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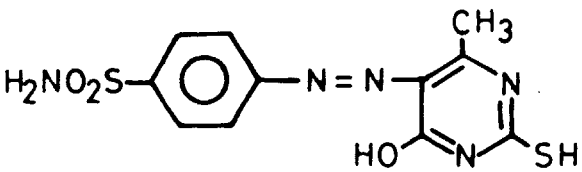
ELECTROCHEMICAL STUDIES ON 4-HYDROXY-2-MERCAPTO-6-METHYL-5-SULPHONAMOYLAZO-PYRIMIDINE

RAJEEV JAIN AND H K PARDASANI

School of Studies in Chemistry, Jiwaji University, Gwalior-474 011, India

Introduction

Aromatic azo compounds have been the subject of many investigations during the last decade[1-4]. Recently, heterocyclic azo compounds have received much attention[5-7]. However, a literature survey reveals the absence of systematic electrochemical study on sulphonamoylazopyrimidines, a class of compounds which have several interesting applications in the field of medicine. In view of the fact that the physiological activity of a molecule is closely related to its redox behaviour in the cell membrane, it was considered worthwhile to study the redox behaviour[8] of a representative member of the class at the glassy carbon and dropping mercury electrodes.



Experimental

4-Hydroxy-2-mercapto-6-methyl-5-sulphonamoylazopyrimidine was synthesised by the method reported from this laboratory[9]. The purity of the compound was ascertained by recrystallisation and TLC. Stock solution (1.0×10^{-3} M) of the arylazopyrimidine was prepared in acetonitrile. All chemicals used were of A.R. grade.

Polarograpic measurements were done on an ELICO-DC CL-25 pen recording polarography. The capillary had a flow rate of 1.25 mg/sec mercury and drop time 2.66 seconds at a zero applied potential *vs.* S.C.E. in 1.0 M KCl solution at a height of 65 cm of mercury column. The polarograms were recorded at 25 ± 1.0°C. The *p*H metric measurements were made on an ELICO-LI-15 expanded scale *p*H meter fitted with a glass electrode and saturated calomel electrode was used as a reference electrode.

Stock solution of the above compound (1.0×10^{-3} M) was prepared in purified[10] N,N-dimethylformamide and acetonitrile (AnalR). In order to evaluate the effects of varying acid strength on this compound, Britton-Robinson buffers[11] in the *p*H range 2.0-12.0, were prepared in doubly distilled water using

*Author for correspondence.

AnalR grade chemicals. For preparing the solutions for polarographic study, 1.0 ml of the depolarizer, 2.0 ml of the DMF (which was necessary to prevent precipitation), 1.0 ml of KCl (1.0 M) and 6.0 ml of the appropriate B.R. buffer were taken in the polarographic cell. The solution was deaerated[12] by passing purified nitrogen gas for about ten minutes and corrections for residual current were made in all the cases. Temperature coefficient was calculated by Nejedly's method[13].

Cyclic voltammetric studies were carried out on a BAS CV-27 cyclio voltammograph in connection with a digital electronic 2000 Omnigraph X-Y/t recorder. The details of experimental set up have been described elsewhere[14].

Results and Discussion

The polarograms of 4-hydroxy-2-mercapto-6-methyl-5-sulphonamoylazopyrimidine were recorded in the *p*H range 2.0-12.0 in 30% dimethylformamide solutions. Electrochemical characteristics have been given in Table I. This compound displayed a single well-defined polarographic wave, the height of which was practically constant within the whole *p*H range. The nature of the wave was investigated through the dependence of the limiting current on the height of the mercury column and on the temperature. The characteristics of polarographic waves were evaluated at various temperatures and at heights of mercury column. The limiting current was found to be diffusion-controlled as evident by the linear plots of i_d *vs* $\sqrt{h}$ (Fig. 1) and the low value of temperature coefficient (below 1.61%/°C). The shift of half-wave potential towards more negative values with increasing concentration of the depolarizer (0.5×10^{-4}M-2.0×10^{-4}M) and logarithmic analysis (by plots of $\log i/i_d - i$ *vs* E) confirmed the irreversible nature of the electrode process.

The $E_{1/2}$ shifted towards negative potential with the increase in *p*H of the solution. The plots of $E_{1/2}$ *vs* *p*H were linear upto *p*H 8.1 with slopes in the range of 0.042 to 0.05 V/*p*H (Fig. 2). Two linear segments intercept at *p*H 8.1, a value which is in accord with the *p*K value. The shift of $E_{1/2}$ with increasing *p*H indicated the participation of protons in the reduction and this led to the conclusion that the proton transfer precedes the main electrode process. Above *p*H 8.1, the $E_{1/2}$ becomes independent of *p*H. This indicated the reduction of

Table I

Polarographic characteristics of 4-hydroxy-2-mercapto-6-methyl-5-sulphonamoylazopyrimidine at p H 5.6, Conc. = 1.0×10^{-4} M

$-E_{1/2}$, V	0.67
i_d, μA	0.40
E_p, V	0.70
i_p, μA	2.42
$dE_{1/2}$, V	
*dp*H, *p*H	0.080
an	0.60
$I \times 10^3$	2.92
P	1.03

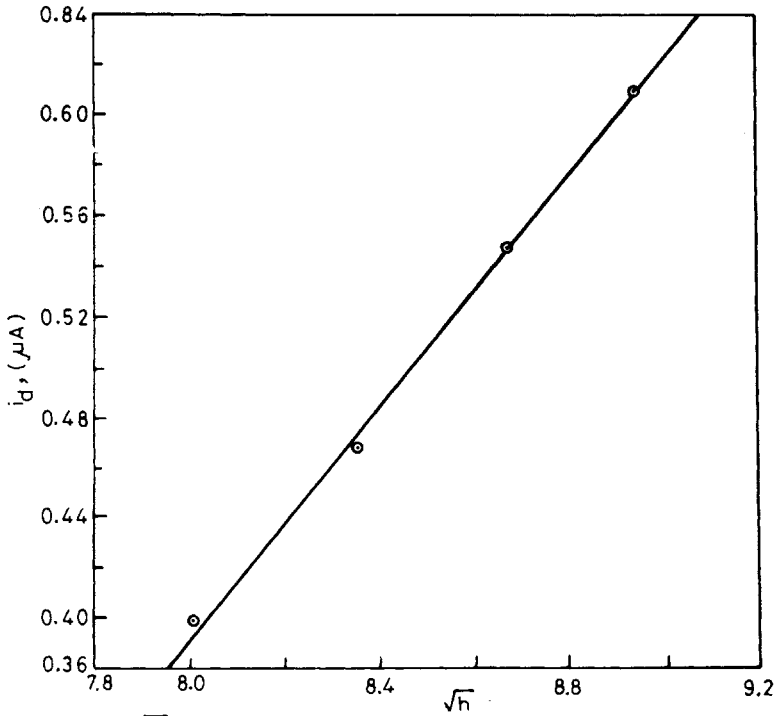


Fig 1 Plot of i_d vs $\sqrt{h}$ for 4-hydroxy-2-mercapto-6-methyl-5-sulphonamoyl azopyrimidine at various heights of mercury column; *p*H 5.6; Conc. = 1.0×10^{-4}M.

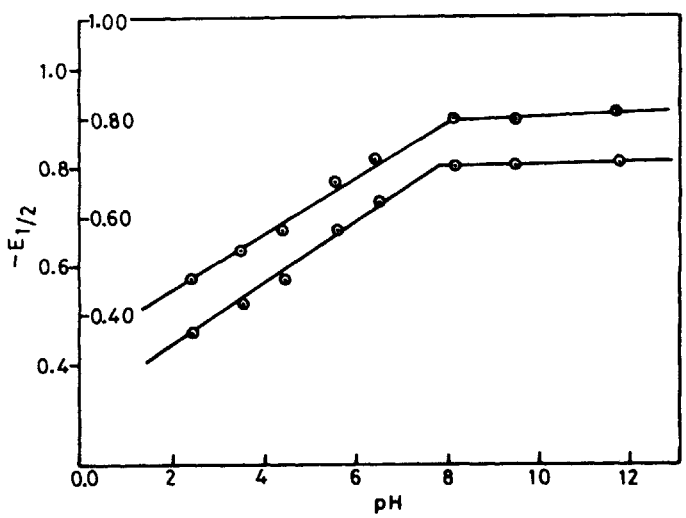


Fig 2 Plots of $-E_{1/2}$ vs *p*H for 4-hydroxy-2-mercapto-6-methyl-5-sulphonamoylazopyrimidines.

R = (1) H; (2) $H_2N-\overset{\overset{NH}{\|}}{C}-$; Conc. = 1.0×10^{-4} M.

unprotonated species. Similar dependence of half-wave potential on *p*H has also been reported by other workers in case of azo compounds[16-18].

Controlled potential electrolysis of the compound at the plateau potential (~1.2 V) using the mercury pool cathode consumed 2.0 electrons. The colour of the starting material faded out at the end of the electrolysis. A polarogram and cyclic voltammogram of the completely reduced solution did not show any reduction peak. This clearly indicates that no electroactive species remained in the solution after complete electroreduction of the compound.

The values of αn_a (product of transfer coefficient and number of electrons involved per molecule of the reactant) and of P (number of protons involved per molecule of the reactant in the rate determining step) were calculated using the following equation[15]:

$$\alpha n_a = -0.0517/E_{1/4} - E_{3/4}$$

and

$$P = (dE_{1/2}/dpH)\alpha n_a/0.0591.$$

Cyclic voltammetry of this pyrimidine derivative was performed at glassy carbon electrode in the pH range 2.0-12.0. Some typical cyclic voltammograms are shown in Fig. 3. The voltammograms were recorded at various scan rates

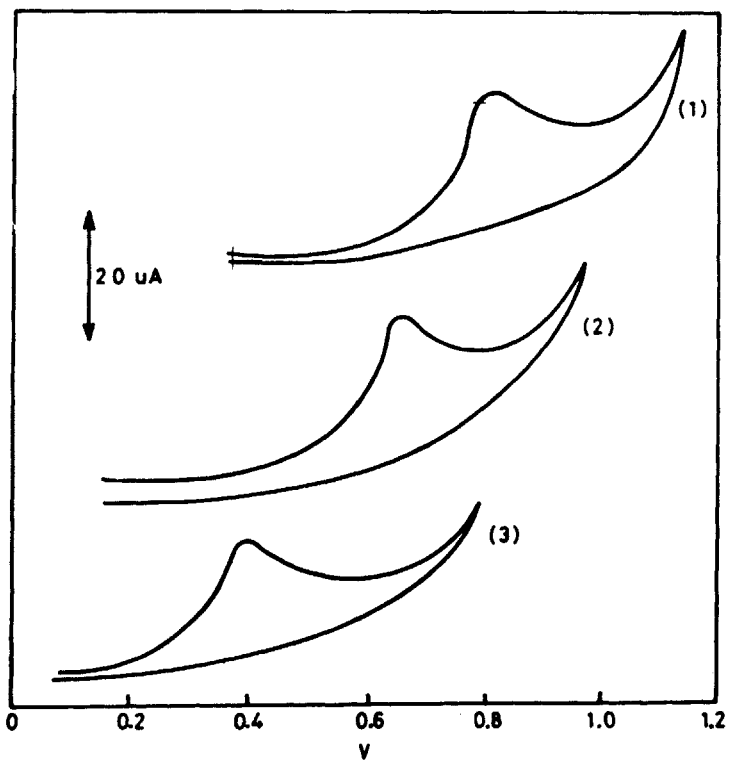


Fig 3 Cyclic voltammograms of 4-hydoxy-2-mercapto-6-methyl-5-sulphonamoyl azopyrimidine at pH (1) 3.6; (2) 5.6; (3) 8.3; Conc. = 1.0×10^{-4}M, ν = 50 mV/s.

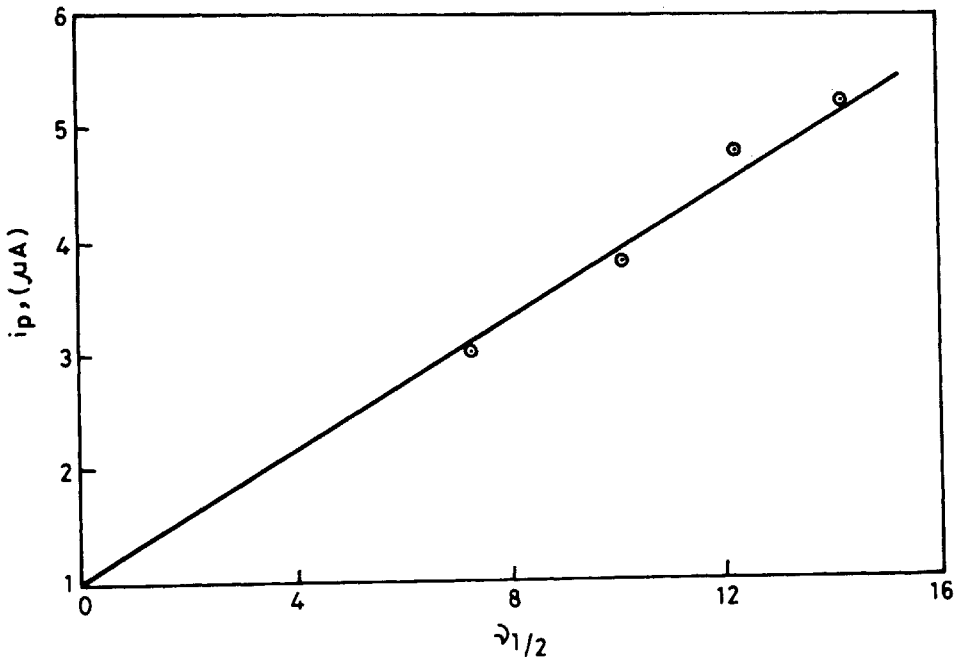
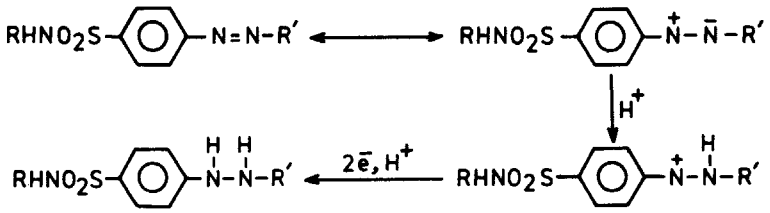


Fig 4 Plot of i_p vs $\nu_{1/2}$ for 4-hydroxy-2-mercapto-6-methyl-5-sulphonamoylazopyrimidine at *p*H 8.3; Conc. 1.0×10^{-4}M.

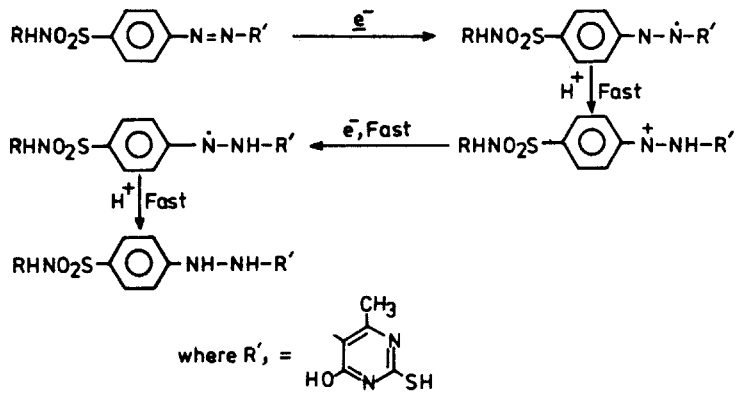
(50-200 mV/sec) and scan ranges. At different scan rates this compound showed only one voltammetric reduction peak at the glassy carbon electrode. The plots of i_{pc} *vs* $\nu^{1/2}$ (scan rate) were found to be straight lines passing through the origin which indicate diffusion-controlled[19] nature of the electrode process (Fig. 4). Further, the effect of change of concentration of these compounds on diffusion current has been examined. The plot of i_d *vs* concentration was a straight line indicating towards the diffusion-controlled nature[19-21] of the electrode process. On the reverse scan no anodic peak could be observed indicating irreversible nature of the electron transfer step as also supported by D.C. polarography.

Keeping in view of the feasibilities[6] of the site of reduction, it was concluded that $-N=N-$ is more susceptible[6] to reduction as its reduction occurs at low potential. Hilson and others[22,23] have reported that reduction of azo compounds takes place in a 2-electron wave at the $-N=N-$ group giving the hydrazo derivative. Nygrad[24] has reported that reduction of azo benzene gives a reversible 2-electron wave at low concentration and low *p*H. The existence of a single irreversible wave observed for this compound may be attributed to the bulky pyrimidine substituent in the molecule.

As the number of electrons involved in the reduction are two and the number of protons involved in the rate determining step is one, and only one product is obtained after exhaustive electrolysis, the following mechanism may be proposed for the reduction of the compound at both the electrodes.



For pH independent ($<p$H 8.1) 2e wave following mechanism may be proposed:



Cyclic voltammetry and DC polarographic studies clearly indicate that at Glassy Carbon (GC) and D.M.E. the compound exhibits diffusion-controlled and irreversible waves. At both the electrodes $E_{1/2}$ and E_p values shift upto pH 8.1 and after that there is a little change in $E_{1/2}$ and E_p values. Similarly, controlled potential electrolysis was carried out at d.m.e. as well as g.c. electrodes. Analysis of products of c.p.e. gave similar results indicating that mechanism of reduction is same at both the electrodes.

The solutions obtained after controlled potential electrolysis at D.M.E. and G.C. electrodes gave negative test for amino group thereby showing that after reduction of $-N=N-$ to $-NH-NH-$ further reduction to aromatic amine does not take place (as also confirmed by the fact that the number of electrons involved is only 2). Furthermore, the above-mentioned electrolysed solution did not give any polarographic or cyclic voltammetric peak, thereby confirming the above reduction mechanism. This mechanism is further supported by the work of others[25,26].

Effect of Solvent Composition

The nature and amount of the solvent can affect the half-wave potential and limiting current[27]. The behaviour as usually observed by changes in both $E_{1/2}$ and i_d was found in the present case. With the increase in the percentage of DMF, the $E_{1/2}$ shifted towards more negative potential with simultaneous decrease in i_d (Table II).

Table II

Effect of increasing percentage of DMF on the polarographic reduction of 4-hydroxy-2-mercapto-6-methyl-5-sulphonamoylazo-pyrimidine at pH 5.6, conc $= 1.0 \times 10^{-4}$ *M*

S. No.	DMF	$-E_{1/2}$, V	i_d, μA
1	30	0.67	0.40
2	40	0.69	0.37
3	50	0.72	0.35
4	60	—	—
5	70	0.74	0.33
6	80	0.75*	0.33

*Drawn out waves.

An increase in the organic solvent content results in a rise in *p*H[28] and in an increase in the dissociation constant of the protonated species[29]. Both these factors lower the rate of protonation and consequently would lead to a shift in half-wave potential of the wave towards more negative potential in all such cases where protonation precedes the electron transfer. It appears that these two factors are not the only one responsible for the observed shift in $E_{1/2}$ because the resulted shift is greater than what it would have been due to change in *p*H and the dissociation constant. An increase in percentage of DMF from 30% to 60% resulted in an increase of *p*H by 1.10 unit.

This additional shift in $E_{1/2}$ may be ascribed to a decrease in adsorbability on the basis of i_p *vs* $v^{1/2}$ plots and hence surface concentration of the depolarizer with an increasing percentage of DMF in aqueous organic mixture[30]. Obviously, decreased surface concentration would retard the electrode process[31] resulting in decrease in $E_{1/2}$ and i_d.

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