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Electrochemical Reduction of 4-(3-Pyridylazo)-3-Amino-2-Pyrazolin-5-One

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Abstract. The electrochemical reduction of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one in universal buffer solutions of different pH values was studied at 268 K. From the results obtained, it was concluded that the azo compound was reduced via an ECEC mechanism (two-electron and two-proton mechanism). The mechanism was confirmed by digital simulation. The heterogeneous electron transfer and homogeneous protonation follow-up reaction parameters were evaluated and the electrode mechanism is discussed.

Keywords: electrochemical reduction, ECEC mechanism, aminopyrazoline, 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one, cyclic voltammetry, azo compounds

Introduction

Numerous azo compounds find important applications in the field of medicine (Jisun *et al.,* 2002; Netto *et al.,* 2001; Rageh *et al.,* 1999; Garg and Singh, 1970; Modest *et al.,* 1957). The electrochemical behaviour of these compounds plays an important role in their biological activity (Bourbonnais *et al.,* 1998; Leontievsky *et al.,* 1997; Solomon *et al.,* 1996). A literature survey reveals that only little work has been carried out on the electorochemical behaviour of heterocyclic azo compounds, such as arylazopyrazolones (Shawali *et al.,* 1992; Abdel-Hamid, 1986; Jain, 1984; Ravindranath *et al.,* 1983), and pyridylazophenol (Al Obaidi *et al.,* 1987; Florence *et al.,* 1974). The objective of the present investigation was to study the electrochemical reduction of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one in universal buffer solutions at different pH values ranging between 2.18 - 10.75. The study was carried out using two electrochemical techniques, namely, cyclic voltammetry and digital simulation, so that the mechanism for the electrochemical reduction of 4-(3-pyridylazo)-3-amino-2-pyrozolin-5-one could be formulated. The behaviour of the electrochemical reduction was investigated at 298 K and a schematic mechanism, consistent with the experimental results, has been proposed. The mechanism was further confirmed and fully characterized by cyclic voltammetric simulation analysis making use of computer programmes CVSIM and CVFIT (Dario *et al.,* 1998; Gosser and Zhang, 1991).

Materials and Methods

For the present electrochemical studies on heterocyclic azo compounds, 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one was prepared according to the method reported earlier (Fahmy *et al.,* 1990; Elnagdi and Abd Allah, 1973). The prepared compound was recrystallised from ethanol and characterized by elemental analysis and IR spectra. Stock solution (5.0×10^{-3} mol dm^{-3}) of the azo compound under study was prepared in 50% aqueous ethanol mixture. Brritton-Robinson modified universal buffers in the pH range of 2.18 - 10.75 were prepared in distilled water using analytical reagent grade chemicals (citric acid, boric acid, phasphoric acid and sodium hydroxide) with ionic strength of 0.4 mol dm^{-3} and were used as the supporting electrolytes (Brritton, 1956). Solutions for cyclic voltammetry measurements were prepared by mixing 1.0 ml of stock solution of the azo compound and 9.0 ml of the appropriate buffer solution. Dissolved Oxygen was removed from these solutions by flushing nitrogen gas for about 15 min. The pH of the buffers was checked with an Orion research model 601A/digital ionalyzer, using combined electrode.

Cyclic voltammograms were recorded using an EG&G PAR model 264 A polarographic analyzer. The measurements were carried out with a conventional three-electrode configuration. An EG&G PAR model SMDE 303A mercury-drop system in small dropping mode was used as the working electrode. The electrode area was 1.05×10^{-2} cm^{-2}. The reference electrode was an Ag/AgCl electrode. A 1.0 cm^2 platinum foil was used as auxiliary electrode throughout the experimental work. Solutions were purged with pure nitrogen before the measurements were done, and an atmosphere of nitrogen was maintained above the working solutions. All experiments were performed at 298 K.

Eversince the pioneering work of Feldberg (Feldberg, 1969), digital simulation techniques have played an important role

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in the analysis of electrochemical data (cyclic voltammetry). Digital simulation, on the basis of general methods developed for the treatment of solution of chemical reactions in the context of the explicit-finite-differences (Gosser and Rieger, 1988; Nielsen *et al.*, 1987), was used. For the purpose of deducing the mechanism, parameters were evaluated by comparing digital simulations with the experimental voltammograms. All digital simulations were done using CVSIM and CVFIT computer programmes. Computations of simulations and treatment of the cyclic voltammetric data were performed on a COPAM PC 3888-25 (80386-25 MHz) with a 80387 mathematical coprocessor. The Harvard Graphics version 2.3 was used for plotting the simulated and experimental cyclic voltammograms.

Results and Discussion

Cyclic voltammetry. The electrochemical reduction of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one was studied using hanging mercury electrode in universal buffer solutions in the pH range of 2.18 - 10.75. It gave cyclic voltammograms of a single well-defined reduction wave in the potential range of -0.4 to -1.6 versus Ag/Ag^+ throughout the pH range of study. At pH 2.18, the cyclic voltammetric wave was located at -0.618 volt at the scan rate of 50 mV per second. On increasing the pH of the solutions, the peak current potential (Ep) shifted to more negative values, and the peak current varied as well. This indicated the participation of hydrogen ions in the electrode process.

Examination of cyclic voltammograms obtained at different scan rate values in the range of 5-200 mV per second at pH 2.18 revealed that no anodic counterpart of the cyclic voltammetric wave was seen on the reverse sweep (Fig. 1). This observation indicated that either the reduction was totally irreversible, which is unlikely, or the reduction product was consumed rapidly by another process, such as protonation. The peak current potential (Ep) thus shifted to more negative potentials on increasing the scan rate. A similar behaviour was obtained at the pH values of 7.11 and 9.13. The effect of scan rate at pH 2.18 is shown as the representative example in Fig. 1. A linear relationship was obtained between the peak current potential (Ep) and logarithm of the scan rate (log ν) at each of the three pH values studied. The regression lines obtained were:

$$Ep = -(0.678\pm0.003) - (0.043\pm0.002) \log \nu;\ r = 0.994 \text{ at pH } 2.18 \quad (1)$$

$$Ep = -(1.204\pm0.001) - (0.052\pm0.009) \log \nu;\ r = 0.991 \text{ at pH } 7.11 \quad (2)$$

$$Ep = -(0.397\pm0.002) - (0.029\pm0.002) \log \nu;\ r = 0.996 \text{ at pH } 9.31 \quad (3)$$

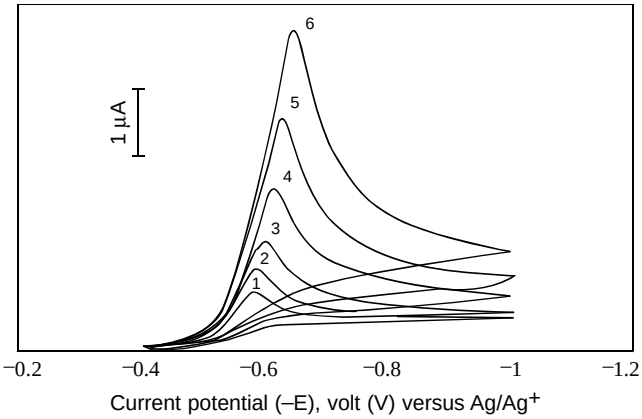


Fig. 1. Cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} of 4-(3-pyradylazo)-3-amino-2-pyrazolin-5-one in buffer solution at pH 2.18 at T = 298 K and different scan rates, (ν) = 5(1), 10(2), 20(3), 50(4), 100(5) and 200(3) mV per second.

The slopes obtained were larger than expected for a reversible process (Mabrouk *et al.*, 1988; Nicholson and Shain, 1964). On the other hand, the dependence of the voltammetric peak current (ip) of the cyclic voltammetric wave on the square root of scan rate ($\nu^{1/2}$) was linear with correlation coefficients close to unity at all the pH values studied. This indicates that the cyclic voltammetric wave was diffusion-controlled in nature (Lerke *et al.*, 1990; Feldberg, 1969). Moreover, the peak potentials were not symmetrical, as indicated from the peak width, Ep-Ep/2, for the cyclic voltammetric wave, which was greater than 28.25 mV at 298 K (Al Obaidi *et al.*, 1987; Bard and Faulkner, 1980) as expected for a two-electron reversible wave (Table 1). From these results it was concluded that the azo compound under investigation was reduced electrochemically in a diffusion controlled irreversible cyclic voltammetric wave involving a transfer of two electrons.

The dependence of the current function ($ip/\nu^{1/2}$), on the scan rate (ν) is an important diagnostic criterion for establishing the type of mechanism by cyclic voltammetry. Table 1 shows the value of $ip/\nu^{1/2}$ for the azo compound under investigation, as a function of scan rate, which decreased as the scan rate increasd.

The cyclic voltammetric wave obtained on the electrochemical reduction of the studied azo compound was also investigated as affected by the solution pH. It was observed that the peak current potential (Ep), of the cyclic voltammetric wave, shifted towards more negative potentials with increase in the pH of the solution. The relationship of Ep versus pH is shown in Fig. 2. The plot mainly shows two intersecting straight lines

for the first and second segments, respectively, as represented by the following regression lines:

Ep = - 0.367 to -0.106; r = 0.999 at 2.18 - 7.11 pH (4)

Ep = - 0.470 to -0.095; r = 0.999 at 7.11 - 10.75 pH (5)

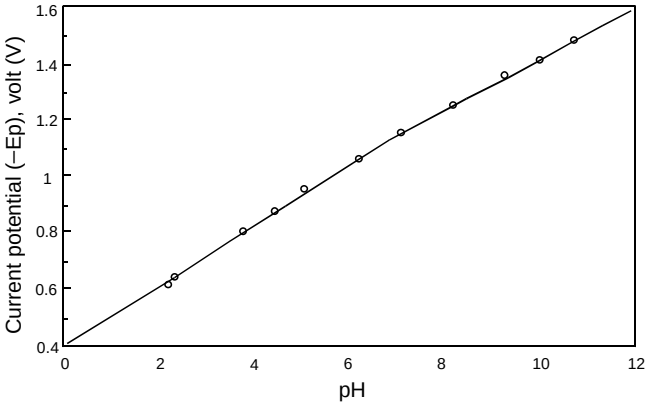


Fig. 2. Relationship of peak current potential (−Ep) and pH of 5.0 x 10^{-4} mol dm^{-3} of 4-(3-pyraylazo)-3-amino-2-pyrazolin-5-one at T = 298 K and scan rate (ν) = 50 mV per second.

The number of protons per molecule of the reactant involved in the electrode process (P) was determined using the following equations:

$$Ep - Ep/2 = \frac{1.857RT}{\alpha n_a F} \quad (6)$$

$$\triangle Ep / \triangle pH = \frac{0.05915}{\alpha n_a} P \quad (7)$$

where:

α = transfer coefficient

n_a = number of electrons involved in the rate determining step

Ep = peak current potential

P = complex coordination

R = gas constant

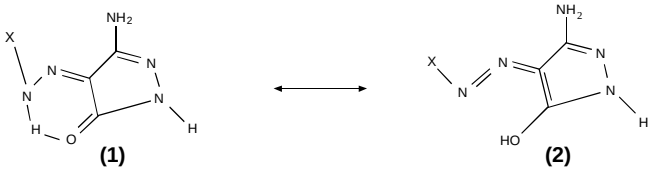
T = absolute temperature

△ Ep /△ pH = slope obtained from equations (4) and (5)

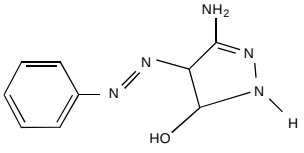
other symbols have their usual significance

On substituting the value of αn_a as obtained from (6) (Goyal and Minocha, 1985; Klingler and Kochi, 1981), the complex coordination values of P were found to be close to two at all the pH values studied.

For understanding the course of the electrode process corresponding to the cyclic voltammetric wave obtained, it was necessary to assign the wave to various electroactive groups in the azo compound under study. It has been concluded earlier that 4-azo-2-pyrazolin-5-ones exists mainly in the solid state, and in the non-aqueous solutions in the hydrazoketo (compound-**1**) and azohydroxy (compound-**2**) in tautomeric equilibrium (Helmy *et al.*, 1996, Aboutabl *et al.*, 1990; Ram and Rao, 1984) as shown below:



In aqueous medium, the equilibrium is however shifted to the azohydroxy form (compound **2**), due to its stabilization through a H-bonding interaction of water molecules with the oxygen atom of its hydroxy group. Thus, 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one is represented by the following structure (**3**):



(3)

Table 1. Cyclic voltammetric data for 5.0 x 10^{-4} mol dm^{-3} of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one at different pH values at 298 K

ν	pH: 2.18			pH: 7.11			pH: 9.31		
(mV/s)	-Ep (V)	Ep-Ep/2 (mV)	$i_p/\nu^{1/2}$ [μA(V/s)$^{-1/2}$]	-Ep (V)	Ep-Ep/2 (mV)	$i_p/\nu^{1/2}$ [μA(V/s)$^{-1/2}$]	$-E_p$ (V)	Ep-Ep/2 (mV)	$i_p/\nu^{1/2}$ [μA(V/s)$^{-1/2}$]
5	0.579	39	11.60	1.090	45	12.16	1.330	48	8.49
10	0.589	39	11.20	1.100	45	12.00	1.340	49	8.30
20	0.600	40	11.03	1.108	43	11.95	1.350	54	7.85
50	0.618	42	10.30	1.130	50	11.50	1.360	55	7.51
100	0.630	50	10.25	1.150	45	11.89	1.366	60	7.21
200	0.650	55	10.06	1.775	60	11.85	1.378	62	6.93

ν = scan rate; -Ep = peak current potential; $i_p/\nu^{1/2}$ = current function; i_p = voltammetric peak current; $\nu^{1/2}$ = square root of scan rate; Ep-Ep/2 = peak width

Therefore, the possible reduction groups in the azo compound under study were the cyclic azomethine groups, /N=C/, of the pyrazole and the pyridine nuclei. The azo /N=N/ groups out of these were more susceptible to reduction than the cyclic azomethine groups, since endocyclic groups required higher potential for reduction.

From the foregoing observations on the reduction of the azo compound under study, it is obvious that the rate-determining steps involved the uptake of protons (H^+) involving chemical reactions. On the basis of this conclusion, a mechanism is suggested, as step-wise detailed in Fig. 3, for $2e^-$ and $2H^+$ reduction of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one (Az).

$$Az + e^- \underset{}{\overset{E_1^o,\ k_s^2,\ \alpha_1}{\rightleftharpoons}} Az^{\bullet -} \qquad (8)$$

$$Az^{\bullet -} + H^+ \underset{}{\overset{k_f^1,\ k_b^1}{\rightleftharpoons}} AzH^{\bullet} \qquad (9)$$

$$AzH^{\bullet} + e^- \underset{}{\overset{E_2^o,\ k_s^2,\ \alpha_2}{\rightleftharpoons}} AzH^- \qquad (10)$$

$$AzH^- + H^+ \xrightarrow{k_f^2,\ k_b^2} AzH_2 \qquad (11)$$

Fig. 3. Scheme showing the mechanism of $2e^-$ and $2H^+$ reduction of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one(Az).

The first step (equation 8) in the proposed mechanism is a moderately fast (reversibly) single electron transfer to form radical anion ($Az^{\bullet -}$). In the second step (equation 9), the radical anion accepts a proton (irreversibly) to form a protonated radical ($AzH^{\bullet}$), which after taking another electron (reversibly) forms a protonated anion(AzH^-) in the third step (equation 10). The product of step three (equation 10) readily takes up one more proton (irreversibly), as shown in equation 11, to give the final product (AzH_2).

A similar two-electron and two-proton reaction mechanism (ECEC) for the reduction of some azo compounds has been proposed (McCleverty, 1986; Ravindranath *et al.*, 1984). The above mechanistic step is supported by the increase of peak current potential (Ep) with pH of the medium.

Digital simulation. The digital simulation at the three pH values studied (2.18, 7.11 and 9.31) was performed to establish the schematic mechanism proposed in Fig. 3 for the reduction of the azo compound. The kinetics of the process can be digitally simulated using the method of finite-differences, as described by Feldberg (1972; 1969). For simulation, the parameters required for the construction of the theoretical cyclic voltammograms according to the proposed mechanism were:

$C_{i,j}$ = respectively, the initial concentrations of the depolarizer and protons
E^o = standard electrode potentials
α = transfer coefficients
D = diffusion coefficients
k_s = standard heterogeneous electron transfer rate constants
k_c = homogeneous rate constants

For a solution of 5.0×10^{-4} mol dm^{-3} of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one in the buffer solution of pH 2.18, at the scan rate of 0.2 V per second, the digital simulated cyclic voltammogram was compared with that obtained experimentally. The best fit digital simulated and the experimental cyclic voltammograms have been recorded in Fig. 4 as the representative example for the above proposed schematic mechanism (Fig. 3).

Complete characterization for the electrochemical reduction kinetics for the azo compound was obtained. Moreover, the heterogeneous electron transfer parameters, as well as the homogeneous rate constants of the follow-up protonatiton reactions, were calculated. Data obtained through simulation-fitting for the azo compound at the pH values of 2.18, 7.11

Table 2. Cyclic voltammetric digital simulation data for 5.0 x 10^{-4} mol dm^{-3} of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one at different pH values at 298 K

	Heterogeneous parameters						Homogeneous parameters						
pH	$-E_1^{0/a}$ [V]	k_s^1 [cm s^{-1}]	α_1^c	$-E_2^{0/a}$ [V]	$k_s^{2/b}$ [cm s^{-1}]	α_2^c	$k_f^{1/d}$ [s^{-1}]	$k_b^{1/e}$ [s^{-1}]	10^3K	$k_f^{2/d}$ [s^{-1}]	$k_b^{2/e}$ [s^{-1}]	10^2K	10^6D^f [$cm^2\ s^{-1}$]
2.18	0.712	0.734	0.499	0.651	1.005	0.456	783.3	0.880	0.890	1800	7.930	2.27	8.50
7.11	1.214	0.527	0.582	1.175	0.593	0.505	560.0	0.573	0.980	1266	6.130	2.07	7.80
9.31	1.383	0.124	0.423	1.370	0.124	0.627	456.7[g]	0.120[g]	3.805	513.3[g]	0.993[g]	5.17	4.75

(a) ± 0.1%; (b) ± 5.7%; (c) ± 6.8%; (d) ± 9.1%; (e) ± 8%; (f) ± 2% $dm^3\ mol^{-1}\ sec^{-1}$

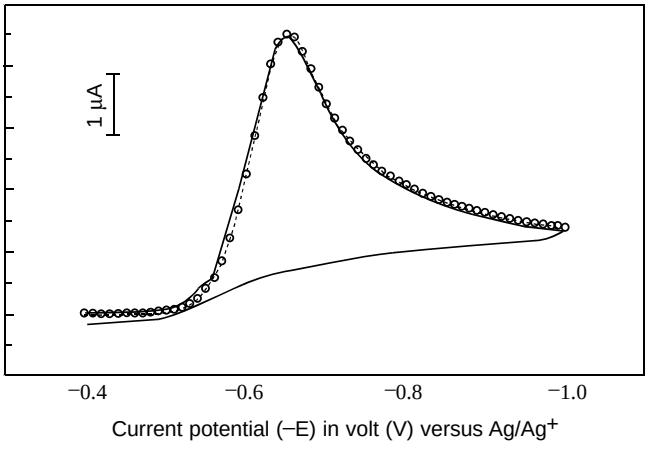


Fig. 4. Cyclic voltammograms of 5.0 x 10^{-4} mol dm^{-3} of 4-(3-pyridylazo)-3-amino-2-pyrazolin-5-one at T = 298 K and ν = 50 mV^{-1}; – background subtracted experimental, oooo digital simulation cyclic voltammograms, see Table 2 for values of parameters used in simulation.

and 9.31 have been summarized in Table 2. It was found that the obtained homogeneous rate constant values decreased with increase in pH, showing that the electrode reaction tended to become more irreversible. Moreover, the heterogeneous rate constant values were observed to be high in acidic medium indicating that the rate of the reaction was fast as the protonated form reduced. Thus, the reduction mechanism follows the proposed schematic mechanism (Fig. 3). It is concluded, therefore, that the electrode reduction kinetics had the same type over the entire pH range. This behaviour is supported by only the small observed difference in the slopes of the two segments of the Ep - pH relationship (Fig. 2; equations 4 and 5).

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