THE ELECTROREDUCTION OF SOME ARYLIDENE DERIVATIVES OF SALICYLIC HYDRAZIDE IN BUFFER SOLUTIONS AT THE DME

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The electroreduction of some arylidene derivatives of salicylic hydrazide is investigated in buffer solutions of different pH values. The reduction involves the uptake of four electrons in acid solutions and two electrons in alkaline media. The number of electrons consumed is calculated from the wave height and confirmed by coulometric analysis. The electrode reaction is also explained. The kinetic parameters of the electrode process are determined and the substituent effect is discussed.

Key words: Polarography of hydrazone, Aryl hydrazone, Arylidene salicylic hydrazide.

INTRODUCTION

The electroreduction of azomethine compounds was the subject of several interesting investigations. Although several authors studied the behaviour of Schiff's bases and arylhydrazones [1-4] yet few articles delt with arylidene derivatives of benzoic hydrazide [5,6]. However, the discussion given by different authors are in conflict so far as the reduction products and the electrode reaction are concerned.

Spectrophotometric studies of arylidene salicylic hydrazide showed that these compounds can exist in different pH dependent equilibrium species with varied excitation energies [7]. These species result from protonation of the C=N linkage or dissociation of protons from the amide and phenolic groups. Thus it seemed of interest to study the electroreduction of these compounds in relation to the nature of the species existing in solution. Also such a study should throw more light on the electrode reaction and contribute to eliminate the conflicts between the results of various authors. The effect of substituent on various electrode parameters are considered as well. The compounds under investigation have the general formula;
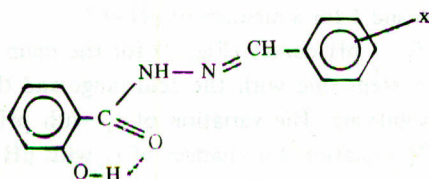
in which x is a substituent with varied electronic character (Table 1).

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EXPERIMENTAL

All compounds used were pure grade chemicals from BDH. The arylidene salicylic hydrazides were prepared as given before [7].

The supporting electrolytes were the components of the Britton and Robinson [8] modified universal buffer series with pH 2-12 containing 30 % by volume DMF.

5×10^{-3} M solutions of the depolarisers were prepared accurately by standard methods in DMF.

The solution for electrolysis was prepared as follows; 10 ml of the doubly concentrated stock of the buffer solutions were placed in the electrolysis cell followed by 4.0 ml of pure water and 4.0 ml of pure DMF. The solution was deaerated by bubbling a pure nitrogen stream for ~ 30 min., then the residual current was recorded. Thereafter 2 ml of the depolariser solution were added and the deaeration was continued for further 4-5 min.

The polarograms were recorded by the aid of the polarecord E 506 using the DME with the characteristics m = 1.677 mg./sec. and t=4.8 sec. All measurements were conducted at $25 \pm 0.5^{\circ}$.

RESULTS AND DISCUSSION

The electroreduction of the benzylidene salicylic hydrazide derivatives (ASH) studied at the DME displays identical behaviour. The polarograms (Fig. 1) reveal that the reduction in media of pH ≤ 7 comprises a single wave with varied heights. The limiting current in solutions of pH (4-5.5) corresponds to the uptake of four electrons. This was confirmed by coulometric analysis and calculated from
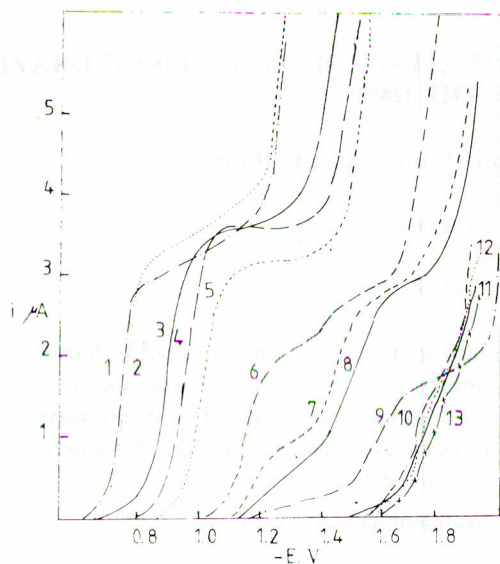
Fig. 1. Effect of polarographic behaviour of 55×10^{-4}M m-Cl (ASH)(I_b) in 30 % DMF.

Fig. 2. Effect of pH on its half wave potential. $E^{1/2}$.

the Ilkovic equation. These results run parallel to those of benzylidene benzoic hydrazide derivatives [5,6]. Within the pH range 5.5 − 7 the reduction current decreases attaining at pH 7 − 7.5 almost half its original value at pH ≤ 5. Thus the number of electrons consumed in media of pH ≥ 7 would be 2.

In solution of pH 7.5 − 9.5 the reduction wave splits into two daughter waves of unequal heights. The height of the second daughter wave increases at the expense of the first one with rise of pH till pH ≥ 10, where one wave only appears at the portion of more negative wave. The splitting of the wave in media of pH 7.5-9.5 can be ascribed to the retarded reduction of a proportion of the depolariser as a result of the decreased H$^+$ ion activity especially in the vicinity of the electrode surface [9]. With rise of pH, the retarded reduction increases till all depolariser species gets reduced at the more negative potential wave. This opinion is supported by the fact that the change of i_1 with pH obeys the Meites equation given for systems of this type [9].

As a matter of fact the $E_{1/2}$ of the reduction waves shift progressively with rise of pH to more negative potentials indicating the contribution of H$^+$ ions to the electrode reaction.

The $E_{1/2}$ − pH curves (Fig. 2) for both waves are satisfactory linear relations with slopes amounting to 0.083 − 0.09 volt.

Analysis of the waves revealed that the electrode reaction is irreversible. From the values of (α_{na}) and slope of $E_{1/2}$- pH curves. The number of protons involved
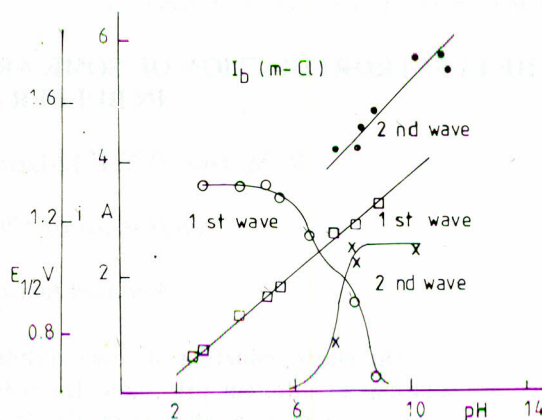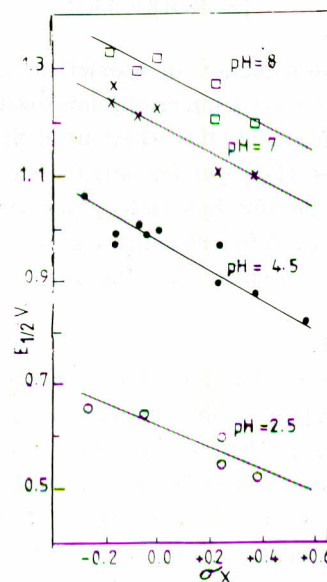

Fig. 3. Dependence of the half wave potential ($E_{1/2}$) of substituted (ASA) on Hammett constant (σ_x) in 30 % DMF at different pH values.

in the rate determining step was found to be 2 in a solution of pH ≤ 6 and 1 for a medium of pH ≥ 8.

The i_1 − pH curves (Fig. 2) for the main wave comprises two steps one with the acid range and the other in alkaline solutions. The variation of i_1 with pH obeys the Meites [9] equation for changes of i_1 with pH in systems governed by the rate of a preceding acid − base reaction from which the following form was derived [10].

$$pH = Log \frac{i_1 - i}{i} + \log 0.886 \sqrt{K_{i/K}}$$

the log $\frac{i_1-i}{i}$ —pH plots are linear relations with almost identical slopes but having varied intercepts. The position of the curve shifts to higher pH range as the donor character of the substituent increase.

The effect of pressure at Hg-head on i_1 revealed that the electrode process is mainly diffusion controlled with partial kinetic contribution. The value of x in the relation $i_1 = Kh^x$ amounts to 0.3 – 0.48.

The electrode reaction. To clarify the conflicta between previous authors [5,6] concerning the final reduction products, a large scale electrolysis for compound I was performed at pH [4,10]. The electrolysis products were then extracted by ether and identified by ir and ^{1}H NMR spectroscopy (Fig. 4 A&B). At pH 4 two products
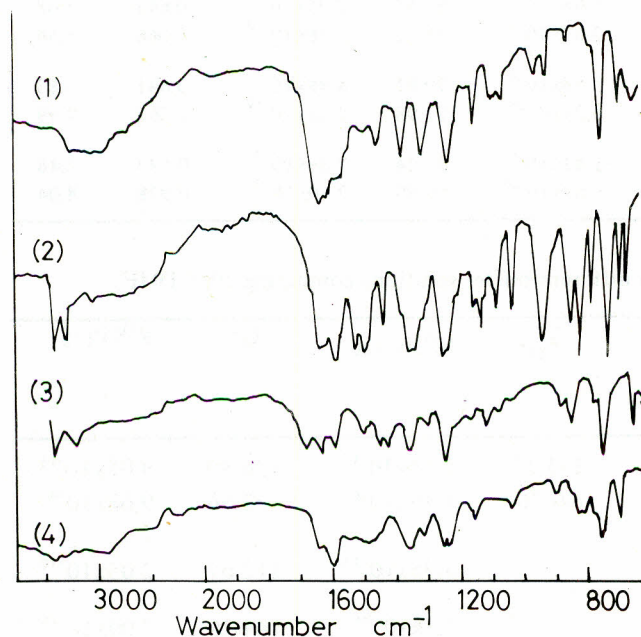

Fig. 4 (A) Infrared spectra of the; 1-Arylidene salicylic hydrazide; 2—Salicylic hydrazide; 3—Reduction product obtained in acid solution; 4—Reduction product obtained in alkaline medium.
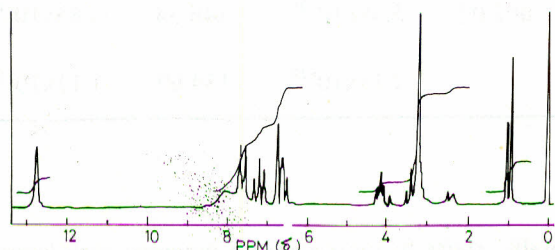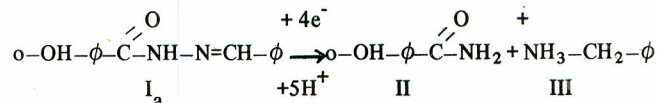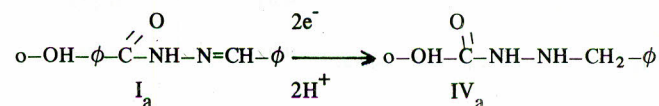

Fig. 4 (B). ^{1}H NMR spectra of the reduction product obtained in acid solution.

were isolated which proved to be benzylamine salt and salicylamide. The formation of these product involves the cleavage of the N—N bond according to the reaction;
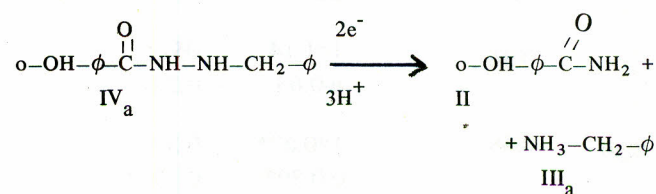
$$o-OH-\phi-\overset{\overset{O}{\diagup\!\!\diagup}}{C}-NH-N=CH-\phi \xrightarrow[+5H^+]{+4e^-} o-OH-\phi-\overset{\overset{O}{\diagup\!\!\diagup}}{C}-NH_2 + \overset{+}{N}H_3-CH_2-\phi$$

$$I_a \qquad\qquad\qquad\qquad II \qquad\qquad III$$

The ratio of the protons to electrons in the overall reaction is gained from the relation $\triangle E_{1/2}/pH = 0.059 (ZH+/n)$. The value obtained amounts to 1.4-1.5.

At pH 10, one product was isolated which was proved from the results of spectral analysis (Fig. 4A, 4B), to be salicyl benzyl hydrazine formed through the solvation of the C=N linkage according to the following reaction ;

$$o-OH-\phi-\overset{\overset{O}{\diagup\!\!\diagup}}{C}-NH-N=CH-\phi \xrightarrow[2H^+]{2e^-} o-OH-\overset{\overset{O}{\parallel}}{C}-NH-NH-CH_2-\phi$$

$$I_a \qquad\qquad\qquad\qquad IV_a$$

A support for the N—N cleavage in acid solution as first step is gained from the results of previous studies as azomethine [10] or azo-azomethine compounds[11].

Confirmation of the electrode reaction was gained by carrying out a large scale electrolysis at pH 9.17 for compound I_a. The resulting solution containing the hydrazone derivative IV_a was acidified to pH 4.8 and its polarogram recorded. The wave obtained, displayed a height equivalent to two electrons and its $E_{1/2}$ was 0.05 volt more positive than for compound I_a. This step corresponds to the N—N bond cleavage according to the equation;

$$o-OH-\phi-\overset{\overset{O}{\parallel}}{C}-NH-NH-CH_2-\phi \xrightarrow[3H^+]{2e^-} o-OH-\phi-\overset{\overset{O}{\diagup\!\!\diagup}}{C}-NH_2 +$$

$$IV_a \qquad\qquad\qquad\qquad\qquad II$$

$$+ NH_3-CH_2-\phi$$

$$III_a$$

Kinetics of the electrode reaction. The various kinetic parameters of the electrode reaction are determined using Koutecky [12] method and its modified form [13]. The results obtained are given in (Table 1 and 2). The $\triangle G^*$ values denotes that the electrode proceeds irreversibly and that the irreversibility decreases as the pH of the medium increases.

The $K^oD^{-1/2}$ values lie within the range 3×10^{-2} -1.2×10^{-27} which accounts for the kinetic character of the electrode reaction. This is in accordance with the effect of Hg height.

The value of the reversible half wave potential $(E_{1/2}^r)$

Table 1. Polarographic Data of salicylic hydrazide derivatives.

Compd. No.	x	Exponent x in $i_1 = Kh^x$	αn_a	n_a	$\triangle E_{1/2}/pH$	Z_{H^+}	K^0	$\triangle G^0$	$K^0 D^{-1/2}$	$-E^r_{1/2}$	pH
I_a	H	0.29–0.50	0.97	2	0.09	2	6.87×10^{-7}	65.07	3.57×10^{-4}	0.586	2.92
			0.52	1	0.28	2	1.7×10^{-21}	149.47	8.85×10^{-19}	1.22	7.99
I_b	m–Cl	0.30,0.48	1.03	2	0.087	2	1.86×10^{-6}	62.56	9.68×10^{-4}	0.408	9.81
			0.76	1	0.119	2	2.13×10^{-22}	154.69	1.11×10^{-19}	0.868	7.39
I_c	p–Cl	0.33–0.47	1.03	2	0.086	2	8.52×10^{-6}	58.75	4.43×10^{-3}	0.468	2.67
			0.91	2	0.19	2	3.33×10^{-28}	138.23	1.73×10^{-25}	0.933	7.47
I_d	p-Br	0.32–0.45	0.94	2	0.08	2	1.3×10^{-6}	63.45	6.79×10^{-4}	0.5513	2.75
			0.67	1	0.187	2	5.39×10^{-27}	181.25	2.80×10^{-24}	0.954	8.29
I_e	m-CH$_3$	0.37–0.48	0.83	2	0.086	2	5.68×10^{-7}	65.55	2.95×10^{-4}	0.641	3.68
			0.41	1	0.116	1	2.67×10^{-17}	125.23	1.38×10^{-14}	1.066	8.54
I_f	p–CH$_3$	0.43–0.54	0.91	2	0.096	2	9.58×10^{-8}	70.01	4.98×10^{-5}	0.641	3.83
			–	–	–	–	4.2×10^{-22}	152.98	2.18×10^{-19}	1.068	7.99
I_g	o–OH	0.41	1.02	2	0.082	2	1.42×10^{-6}	63.24	7.39×10^{-4}	0.543	2.48
			0.49	1	0.117	1	5.01×10^{-25}	169.88	2.60×10^{-22}	0.978	8.04

Table 2. Results obtained for 5×10^{-4} M m-Cl ASH (I_b) in different buffer solutions containing 30 % DMF.

pH	Exponent x in il - Kh^x	na	Most probable -value	n_a	Z_{H^+}	K^0cm/sec	G*	$K^0 D^{-1/2}$
2.8		1=1.57	0.78	2	1=1.52	1.74×10^{-17}	126.30	9.05×10^{-15}
		u=o.39	0.19	1	u-0.76	1.86×10^{-6}	62.56	9.68×10^{-4}
5.47	0.39	0.88	0.44	2		3.95×10^{-15}	112.69	2.05×10^{-12}
	0.36	1=1.14	057	2		1.3×10^{-20}	144.25	7.09×10^{-18}
		u-0.63	0.32	1		$5.45 \times 1-^{/13}$	100.32	2.83×10^{-10}
7.39	0.48	1=0.67*	0.33	2		1.64×10^{-17}	126.44	8.55×10^{-15}
		0.0.39*	0.19	1		7.81×10^{-12}	93.64	4.06×10^{-9}
8.14	0.30	0.52	0.26	1	1=2.07	2.16×10^{-11}	90.86	1.23×10^{-8}
	0.46*	0.84*	0.42	2*	u=1.07	5.48×10^{-21}	146.54	2.85×10^{-18}
11.34		0.74	0.37	2*		2.13×10^{-22}	154.69	1.11×10^{-19}

*Second wave; l=lower; u=upper.

was determined using the method of Gelling [14] (Table 1).

Effect of substituent on $E_{1/2}$ and pK'_a. The position of the reduction waves, compared at one and the same pH, generally, shifts to more negative potential with increased donor property of the substituent on the arylidene ring.

The plot of $E_{1/2}$ as a function of σ_x – (Hammett constant) is a satisfactory linear relation with a negative

slope (fig. 3). This reveals the validity of the Hammett linear free energy relationship in the form;

$$E_{½ (x)} = E_{½ (H)} - \rho \, {}^{\sigma}x$$

with *p* values amount to 0.2–0.3 depending on the pH of the medium and the reduction wave under consideration.

The negative slope denotes that the electrode reaction is facilitated by acceptor substituent and antagonised by the donors. The shift of the $E_{½}$ to more negative potential with increased donor character of the substituent can be explained by the easy activating π-electrons of the arylidene ring to a π^*-level on the C=N linkage which antagonises the acquisition of reducing electron. Hence the latter process requires a higher energy compared to monosubstituted compound.

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