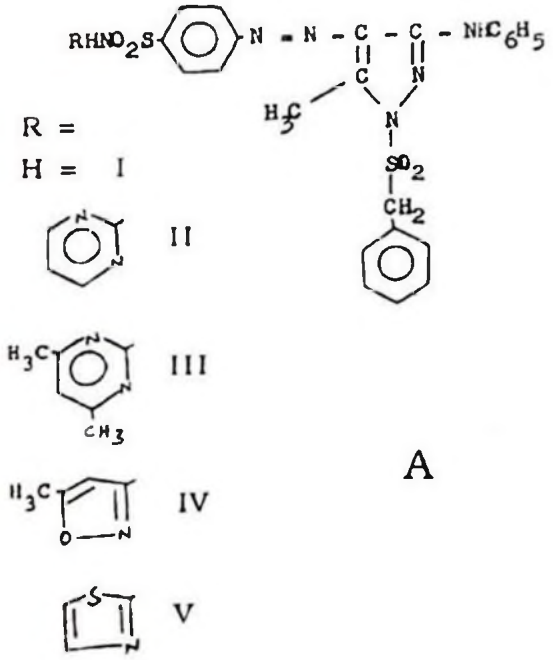
Polarographic and Cyclic - Voltammetric Studies on Some Phenylmethylsulphonylazopyrazoles

Rajeev Jain, Seema Gupta and Sandeep Tomar

School of Studies in Chemistry, Jiwaji University, GWALIOR - 474 001

The -N=N- group of 1-phenylmethylsulphonyl-3-aminophenyl- 5-methyl-4-(4'-sulphonamoyl) azopyrazoles is reduced at dme and GC to -NH-NH- grouping by consuming 2 e⁻ in one well-defined, diffusion-controlled and irreversible step in BR buffer solutions of pH 2.0 to 12.0.

Sulphonamides possess wide spectrum of antibacterial activity and they are the first effective chemotherapeutic agents to be used as antibacterial compounds [1]. The importance of azo dyes in biology and medicines has been extensively reported in literature [2]. In recent years, the electrochemical reduction of azopyrazoles is the subject of several investigations [3-8]. In continuation of these studies, polarographic and cyclic voltammetric studies on some 1-phenylmethylsulphonyl-3-aminophenyl- 5-methyl-4-(4'-sulphonamoyl) azopyrazoles (A Compounds I - V) are reported here.



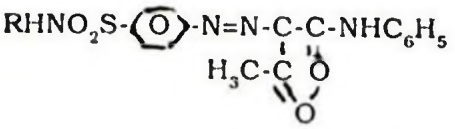
A

EXPERIMENTAL

Reagents and Solutions

1-Phenylmethylsulphonyl-3-aminophenyl-5-methyl-4-(4'-sulphonamoyl)azopyrazoles (A, compounds I-V) were prepared in the laboratory following a three step preparation procedure as follows:

In the first step appropriately substituted sulphanilamide ($RHNO_2S$-⬡-NH_2) was diazotized and condensed with 4-phenylamino butane-2, 4-dione (CH_3-CO-CH_2-CO-NHC_6H_5) to get the 3-(4' sulphonamoyl) hydrazono-4-phenylamino butane-2,4-dione



This was purified by recrystallisation and

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identified by melting point, elemental analysis, ir spectra and PMR spectra.

In the step 2, acetanilide was made to react with chlorosulphonic acid; the product was purified by recrystallisation and condensed with hydrazine hydrate to yield 4-acetamido benzene sulphonyl-hydrazide (C_6H_5-CH_2-SO_2-NH-NH_2). This was purified.

In the step 3, the above two intermediates were condensed and the product was purified by recrystallization. Identity of the compounds were confirmed by melting point, elemental analysis and spectral studies.

Stock solutions (2.0×10^{-3} M) of all the dipolarizers (A, I to V) were prepared in purified DMF (AnalaR). Potassium chloride (1.0 M) was prepared from AnalaR grade salt in doubly distilled water. Britton-Robinson buffers [9] of varying acid strength were prepared in doubly distilled water using A.R. grade chemicals.

Working solutions were prepared by taking 1.0 ml of the stock solution and mixed with 2.0 ml of DMF, 1.0 ml of KCl and 6.0 ml of appropriate B.R. buffer solution. Final volume was 10 ml and concentration of depolariser was 2.0×10^{-4} M. The solutions were deaerated by passing a stream of purified nitrogen gas for 15 minutes before recording the polarograms and a blanket of nitrogen gas was maintained throughout the experiment in all the cases.

Polarographic Measurements

Polarographic measurements were carried out on ELICO DC CL-25 polarograph using dropping mercury and saturated calomel electrodes (SCE). DP 510 Digital pH meter with glass electrode was standardised and all potentiometric studies were carried out on this. Voltammograms were recorded using a three electrode system (glassy carbon, Ag/AgCl and platinum wire) with BAS CV-27 cyclic voltammograph in conjunction with a Digital Electronic 2000 Omnigraph x-y/t recorder.

Controlled Potential Electrolysis and Coulometry

Controlled potential electrolysis at dropping mercury electrode and glassy carbon electrode were carried out in a micro cell. Solution was prepared by taking 2.0 ml of depolariser, 6.0 ml of B.R. buffer, 1.0 ml of dimethyl formamide and 1.0 ml of KCl; it was electrolysed at a potential which corresponds to the limiting current on the polarographic wave. At the end of the electrolysis, current decreased to the background level and the solution became colourless. Only one product was identified by TLC (CCl_4 as solvent system). The number of electrons involved in the reduction process was also determined by coulometry, by reading the value of Q from the coulometer and value of 'n' was calculated using following expression :

$$Q = nFN$$

RESULTS AND DISCUSSION

All compounds gave a single, two-electron, reduction wave in B.R. buffers of pH range 2.3 to 11.8 (Table 1). The nature of the polarographic wave is diffusion controlled [10] (limiting current is proportional to $h^{1/2}$ and to C). The $E_{1/2}$ values were found to be pH dependent and shifted towards more negative potential with increasing concentration of the depolariser indicating the irreversible nature of the waves. Coulometry indicated n as 2. The reduction is that of azo group.

Azobenzene [11] is reduced reversibly at low concentration and at low pH values; however, though the reduction is that of azo group in the present set of compounds, they give irreversible waves. This deviation can be attributed to substitution of bulky pyrazole moiety at one end of -N=N- group. A comparison of limiting current shows that most of the compounds involve same number of electrons in the reduction process. Values of αn were calculated [12] using the equation.

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

Half-wave potential shifted towards more negative values with the increase in pH [13]. The plots of $E_{1/2}$ *vs* pH (Fig. 1) are linear up to pH 7.7 (slope nearly 0.95) and thereafter variation in $E_{1/2}$ with rise in pH is slight. The pH at the intersecting point is nearly equal to pK. This is a common behaviour of organic reductions involving H^+ [15].

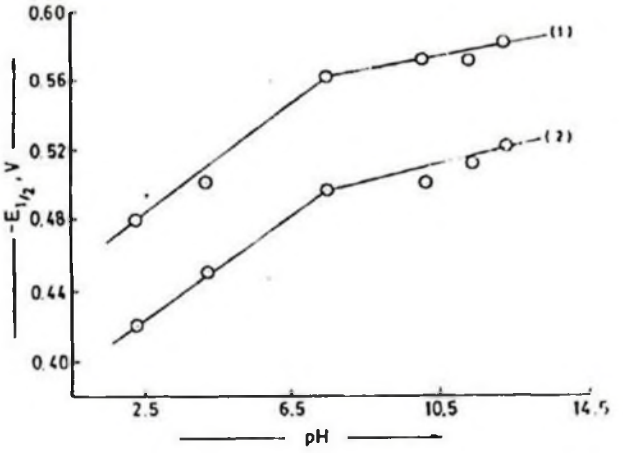


Fig. 1 : Plot of $-E_{1/2}$ *vs* pH
1. Compound A-I 2. Compound A-III
Concentration 2.0 x 10^{-4}M

The number of protons involved in the rate determining step of the reduction of acidic form [12] was determined by the expression.

$$P = \frac{dE_{1/2}}{dpH} \cdot \frac{\alpha n}{0.05915}$$

These values are included in Table 1.

Table 1

Polarographic Characteristics

Depolariser: 1-phenylmethylsulphonyl-3-aminophenyl-5-methyl-4-(4'-sulphonamoyl) azopyrazoles (compounds A - I to V)
pH 4.2: Conc. = 2.0 x 10^{-4} M.

Sl.No	$E_{1/2}$.V	i_d, μA	αn	I x 10^2	P
A-I	0.50	1.65	0.182	17.55	1.10
A-II	0.46	1.50	0.111	15.95	1.15
A-III	0.59	1.66	0.086	17.65	1.02
A-IV	0.60	1.65	0.085	17.55	1.11
A-V	0.59	1.78	0.086	18.93	1.15

Cyclic Voltammetry

Cyclic voltammetric measurements were carried out at glassy carbon and also at Pt electrode. Voltammograms of all the azopyrazoles were recorded in the pH range 2.3-11.8 and at different concentrations of the depolariser (2.0 x 10^{-4} M to 5.0 x 10^{-4} M). The CV behaviour is in agreement with that observed from the polarographic measurements. All the azopyrazoles showed a single, well defined, two electron reduction. One cathodic peak is observed in the entire pH range studied. The peak height increased with the increase in the concentration of the depolariser and also with the increase in scan rate (50 mV/sec to 250 mV/sec.). These indicate diffusion controlled nature of the reduction process. It was observed that the peak potential (E_p) shifted towards more negative side with increase in concentration of the depolariser. No anodic peak (for oxidation of the product) was observed in reverse scan, showing that the electrode process is irreversible.

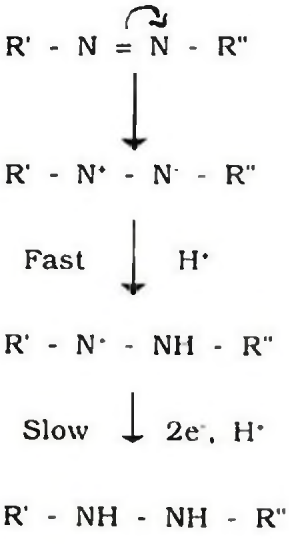
Identification of Product

The solution was electrolysed at controlled potential. Completely electrolysed solution did not give any polarographic wave or cyclic voltammetric peak. During electrolysis, UV-vis spectra of the solutions were recorded at different time intervals. λ_{max} at 415 nm due to -N=N- grouping showed a decrease in the peak intensity after each interval of electrolysis and finally the peak disappeared, confirming the reduction of -N=N- group. Only one product was identified in thin layer chromatographic analysis (Silica gel G as adsorbent and CCl_4 as solvent system).

The reduced solution did not give dye test for primary amines showing that -N=N- group is reduced only upto -NH-NH stage.

Mechanism

As the number of electrons involved in the reduction process is two and the number of protons involved in the rate determining step is one, the following mechanism may be proposed for the reduction of these azopyrazoles. Similar mechanism has also been proposed by other workers [14] for analogous systems.



This mechanism accounts for the effect of pH. The number of protons participating in the reduction at acidic pH (P) is one. As the equilibrium shifts towards unprotonated form, the $E_{1/2}$ tends to become constant.

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