Hammett Substituent Effects and Correleation between $E_{\frac{1}{2}}$ and pK Values of Azo Dyes

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THE $E_{\frac{1}{2}}$ -pH relationship studied polarographically is connnected with dissociation constant of the azo dyes. The Hammet substituent effects of the groups attached in the dye molecules have been correlated with $E_{\frac{1}{2}}$ and pK values by the equation

$$\Delta E_{\frac{1}{2}} = (pK\text{-}N)\ \rho\pi_{,R}/m$$

$\Delta E_{\frac{1}{2}}$ calculated as above differs from experimental value in cases involving structural modifications due to the presence of poly substituents.

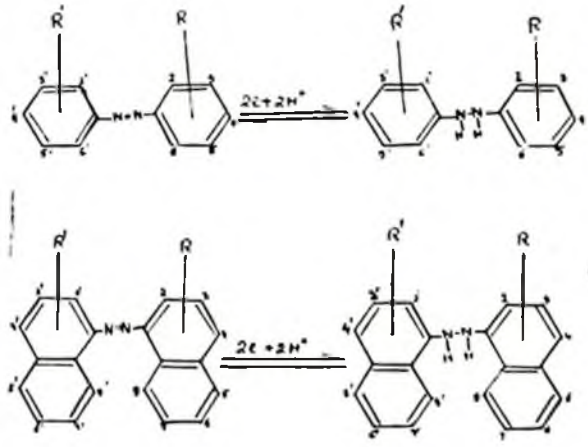
THE polarographic reduction behaviour of various azo dyes in several buffer systems has been reported by Gupta, Kachru and Bhat[1]. The $E_{\frac{1}{2}}$-pH relations agree fairly well with the values reported by various authors. No break at higher pH was observed. The pK values of the azo compounds have been determined by potentiometric[2,3], Spectrophotometric[2,3] and conductometric techniques[2] in aqueous medium at 25±0.1°C. The pK values of these compounds have been related to the nature of the substituents present. An attempt has been made to correlate the Hammett's substituent constants with pK values.

EXPERIMENTAL

Reagent grade chemicals were used throughout. Ionic strength (μ) was kept constant by adding KCl in the case of polarographic measurements. The pH of solutions was maintained by Britton and and Robinson buffer, Clark-Lubs buffer and in some cases even by adding 0.12 N NaOH. The pH was measured by Philips pH meter PR 9405 using glass and calomel electrodes. Potentiometric, conductometric and spectrophotometric measurements were made by OSAW (India) Vernier potentiometer 300-70, Philips conductivity bridge PR 9500, and Carl Zeiss (DDR Germany) VSU 2-P spectrophotometer respectively. A manual polarographic unit (Toshniwal, India) was used in conjuction with multiflex spot galvanometer. The dme had the following characteristics ($m^{2/3}\ t^{1/6} = 3.82\ mg^{2/3}\ S^{-\frac{1}{2}}$). Temperature was kept constant at 25± .1°C by a thermostatic water bath. For polarographic measurements 1 mM concentration of each dye was prepared by diluting the 0.01 stock solutions with requisite amount of buffer. The solutions were deaerated by bubbling pure hydrogen for five minutes before subjecting to current voltage measurements.

RESULTS AND DISCUSIONS

The dyes gave a single, two electron diffusion controlled reduction wave. The $k^{o}_{f,h}$ ranges between 1×10^{-3} to 1×10^{-4}, which indicates the partly irreversible nature of the electrode reduction, contrary to the views of some authors[4]. The increase in $E_{\frac{1}{2}}$ with increasing pH indicates that prior to the first electron intake proton transfer takes place[4,5]. Since all the dyes are reduced in a single two electron wave, the course of reduction is represented as indicated below, a view in accordance with the work of Hillson and Birnbaum[6] and Pezzatini[7].



In all the dyes the degree of reversibility is the same, so Hammett equation can be used successfully. The values of $E_{\frac{1}{2}}$ are plotted against Hammett substituent constant ($\Sigma\sigma^{*}_{x}$) in order to evolve the effect of different substituents on the aromatic ring system. When values of $E_{\frac{1}{2}}$ are available for compounds containing substituents at two different positions (e.g.) position n=1 and n=2 of the aromatic system), the two reaction constants $\rho^{*}\pi$, R_1 and $\rho^{*}\pi$, R_2 can be determined. For approximately

TABLE I

Calculated values of $\Sigma\sigma_X^*$ pK_a, $E_{\frac{1}{2}}^I$ and $\Delta E_{\frac{1}{2}}^{I\,a,b}$

Compound	Substituents	$\Sigma\sigma_X^*$ Theoretical	$\Sigma\sigma_X^*$ Calculated	Ref. 1 $\rho\pi_R$	Ref. 2 pK_a	$E_{\frac{1}{2}}^I$ at pH 5.4/V [SEC]	$\Delta E^a{}_{\frac{1}{2}}$	$\Delta E^b{}_{\frac{1}{2}}$	Difference $\Delta\Delta E_{\frac{1}{2}}$
Azobenzene	none	—	—	—	—	(0.33)	—	—	—
Solochrome yellow 2 GS	3(COOH),4(OH), 4'(SO_3Na)	+ 0.36	+ 0.571	0.14	6.23	0.27	+ 0.06	+ 0.002	+ 0.058
1-Naphthyl azobenzene	none	—	—	—	—	(0.365)	—	—	—
Solochrome fast navy 2 RS	6,3'(SO_3Na) 5 Cl,2,2'(CH)	+ 0.56	+ 0.406	0.16	6.50	0.32	+ 0.045	+ 0.096	− 0.051
Solochrome black PVS	5(OH),5'(SO_3H) 2,2'(OH)	− 0.22	+ 0.344	0.16	6.01	− 0.330	+ 0.035	+ 0.065	− 0.030
Azonaphthylene	none	—	—	—	—	(0.40)	—	—	—
Solochrome black WDFA	3(SO_3H),5(NO_2) 2,2'(OH)	− 0.12	+ 0.22	0.18	6.30	0.33	+ 0.02	+ 0.046	− 0.026
Solochrome dark blue B150	4(SO_3Na),2,2'(OH)	+ 0.38	+ 0.618	0.18	6.36	0.31	0.09	+ 0.065	+ 0.025

a Polarographically $E_{\frac{1}{2}}^I - pH$ equation, $\Delta E_{\frac{1}{2}}^I = [E_{\frac{1}{2}}^I]_s - [E_{\frac{1}{2}}^I]_u$

b From dissociation constants $\Delta E_{\frac{1}{2}}^I = \left(\frac{pK_a - 6.15}{0.58}\right) \rho\pi_R$

equal values of $\rho^*\pi_{,R1}$ and $\rho^*\alpha_{,R2}$ use of a simplified equation is recommended.

$$\Delta E_{\frac{1}{2}} = \rho^*\pi_{,Rn}\,\Sigma\sigma_x^* \qquad 1$$

considering toe substituents in b valent azo group the shifts in $E_{\frac{1}{2}}$ can be expressed

$$\Delta E_{\frac{1}{2}}^1 = \rho'\pi_{,R}\,\Sigma\sigma_x^* + \rho''\pi,e\,\Sigma_x^* \qquad 2$$

For not highly unsymmetrical sh pes of the molecules, it can be expected hat

$$\rho'\,\pi_{,R} = \rho^2\,\pi_{,R} = \rho\,\pi_{,R}$$

Thus $\Delta E_{\frac{1}{2}} = \rho'\,\pi,\,R\,\Sigma\sigma_x^* \qquad 3$

where $\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_1 - (\Gamma_{\frac{1}{2}})_H$

The calculated values of $\Sigma\sigma_x^*$ obtained from relation [3] are presented in Table 1. The theoretical values are also given in the Table 1 for reference.

The values of the substituent constant $\Sigma\sigma_x^*$ is logically derived from the dissociation constants[8,9] as follows :

$$pK = m\,\Sigma\sigma_x^* + N \qquad 4$$

Thus from equation [3] and [4]

$$\left[E_{\frac{1}{2}} = \left(\frac{pK - N}{m}\right)\rho\,\pi,\,R\right] \qquad 5$$

where m is the slope and N is the intercept of the plot of pK VS $\Sigma\sigma_x^*$. The plot of pK VS $\Sigma\sigma_x^*$ and $E_{\frac{1}{2}}$ VS $\Sigma\sigma_x^*$ are shown in Fig. 1. The values of m

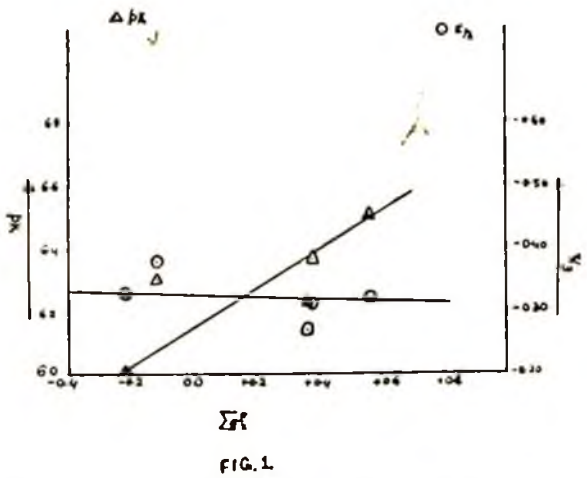


Fig. 1 Plots of $\Sigma\sigma_x^*$ Vs. pK and $E_{\frac{1}{2}}$ azo dyes

nad N are 0.58 and 6.15 respectively [with correlation coefficient = − 0.967, and standard deviation = 0.0326].

It can be realised from Table 1 that the $\Delta E_{\frac{1}{2}}$ values calculated from polarographic and dissociation [pK] methods are fairly close to each other in most cases. The $\Delta\Delta E_{\frac{1}{2}}$ obtained by substracting the polarographic $\Delta E_{\frac{1}{2}}$ values from $\Delta E_{\frac{1}{2}}$ obtained from pK value is fairly small. A linear relationship between $E_{\frac{1}{2}}$ VS $\Sigma\sigma_x^*$ and pK VS $\Sigma\sigma_x^*$ is obtained in all dyes except solochrome yellow 2 GS and Solochrome black WDFA which show slight deviation, which can be explained as follows :

In solochrome yellow 2 GS the azo group enhances the electron density at the carbonyl group of carboxylic acid which strengthen the OH bond and inhibits the loss of proton. Further, the hydrogen bonding between —OH and —COOH ortho to each other may also increase the pK values. In Solochrome black WDFA deactivation of the ring is predominant factor by the presence of SO_3^- situated at the m-position as compared to ortho or para position where it activates the electro active group[10].

The dye molecules under consideration are unsymmtrical due to the substituents attached to the phenyl and naphthyl rings. The polarographic $\Sigma\sigma_x^*$ obtained differs from the theoretically[11] calculated $\Sigma\sigma_x^*$ due to the kind of aromatic ring system and also due to the reducibility of the groups in the side chain. The position of the substituent group affects substantially the charge density at the reducible group which subsequently changes the $E_{\frac{1}{2}}$ and in turn alterations of $\Sigma\sigma_x^*$ are observed. Thus the calculations made theoretically determines the effects of singly substituted groups while in polysubstituted molecule it can be concluded that the resultant effect is different due to the steric, mesomeric inductive and polar effects operating simultaneously in these compounds. The hydrogen bonding is another possibility in some compounds, as for example, in solochrome yellow 2 GS. The difference may also be due to the partly irreversible reduction behaviour of these molecules at dme.

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