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Electrochemical studies of certain novel N|-(benzenesulfonyl)-3-methyl-4-(2|-substituted-aryl hydrazono)- pyrazolin-5-ones

Estudios electroquímicos de ciertos N|-(benceno sulfonilo)-3-metil-4-(2|-sustituido-arílico hydrazono)- pyrazolina-5-ones novedosos

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ABSTRACT

Polarographic and cyclic voltammetric reduction of N|-(benzenesulfonyl)-3-methyl-4-(2|-substituted-aryl hydrazono)-pyrazolin-5-ones was carried out in 40% (v/v) dimethylformamide in Britton-Robinson buffer solutions of pH 1.1-10.1. Thermodynamic parameters i.e. enthalpy of activation 'ΔH^*_p', heat of activation at constant volume 'ΔH^*_v' and entropy of activation 'ΔS^*' were evaluated. The reduction was found to be diffusion controlled and irreversible at all temperatures. The compound exhibits two polarographic waves in the entire pH range of study. The results obtained in polarography were compared with the results obtained in cyclic voltammetry and a mechanism for the electrode process was proposed in acidic and basic media.

RESUMEN

La reducción polarográfica y voltamperometría cíclica de N|-(benceno sulfonal)-3-metil-4-(2|-sustituido-arílico hydrazono)-pyrazolina-5-ones fue realizado en 40% (v/v) dimetil formamida en un amortiguador de Britton-Robinson con soluciones de pH 1.1-10.1. Fueron evaluados parámetros termodinámicos, por ejemplo, entalpía de activación 'ΔH^*_p', calor de activación a un volumen constante 'ΔH^*_v' y entropía de activación 'ΔS^*'. Se encontró que la reducción es controlada por la difusión así como que es irreversible en todas las temperaturas. El compuesto exhibe dos ondas polarográficas en el rango de estudio entero de pH. Se realizó una comparación entre los resultados obtenidos en la polarografía y los obtenidos en la voltamperometría cíclica; el proceso del mecanismo para el electrodo fue propuesto en materiales ácidos y bases.

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Keywords:
Aryl-hydrazono-pyrazolin-5-ones; polarography; cyclic voltammetry; reduction mechanism.

Palabras clave:
Arílico hydrazono-pyrazolina-5-ones; polarografía; voltametría cíclica; mecanismo de reducción.

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INTRODUCTION

Pyrazolin-5-ones possess a diverse spectrum of medicinal applications (Dastagiri, Prasad, Spoorthy & Ravindranath, 2013; Naik, Prasad, Spoorthy & Ravindranath, 2013; Gupta & Arora, 1983; Gürsoy, Demirayak, Capan, Erol & Vural, 2000; Hawash, El-Badawey & El-Ashmawey, 2006; Makhija, Kasliwal, Kulkarni & Neamati, 2004; Sivakumar & Rajasekaran, 2013; Narasimhan, Sharma, Kumar, Yogeeswari & Sriram, 2011). The medicinal applications are due to their ready accessibility, diverse chemical activity and broad spectrum of biological and pharmacological properties. Electrochemistry has become an important tool in drug discovery and research. The medicinal applications are due to the close resemblance between biological and electrochemical reduction patterns (Shirinzadeh, Yilmaz, Gumustas, Suzen, Ozden & Ozkan, 2010; Vire & Kauffmann, 1994). Research in electrochemistry suggest that the nature of the medium influences the redox pathway of the drug (Perlin & Dempsy, 1974).

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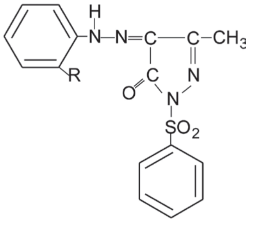
In the current study, the authors attempt to determine the nature of the wave, the formal heterogeneous rate constant, thermodynamic functions and the effect of substituents for the series of arylazopyrazoline-5-ones in Britton-Robinson buffer solutions.

MATERIALS AND METHODS

All reagents used were of analytical reagent grade procured from Merck, India. The working solutions were prepared by using double distilled water. pH measurements were made using pH meter Model L1-10 manufactured by Elico Private Limited, Hyderabad, India. The instrument consists of three units: (1) a dropping mercury electrode assembly, (2) a mains operated direct current (DC) polarographic unit CL-25, and (3) mains operated self-balancing strip chart recorder model LR 101P. The polarographic unit is capable of recording polarograms either with increasing or decreasing applied voltage continuously ranging from -3.0 V to 0 V or 0 V to +3.0 V with an accuracy of ±1 mV. Lingane type of H-cell with a capacity of 25 mL was used in polarographic studies. The dropping mercury electrode had the capillary characteristics, m = 2.422 mg/s, t = 2.5 s, h = 60 cm. The cyclic voltammetric unit consists of an x-y recorder (Model RE.00074), PAR 173 potentiostat and PAR 175 Universal Programmer. A single compartment cell model 303 HMDE supplied by PAR with silver wire as reference electrode and platinum wire as counter electrode was used in the studies. A static mercury drop electrode (HMDE 303) with a drop area of 0.0096 cm^2 was used as working electrode.

Title compounds were synthesized by the procedure reported in the literature (Srenivasan, Prasad, Swami & Ravindranath, 2013).



Compound	1	2	3	4	5
-R	H	CH_3	OCH_3	OH	Cl

General procedure for electrochemical studies

10 mL of buffer solution of required pH, 2.5 mL of aryl hydrazono pyrazolin-5-one of required concentration and 10 mL of dimethylformamide were pipette out into polarographic cells or cyclic voltammetric cell. The total volume reached 25 mL with distilled water. Polarograms/cyclic voltammograms were recorded after creating a vacuum over the experimental solution with nitrogen gas.

RESULTS AND DISCUSSION

Polarographic studies

Among the sites susceptible for reduction namely, the exocyclic >C=N–, the cyclic >C=N– and cyclic amide, exocyclic >C=N– is more susceptible for reduction than cyclic >C=N– and cyclic amide. This was confirmed by the fact that N-(benzenesulfonyl)-pyrazolin-5-one does not undergo reduction under the experimental conditions of study. Hence polarographic waves observed in the present studies were due to the reduction of exocyclic >C=N– group. Aryl hydrazono pyrazolin-5-ones under study exhibit two waves in the pH range 1.1-10.1. Model polarograms are shown in the figure 1. The results are shown in the table 1 (see page 13). The linear dependence of the limiting current (i_L) on the square root of the height of the mercury column ($h^{1/2}$) and the concentration of the depolarizer (C) suggests that the nature of the electrochemical process is controlled by diffusion (figure 2 and figure 3). Semi logarithmic analysis of the waves also suggests that the nature of the wave is irreversible (figure 4). This was further confirmed by the shift of half wave potentials towards more negative values with the increase in the concentration of the depolarizer (Meites, 1967). The irreversible nature may be due to the bulky aryl hydrazono group at the end of >C=N- linkage (Malik & Goral, 1978).

It can be seen from table 1 (see page 13) that limiting current in the first wave was unaltered with pH (1.1-10.1). The first wave was due to the two electron reductive cleavage of >N-N< in the azomethine group (>C=N-NH-). The reductive cleavage involves the same number of electrons in the entire pH range of study and was not affected by the acid-base equilibrium.

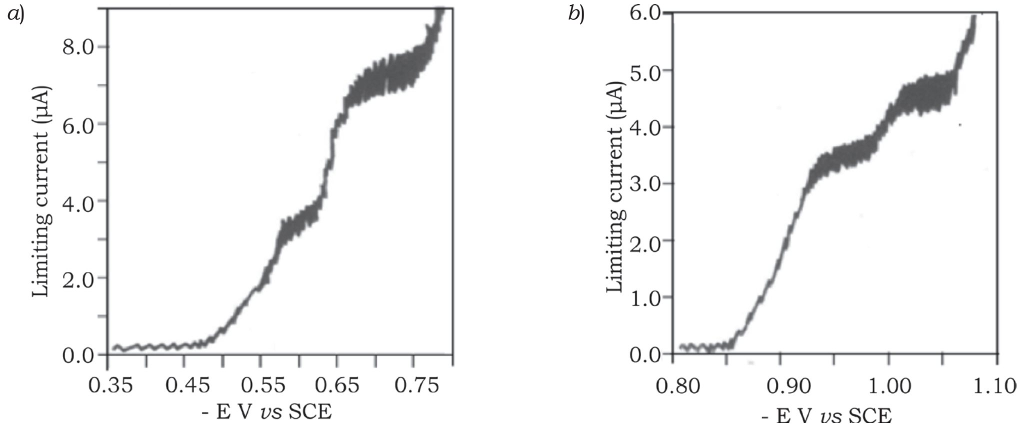


Figure 1. Polarograms of N|-(benzenesulfonyl)-3-methyl-4-(2|-methoxy-benzene hydrazono)-pyrazolin-5-ones. *a*) indicates polarogram drawn at pH 4.1 and *b*) that at 8.1.
Source: Authors own elaboration.

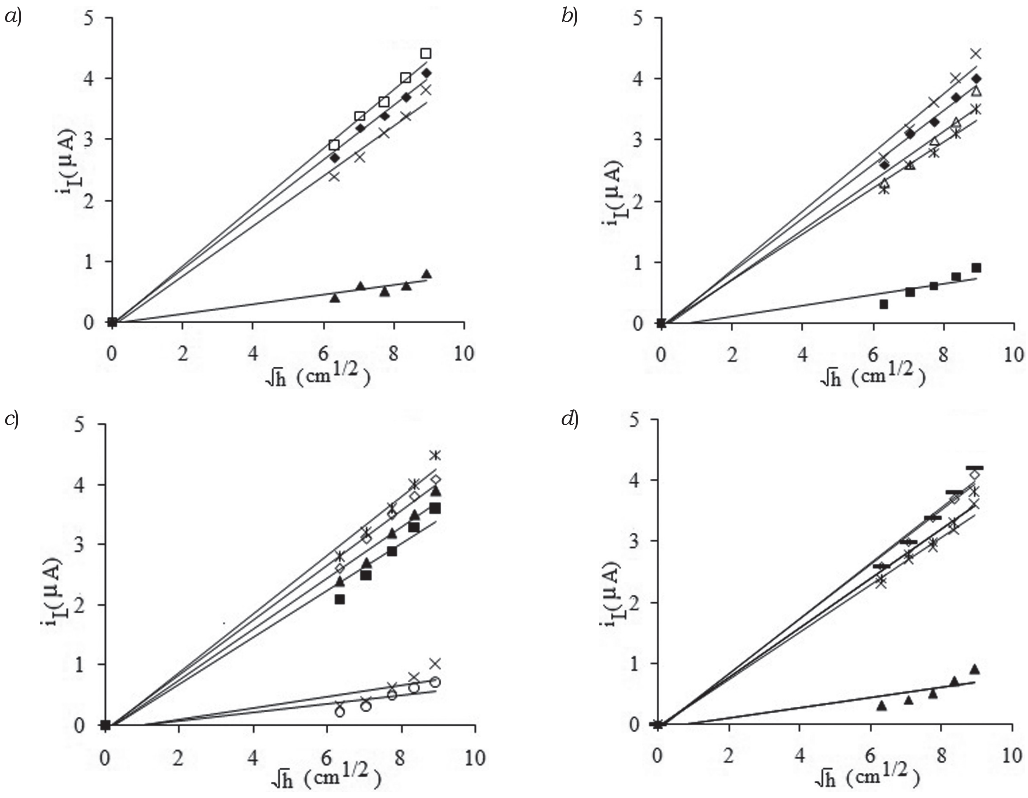


Figure 2. Influence of limiting current on the square root of the height of the mercury column in aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M). *a*): ◆H,4.1,I; □H,8.1,I; ▲H,8.1,II; ×Met,4.1,I, *b*): ◆H,4.1,II; ■Met,8.1,II; △Mxy,4.1,II; ✳Cl,4.1,I, ×Hxy,4.1,II; *c*): ◇Met,4.1,II; ■Mxy,4.1,I; ▲Mxy,8.1,I; ×Mxy,8.1,II; ✳Hxy,8.1,I; ○Cl,8.1,I, *d*): ◇Met,8.1,I; ‾Hxy,4.1,I; ▲Hxy,8.1,II; ×Cl,4.1,II and ✳Cl,8.1,I. 4.1 and 8.1 indicate the pH, I and II indicate first and second wave respectively.
Source: Authors own elaboration.

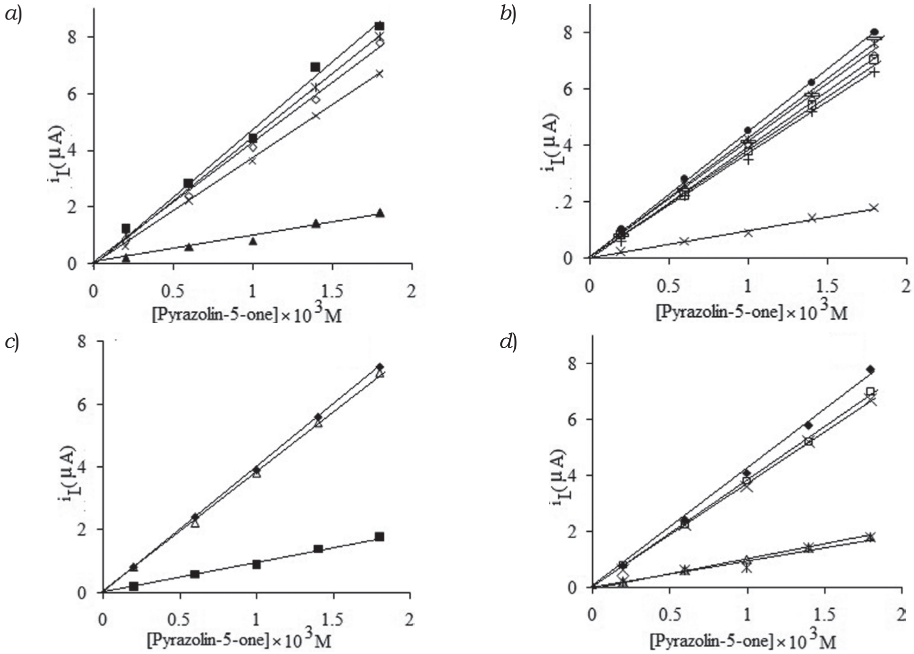


Figure 3. Influence of limiting current on the concentration of aryl hydrazono-pyrazolin-5-ones. (1×10^{-3} M). *a*): ◇H,4.1,I; ■H,8.1,I; ▲H,8.1,II; ×Mxy,4.1,I; ✳Hxy,4.1,II, *b*): ×Met,8.1,II; ◇H,4.1,II; ✳Hxy,4.1,I; □Met,4.1,I; ●Hxy,8.1,I; ═Met,4.1,II; +Cl,4.1,I, *c*): ◆Mxy,8.1,I; ■Hxy,8.1,II; △Cl,8.1,I, *d*): ◆Met,8.1,I; ×Cl,4.1,II; □Mxy,4.1,II; ✳Cl,8.1,I and △Mxy,8.1,II. 4.1 and 8.1 indicate the pH, I and II indicate first and second wave respectively.
Source: Authors own elaboration.

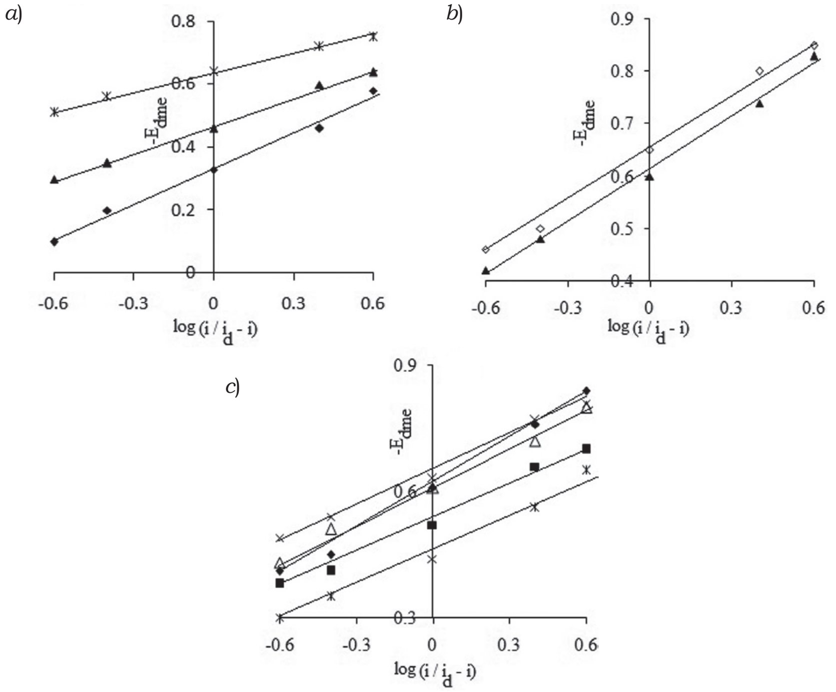
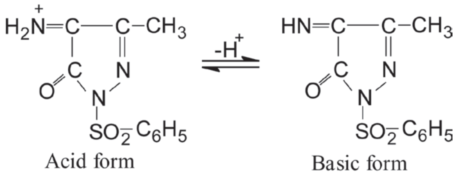


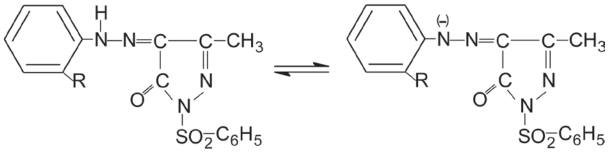
Figure 4. Semi log plots of aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M). *a*): ◆H,I; ▲Met,I; ✳Cl,II, *b*): ◇H,II; ▲Hxy,I, *c*): ◆Met,II; ■Mxy,I; ▲Mxy,II; ×Hxy,II and ✳Cl,I. 4.1 and 8.1 indicate the pH, I and II indicate first and second wave respectively.
Source: Authors own elaboration.

This further reveals that both the protonated and non-protonated forms of the depolarizer were electro active. However, both the half wave potentials and the limiting currents of the second wave changed with pH (1.1-7.1). The second wave was due to the two electron reduction of the exocyclic imino group (>C=NH) formed in the >N-N< reductive cleavage of azomethine group (>C=N-NH-). The limiting current of the second wave decreases with an increase in pH and was attributed to the electro active nature of protonated form of the depolarizer.

The decrease in the height of the second wave with increasing pH was due to the decrease in the rate of protonation with increase in pH.



In alkaline solutions, aryl hydrazono pyrazolin-5-ones exist in azomethine anionic form and the later undergoes chemical cleavage partially into heterocyclic carbonyl compound (Fahmy, Abdel & Badran, 1981). Equilibrium exists between the azomethine anionic form and heterocyclic carbonyl compound. The decrease in limiting current with increased pH could be attributed to either the chemical cleavage of depolarizer and or the acid-base equilibrium.



Half wave potentials of the first and second waves become more negative with increase in pH within the range 1.1-7.1 and remain constant in alkaline media. A plot of $E_{1/2}$ *vs* pH is shown in figure 5 (see page 15). This indicates the participation of protons in the reduction process. The fractional value of *P* indicates that heterogeneous proton transfer was taking place in the electrode process (Ravindranath, Rama, Brahmaji, 1983).

The coulometric data (De Vries & Kroon, 1953) of $N^{|}$-(benzenesulfonyl)-3-methyl-4-(benzene hydrazono)-pyrazolin-5-one is given in table 2.

Taking the following all together; the decrease in the heterogeneous rate constant value ($k^{o}_{f,h}$), the increase of activation free energy change (ΔG^{*}), and the increase in pH (table 1), it may be concluded that the electrode reaction was rendered increasingly difficult with increases in pH.

Effect of temperature

The values of $k^{o}_{f,h}$ and other thermodynamic parameters (enthalpy of activation 'ΔH^{*}_{p}', heat of activation at constant volume 'ΔH^{*}_{v}' and entropy of activation 'ΔS^{*}') were evaluated from three different methods (Gaur & Bhargava, 1973; Meites & Israel, 1961; Oldham & Parry 1968) proposed in the literature. The increase in the value of $k^{o}_{f,h}$ with increase in temperature (table 3 and table 4) suggest that the irreversibility of electrode reaction was increasing with increase in temperature. This observation was in harmony with the decrease in αn_a values (Jha, Jha & Srivastava, 1975; Meites, 1965; Sharma, Jha & Singh, 1975; Sharma & Singh, 1979) (α is the transfer coefficient and n_a is the number of electrons involved) with increase in temperature as shown in the table 5 (see page 16). The negative value of ΔS^{*} indicates the formation of activated state with a decreased entropy (Glasstone & Lewis, 1982). The positive and high values of ΔG^{*} indicate the non spontaneous process of the electrode reaction (Glasstone & Lewis, 1982). The high values of ΔG^{*} indicate that the reaction rate was low (Glasstone & Lewis, 1982).

Effect of substituents on reduction process

For the purpose of establishing the effect of substituent on the reduction process, $E_{1/2}$ was plotted against Hammett substituent constant. The substituent values were taken from the literature (Meites, 1967). The values of specific reaction constant (ρ) calculated from $E_{1/2}$-σ_o plot were positive (Hammett, 1940) (table 6, see page 16) indicating the significance of the electron addition step.

The position of the first wave on the potential axis suggests that the wave was due to the two electron reductive cleavage of >N-N< in the azomethine group (>C=N-NH-). $E_{1/2}$ values were not affected by the acid-base equilibrium but were affected by the position of the substituent in the aromatic ring. It can be observed from the plots that electron donating substituents i.e. $-CH_3$, $-OCH_3$ and –OH shift $E_{1/2}$ towards more negative values whereas the electron withdrawing substituents i.e. –Cl shift $E_{1/2}$ towards more positive values. The presence of electron withdrawing substituent has facilitated while the presence of electron donating substituent has impeded the reductive cleavage of >N-N< bond.

Table 1.
Polarographic characteristics and kinetic parameters of aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M).

-R	pH	$-E_{1/2}$ V *vs* SCE		Limiting current (µA)		$\Delta E_{1/2}/\Delta pH$ (mv)		αn_a		No of protons (P)		$D\times10^6$ cm sec^{-1}		$I\times10^3$		$K^o_{f,h}$ cm sec^{-1}		ΔG^* K cal mol^{-1}	
		I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave
H	2.1	0.3	0.51	4.8	5.1	0.077	0.077	0.57	0.86	0.74	1.12	4.79	5.42	2.66	2.83	2.40×10^{-4}	2.10×10^{-7}	5.19	7.01
	4.1	0.45	0.66	4.1	4	0.077	0.077	0.57	0.86	0.74	1.12	3.49	3.34	2.27	2.22	1.34×10^{-5}	1.11×10^{-9}	5.94	9.37
	6.1	0.63	0.84	4.1	2.7	0.077	0.077	0.43	0.57	0.56	0.74	3.49	1.51	2.27	1.50	2.00×10^{-6}	1.55×10^{-9}	6.43	8.29
	8.1	0.78	0.99	4.4	0.8	0.077	0.077	0.34	0.15	0.44	0.19	4.00	0.13	2.44	0.44	1.10×10^{-6}	3.30×10^{-6}	6.7	6.30
	10.1	0.78	0.99	4.4	0.8	0.077	0.077	0.34	0.15	0.44	0.19	4.00	0.13	2.44	0.44	1.10×10^{-6}	3.30×10^{-6}	6.57	6.30
CH_3	2.1	0.34	0.54	4.3	5.3	0.79	0.81	0.49	0.74	0.65	1.01	3.84	5.85	2.39	2.94	2.21×10^{-4}	3.20×10^{-7}	5.22	6.90
	4.1	0.49	0.64	3.8	4.1	0.79	0.81	0.49	0.74	0.65	1.01	3.02	3.49	2.11	2.27	1.12×10^{-5}	1.41×10^{-8}	5.98	7.72
	6.1	0.67	0.87	3.8	3.8	0.79	0.81	0.40	0.52	0.53	0.71	2.99	2.99	2.11	2.11	2.00×10^{-6}	3.78×10^{-9}	6.49	8.06
	8.1	0.83	1.02	4.1	0.9	0.79	0.81	0.32	0.40	0.43	0.5	3.49	0.17	2.27	0.50	8.80×10^{-7}	1.63×10^{-9}	6.65	8.27
	10.1	0.83	1.02	4.1	0.9	0.79	0.81	0.32	0.40	0.43	0.5	3.49	0.17	2.27	0.50	8.80×10^{-7}	1.63×10^{-9}	6.65	8.27
OCH_3	2.1	0.39	0.49	4.2	4.8	0.08	0.081	0.43	0.62	0.58	0.85	3.68	4.79	2.33	2.66	1.17×10^{-4}	4.00×10^{-6}	5.38	6.25
	4.1	0.55	0.64	3.6	3.8	0.08	0.081	0.43	0.62	0.58	0.85	2.69	3.03	2.00	2.11	6.80×10^{-6}	8.50×10^{-8}	6.11	7.25
	6.1	0.72	0.83	3.6	2.9	0.08	0.081	0.34	0.45	0.46	0.62	2.69	1.74	2.00	1.61	2.10×10^{-6}	3.23×10^{-8}	6.41	7.50
	8.1	0.9	0.98	3.9	1.00	0.08	0.081	0.30	0.36	0.41	0.49	3.17	0.21	2.16	0.55	6.00×10^{-7}	1.08×10^{-8}	6.74	7.78
	10.1	0.9	0.98	3.9	1.00	0.08	0.081	0.30	0.36	0.41	0.49	3.17	0.21	2.16	0.55	6.00×10^{-7}	1.08×10^{-8}	6.74	7.78
OH	2.1	0.47	0.53	4.7	5.4	0.083	0.082	0.43	0.62	0.60	0.86	4.62	6.10	2.61	3.00	3.45×10^{-5}	1.70×10^{-6}	5.69	6.47
	4.1	0.63	0.67	4.2	4.4	0.083	0.082	0.43	0.62	0.60	0.86	3.68	4.00	2.33	2.44	2.10×10^{-6}	4.70×10^{-8}	6.42	7.40
	6.1	0.8	0.85	4.2	3.1	0.083	0.082	0.34	0.45	0.48	0.62	3.68	2.01	2.33	1.72	8.00×10^{-7}	2.45×10^{-8}	6.66	7.57
	8.1	0.98	1.01	4.5	0.9	0.083	0.082	0.30	0.36	0.42	0.50	4.20	0.17	2.50	0.50	2.70×10^{-7}	6.35×10^{-9}	6.95	7.92
	10.1	0.98	1.01	4.5	0.9	0.083	0.082	0.30	0.36	0.42	0.50	4.20	0.17	2.50	0.50	2.70×10^{-7}	6.35×10^{-9}	6.95	7.92
Cl	2.1	0.32	0.51	3.5	4.9	0.079	0.08	0.069	0.86	0.92	1.18	1.60	2.24	1.94	2.72	1.17×10^{-4}	4.00×10^{-6}	5.39	7.14
	4.1	0.46	0.66	3.5	3.6	0.079	0.08	0.069	0.86	0.92	1.18	1.60	1.64	1.94	2.00	6.80×10^{-6}	8.50×10^{-8}	6.37	8.47
	6.1	0.64	0.84	3.5	2.4	0.079	0.08	0.50	0.62	0.67	0.85	1.60	1.10	1.94	1.33	2.10×10^{-6}	3.23×10^{-8}	6.86	9.63
	8.1	0.78	0.99	3.8	0.7	0.079	0.08	0.40	0.50	0.53	0.68	0.74	0.32	2.11	0.39	2.00×10^{-7}	1.90×10^{-10}	7.03	8.83
	10.1	0.78	0.99	3.8	0.7	0.079	0.08	0.40	0.50	0.53	0.68	0.74	0.32	2.11	0.39	2.00×10^{-7}	1.90×10^{-10}	7.03	8.83

Source: Authors own elaboration.

Table 2.
Millicoulometric data for aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M); Medium: Aqueous DMF (40% v/v).

pH	First wave			Second wave		
	Limiting current (µA)	Time (sec)	*n* value	Limiting current (µA)	Time (sec)	*n* value
4.1	4.1	0	---	4.0	0	---
	3.1	7200	1.9	3.1	7200	1.9
	2.7	10 800	1.8	2.6	10 800	1.8
8.1	4.4	0	---	0.8	0	---
	3.3	7200	1.9	0.72	7200	1.9
	2.8	10 800	1.8	0.68	10 800	1.8

Source: Authors own elaboration.

Table 3.
Kinetic and thermodynamic parameters for the polarographic reduction of aryl hydrazono-pyrazolin-5-ones (1×10^{-3}M) at pH 4.1 (#MI, OP and GB stand for Meites & Israel (1961) treatment, Oldham & Parry (1968) treatment, and Gaur & Bhargava (1973) treatment respectively).

Method#	Parameter	Temperature (K)				Parameter	Temperature (K)				Parameter	Temperature (K)				Parameter	Temperature (K)			
		303	313	323	333		303	313	323	333		303	313	323	333		303	313	323	333
	-H	First wave					Second wave				$-CH_3$	First wave					Second wave			
MI	$K^{o}_{f,h}\times10^{7}$	7.75	4.20	1.50	1.10	$K^{o}_{f,h}\times10^{11}$	6.40	1.12	0.009	0.235	$K^{o}_{f,h}\times10^{7}$	6.40	3.40	3.46	1.50	$K^{o}_{f,h}\times10^{11}$	81.26	2.56	2.50	1.16
	ΔH^{*}_{p}	12.81	12.81	12.81	12.81	ΔH^{*}_{p}	21.87	21.87	21.87	21.87	ΔH^{*}_{p}	9.47	9.47	9.47	9.47	ΔH^{*}_{p}	19.36	19.36	19.36	19.36
	ΔH^{*}_{v}	12.21	12.19	12.17	12.51	ΔH^{*}_{v}	21.27	21.25	21.23	21.21	ΔH^{*}_{v}	8.87	8.85	8.83	8.81	ΔH^{*}_{v}	18.75	18.73	18.71	18.69
	ΔG^{*}	15.54	16.45	17.65	18.43	ΔG^{*}	2.12	2.30	2.68	2.55	ΔG^{*}	15.65	16.59	17.13	18.24	ΔG^{*}	19.67	22.49	23.24	24.50
	$-\Delta S^{*}$	11.00	13.60	16.90	18.86	$-\Delta S^{*}$	0.22	5.62	17.42	13.06	$-\Delta S^{*}$	22.34	24.74	25.70	28.33	$-\Delta S^{*}$	3.02	12.00	14.02	16.44
OP	$K^{o}_{f,h}\times10^{7}$	7.70	4.20	1.56	1.00	$K^{o}_{f,h}\times10^{11}$	6.40	1.15	0.46	0.24	$K^{o}_{f,h}\times10^{7}$	6.40	3.40	3.48	1.50	$K^{o}_{f,h}\times10^{11}$	76.00	2.60	2.50	1.80
	ΔH^{*}_{p}	13.17	13.17	13.17	13.17	ΔH^{*}_{p}	16.02	16.02	16.02	16.02	ΔH^{*}_{p}	9.42	9.42	9.42	9.42	ΔH^{*}_{p}	21.05	21.05	21.05	21.05
	ΔH^{*}_{v}	12.57	12.55	12.53	12.51	ΔH^{*}_{v}	15.41	15.39	15.37	15.35	ΔH^{*}_{v}	8.82	8.80	8.78	8.76	ΔH^{*}_{v}	20.44	20.42	20.40	2.38
	ΔG^{*}	15.54	16.45	17.63	18.43	ΔG^{*}	2.12	2.29	2.43	2.55	ΔG^{*}	15.94	16.58	17.13	18.19	ΔG^{*}	19.71	22.47	23.23	24.29
	$-\Delta S^{*}$	9.78	12.43	15.78	17.76	$-\Delta S^{*}$	19.09	24.28	27.72	30.17	$-\Delta S^{*}$	23.50	24.84	24.13	28.30	$-\Delta S^{*}$	2.43	6.54	8.76	12.32
GB	$K^{o}_{f,h}\times10^{7}$	8.60	5.10	1.80	1.30	$K^{o}_{f,h}\times10^{11}$	5.44	0.81	0.36	0.18	$K^{o}_{f,h}\times10^{7}$	8.50	4.10	4.20	1.80	$K^{o}_{f,h}\times10^{11}$	17.40	2.18	2.13	0.95
	ΔH^{*}_{p}	12.63	12.63	12.63	12.63	ΔH^{*}_{p}	15.94	15.94	15.94	15.94	ΔH^{*}_{p}	9.88	9.88	9.88	9.88	ΔH^{*}_{p}	20.59	20.59	20.59	20.59
	ΔH^{*}_{v}	12.03	12.00	11.98	11.96	ΔH^{*}_{v}	15.34	15.32	15.30	15.28	ΔH^{*}_{v}	9.28	9.26	9.24	9.22	ΔH^{*}_{v}	19.99	19.97	19.95	19.93
	ΔG^{*}	15.47	16.32	17.53	18.32	ΔG^{*}	2.13	2.32	2.45	2.57	ΔG^{*}	15.53	16.46	16.99	18.09	ΔG^{*}	20.60	22.59	23.35	24.64
	$-\Delta S^{*}$	11.37	13.78	17.16	19.10	$-\Delta S^{*}$	19.67	25.25	28.46	31.40	$-\Delta S^{*}$	20.62	23.00	24.01	26.65	$-\Delta S^{*}$	2.10	8.38	10.54	14.15
	$-OCH_3$										$-OH$									
MI	$K^{o}_{f,h}\times10^{7}$	3.90	7.00	7.90	1.90	$K^{o}_{f,h}\times10^{10}$	14.72	3.45	1.30	0.67	$K^{o}_{f,h}\times10^{7}$	1.20	2.90	2.00	2.5	$K^{o}_{f,h}\times10^{10}$	91.70	2.54	1.47	0.89
	ΔH^{*}_{p}	12.90	12.90	12.90	12.90	ΔH^{*}_{p}	17.39	17.39	17.39	17.39	ΔH^{*}_{p}	7.18	7.18	7.18	7.18	ΔH^{*}_{p}	11.94	11.94	11.94	11.94
	ΔH^{*}_{v}	12.30	12.28	12.26	12.24	ΔH^{*}_{v}	16.78	16.76	16.74	16.72	ΔH^{*}_{v}	6.58	6.56	6.54	6.52	ΔH^{*}_{v}	11.34	11.32	11.30	11.28
	ΔG^{*}	15.94	16.13	16.59	18.06	ΔG^{*}	18.61	20.87	22.18	23.34	ΔG^{*}	16.65	16.67	17.47	17.89	ΔG^{*}	18.20	21.06	22.11	23.15
	$-\Delta S^{*}$	12.02	12.31	13.43	17.49	$-\Delta S^{*}$	6.02	13.14	16.84	19.86	$-\Delta S^{*}$	32.32	32.32	33.83	34.16	$-\Delta S^{*}$	22.65	31.12	33.47	35.60
OP	$K^{o}_{f,h}\times10^{7}$	3.98	7.10	7.90	1.90	$K^{o}_{f,h}\times10^{10}$	48.00	3.50	1.30	0.68	$K^{o}_{f,h}\times10^{7}$	1.20	2.9	2.00	2.50	$K^{o}_{f,h}\times10^{10}$	27.00	2.60	1.50	0.80
	ΔH^{*}_{p}	13.22	13.22	13.22	13.22	ΔH^{*}_{p}	17.16	17.16	17.16	17.16	ΔH^{*}_{p}	9.15	9.15	9.15	9.15	ΔH^{*}_{p}	11.70	11.70	11.70	11.70
	ΔH^{*}_{v}	12.62	12.60	12.58	12.56	ΔH^{*}_{v}	16.56	16.54	16.52	16.50	ΔH^{*}_{v}	8.55	8.53	8.51	8.49	ΔH^{*}_{v}	11.10	11.08	11.06	11.04
	ΔG^{*}	15.94	16.13	16.60	18.05	ΔG^{*}	18.59	20.87	22.17	23.34	ΔG^{*}	16.65	16.68	17.47	17.89	ΔG^{*}	18.94	21.06	22.09	23.22
	$-\Delta S^{*}$	10.96	11.28	12.43	16.48	$-\Delta S^{*}$	6.71	13.84	17.50	20.54	$-\Delta S^{*}$	26.74	26.83	27.74	28.25	$-\Delta S^{*}$	25.85	31.87	34.16	36.56
GB	$K^{o}_{f,h}\times10^{7}$	4.91	8.90	9.90	2.33	$K^{o}_{f,h}\times10^{10}$	50.00	3.21	1.16	0.58	$K^{o}_{f,h}\times10^{7}$	1.40	3.50	2.40	3.00	$K^{o}_{f,h}\times10^{10}$	27.40	2.33	1.30	0.77
	ΔH^{*}_{p}	13.04	13.40	13.04	13.04	ΔH^{*}_{p}	18.94	18.94	18.94	18.94	ΔH^{*}_{p}	7.91	7.91	7.91	7.91	ΔH^{*}_{p}	12.12	12.12	12.12	12.12
	ΔH^{*}_{v}	12.44	12.42	12.40	12.38	ΔH^{*}_{v}	18.34	18.32	18.30	18.28	ΔH^{*}_{v}	7.31	7.29	7.27	7.25	ΔH^{*}_{v}	11.52	11.50	11.48	11.46
	ΔG^{*}	15.82	15.99	16.45	17.94	ΔG^{*}	18.57	20.91	22.26	23.44	ΔG^{*}	16.55	16.57	17.35	7.77	ΔG^{*}	18.93	21.12	22.18	23.25
	$-\Delta S^{*}$	11.15	11.41	12.54	16.71	$-\Delta S^{*}$	0.78	8.30	12.25	15.59	$-\Delta S^{*}$	30.50	29.64	31.20	31.60	$-\Delta S^{*}$	24.50	30.72	33.13	35.39

Source: Authors own elaboration.

Table 4.
Kinetic and thermodynamic parameters for the polarographic reduction of aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M) at pH 4.1.

Method#	Parameter	Temperature (K)				Parameter	Temperature (K)			
		303	313	323	333		303	313	323	333
	-Cl	First wave					Second wave			
MI	$K^{o}_{f,h}\times10^{7}$	1.90	5.9	1.90	1.70	$K^{o}_{f,h}\times10^{11}$	5.73	9.28	2.30	1.89
	ΔH^{*}_{p}	12.40	12.40	12.40	12.40	ΔH^{*}_{p}	7.09	7.09	7.09	7.09
	ΔH^{*}_{v}	11.79	11.77	11.75	11.73	ΔH^{*}_{v}	6.49	6.47	6.45	6.43
	ΔG^{*}	16.38	16.25	17.51	18.16	ΔG^{*}	21.26	21.69	23.29	24.17
	$-\Delta S^{*}$	15.14	14.28	17.82	19.27	$-\Delta S^{*}$	48.77	48.62	52.15	53.30
OP	$K^{o}_{f,h}\times10^{7}$	1.90	5.80	1.90	1.70	$K^{o}_{f,h}\times10^{11}$	5.73	9.50	2.30	1.90
	ΔH^{*}_{p}	13.04	13.04	13.04	13.04	ΔH^{*}_{p}	7.36	7.36	7.36	7.36
	ΔH^{*}_{v}	12.43	12.41	12.39	12.37	ΔH^{*}_{v}	6.76	6.74	6.72	6.70
	ΔG^{*}	13.68	16.25	17.50	18.14	ΔG^{*}	21.26	21.67	23.31	24.18
	$-\Delta S^{*}$	13.03	12.23	15.79	17.29	$-\Delta S^{*}$	47.86	47.70	51.30	52.58
GB	$K^{o}_{f,h}\times10^{7}$	2.00	7.00	2.00	2.00	$K^{o}_{f,h}\times10^{11}$	4.98	8.24	1.92	1.56
	ΔH^{*}_{p}	13.17	13.17	13.17	13.17	ΔH^{*}_{p}	7.36	7.36	7.36	7.36
	ΔH^{*}_{v}	12.89	12.87	12.85	12.83	ΔH^{*}_{v}	6.76	6.74	6.72	6.70
	ΔG^{*}	16.27	16.13	17.38	18.02	ΔG^{*}	21.26	21.76	23.42	24.31
	$-\Delta S^{*}$	11.15	10.40	14.01	15.56	$-\Delta S^{*}$	48.12	47.98	51.70	52.28

Units for each of the parameter: cm sec^{-1} for $K^{o}_{f,h}$; k cal mol^{-1} for ΔH^{*}_{p}, ΔH^{*}_{v} and ΔG^{*}; eu for ΔS^{*}; #MI, OP and GB stand for Meites & Israel (1961) treatment, Oldham & Parry (1968) treatment and Gaur & Bhargava (1973) treatment respectively.
Source: Authors own elaboration.

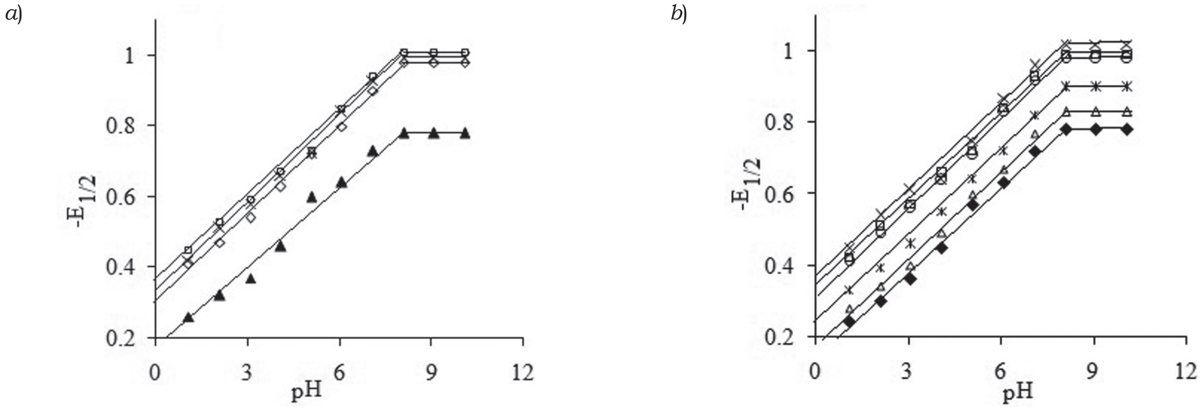


Figure 5. Influence of pH on half wave potential of aryl hydrazono-pyrazolin-5-ones. (1×10^{-3} M). *a*): ◇Hxy,I; □Hxy,II; ▲Cl,I; ×Cl,II, *b*): ◆H,I; □H,II; △Met,II; ×Met,I; ✱Mxy,I and ○Mxy,II. I and II indicate the first and second waves respectively.
Source: Authors own elaboration.

Table 5.
Effect of temperature on polarographic characteristics of aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M), Medium: Aqueous DMF (40% v/v).

Temp (K)	-$E_{1/2}$ V *vs* SCE		Limiting current (μA)		Temperature coefficient		αn_a		$D^{1/2}\times10^6$ cm sec^{-1}	
	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave	I wave	II wave
-H										
303	0.45	0.66	4.1	4.0	---	---	0.57	0.86	1.87	1.83
313	0.51	0.75	4.6	4.5	1.15	1.17	0.51	0.80	2.10	2.05
323	0.60	0.81	5.1	5.1	1.03	1.25	0.46	0.76	2.33	2.33
333	0.66	0.87	5.7	5.8	1.11	1.28	0.42	0.72	2.60	2.65
-CH_3										
303	0.49	0.64	3.8	4.1	---	---	0.49	0.78	1.73	1.87
313	0.57	0.81	4.4	4.7	1.46	1.36	0.43	0.68	2.00	2.15
323	0.62	0.86	5.0	5.3	1.28	1.20	0.38	0.63	2.28	2.42
333	0.73	0.94	5.5	5.9	0.95	1.07	0.34	0.29	2.51	2.69
-OCH_3										
303	0.55	0.64	3.6	3.8	---	---	0.43	0.62	1.64	1.73
313	0.57	0.81	4.2	4.4	1.54	1.46	0.37	0.56	1.92	2.00
323	0.62	0.92	4.7	5.0	1.12	1.27	0.32	0.51	2.15	2.28
333	0.81	1.02	5.2	5.6	1.01	1.01	0.28	0.47	2.37	2.56
-OH										
303	0.63	0.67	4.2	4.4	---	---	0.43	0.62	1.92	2.01
313	0.64	0.83	4.8	5.0	1.33	1.28	0.37	0.56	2.19	2.28
323	0.74	0.92	5.4	5.6	1.17	1.13	0.32	0.51	2.47	2.56
333	0.80	1.01	6.0	6.2	1.02	1.02	0.28	0.47	2.74	2.83
-Cl										
303	0.46	0.66	3.5	3.6	---	---	0.69	0.86	1.60	1.64
313	0.44	0.68	4.0	4.2	1.33	1.54	0.63	0.80	1.83	1.92
323	0.51	0.76	4.5	4.7	1.17	1.12	0.58	0.75	2.05	2.15
333	0.54	0.80	5.0	5.2	1.05	1.01	0.54	0.71	2.28	2.38

Source: Authors own elaboration.

Table 6.
Effect of pH on reaction constant for the reduction of aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M), medium: aqueous DMF (40% v/v).

pH	ρ value
2.1	0.14
4.1	0.15
6.1	0.14
8.1	0.13

Source: Authors own elaboration.

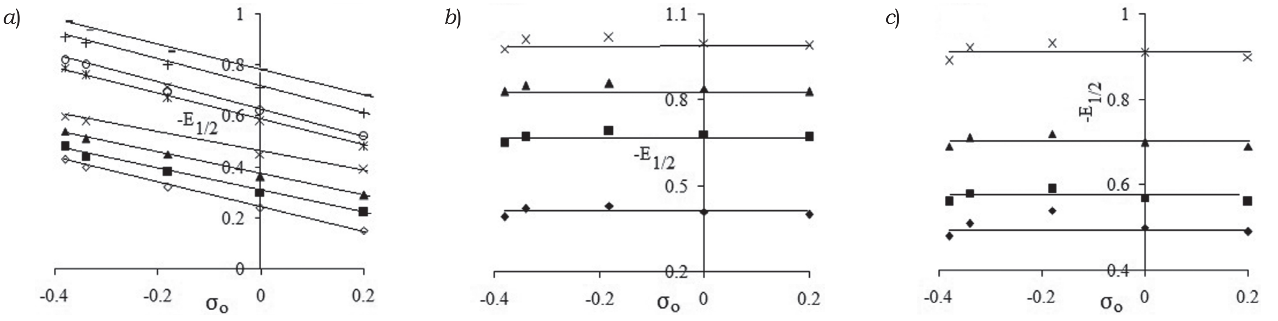


Figure 6. -$E_{1/2}$ *vs* σ_o plots of aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M). a): ◇1.1,I; ■2.1,I; ▲3.1,I; ×4.1,I; ✱5.1,I; ○6.1,I; +7.1,I; ═8.1,I, b): ◆1.1,II; ■4.1,II; ▲6.1,II; ×8.1,II, c) ◆2.1,II; ■3.1,II; ▲5.1,II and ×7.1,II. 1.1, 2.1 etc. indicate the pH, I and II indicate first and second wave respectively.
Source: Authors own elaboration.

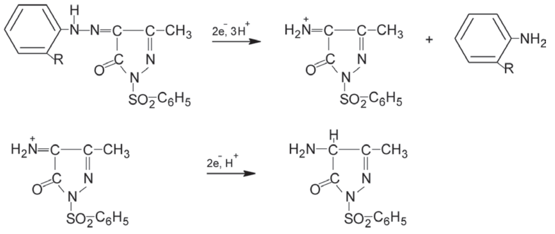
The position of the second wave on the potential axis suggests that the wave was ascribed to the two electron reduction of imine in acidic medium and the hetero cyclic diketone in alkaline medium. It can be noticed from the table 1 and figure 6 (b), (c) that the $E_{1/2}$ values for the process depend upon the acid-base equilibrium and was independent of position and nature of substituent in the aromatic ring.

Mechanism of reduction

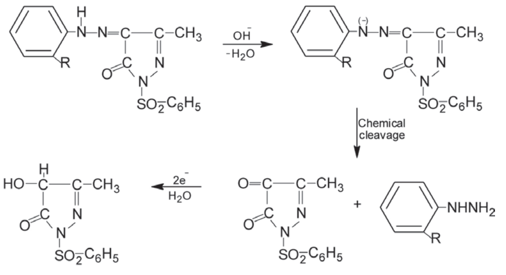
In an acidic medium, the first step involves the two electron reductive cleavage of >N-N< bond leading to the formation of N-(benzenesulfonyl)-3-methyl-4-imino-pyrazolin-5-one and substituted aniline. The second step involves the two electron reduction of ketimine to the corresponding amine. The variation of wave height with pH was similar to the trend reported in the literature for acid hydrolysis of imides (Cordes & Jemcks, 1963).

In an alkaline medium, the azomethine group exists in anionic form. The first wave was attributed to the two electron reductive cleavage of >N-N< bond to azomethine anion. The azomethine anion form was susceptible for chemical cleavage to the corresponding heterocyclic carbonyl compound. The second wave was due to two electron reduction of heterocyclic carbonyl compound to corresponding alcohol. The observed reduction behavior of carbonyl group was similar to that reported in literature (Zuman, 1970).

The reduction mechanism is shown in scheme 1 and scheme 2.



Scheme 1. Reduction mechanism in acidic medium



Scheme 2. Reduction mechanism in basic medium.

Cyclic voltammetric studies

Cyclic voltammetry studies resulted in two cathodic peaks at all scan rates and in different pH media studied. Model cyclic voltammograms are shown in figure 7. The cathodic peaks observed correspond to the waves observed in polarography. The linear plot of i_p *vs* $\upsilon^{1/2}$ passing through the origin suggests the diffusion controlled nature of the electrode process. The absence of anodic peak in the reverse scan suggests the irreversible nature of the reduction. This was further confirmed by the negative shift of peak potentials with increase in scan rate. Plots, drawn between Hammett substituent constant and first cathodic peak potential, shown in figure 8, display a straight line with positive slope once again confirming the significant role of nucleophilic addition of electron. The data presented in table 7 reveals that the results were similar to those obtained in polarography. Hence the reduction mechanism observed in cyclic voltammetry was similar to that in polarography.

CONCLUSIONS

The present research reports the electrochemical studies of five novel aryl hydrazono pyrazolin-5-ones. Two well defined diffusion controlled and irreversible polarographic waves were observed for all compounds under study in the pH range 1.1-10.1. The number of electrons consumed in the reduction process was determined and plausible reduction mechanism in acidic and basic media was proposed. The results obtained in polarographic studies were compared with those obtained in cyclic voltammetric studies.

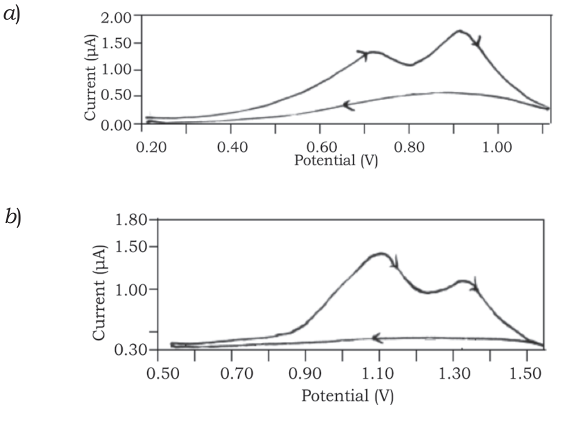


Figure 7. Cyclic voltammograms of N$^{|}$-(benzenesulfonyl)-3-methyl-4-(2$^{|}$-methoxy-benzene hydrazono)-pyrazolin-5-ones. *a*) indicates voltammogram drawn at pH 4.1 and *b*) that at 8.1.

Table 7.
Cyclic voltammetry data for aryl hydrazono-pyrazolin-5-ones (1×10^{-3} M); medium: 40% (v/v) aqueous DMF.

pH	Scan rate vs^{-1}	$-E_{pc}$ 1 V	$-E_{pc}$ 1I V	$-i_{pc}$ 1 μA	$-i_{pc}$ 1I μA	$-E_{pc}$ 1 V	$-E_{pc}$ 1I V	$-i_{pc}$ 1 μA	$-i_{pc}$ 1I μA	$-E_{pc}$ 1 V	$-E_{pc}$ 1I V	$-i_{pc}$ 1 μA	$-i_{pc}$ 1I μA	$-E_{pc}$ 1 V	$-E_{pc}$ 1I V	$-i_{pc}$ 1 μA	$-i_{pc}$ 1I μA	$-E_{pc}$ 1 V	$-E_{pc}$ 1I V	$-i_{pc}$ 1 μA	$-i_{pc}$ 1I μA
Compound		-H				$-CH_3$				$-OCH_3$				-OH				-Cl			
2.1	0.010	0.33	0.51	0.7	0.8	0.35	0.55	0.7	1.0	0.45	0.67	0.4	0.7	0.48	0.66	0.5	0.6	0.30	0.47	0.7	0.8
	0.050	0.39	0.57	1.6	1.7	0.43	0.63	1.5	2.1	0.51	0.73	1.0	1.4	0.54	0.72	1.1	1.4	0.36	0.53	1.6	1.9
	0.100	0.42	0.60	2.3	2.4	0.47	0.67	2.1	2.9	0.54	0.76	1.5	1.9	0.57	0.75	1.6	2.0	0.39	0.56	2.3	2.6
	0.200	0.48	0.66	3.3	3.5	0.52	0.72	3.0	4.2	0.59	0.81	2.2	2.7	0.62	0.80	2.3	2.9	0.44	0.61	3.3	3.8
	0.500	0.60	0.78	5.2	5.5	0.62	0.82	4.8	6.1	0.69	0.91	3.4	4.2	0.72	0.90	3.6	4.6	0.54	0.71	5.2	6.0
4.1	0.010	0.48	0.66	0.5	0.4	0.52	0.71	0.5	0.6	0.33	0.83	0.4	0.6	0.60	0.78	0.4	0.5	0.42	0.63	0.7	0.8
	0.050	0.54	0.72	1.1	0.9	0.60	0.79	1.1	1.2	0.69	0.89	0.9	1.2	0.66	0.84	1.0	1.1	0.48	0.69	1.4	1.7
	0.100	0.57	0.75	1.6	1.3	0.64	0.83	1.6	1.7	0.72	0.92	1.3	1.7	0.69	0.87	1.4	1.6	0.51	0.72	1.9	2.3
	0.200	0.63	0.81	2.3	1.9	0.69	0.88	2.3	2.4	0.77	0.97	1.9	2.4	0.74	0.92	2.0	2.3	0.56	0.77	2.7	3.4
	0.500	0.75	0.93	3.6	3.0	0.79	0.98	3.6	3.8	0.87	1.07	3.0	3.8	0.84	1.02	3.1	3.6	0.66	0.87	4.3	5.3
6.1	0.010	0.81	0.99	0.5	0.4	0.84	1.03	0.5	0.4	0.95	1.14	0.3	0.4	0.92	1.11	0.3	0.4	0.78	0.95	0.5	0.4
	0.050	0.87	1.05	1.1	0.9	0.92	1.11	1.1	1.0	1.01	1.20	0.8	0.9	0.98	1.17	0.8	0.9	0.84	1.01	1.0	0.8
	0.100	0.90	1.08	1.6	1.3	0.96	1.15	1.6	1.4	1.04	1.23	1.1	1.2	1.01	1.20	1.1	1.2	0.87	1.04	1.4	1.1
	0.200	0.96	1.14	2.3	1.9	1.01	1.20	2.3	2.0	1.09	1.28	1.6	1.8	1.06	1.25	1.6	1.8	0.92	1.09	2.0	1.6
	0.500	1.08	1.26	3.6	3.0	1.11	1.30	3.6	3.1	1.19	1.38	2.5	2.8	1.16	1.35	2.5	2.8	1.02	1.19	3.2	2.6
8.1	0.010	0.86	1.06	0.6	0.4	1.10	1.10	0.5	0.6	1.01	1.24	0.5	0.4	1.00	1.23	0.5	0.5	0.75	0.87	0.4	0.3
	0.050	0.92	1.12	1.3	0.8	1.18	1.18	1.2	0.9	1.07	1.30	1.0	0.8	1.06	1.29	1.1	1.1	0.81	0.93	0.7	0.7
	0.100	0.95	1.15	1.7	1.1	1.22	1.22	1.5	1.3	1.10	1.33	1.4	1.1	1.09	1.32	1.6	1.5	0.84	0.96	1.2	1.0
	0.200	1.01	1.21	2.4	1.7	1.27	1.27	2.2	1.8	1.15	1.38	2.0	1.6	1.14	1.37	2.3	2.3	0.89	1.01	1.7	1.4
	0.500	1.13	1.33	3.8	2.6	1.37	1.37	3.5	3.0	1.25	1.48	3.2	2.5	1.24	1.47	3.7	3.7	0.99	1.11	2.7	2.2

Source: Authors own elaboration.

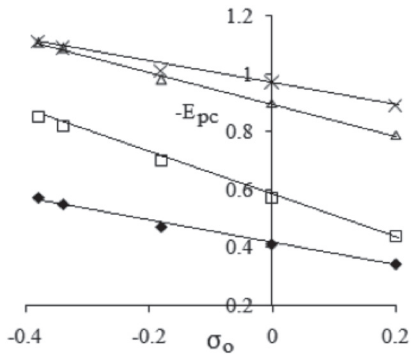


Figure 8. -Epc *vs* σ_o plots of aryl hydrazono-pyrazolin-5-ones; Scan rate =100 mVs^{-1}; ◆2.1,I; □4.1,I; △6.1,I and ×8.1,I. 4.1 and 8.1 indicate the pH respectively; I indicate the first cathodic peak.

APPENDIX

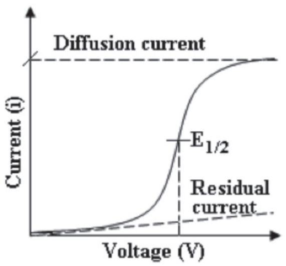


Figure 9. The i - E Curve (Polarogram).

Half-wave potential: The potential corresponding to the point of inflection of the curve is the Half-wave potential and is characteristic of the nature of the reacting material.

Diffusion current: The height of the curve is the diffusion current and is the function of concentration of the electroactive species.

Limiting current: The current corresponding to the plateau of the polarographic wave is called a limiting current.

Reaction constant: The reaction constant (ρ) is the measurement of sensitive of a particular reaction to the changes in electronic effects of substituent groups. The reaction constant depends on the nature of the chemical reaction, as well as reaction conditions (solvent, temperature, etc.). Both the sign and magnitude of the reaction constant are indicative of the extent of charge built-up during the reaction progress.

D is the diffusion coefficient and is an important parameter indicative of the diffusion mobility.

REFERENCES

Cordes, B. H. & Jemcks, W. P. (1963). The Mechanism of Hydrolysis of Schiff Bases Derived from Aliphatic Amines. *Journal of the American Chemical Society, 85*(18), 2843-2848.

Dastagiri Reddy, M. R., Prasad, A. R. G., Spoorthy, Y. N. & Ravindranath, L. K. (2013) Synthesis, Characterization and Antimicrobial Activity of Certain novel Aryl Hydrazone Pyrazoline-5-Ones Containing Thiazole Moiety. *Advanced Pharmaceutical Bulletin, 3*(1), 153-159.

De Vries, T. & Kroon, J. L. (1953). A Millicoulometer Method for the Determination of Polarographic n-Values. *Journal of the American Chemical Society, 75*(10), 2484-2486.

Fahmy, H. M., Abdel Aziz, M. A. & Badran, A. H. (1981). Electro reduction of a series of arylazo thiohydantoin derivatives at the DME. *Journal Electroanalytical Chemistry, 127*(1-3), 103-112.

Gaur, J. N. & Bhargava, S. K. (1973). A note on the kinetic parameter determination at the DME by koutecky's method. *Bulletin of the Chemical Society of Japan*, 46(10), 3314-3315.

Glasstone, S. & Lewis, D. (1982). *Elements of Physical Chemistry* (2nd Edition). India, New Delhi: Macmillan.

Gupta, D. R. & Arora, R. K. (1983). Characterization of Derivatives of Some Closely Related 1-Picolinoyl-3-methyl-4-(substituted)-pyrazoline-5-ones by Thin-Layer Chromatography. *Journal of Liquid Chromatography, 6*(14), 2695-2697.

Gürsoy, A., Demirayak, S., Capan, G., Erol, K. & Vural, K. (2000). Synthesis and preliminary evaluation of new 5-pyrazolinone derivatives as analgesic agents. *European Journal of Medicinal Chemistry, 35*(3), 359-364.

Hammett, L. P. (1940). *Physical Organic Chemistry.* New York: Mc Graw-Hill.

Hawash, S. A., El-Badawey, S. A. & El-Ashmawey, I. M. (2006). Nonsteroidal antiinflammatory agents-part 2 antiinflammatory, analgesic and antipyretic activity of some substituted 3-pyrazolin-5-ones and 1,2,4,5,6,7-3H-hexahydroindazol-3-ones. *European Journal of Medicinal Chemistry, 41*(2), 155–165.

Jha, S. K., Jha, S. & Srivastava, S. N. (1975). Influence of aqueous mixture of amides on the kinetics of electrode reduction of nickel(II) and cobalt(II) at dropping mercury electrode. *Z. Naturforsch, 30*B, 859-865.

Makhija, M. T., Kasliwal, R. T., Kulkarni, V. M. & Neamati, N. (2004). De novo design and synthesis of HIV-1 integrase inhibitors. *Bioorganic & Medicinal Chemistry, 12*(9), 2317-2333.

Malik, W. V. & Goral, N. (1978). Polarographic reduction of some aryl azopyrazoles in N, N'-dimethylformamide. *Journal Electroanalytical Chemistry, 87*, 129-135.

Meites, L. (1965). *Polarographic Techniques.* New York: Inter Science.

Meites, L. (1967). *Polarographic Techniques.* New York: Inter Science.

Meites, L. & Israel, Y. (1961). The calculation of electrochemical kinetic parameters from polarographic current-potential curves. *Journal of the American Chemical Society,* 83(24), 4903-4096.

Naik, K., Prasad, A. R. G., Spoorthy, Y. N. & Ravindranath, L. K. (2013). Design, synthesis, characterization and antimicrobial evaluation of new pyrazoline-5-ones. *Journal of Applied Pharmacy, 4,* 720-730.

Narasimhan, B., Sharma, D., Kumar, P., Yogeeswari, P. & Sriram, D. (2011). Synthesis, antimicrobial and antimycobacterial evaluation of 2-(substituted phenyl)-imidazol-1-yl -pyridin-3-yl-methanones. *Journal of Enzyme Inhibition and Medicinal Chemistry, 26*, 720-727.

Oldham, K. B. & Parry, E. P. (1968). Use of polarography and pulse-polarography in the determination of the kinetic parameters of totally irreversible electro reductions. *Analytical Chemistry, 40*(1), 65-69.

Perlin, M. D. D. & Dempsy, B. (1974). *Buffers for pH and Metal ion control.* London: Chapman & Hall.

Sharma, S. S., Jha, S. K. & Singh, M. (1975). Effect of TritonX-100 on the kinetics of irreversible electrode process: polarograpic reduction of Ni(II), Co(II), Zn(II) and Mn(II). *Indian Journal of Chemistry, 15*A, 742-746.

Sharma, S. S. & Singh, M. (1979). Polarographic studies on the influence of concentration and nature of different supporting electrolytes on the kinetics of irreversible electrode process of Ni(II) and Co(II). *Journal Indian Chemical Society, 56,* 183-191.

Shirinzadeh, H., Yilmaz, A. D., Gumustas, M., Suzen, S., Ozden, S. & Ozkan, S. A. (2010). Electrochemical behavior of indole-3-carboxaldehyde izonicotinoyl hydrazones: discussion on possible biological behavior. *Combinatorial Chemistry and High Throughput Screening, 13*, 619-627.

Sivakumar, K. K. & Rajasekaran, A. (2013). Synthesis, *in-vitro* antimicrobial and antitubercular screening of Schiff bases of 3-amino-1-phenyl-4- [2-(4-phenyl-1,3-thiazol-2-yl) hydrazin-1-ylidene]-4,5-dihydro-1H-pyrazol-5-one. *Journal of Pharmacy and Bioallied Sciencies., 5*(2): 126–135.

Srenivasan, P., Prasad, A. R. G., Swami, G. N., Ravindranath, L. K. (2013) Synthesis and Characterization of Certain Medicinally Important Novel Pyrazolin-5-ones. *Hecettepe Journal of Biological & Chemistry, 41*(1), 73-79.

Ravindranath, L. K., Rama Das, S. R. & Brahmaji Rao, S. (1983). Polarographic behaviour of arylazo pyrazoles. *Electochimica Acta*, *28*(5), 601-603.

Vire, J. C. & Kauffmann, J. M. (1994). Trends in electrochemistry in drug analysis. *Current Topics in Electrochemistry, 3,* 493-515.

Zuman, P. (1970). *Topics in Organic Polarography*. New York: Plenum Press.