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Electrochemical studies on some synthesised N-sulphonamoylphenyl-3-aminophenyl-5-methyl-4-[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles

Pratibha Sharma*, Archana Dave, Nirankar N Mishra, Sandeep R Narad & Neeta Kapoor

Microanalysis Research Laboratory, Institute of Chemical Sciences, D A University, Indore 452 001, India

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Present note deals with the electrochemical behaviour of N-sulphonamoylphenyl-3-aminophenyl-5-methyl-4 -[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles. All the studies have been carried out in DMF-water admixture using Britton-Robinson buffers of varying *p*H. A single, well defined, diffusion-controlled reduction wave is obtained which shifted towards more negative potential with increase in the *p*H. On the basis of number of protons consumed and electron transferred, a plausible mechanism has also been suggested.

A systematic perusal of earlier literature reveals that inspite of the pharmaceutical importance associated with arylazo compounds, relatively few reports[1-3] exist on the electrochemical behaviour of azo compounds having heterocyclic moiety attached at one of the ends of azo group. However, electrochemical studies on aromatic azo compounds have been the subject of many investigations during the last few years[4-8]. Hence, it was thought worthwhile to undertake systematic and comprehensive electrochemical studies on some synthesised N-sulphonamoylphenyl-3-aminophenyl- 5 -methyl-4-[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles(I) with a view (i) to decide about the fate of electroreduction process, (ii) to elucidate the mechanism of electroreduction, and (iii) to find out the effect of vairous experimental conditions.

Experimental

All the chemicals used were of AR grade. The purity of all the synthesised compounds was ascertained by recrystallization and TLC (xylene : ethyl acetate = 7 : 3). Stock solutions (1×10^{-3} *M*) of all the substituted N-sulphonamoylphenyl- 3 -aminophenyl- 5 -methyl-4-[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles were prepared in DMF. Potassium chloride (1.0 *M*) was used as a supporting electrolyte to maintain the ionic strength as well as to eliminate the effect of migration current. Britton-Robinson (BR) buffer[9] of different *p*H (2.0-12.0) values were prepared in distilled water. Test aliquots were prepared by taking 1.0 ml aliquot of stock solution mixed with 2.0 ml of DMF, 1.0 ml of potassium chloride and 6.0 ml of BR buffer solution of desired *p*H value. The solutions were deaerated by purging a stream of nitrogen gas for 15 min before recording the current-voltage curves. Cyclic voltammetric (CV) studies were carried out on computerised VSM/EC/30-S potentiostat and polarograms were recorded on Toshinwal digital polarograph. The capillary characteristic ($m^{2/3}\ t^{1/6}$) was 1.18 $mg^{2/3}\ s^{-1/2}$ in 1 *M* KCl solution. A three electrode cell assembly was used for the purpose. Saturated calomal and silver/silver chloride electrodes were used as reference electrodes whereas dropping mercury and glassy carbon electrodes served the purpose of working electrode for D C polarographic (DCP) and cyclic voltammetric measurements, respectively.

Results and discussion

All the substituted arylazopyrazoles reduced in a one well defined wave in the *p*H range 2.0-12.0. An overview of polarograms is exhibited in Fig. 1.

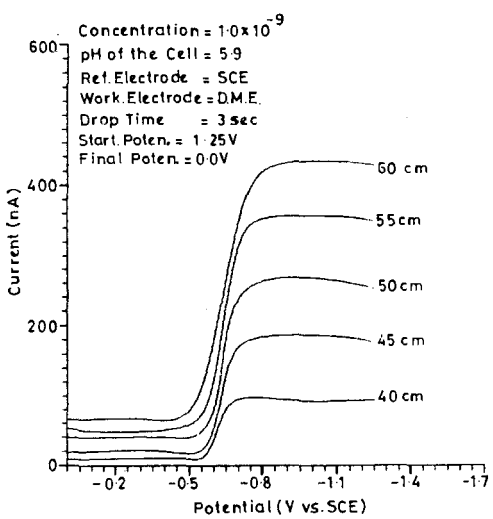


Fig. 1—Polarograms of N-4′-(2″-methiazolyl)sulphonamoyl phenyl- 3 -aminophenyl- 5 -methyl-4′-(2″-pyrimidinyl)sulphonamoyl phenylazopyrazoles at different height of DME

The wave height was found to be diffusion controlled as evidenced by the linearity of plots of i_d versus $\sqrt{h}$ and the shift of $E_{1/2}$ towards more negative potential with increasing concentration of the depolarizer. The cyclic voltammograms of substituted N-phenylsulphonamoylpyrazoles in buffer solutions of *p*H 2.0-12.0 were recorded at different scan rates and concentrations. At different scan rates, all these compounds showed only one voltammetric reduction peak at the glassy carbon electrode. The cathodic peak potentials of the waves were found to shift towards more negative potential and on reversing the scan no anodic peak could be observed with increase in scan rate indicating that the process was irreversible. The typical cyclic voltammogram of N-sulphonamoylphenyl-3-aminophenyl- 5 -methyl-4-[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles at scan rates of 20 mV s^{-1} and 100 mV s^{-1} is shown in Fig. 2. The dependence of peak current (i_p) on the square root of scan rate ($\nu^{1/2}$) was found to be linear passing through the origin indicating diffusion-controlled nature of the electrode process.

Mechanism of electrode process

Keeping in view the feasibilities of the different

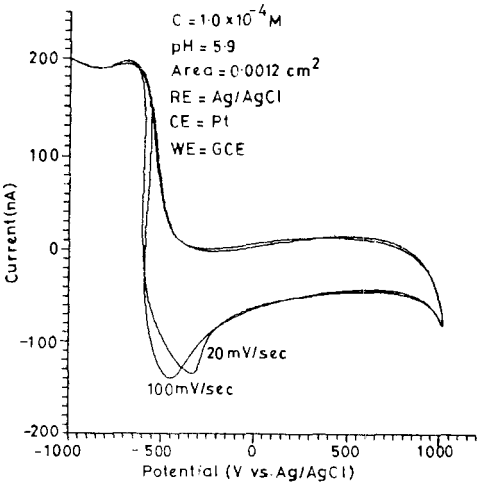


Fig. 2—Cyclic voltammogram of N-4′-(2″-methiazolyl)sulphonamoyl phenyl-3-aminophenyl-5-methyl-4′-(2″-pyrimidinyl)sulphonamoyl phenylazopyrazoles

Table 1—Electrochemical characteristic of some N-sulphonamoylphenyl-3-aminophenyl-5-methyl-4-[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles at *p*H 5.92, $C = 1.0 \times 10^{-4}$ *M*

R	$-E_{1/2}$ (V)	i_d (uA)	$E_{1/2}$ (V)	$\Delta E_{1/2}$ (V)	d*p*H *p*H	$Do^{1/2}$ cm^2/sec ($\times 10^{-3}$)	$K^0_{f,h}$ cm/sec ($\times 10^{-6}$)	pK_a	I
I	0.59	3.35	0.00	0.042	0.516	4.66	2.24	8.80	2.83
II	0.60	3.14	−0.01	0.045	0.602	4.76	6.63	9.20	2.66
III	0.60	3.39	−0.01	0.052	0.602	4.74	1.27	9.10	2.87
IV	0.62	2.71	−0.03	0.038	0.542	3.77	6.67	9.00	2.29
V	0.58	2.62	0.01	0.058	0.516	3.64	2.11	8.70	2.22
VI	0.63	3.33	−0.04	0.055	0.542	4.63	6.64	8.20	2.82
VII	0.68	2.72	−0.09	0.046	0.542	3.78	1.88	8.60	2.30
VIII	0.60	2.57	−0.01	0.040	0.542	3.57	1.19	7.80	2.17
IX	0.62	2.92	−0.03	0.038	0.542	4.06	1.05	8.00	2.47
X	0.63	2.90	−0.04	0.048	0.502	4.33	7.67	8.90	2.45

sites of reduction on the basis of DCP, CV and CPE viz., $-N=C-$ or $-C=C-$ of the ring or the extranuclear $-N=N-$, it was inferred that possible reduction site is $-N=N$[10], since $-C=N$ and $-C=C-$ require much higher potential for reduction. The dependene of wave height and half-wave potential on *p*H was investigated in buffer solution of varying *p*H (2.0-12.0). For all the compounds the wave height was practically independent of *p*H, whereas half wave potential shifted towards negative side with increase in *p*H (Table 1; Fig. 3). To get an indication of reversibility, the polarograms of these compounds were taken at different concentrations of depolarizer. The concentration was varied in the range 0.5×10^{-4} *M*-2.0×10^{-4} *M*. The shift of $E_{1/2}$ towards more negative potential with increase in concentration, from 0.5×10^{-4} *M* to 2.0×10^{-4} *M* indicates irreversible nature of the process. Since

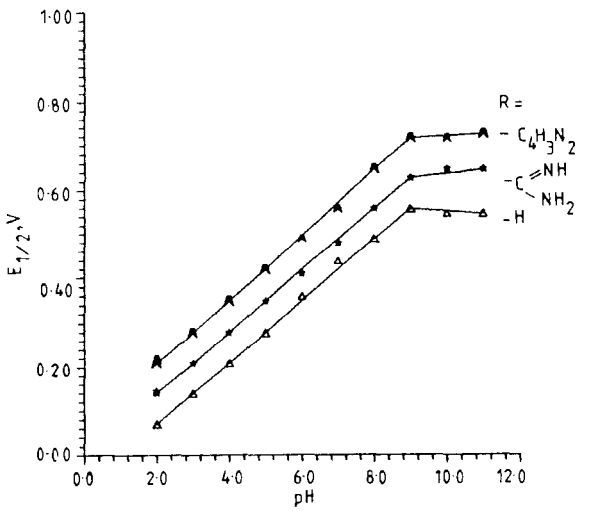
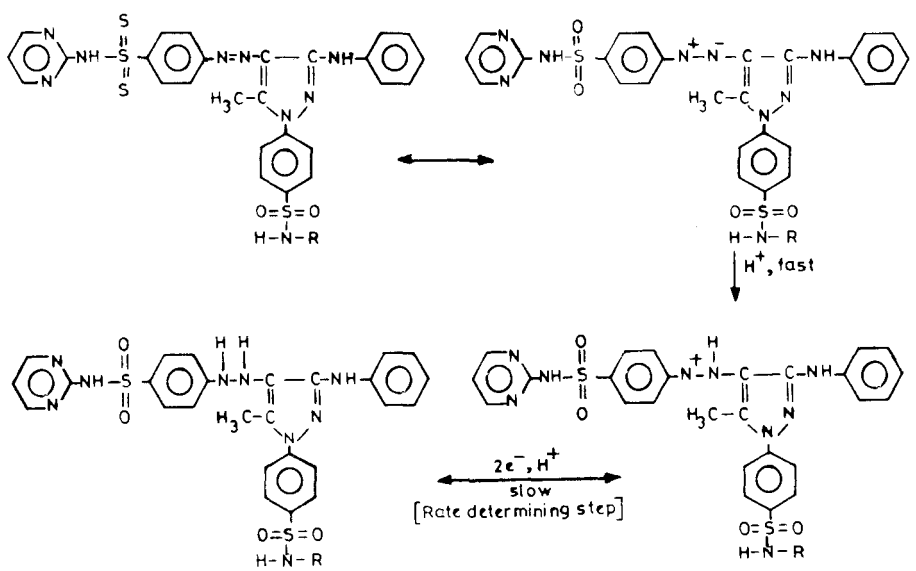
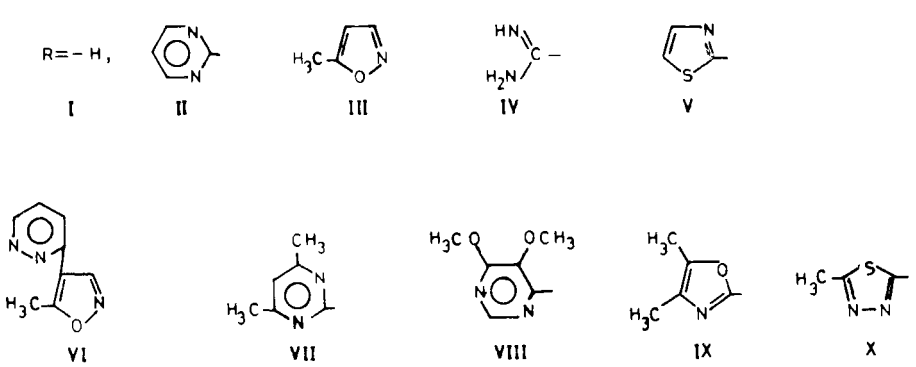


Fig. 3—Plots of $-E_{1/2}$ vs *p*H of N-sulphonamoylphenyl-3-aminophenyl- 5 -methyl- 4-4'- (2" -pyrimidinyl)sulphonamoyl phenylazopyrazoles





Scheme 1

Table 2—Values of half-wave potential ($E_{1/2}$) for the reduction of N-sulphonamoylphenyl-3-aminophenyl-5-methyl-4-[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles at various *p*H, $C = 1.0 \times 10^{-4}$ *M*

R	*p*H					
	2.56	4.86	6.03	8.12	10.80	11.50
I	0.52	0.60	0.62	0.71	0.72	0.72
IV	0.51	0.53	0.60	0.68	0.75	0.76
II	0.42	0.56	0.61	0.70	0.75	0.74

two electrons and one proton were required for the rate determining step, a mechanism similar to that reported in literature[12] may be proposed for the reduction of N-sulphonamoylphenyl-3-aminophenyl- 5 -methyl- 4 -[4′(2″-pyrimidinyl)sulphonamoyl]-phenylazopyrazoles (Scheme 1).

The solution after controlled potential electrolysis gave negative test for amino group, thereby confirming the above reduction mechanism.

Controlled potential electrolysis (CPE) of azopyrazoles was carried at the plateau potential (−1.2V) of the wave to determine the number of electrons in the reduction. The value of *n* was found to be ~ 2(I = 1.6 × n) as confirmed by diffusion-current constant (I) value given in Table 2 and millicoulometric method of deVries and Kroon[12].

Acknowledgement

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