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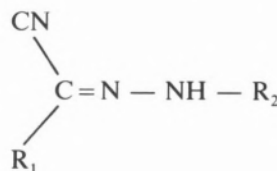


EFFECT OF RING TYPE ON IONIZATION OF THE HYDRAZONO LINKAGE IN AQUEOUS MEDIA

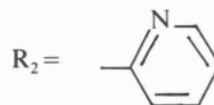
1 — INTRODUCTION

It was generally accepted up till this last decade that phenylhydrazones are inactive in alkaline media. This inactivity was rationalized for by assuming hydrolysis of this linkage, or to the lack of hydrogen ions in these media which are considered a prerequisite for the reduction sequence and the general scheme suggested by LUND [1] for their electroreduction was followed. However, recently the results of several comprehensive papers showed [2,3,4], that in contrast to previously reported behaviour of these compounds, they may be reduced in both acid and alkaline media respectively depending on the degree of ionization of the NH of their $—C=N=NH$ linkage [5].

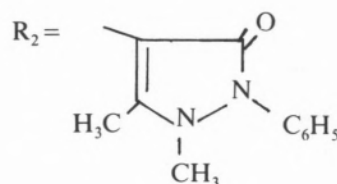
In connection, we report the polarographic and potentiometric data for compounds **I**, **II** and **III**



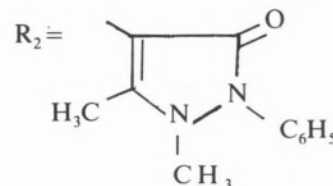
I, $\text{R}_1 = \text{CN}$



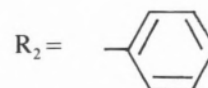
II, $\text{R}_1 = \text{CN}$



III, $\text{R}_1 = \text{COOC}_2\text{H}_5$



IV, $\text{R}_1 = \text{CN}$



2 — EXPERIMENTAL

2.1 — ORGANIC SYNTHESSES

Diazotized 4-aminoantipyrene (prepared from 0.1 mole of 4-amino antipyrene and the appropriate

The acid-base equilibria for a series of hydrazones in ethanolic aqueous media is reported and discussed through correlation of polarographic and potentiometric data.

quantities of concentrated hydrochloric acid and NaNO_2 as has been previously described [6] was added to a solution of 0.1 mole of malononitrile (**II**) or ethylcyano acetate (**III**) in ethanol (100 ml) containing sodium acetate (10.0 g). The solid product formed on standing was filtered and crystallized from ethanol.

The pyridin-3-yl azo derivative (**I**) was prepared by coupling diazotized 3-aminopyridine with malononitrile utilizing similar procedure.

The obtained compounds gave correct spectral data (IR, ^1H NMR and MS) in excellent agreement with the proposed structures. These data together with their chemistry will be published in a separate communication now in preparation.

2.2 — POLAROGRAPHIC MEASUREMENTS

2.2.1 — APPARATUS

Polarograms were recorded with a pen type recorder E506 polarograph-Metrohm-Switzerland product. The capillary possessed the following characteristics in H_2O open circuit: $t = 5.1 \text{ s/drop}$, $m = 1.49 \text{ mg. s}^{-1}$ for $h = 40 \text{ cm}$.

2.2.2 — SOLUTION

10^{-3}M stock solutions were prepared by dissolving an accurately weighed quantity of material in the appropriate volume of absolute ethanol. Britton-Robinson modified universal buffers [7] were used as supporting electrolyte.

2.2.3 — MEASUREMENTS

All experiments were carried at $25^\circ \pm 2^\circ\text{C}$; the half-wave potentials were measured graphically and expressed *versus* SCE with an accuracy of $\pm 0.005\text{V}$.

2.2.4 — PROCEDURE

16 ml of buffer solution and 2 ml of ethanol were introduced into the polarographic cell. The mixture was then deaerated with H_2 gas for 12 minutes. 2 ml of 10^{-3}M depolarizer was then introduced into the cell so that the final concentration was 10^{-4}M in 20 ml of 20% (v/v) ethanolic buffer.

2.3 — DETERMINATION OF THE ACID DISSOCIATION CONSTANT

Potentiometric titrations were carried out using an electronically controlled syringe burette, Electro-burex type in conjunction with automatic recording TAT-5 unit (Solea Tacussel-France) accurate to ± 0.01 pH unit. The pK_a values were conventionally calculated [8] from the registered graphs obtained by titrating a 10^{-3}M solution (30 ml; 1:4 $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$) of each compound.

3 — RESULTS AND DISCUSSION

The polarographic behaviour of compounds **I-III** are illustrated graphically in fig. 1, by **I**. As is clear the shift of $E_{1/2}$ with increase of pH is described by a straight line. At pH 9, $E_{1/2}$ is independent of any variation in pH. The i_1 -pH plot shows a deep well defined dissociation curve. pK value (apparent

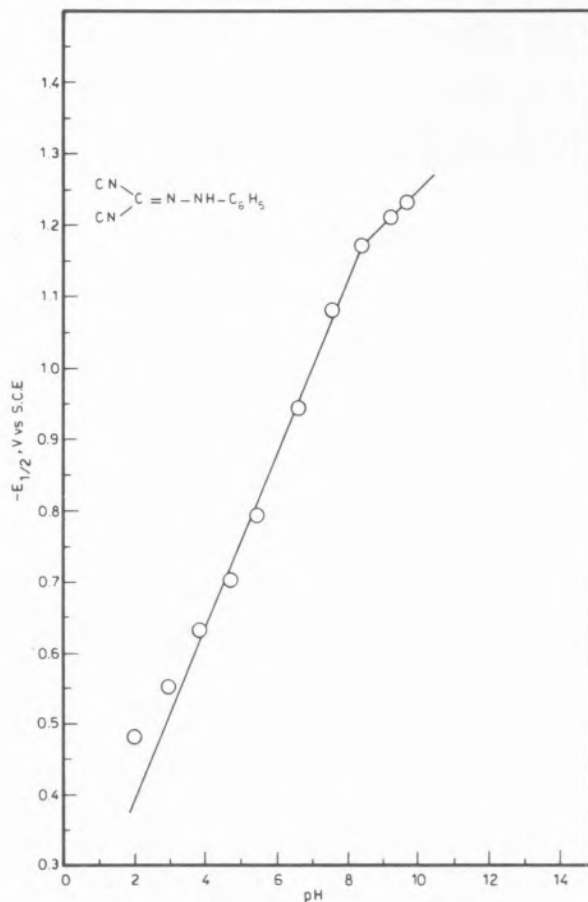
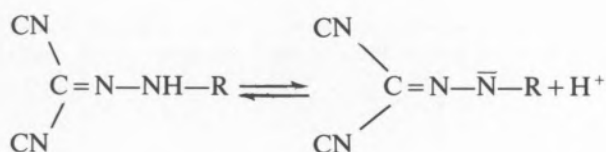


Fig. 1
 $E_{1/2}$ — pH relation for compound **I**

dissociation constant) obtained from the i_l -pH plot, as the value of pH at $i_{lim}/2$, is in good agreement with that obtained by the intersection of the two segments of the $E_{1/2}$ -pH plot [9]. The obtained dissociation curves assigned two main points whether these are strong acids or hydrolysed in alkaline media. Thus at this stage it was found mandatory to calculate the pK_a of such compounds which we assumed by similarity to arylhydrazonomesoxalonitrile [5] **IV** to be due to the ionization of NH of the hydrazone linkage according to



That these compounds are polarographically inert in alkaline medium is due to the fact that the negative charge is distributed over the whole molecule in a way that prevents further reduction. This type of behaviour is analogous to those of monobasic acids [10] and is represented by the following acid-base equilibrium,



where the ratio k_d/k_r equals to K' .

From the difference between the polarographic and potentiometric pK 's it is possible to calculate the value of the rate constant k_r using the following equation

$$\log k_r = 2 \text{ pK}' - \text{pK}_1 - 2 \log 0.886 - \log t$$

and from k_r values one may obtain the appropriate theoretical curve using the following relation [10]

$$\frac{i_{\text{HA}}}{i_d} = \frac{0.886 \left(\frac{k_r t_1}{K_1} \right)^{1/2} [\text{H}^+]}{1 + 0.886 \left(\frac{k_r t_1}{K_1} \right)^{1/2} [\text{H}^+]}$$

From fig. 2 it is obvious that the theoretical curve is superimposed on the experimental results indicating that these compounds behave as acids with one ionizable center. At this point it was found

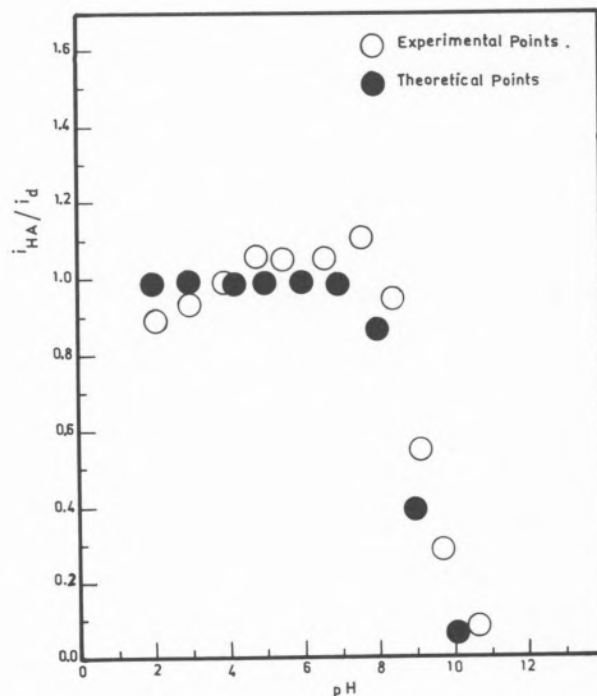


Fig. 2
Theoretical and experimental pH dependence of the limiting current i_{HA}/i_d vs. pH

worthwhile to investigate the effect of ring substitution on the ionization process. As is clear the variation of ring structure has no effect on the ionization of the NH group as reflected from the more or less constant values of pK_a and pK' of the compounds **I**, **II** and **IV** compiled in table 1 while when the substitution is in the carbon of the $-\text{C}=\text{N}-\text{NH}$ linkage, compound **III**, the pK_a and pK' changed significantly indicating that substitution on the carbon of the hydrazone $-\text{C}=\text{N}-\text{NH}-$ linkage has a straightforward effect on the ionization process in such molecules.

Table 1

Compound	$E_{1/2}$ vs pH (mV/pH)	pK	pK _a	$K_f/\text{mol}^{-1}\text{sec}^{-1}$	k_d/sec^{-1}
I	$E_{1/2} = -0.160 - 0.117 \text{ pH}$	9.20	6.00	9.84×10^{11}	9.84×10^5
II	$E_{1/2} = -0.305 - 0.098 \text{ pH}$	9.20	5.90	7.82×10^{11}	9.84×10^5
III	$E_{1/2} = -0.235 - 0.101 \text{ pH}$	10.10	7.20	3.92×10^{12}	2.47×10^5
IV*	$E_{1/2} = -0.570 - 0.076 \text{ pH}$	9.20	6.23	4.90×10^{11}	2.90×10^5

* Data obtained for IV in 40% by volume ethanolic Britton-Robinson buffers [5].

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RESUMO

Efeito do tipo de anel na ionização de hidrazonas em soluções aquosas.

Os equilíbrios ácido-base de uma série de hidrazonas em soluções em água + etanol são estudados por meio de polarografia e potenciometria.