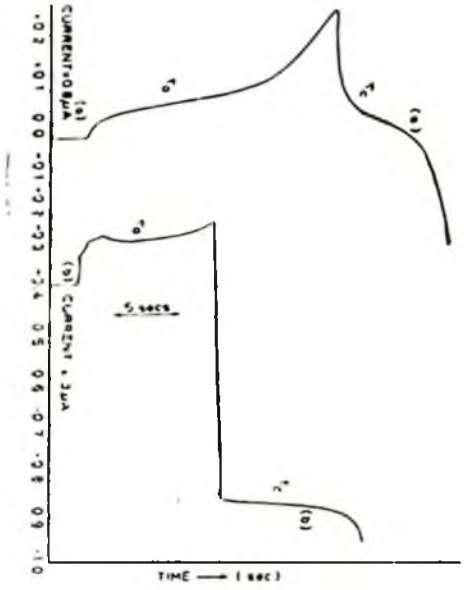


FIG. 2 CHRONOPOTENTIOGRAMS OF (a) 0.4mM THIOUREA IN 0.1M $HClO_4$ AND (b) 1.2mM THIOUREA IN 0.1M NaOH A = 0.02613 cm^2

were almost equal. The ratio of the forward transition time (τ_f) to reverse transition time (τ_r) is about 3, indicating the solubility of reaction product and reversibility of electrode reaction It was also found that the $i\tau_a^{1/2}/Co^*$ ratio was independent of the $1/Co^*$ ratio and that τ_a/τ_c ratio was always equal to 3 ± 0.2 being unaffected by changes in τ_c. These facts indicate the absence of any kinetic or catalytic process interfering with the electrode reaction [6,7].

A plot of $\log \frac{(\tau_{\frac{3}{4}}^{\frac{1}{2}} - t_{\frac{1}{4}}^{\frac{1}{2}})'}{t_{\frac{1}{4}}^{\frac{1}{2}}}$ Vs E gave a slope of about 30 mV which confirms that the electrode reaction is of second order[8] involving two electrons as

$$Hg + 2\ (T.U.) \rightleftharpoons Hg\ (T.U.)_2^{2+} + 2e$$

In alkaline medium (0.1 M NaOH), the ratio ($\tau a/\tau c$) is almost unity indicating the insolubility of reaction product at the electrode surface[8]. The quarter wave potentials of forward and reverse cycle differ by about 600 mV. This indicates that the electrode process is irreversible. The shape of chronoamperograms is abnormal as shown in Fig. 3(b).

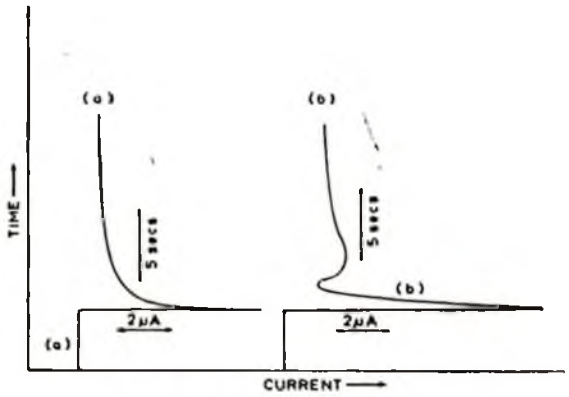


FIG 3 CHRONOAMPEROGRAMS OF 0.4mM THIOUREA IN (a) 0.1M KNO_3 AT +0.20V (b) 0.1M IN NaOH AT -0.30V A = 0.02613 cm^2

The values of diffusion coefficients in various supporting electrolytes obtained by chronoamperometric and chronopotentiometric data are given below.

S.E.	D (by chrono-amperometry (cm^2 sec)	D (by chrono-potentiometry (cm^2 sec)
0.1 M $HClO_4$	1.12×10^{-5}	1.13×10^{-5}
0.1 M H_2SO_4	1.4×10^{-5}	1.3×10^{-5}
0.1 M KNO_3	1.35×10^{-5}	1.32×10^{-5}
0.1 M NaOH	—	1.19×10^{-5}

SUMMARY AND CONCLUSION

The cyclic voltametric and chronopotentiometric data of T.U. in acidic and in 0.1 M KNO_3 media, indicate that the electrode reaction is reversible and diffusion controlled. The product of electrode reaction is the soluble species, $[Hg(TU)_2^{2+}]$. The electrode reaction is of second order involving two electrons.

In alkaline medium, the electrode process is totally irreversible. The reaction product is insoluble which was confirmed to be HgS.

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REFERENCES

1. R. I. Edsgberg, *Anal. Chem.* 26 (1954) 724.
2. C. J. Nyman and E. P. Parry, *Anal. Chem.* 30 (1958) 1255.
3. Halcolm R. Smyth & Janet G. Osteryoung. *Anal. Chem.* 49 (1977) 2310.
4. C. A. Mairesse-Ducarmois, J. L. Vandenblack et G. J. Ratriarche, *Electrochimica Acta.*, 23 (1978) 95.
5. M. S. Shuman, *Anal. Chem.*, 41 (1969) 142.
6. P. Delahay and T. Berzins, *J. Amer. Chem. Soc.*, 75, 2486 (1953).
7. C. Furlani and G. Morpurgo, *J. Electroanal. Chem.*, 1, 351 (1959-60).
8. W. H. Reinmuth, *Anal. Chem.*, 32 (1960) 1514.