POLAROGRAPHIC STUDY OF SOME ARYLIDENE −2− PYRIDYLHYDRAZONES

BY

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ملخـــص

لقد تمت دراسة السلوك البولاروجرافي لبعض مشتقات ٢ـ بريديل هايدرازون في محلول (برايتون ـ روبنسون) المائي المنظم المحتوي على ٤٠٪ ايثانول وذلك باستعمال طريقة التيار البولاروجرافي المستمر .

وقـد لوحظ في درجـات الحمـوضة المتراوحة بين (١,٩ ـ ٦,٤) ، أن موجة الاختزال ذات الاتجاه الواحد والتي تتضمن اكتساب ٤ الكترونات تعزى الى كسر رابطة N – N والى اشباع مركز الرابطة المزدوجة (C = N) . ان جميع المواد التي درست كانت غير فعالة بولاروجرافياً في الوسط القاعدي .

لقد نوقش تأثير درجة الحموضة على التيار المحدد ، $E_{1/2}$ ، كذلك على ميكانيكية الاختزال وتأثير المعـوضـات وقد قورنت هذه المعطيات بمواد مشابهة ، كما تم حساب المتغيرات الحركية لتفاعل القطب الكهربائي .

Abstract

The polarographich behaviours of some arylidene 2− pyridyl hydrazones have been studied in aqueous Britton - Robinson buffer solution containing 40% ethanol using DC polarographic technique. In the pH range 1.9 – 6.4 the observed single irreversible 4− electron reduction wave is attributed to the splitting of the N – N bond and saturation of C = N centre. All compounds studied are polarographically inactive in alkaline medium .

The effect of pH on the limiting current and $E_{1/2}$ as well as the reduction mechanism and the effect of substituents are discussed and compared with similar compounds . The kinetic parameters of the electrode reaction have been calculated .

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Introduction

The use of hydrazones in analytical chemistry is very interesting because of their simple synthesis , high sensitivity , and high selectivity towards various metal ions . They are widely used as colorimetric , flourimetric and gravimetric reagents , and acid – base indicators . Their analytical applications have been reviewed[1] . The nitrogen containing heterocyclic hydrazones have have been widely studied as analytical reagents[1-11].

On the other hand , the polarographic behaviour of hydrazone compounds has been the subject of many investigations[12-15] , but those related to nitrogen containing heterocyclic hydrazones are scarce .

Following our studies on the polarographic behaviour of nitrogen-containing hetercocyclic hydrazones[16-18] , we investigate the polarographic behaviour of some arylidene 2– pyridyl hydrazones to elucidate the nature and mechanism of electrode process and to test the applicability of the polarographic method for quantitative determination of these hydrazones . No work on these compounds from the present standpoint has been published .

Experimental

a – Solutions :

Arylidene -2- pyridylhydrazones (Py – NH – N = CH  R) were prepared by refluxing the aromatic aldehyde with 2- pyridylhydrazine in ethanolic solution. 10^{-2}M solutions of the organic hydrazones were prepared by dissolving the appropriate amount of the solid compound in hot absolute ethanol . The investigated compounds are listed in Table 1 . As a supporting electrolyte , the universal buffer series of Britton and Robinson[19] covering the pH range 1.8 – 11.8 was used .

Table (1) : Abbreviated and full names for hydrazones

Number	R	Full Name	Abbreviated Form
I_a	H	Benzylidene–2–pyridylhydrazone	BAPH
I_b	m–Cl	m–Chlorobenzylidene–2– pyridylhydrazone	m–Cl–BAPH
I_c	m–Br	m–Bromobenzylidene –2– pyridylhydrazone	m–Br–BAPH
I_d	m–CH_3	m–Methylbenzylidene –2– pyridylhydrazone	m–CH_3–BAPH
I_e	o–OCH_3	o–Anisylidene –2– pyridylhydrazone	o–AAPH
I_f	p–OCH_3	p–Anisylidene –2– pyridylhydrazone	P–AAPH

b – Apparatus :

The average current – voltage curves were recorded on a Sargent Welch A–3001 Polarograph . The Dropping Mercury Electrode (DME) has the following characters : m = 2.35 mg / sec and t = 3.4 sec , at mercury height (h) = 60 cm. Hg. The pH values of the solutions were measured with a Corning Model 12 pH Meter .

Results and Discussion

Effect of pH :

The polarograms of 5.0 x 10^{-4}M solutions of different arylidene -2- pyridyl – hydrazones have been recorded using the DME over the pH range 1.8 – 11.8 . Each consists of a single developed wave in acidic medium (pH 1.8 – 7.0) . Above pH 7.0, all the compounds are polarographically inactive . The half – wave potential of this wave is pH – independent , and the $\triangle E_{1/2} / \triangle pH$ relation is linear with a slope equal to zero within the pH range 1.8 – 7.0 . This behaviour indicates that , the protonation is very fast in the electroreduction process . The rate determining step (RDS) should be either the diffusion process or the electron transfer process . Consequently , the whole electroreduction process becomes pH – independent . Furthermore, the height of the limiting current , for the compounds (I_{a-f}) , is pH – independent in the pH range (1.9 – 6.0) . At pH 7.5 , the wave has completely disappeared .

Effect of Mercury Height :

The effect of mercury height (h) on the polarograms indicates that the reduction process is mainly under diffusion control for all compounds . This is obvious for the values of the exponent in the relation ($i_{id} = Kh^x$) which vary between 0.54 – 0.59 , and the perfect linearity of i_d vs . $\sqrt{h}$ plots .

Calculation of Rate Constant and Free Energy :

Analysis of the waves by applying the fundamental equation for the polarographic waves[20] showed that the waves are irreversible in nature as is evident from the values of kinetic parameters ($\propto n_a$, K_s and $\triangle G^*$) which are listed in Table2.

Reduction Mechanism :

In order to find out the mode of reduction of arylidene –2– pyridylhydrazones, it was necessarily deemed to calculate the number of electrons involved in the reduction process . This was done by applying the Ilkovic equation and substituting for the different terms as reported previously by us.[16]

Table (2) : Kinetic Parameters for 5.0×10^{-4} M arylidene −2− pyridhydrazones at pH 3.6 in presence of 40% ethanol .

Compound	$E_{1/2}$,v vs SCE	$\propto n_a$	K_o cm/sec	$\triangle G^*$Kcal/mol
I_a	1.59	0.54	4.60×10^{-18}	129.64
I_b	1.55	0.54	1.18×10^{-17}	127.27
I_c	1.56	0.54	4.20×10^{-18}	129.87
I_d	1.61	0.58	1.52×10^{-19}	138.19
I_e	1.56	0.59	3.92×10^{-19}	135.82
I_f	1.62	0.57	6.35×10^{-19}	134.61

In acidic media , the number of electrons involved in the process of reduction is 4 electrons . Evidently , the reduction involves an N – N bond cleavage followed by a C = N bond saturation . This behaviour is similar to the one proposed by Lund[12] , Gomez, et al[21] . and recently by us[16–18] .

$$Py - NH - N = CH - \langle Q \rangle_R + 2e \rightarrow Py - \bar{N}H + \bar{N} = CH - \langle Q \rangle_R \quad \ldots. (1)$$

(III) (rate – determining step).

$$(II) + (III) + 2H^+ \rightarrow \underset{(IV)}{Py - NH_2} + \underset{(V)}{NH = CH - \langle Q \rangle_R} \quad \ldots. (2)$$

$$(V) + 2e + 2H^+ \rightarrow R - \langle Q \rangle - CH_2 - NH_2 \quad \ldots.(3)$$

Effect of Concentration of Hydrazones :

It was found that the DC wave could have been used for analytical purposes . The i_d is plotted as a function of the concentration of BAPH (as a representative compound) at pH 3.6 in the presence of 40% ethanol ; at this value of pH , a single well defined wave is obtained . A perfect linear relation between current and concentration is obtained with a slope equal to 11.58 μ A/mmol and a correlation coefficient of 0.9999 . At higher concentration (above 1.0 mM) , a negative deviation is observed , which may be due to the adsorption of the depolarizer or its reduction product . On the other hand , the applicability of the DC polarographic method for the analysis is also supported by the constancy of the i_d/C values .

It is an evidence that , the $E_{1/2}$ of the polarographic wave is shifted to more negative values by increasing the concentration of the depolarizer. This phenomenon has been observed in the reduction of organic compounds[21,22,23] and is characteristic of the irreversible processes .

Effect of Substituents :

The effect of substituents on $E_{1/2}$ values can be treated quantitatively only when the slopes of $E_{1/2}$ vs. pH plots , and the degree of irreversibility ($\propto$) remain constant in the entire reaction series[24] .

Since the values of $\propto n_a$ are practically constant as shown in Table 2 and $dE_{1/2}/dpH$ are constant since $E_{1/2}$ are pH independent in these hydrazones ; a correlation of the half wave potentials with Hammett substituent constants was considered . This was to quantitatively express the substituent effect . Figure (1)

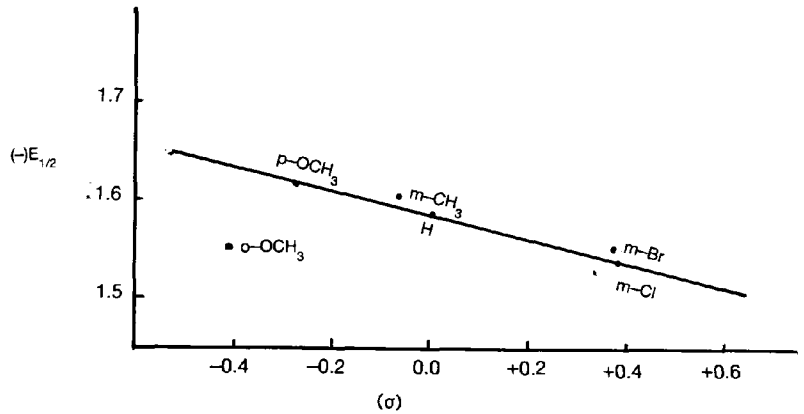

Fig. 1 : Dependence of $E_{1/2}$ on σ for some Arylidene –2– pyridylhydrazone at pH 3.6 (concentration = 5.0×10^{-4} M) .

represents a linear plot of $E_{1/2}$ vs. σ in Britton – Bobinson buffer of pH 3.6 . It was observed that all meta– and para– derivatives fit the straight line , with value of the specific reaction constant (ρ = slope) of 0.12 . The deviation of the ortho derivatives from the straight line can be attributed as usual to steric hindrance to coplanarity[25] .

The magnitude of the polarographic ortho shift ($\triangle o$)[26] , can be expressed by the following relation :

$$\triangle o = (E_{1/2})_{o\text{-}R} - (E_{1/2})_{p\text{-}R}$$

where its value for the methoxy group was 0.60 . The positive value of $\triangle o$ indicates that the p–substituted compounds are more easily reduced compared to their o–analogues .

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