

## INVESTIGATIONS ON REDOX BEHAVIOUR OF SOME 2-BENZOTHAZOLYLHYDRAZONO ETHYL-2-CYANOETHANOATES

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Polarographic reduction of 2-benzothiazolylhydrazono ethyl 2-cyanoethanoates takes place in a single 4-electron transfer, giving a diffusion controlled irreversible wave in B. R. buffers of pH range 2.0-4.2 and in 0.1N HCl. Unlike other compounds of the series, the nitro compound gave two well-defined waves. The first wave at a less negative potential was attributed to the reduction of nitro group which was also found to be diffusion controlled and irreversible. The reduction in these compounds takes place at the  $-\text{NH}-\text{N}=\text{C}-$  bond and mechanism has been proposed for the reduction process.

Effect of supporting electrolyte concentration and solvent percentage on the reduction have been discussed. The polarograms recorded with chlorides of lithium, sodium, potassium, rubidium and tetraethylammonium iodide as base electrolytes revealed that the value of the specific reaction constant increases in direct proportions of the size of cation.

A further check was made by recording the polarograms with supporting electrolytes having a common cation and different anions. No change in  $E_{1/2}$  or  $i_d$  was observed which showed that only the cation influences the electrical double layer at the cathode.

For studying the effect of various solvents and solvent percentage on the ease of reduction, polarograms were recorded in different percentage of acetonitril, cellosolve and dimethylformamide. It was observed that as the concentration of the solvents varies from 20 per cent to 70 per cent the  $E_{1/2}$  shifted towards more negative potential with decrease in wave height. The results have been discussed in terms of potential variations in the electrical double layer.

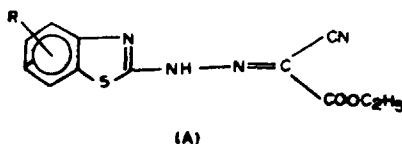
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### INTRODUCTION

THIAZOLES and benzothiazoles play an important role in the field of medicinal chemistry as they possess interesting biological activity (Tirouflet *et al.*, 1960; and Malik *et al.*, 1975). A knowledge of their redox behaviour at the solution-mercury interface may prove quite useful from physiological point of view. Polarographic studies on the reduction of these compounds at DME were therefore, undertaken.

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The present paper describes the results of such studies on some recently synthesised hydrazono derivatives of 2-aminobenzothiazoles (A) (Goyal *et al.*, 1981).



### EXPERIMENTAL

The hydrazono derivatives of 2-aminobenzothiazoles with substituents in the benzene ring were synthesised by the method reported from this laboratory (Goyal *et al.*, 1981).

### MATERIALS AND METHODS

Stock solutions of ( $1 \times 10^{-3}$  M) the above mentioned compounds were prepared in distilled DMF (AnalaR). Britton-Robinson buffers in the *pH* range 2.0–12.0 were prepared by adding requisite amounts of 0.2M sodium hydroxide solution in stock B. R. buffer of *pH* 1.8, composed of boric acid, phosphoric acid and acetic acid. The chemicals used were of A. R. grade.

A Cambridge pen recording polarograph was used. The capillary characteristic was  $2.040 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ . SCE was used as the reference electrode.

For recording polarograms, 2.0ml of stock solution ( $1.0 \times 10^{-3}$ M) of compound, 1.0ml of 1M KCl and 7.0ml of buffer were mixed and a stream of pure hydrogen gas was passed for about 5 minutes so as to ensure complete deaeration. Studies could not be carried out in buffers of *pH* more than 4.2, due to the precipitation of compound in higher *pH* range, so polarographic studies were carried out in 0.1N HCl and in buffers upto *pH* 4.2. The cell was kept in a thermostatic water bath (temp.  $25 \pm 0.1$  °C). The number of electrons involved in the reduction process was calculated by milli-coulometry method (DeVries & Kroon, 1953) using  $\text{CdSO}_4$  as a reference solution. The controlled potential electrolysis was carried out at potential corresponding to the plateau (1.6V) of the wave. The electrolysis cell was a H-shaped cell, the cathodic and anodic compartment being separated by a diaphragm of sintered glass. Mercury was used as electrode material. After complete electrolysis (about 6hrs) the catholyte was analysed for the identification of the end product.

### RESULTS AND DISCUSSION

The compounds listed in Table I gave a single  $4e$  reduction wave in B. R. buffer of *pH* range 2.0–4.2 and in 0.1N HCl. The nature of the wave was found to be diffusion-controlled as evident by the linear dependence of limiting current on  $\sqrt{h}$  and concentration of depolariser. The constancy of wave height in the *pH* range studied together with the fact that  $di/dt$  had a very low value of temperature coefficient further confirmed that the reduction waves were fully diffusion controlled. The wave characteristics are shown in Table I.

TABLE I

*Polarographic characteristics of 2-benzothiazolyldiazono ethyl 2-cyanoethanoates at pH 4.2 concn.  $2.0 \times 10^{-4}M$*

S. No.	R	$E_{1/2}, V$	$i_d/\mu A$	$\Delta E_{1/2}/V$	$\alpha n$		p
					I method*	II method**	
1.	H	0.65	0.60	0.00	0.86	0.82	1.20
2.	3-CH <sub>3</sub>	0.70	0.60	0.05	0.86	0.81	1.14
3.	4-CH <sub>3</sub>	0.80	0.70	0.15	0.76	0.81	1.20
4.	2-OCH <sub>3</sub>	0.64	0.55	0.01	0.76	0.79	1.20
5.	4-OCH <sub>3</sub>	0.66	0.55	0.01	0.71	0.68	1.12
6.	4-NO <sub>2</sub>	0.98	0.60	0.33	0.66	0.70	1.14
7.	2,3-(CH <sub>3</sub> ) <sub>2</sub>	0.70	0.55	0.05	0.86	0.80	1.14

\*Log plot method

\*\*Oldham and Perry method.

The half-wave potential of these compounds was found to be dependent on pH and shifted towards more negative potential with increase in pH. The plots of  $E_{1/2}$  vs pH were linear. The irreversible nature of the waves was confirmed by log plots (Meites, 1967). The fact that  $E_{1/2}$  shifted towards more negative potential with increasing concentration of depolariser further pointed towards the irreversible nature of the waves. The value of  $\alpha n_a$  (product of transfer coefficient and number of electrons transferred in the rate determining step) and p (number of protons involved during the rate determining step of the reaction) was determined using the expressions,

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

$$\frac{dE_{1/2}}{dpH} = - \frac{0.05915}{\alpha n_a} \cdot p$$

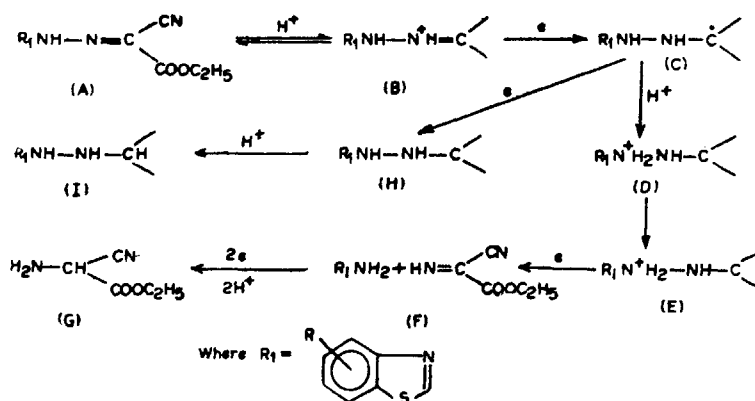
The values of  $\alpha n$  and rate constant  $Kr$  were also determined by the method of Oldham and Perry (1968) using the expression,

$$E_{1/2} = E_r + \frac{0.0592}{\alpha n} \log \left[ 1.35 K_r \frac{t}{D} \right]$$

where  $t$  is the drop time at the potential  $E_r$ . The values of half-wave potentials together with  $\alpha n$ , and p are given in Table I.

Since the half-wave potential of these thiazoles were pH dependent and the limiting current pH independent, it was concluded that both acidic and basic forms of the compounds reached the electrode surface and are electroactive. Thus the proton transfer reaction precedes the electrode process in such cases. Out of the two general sequences (Zuman, 1969) for the proton and electron addition viz.,

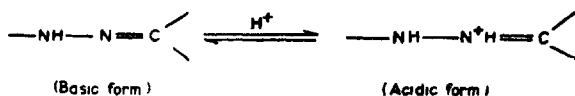
$H^+$ ,  $e$ ,  $H^+$ ,  $e$  and  $H^+$ ,  $e$ ,  $e$ ,  $H^+$ . The former sequence was more probable for these compounds in the light of their structural genesis. After the uptake of a proton and one electron the radical (C) would accept a proton to form a protonated radical (D) which after taking one electron got cleaved at nitrogen bond with the formation of aniline. The imine (F) formed was further protonated and got reduced.



Alternatively, the radical (C) could also combine with an electron instead of proton but this possibility was cancelled out by the fact that such a reduction would involve only 2 electrons whereas polarographic data clearly indicate 4-electron transfer reaction at the DME.

These mechanistic steps found support from the increase of  $E_{1/2}$  with  $pH$  as protons are consumed in the reduction. In the  $pH$  range studied where both the electroactive form (acidic as well as basic) are reduced half-wave potential of the two forms are so close that the waves merge and no separation of two waves can be observed.

Similar steps for the reduction of hydrazono group have also been proposed by other workers (Lund, 1959; and Hass & Lynch, 1957, 1964), involving cleavage of the nitrogen-nitrogen bond. Due to an acid-base equilibria that exist between two structural forms of the compounds, wave height of the wave remains  $pH$ -independent as long as the formation of the acidic from the basic form is fast enough, when  $pH$  increases, rate of protonation decreases, the wave height decreases as well.



When a depolariser solution was tested after controlled potential electrolysis, gave dye test thereby showing that at least one of the reduction product is aromatic amine. UV spectra of the solution during electrolysis were recorded at different intervals of time at UV-VIS spectrophotometer.  $\nu_{\max}^-$   $CH_3OH$  at 425nm for

—NH—N=C— grouping showed a decrease in the peak height after each interval of time and finally disappearance of the peak, confirmed the above reduction mechanism.

#### *Effect of Supporting Electrolyte Concentration*

The effect of the double layer structure on  $E_{1/2}$  of a process preceded by the protonation is given by the equation (Mairanovsky, 1962),

$$\Delta E_{1/2} \approx \Delta \psi_1 \left( \frac{\alpha n_a - Z}{\alpha n_a} - \frac{\partial E_{1/2} \cdot F}{\partial pH \cdot 2.30 RT} \right) \quad \dots(1)$$

where  $\psi_1$  is the variation in the double layer potential,  $\alpha$  is the transfer coefficient,  $n_a$  is the number of electrons transferred in the rate determining step,  $Z$  is the charge of the particle being discharged. Undoubtedly a marked effect of change in ionic strength on  $E_{1/2}$  should be observed in cases where the depolarizer is in the ionic form, no such effect should be observed when it is in the non-ionic form, i.e., when  $Z = 0$ . Since the second term in the bracket of equation (1) is nearly  $-1$  and  $Z = 0$ ,  $E_{1/2}$  will be almost independent of  $\psi_1$  or of ionic strength. This was verified by carrying out experiments with varying concentrations of KCl (0.01M to 0.25M). The values of  $dE_{1/2}/dpH$ , thus obtained fell in the range 60–70 mV/pH and  $E_{1/2}$  and  $i_a$  remained unaffected by the change in concentration of the supporting electrolyte.

#### *Effect of Cations and Anions*

The effect of the size of the cation of the supporting electrolyte on the nature and shape of the wave was determined by recording the polarograms of compounds (I-VII) in chlorides of lithium, sodium, rubidium and tetraethylammonium bromide. In all these cases the usual one well-defined wave was obtained. However,  $E_{1/2}$  shifted towards more negative potential with increase in size of the cation without influencing the wave height. A further check was made by recording the polarograms with supporting electrolyte, having a common cation and different anions. No change in  $E_{1/2}$  and  $i_a$  is observed, which goes to show that only the cation influences the electrical double layer at the cathode. It is interesting to observe that the nature of cation also influences the value of specific reaction constant ( $\rho$ ), with increase in size of the cation the value of specific reaction constant increases. This is in agreement to the wellknown fact that reduction of —NH — N = C < group depends on the components of the supporting electrolyte in addition to the nature of the substituent present. The value of the specific reaction constant ( $\rho$ ) is a linear function of the  $(E_{1/2})_H$  (half-wave potential of the parent unsubstituted compound in the same supporting electrolyte). The effect of the cations on the reduction was found similar to that of crystallographic ionic radii  $(C_2H_5)_4N^+ > Rb^+ > K^+ > Na^+ > Li^+$ . Incidentally, this order is almost reverse of the order of ions of the Hofmeister series for hydrophilic colloidal solutions.

#### *Effects of Solvent Compositions*

Firstly, the polarograms of benzothiazoles were recorded in the minimum amount of D.M.F. (20 per cent) necessary for the dissolving of the compound.

The D. M. F. was then progressively increased from 20 per cent to 70 per cent to see the effect of solvent composition on the electrode process. It was observed that  $E_{1/2}$  shifted to more negative potential with increasing concentration of DMF in the solvent mixture. In electrode processes accompanied by preprotonation, the shift in  $E_{1/2}$  can be due to a rise of pH of solution and an increase in the dissociation constant of the protonated species. Both these factors sharply lower the rate of preprotonation (Mairanovsky, 1965) and consequently lead to the shift in  $E_{1/2}$  towards more negative potential. Schwabe (1962) supposed that the shift of the  $E_{1/2}$  be caused by inhibition of the electrode process by the solvent molecules adsorbed on the electrode. There is yet another factor which exerts a great influence in such cases and it is the viscosity of the solvent. With increasing concentration of D.M.F. in the solvent mixture, there is a gradual increase in viscosity upto a certain concentration (60% DMF) after which it decreases. This optimum concentration points towards complete association of the solvent.

TABLE II

*Effect of D.M.F. percentage on the polarographic reduction of 2-benzothiazolyldrazono ethyl 2-cyanoethanoates at pH 2.2*

S. No.	DMF%	$E_{1/2}/V$	$i_d/\mu A$
1.	30	0.49	0.77
2.	40	0.56	0.65
3.	50	0.63	0.52
4.	60	0.74	0.48
5.	70	0.75	0.42
6.	80	—	—

A survey of the data (Table II) on the variation of  $E_{1/2}$  with solvent composition would reveal that potential reaches its peak value at about 60 per cent DMF and after that remains independent of the concentration of the organic solvent. The  $i_d$  values, as expected, however goes on decreasing and at a very high percentage of DMF in the solvent mixture, very ill-defined waves are obtained.

## REFERENCES

- DeVries, T., and Kroon, J. L. (1953) A millicoulometer method of the determination of polarographic  $n$ -values. *J. Am. chem. Soc.*, **75**, 2484.
- Goyal, R. N., Jain, R., and Tyagi, S. (1981) Polarographic reduction of some potential antineoplastic-5-arylazopyrimidines. *J. Indian chem. Soc.*, **58**, 504.
- Haas, J. W., and Lynch, C. C. (1957) Derivative polarography of carbohydrates aldopentose hydrazone. *Anal. Chem.*, **29**, 479.
- (1964) Polarographic reduction of some semicarbazones. *Acta Chem. Scand.*, **18**, 563.
- Lund, M. (1959) Electroorganic preparations V. Polarographic determination of phenols after treatment with nitrous acid. *Acta Chem. Scand.*, **13**, 249.
- Mairanovsky, S. G. (1962) Effect of the double layer structure and of the adsorption of electrode reaction participation upon polarographic waves in the reduction of organic substances. *J. electroanal. Chem.*, **4**, 166.

- Mairanovsky, S. G. (1965) Effect of composition of aqueous-organic solvent on polarographic behaviour of organic compounds. *Talanta*, **12**, 1299.
- Malik, W. U., Goyal, R. N., and Bhavikati, M. R. (1975) Polarographic reduction of 2-amino-4-methyl-5-arylazthiazoles. *Indian J. Chem.*, **13**, 955.
- Meites, L. (1967) *Polarographic Techniques*. Interscience, New York.
- Oldham, K. B., and Perry, E. P. (1968) Use of polarography and pulse polarography in the determination of the kinetic parameters of totally irreversible electroreductions. *Anal. Chem.*, **40**, 65.
- Schwabe, K. (1962) In : *Progress in Polarography*, **1**. [Ed. P. Zuman & I M. Kolthoff]. Interscience, New York.
- Tirouflet, J., Loviron, E., Metzger, J., and Biochard, J. (1960) The polarographic behaviour of various heterocyclic aldehydes and chalcones. *Colln. Czech. Chem. Commun.*, **25**, 3277.
- Zuman, P. (1967) *Substituent Effects in Organic Polarography*. Plenum Press, New York.
- (1969) *The Elucidation of Organic Electrode Process*. Academic Press, New York.