ELECTROCHEMICAL BEHAVIOUR OF THE MESOIONIC HETEROCYCLE: ANHIDRO

1-AMINO-5-PHENYL-2-MERCAPTO-1,3,4-TRIAZOLO-(3,2-c)-QUINAZOLIN-4-IUM

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ABSTRACT

An electrochemical study on the mesoionic heterocycle mentioned above is carried out, using dc polarography, cyclic voltammetry and controlled potential electrolysis. A reduction mechanism with a consumption of four electrons in each polarographic wave is proposed. On the other hand, we detect a kinetic response of CE type caused by an equilibrium between hydrolysis products ot the heterocycle.

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INTRODUCTION

Mesoionic heterocycles have a great interest both from theoretical point of wiew and also owing to its many biological and pharmacological applications (1).

Electrochemical studies of mesoionic compounds are rare. As far as we know, the only attempt is that of P. Zuman, which found that Sydnones are polarographically reducible both in acid and in alkaline medium. In the former case the electrons consumed per molecule is $n = 6$, whereas at high pH $n=4$ (2).

The aim of this paper is the study of the electrochemical behaviour of a mesoionic compound derived from 1,3,4-triazolo-(3,2-c)-quinazoline, anhidro 1-amino-5-phenyl-2-mercapto-1,3,4-triazolo-(3,2-c)-quinazolin-4-ium (I), which has been recently synthesized (3), in order to elucidate its reduction mechanism on the DME, using dc polarography, cyclic voltammetry and controlled potential electrolysis.

(I)
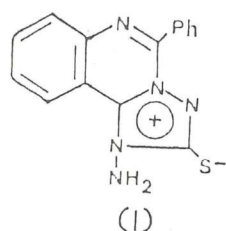
EXPERIMENTAL

CHEMICALS

The mesoinic compound (I) was prepared by reaction of 2-phenyl-4-tioxo-1,3-benzotiazine with thiocarbohydrazide (3). All other chemicals were of Merck reagent grade and their solutions were prepared in twice-distilled water. Mercury was first electrolytically purified and distilled three times.

APPÀRATUS

Dc polarograms were recorded on an AMEL 471 multipolarograph with a three-electrode system, using a thermostated cell ($25\pm0.1°C$). Potentials were referred to the SCE. The capillary used had the following characteristics when immersed in a Britton-Robinson buffer (pH = 7.0), at h = 50 cm and -1.0 V: m = 1.46 mg/s and t = 4.20 s. Voltammetric studies were carried out using an AMEL 448 oscilloscope with a METROHM EA 290 HMDE working electrode. Coulometric determinations of the electrons involved were made in an AMEL 551 potentiostat with an AMEL 563 integrator and an AMEL 862/D recorder, using a mercury pool electrode (area = 7 cm2) stirred by a magnetic stirrer. The pH values were measured with a Philips pH-meter, Model pw 9408.

PROCEDURES

Owing to the poor solubility of the mesoionic compund, the use of a great percentage of organic solvent was imperative. Therefore, ternary mixtures of water-ethanol-DMF 3:14:3 (vol.) were used. However, the maximum concentration of heterocycle obtained has been 1.5×10^{-4} M. An 1×10^{-3} M stock solution of compound (I) in DMF was used. The aqueous

part was an acetate or ammonia buffer in which acetate or ammonia concentration was hold constant at 1 M. Sodium perclorate at a final concentration 0.1 M was added also.

The potential selected for controlled potential electrolysis corresponded to the crest of polarographic waves. The electrolysis was continued until the current decayed to the background level.

The values $n\alpha$ were computed from the slope of plots of E vs $\log (\bar{i}/(\bar{i}_l - \bar{i}))$.

RESULTS AND DISCUSSION

In neutral an basic medium, compound (I) shows two polarographic waves (A and B) of similar intensity. In acidic medium wave A splits in two waves A1 and A2. Simultaneously, wave B tends to overlap with the background (Fig. 1). Waves A, B and A1+A2 are diffusion controlled as proved by the dependence on heterocycle concentration, dropping time, mercury pressure and temperature. However, wave A1 shows a clear kinetic character as shown, for example, by the logarithmic analysis of i_l-t curves (Fig. 2) which shows a slope of about 0.6. The behaviour of waves A1 and A2 is very similar to those observed in some acid-base equilibria (4) or complex dissotiations reactions (5) and it is characteristic of a CE mechanism. In the case of the heterocycle, the two species in chemical equilibrium are both reducible and each one is responsible for waves A1 and A2, respectively. The kinetic character detected in wave A1 is due to the tendency of the system to re-establish the equilibrium disturbed by the electrode process. On the other hand, the fact that the kinetic character is so clear indicates that the species responsible for wave A1 is scarce in solution (6), ie, chemical
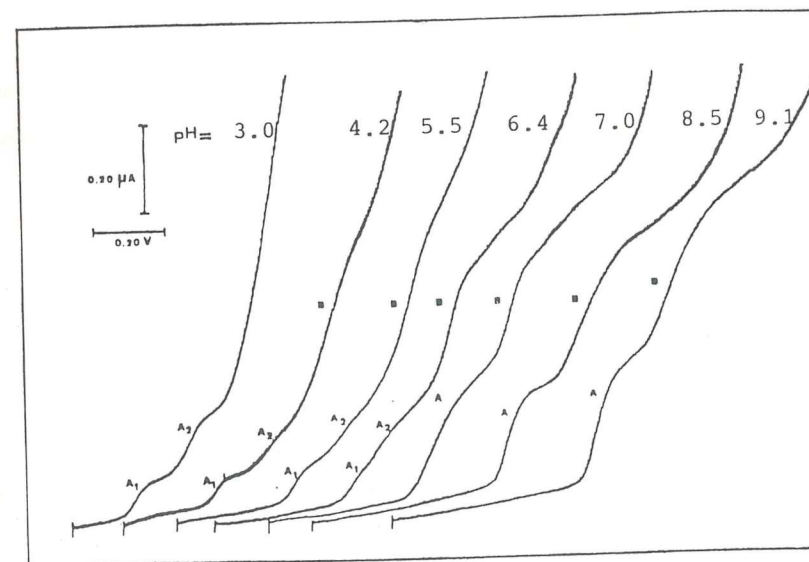
Figure 1.- pH dependence of the polarographic waves of heterocycle (I). Acetate buffer for pH 3 to 7, ammonia buffer for others pH. Drop time: 2 s. Scan starts at −0.5 V.
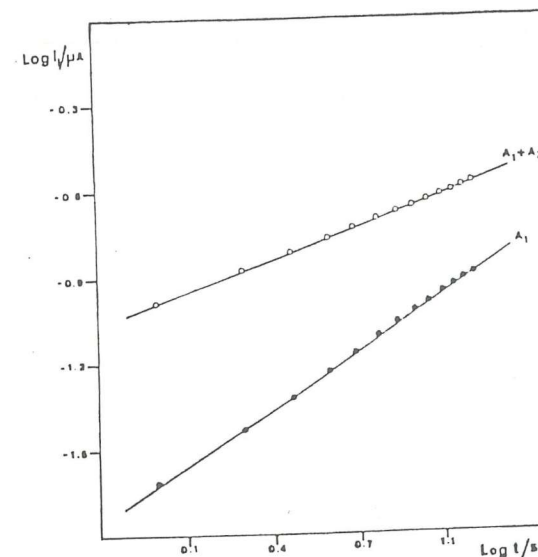

Figure 2.- Logarithmic analysis of i_l-t dependence for wave A1 and A1+A2. pH = 3.0

equilibrium is highly displaced to species responsible for wave A2.

Logarithmic analysis of polarographic waves were carried out (Fig. 3). The values obtained for slopes and other polarographic data are shown in Table 1.
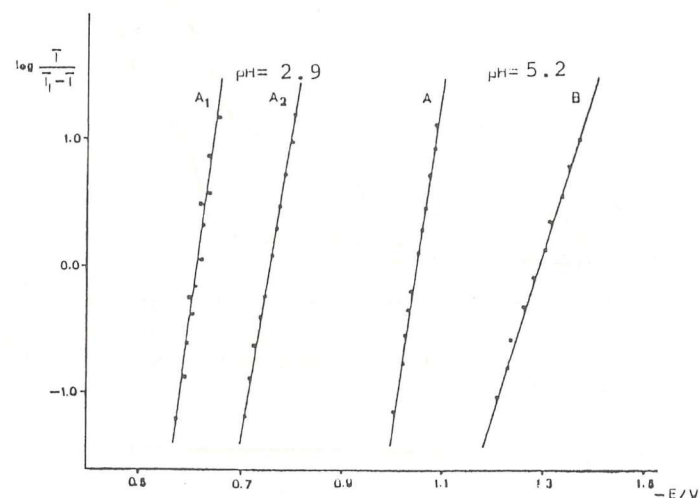

Figure 3.- Logarithmic analysis of polarographic waves of heterocycle (I). Acetate buffer. Drop time: 2 s.

Table 1

Polarographic data obtained for the reduction of compound (I). Conditions as in Fig. 1

pH range	wave	$dE_{1/2}/dpH$	Δ (*)	αn
1.9 - 5.0	A1	0.057	0.029	2.06
1.9 - 5.0	A2	0.048	0.040	1.46
5.5 - 7.5	B	0.083	0.070	0.85
8.5 - 9.6	A	---	0.035	1.70
8.5 - 9.6	B	---	0.094	0.62

(*): Slope of logarithmic analysis.

Limiting currents are essentially pH-independent (Fig. 1). However, below pH 7, half-wave potentials of waves A2 and B are shifted to more negative values with increasing pH (Table 1, Fig. 4), taking into account the slope of polarographic waves and the value of $dE_{1/2}/dpH$, we can conclude that a monoprotonic transfer takes place before the electronic one in each of these waves (7). In basic medium, half-wave potentials and limiting currents of waves A and B remain pH-independent, which indicates direct reduction of the species
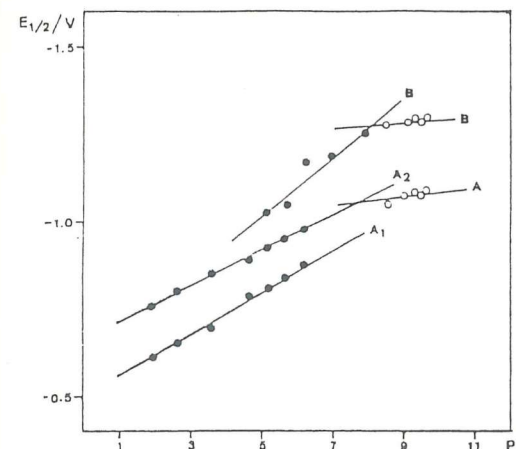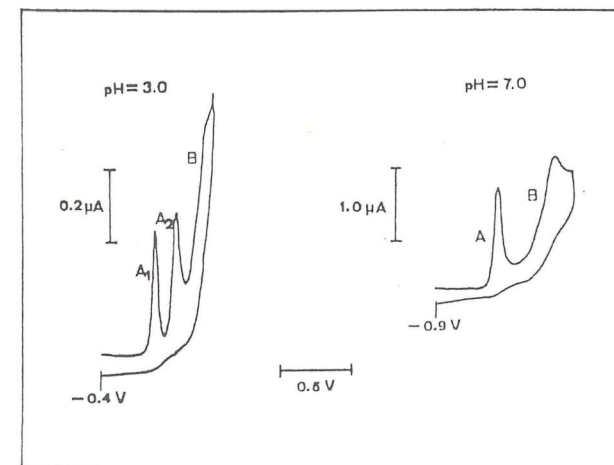

Figure 4.- pH dependence of half-wave potentials of individual waves of heterocycle (I). Conditions as in Fig. 1.

Figure 5.- pH dependence of voltammetric peaks of heterocycle (I). Acetate buffer. Scan rate: 0.2 V/s.

predominat in the bulk of solution (8). From logarithmic analysis and pH-dependence of wave Al no direct mechanistics consecuences are extraible, due to its kinetic character, but its analogy with wave A2 (see below) indicates a similar behaviour.

Over the entire pH range studied we have obtained voltammetric peaks according to the polarographic waves. Anodic peaks were never observed whic indicates the overall irreversible character of the reduction process of (I) (Fig. 5), moreover, peak-potentials shifts to more negative values increasing scan rate, which confirms this irreversible character. On the other hand, in all the peaks, the current function $(i_p/cAv^{1/2})$ increases when concentration decreases or scan rate increases. This indicates that adsorption of electroactive species takes place (9). As ilustration of this behaviour, Table 2 shows the values of the current function of peak A in several conditions. This adsorption is not sufficiently strong to origine pre or post-peaks, consecuently no differences between molecules which are adsorbed or diffuse to the electrode can be observed, and no adsorption step will be included in the reduction mechanism.

Table 2

Influence of scan rate and concentration of compound (I) on current function $(i_p/cAv^{1/2}, \mu A.mM^{-1}.mm^{-2}.V^{-1/2}.s^{1/2})$ of peak A. pH = 8.4. Ammonia buffer.

| Concentration/M	Scan Rate/V.s^{-1}				
	0.2	0.5	1.0	3.0	5.0
$1.5.10^{-5}$	40	45	65	83	95
$2.5.10^{-5}$	36	40	51	59	64
$5.0.10^{-5}$	31	34	43	57	65
$7.5.10^{-5}$	28	27	34	47	50
$1.0.10^{-4}$	26	27	33	43	44
$1.2.10^{-4}$	21	20	24	31	34

Controlled potential electrolysis were carried out in order to determine the number of electrons per molecule involved in each electrode process.

Coulometry at a potential on the crest of wave Al gives a n value of 4. In the course of electrolysis, the height of wave A2 gradually decreases until it disappears, while the wave B remains unaltered with electrolysis. Identical results are obtained if electrolysis is carried out at a potential corresponding to the limiting current of waves A2 or A. This behaviour confirms the existence of an equilibrium between species responsible of waves Al and A2. In both waves, a number of four electrons per molecule are involved.

Electrolysis at a potential corresponding to the limiting current of wave B gives a n value nearly four, but it is difficult to determine exactly this n value, due to the proximity of wave B to the background.

REDUCTION MECHANISM

In acidic medium, hydrolysis of mesoionic compound takes place (which causes a loss of color in solutions), according to the following scheme (3):
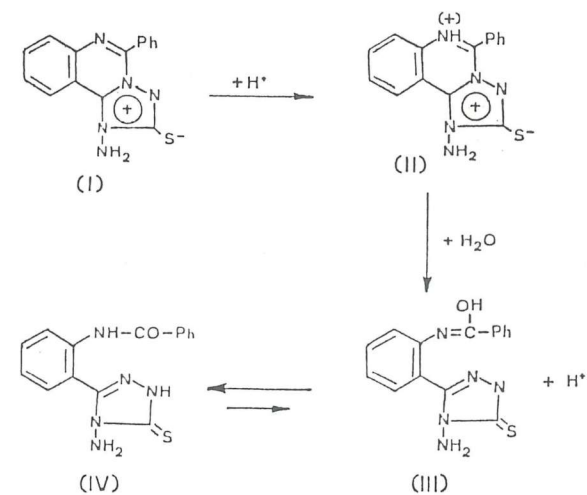
The waves Al and A2 will be originated by the reduction of a part of molecule which is not hydrolized (after hydrolysis the waves Al and A2 do not disappear). On the other hand, the hydrolysis products of heterocycle ((III) and (IV)) show a tautomeric equilibrium, being the species (IV) the one which prevails in solution. Waves Al and A2 are due to tautomeric forms (III) and (IV), respectively. This justifies the kinetic response observed in wave Al, and the existence of an equilibrium detected in controlled potential electrolysis. The reduction responsible of waves Al and A2 will occur in the five membered ring, in which a N-N bond is contiguous to a C=N double bond, similarly to some aldimines (10,11) and hydrazones (12,13). In these compounds the hydrogenolysis of N-N bond takes place before the saturation of C=N double bond, if we assume this step as the rate determining for wave A2 (This implies $\alpha \approx 0.7$, see table 1) and taking into account preprotonation, we can write for wave A2 the following mechanism:
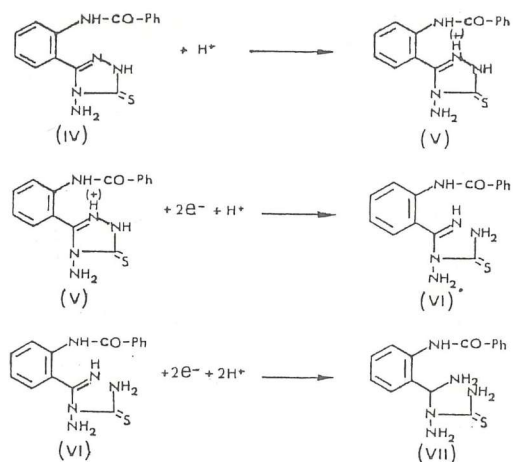
and, similarly, for wave Al:
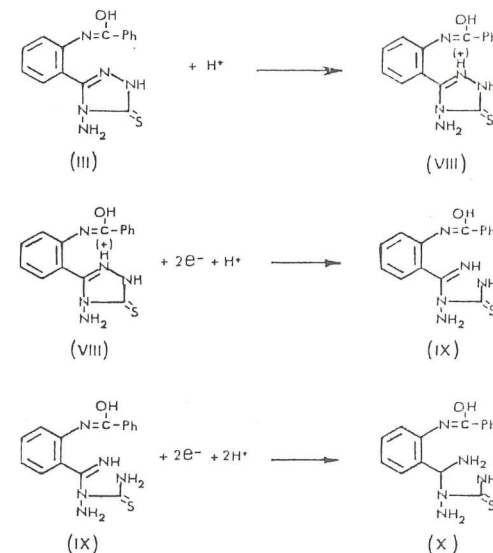
Taking into account the similarity between the wave A and the waves Al and A2, the reduction responsible for wave A takes place in the same region of the molecule (without hydrolyisis) that waves Al and A2. In this case there is not direct evidences for mechanistics details, because the decrease in slope of polarographic wave (related to A2) can indicate the control simultaneous of more than one step. Consecuently, we propose the following overall mechanism:
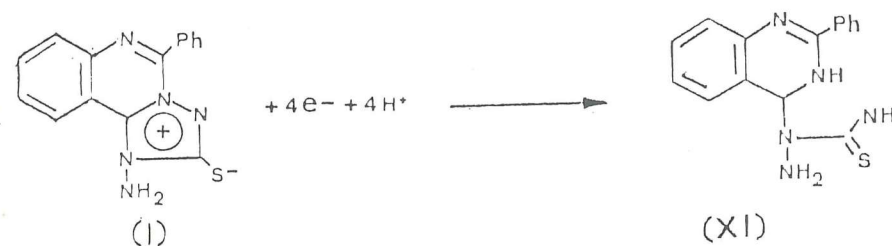
It is difficult to propose a reduction mechanism for wave B. However, taking into account the similar intensity of waves A and B, the number of electrons obtained in controlled potential electrolysis for wave B, and the fact that wave B remains unaltered after hydrolyisis, we propose for wave B the following overall mechanism:

$$+4e^- +4H^+$$

(XI)

(XII)
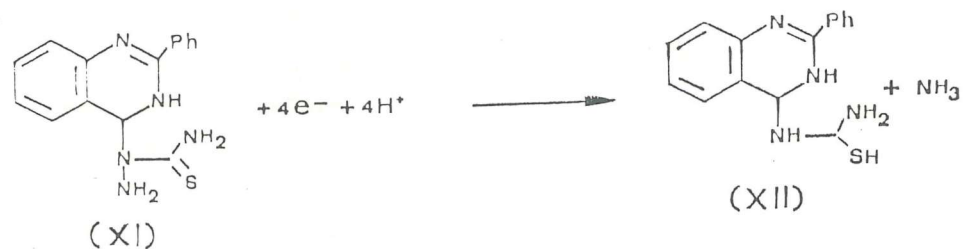
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TEMPERATURE EFFECT ON POLAROGRAPHIC BEHAVIOUR OF Co(II) and Zn(II) 2:1 COMPLEXES WITH PALUDRINE

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SUMMARY

The polarographic reduction of Zn(II) and Co(II) complexes with paludrine has been studied in moderated acid media. The Zn(II) 2:1 complex shows two well defined waves. The Co(II) 2:1 complex shows only one wave. Arrhenius activation energies, obtained from diffusion currents of np, dp, ac_1, ac_2, K_1 and K_2 polarograms, show that all cathodic and anodic processes are controlled by diffusion. The mechanism of these processes is proposed.

INTRODUCTION

The first published studies on polarography of biguanides were related to their complexes[1,2]. In order to reduce the biguanide group at the d.m.e., it is required that the nitrogen bridge between the biguanide plane is protonated at the electronic delocalization on the biguanide group thus lost, which makes them susceptible to saturation and reduction, producing the corresponding amino groups[3-5].

In the present study, direct current (dc), normal (np) and differential pulse (dp), first (ac_1) and second (ac_2) armonic superimposed alternating current polarography and methods based on the Kalousek commutator are employed to elucidate the behaviour of 2:1 biguanide complexes on the d.m.e. of paludrine-cobalt and paludrine-zinc buffer aqueous solutions.

EXPERIMENTAL

Polarographic measurements were made with a Polarecord E-506 (Metrhom S.A.). A digital Radiometer pHmeter with a combined electrode enabled us to obtain a pH accuracy of +0.01 units. The temperature was kept constant to +0.1°C using a Heto 03T623 cryostat and a Heto 05E623 thermostat.