

Synthesis, Electrochemical Oxidation of 2-Hydroxy-5-Nitrophenyl Azo1-(2,5-Dichloro-4-Sulfophenyl)-3-Methyl-5- Pyrazolone Reagent at Mercury Electrode

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Abstract: 2-hydroxy-5-nitrophenylazo1-(2,5-dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone (2HNAP) was synthesized. The solid state of reagent isolated and characterized by FT-IR, ¹H-NMR and mass spectroscopy. The electrochemical oxidation of reagent at a mercury electrode was studied by differential pulse polarography in a wide pH range. Electrolyte with pH less than 10 diffusion of control, pH-dependent process that involves the transfer of one electron and one proton from the OH group.

Keywords: 2-Hydroxy-5-Nitrophenyl Azo Pyroalone, Differential Pulse Paleography, Oxidation Mechanism.

INTRODUCTION

The azo compounds are the most openly used class of dyes due to their used in different effective applications such as optics properties, sensors, indicators and photochromic materials [1-8]. The electrochemical methods such as differential pulse polarography (DPP) allows for an analysis without samples pre-treatment, has comparable selectivity and sensitivity over many analytical methods due to able to perform both individual and simultaneous analysis [9-12]. In connection with 2-HNAP redox mechanism less information is obtainable.

Azo-phenolic and carboxylic compounds subject electrochemical reduction at the azo nitrogen atom obeyed by the cleavage of the azo bond [13,14]. The aim of the present work is our ongoing concern in the synthesis and spectral characterization azo the investigation of 2-HNAP anodic oxidation behavior, using differential pulse voltammetry, at a mercury electrode, in order to explain the 2-HNAP redox mechanism.

EXPERIMENTAL

The infrared spectra were measured as KBr disc using Shimadzu FTIR 8400 spectrophotometer with scanning 4000-400cm⁻¹. ¹H-NMR spectra were recorded on a Bruker AV 300 Avance-III 300MHz using DMSO-d₆ as a solvent and TMS as internal standard. Mass spectrum was performed using an ESI Mass AB SCIEX 3200 QTRAP mass spectrometer at 70 eV. Polarograms were recorded with a polarographic analyzer model 797VA (Metrohm Swiss) three electrodes, a mercury electrode, a silver-silver chloride and a platinum wire electrode, were used as working, reference and auxiliary electrodes respectively.

Reagents

The buffer solutions used in this study was boric buffers, which were prepared (pH 2.0- 11.0) by mixing a solution containing 0.04 M acetic acid, 0.04 M boric acid and orthophosphoric acid. Stock solution of 1x10⁻³ M 2HNAP azo dye was prepared by dissolving 0.0486 g in 100 mL of ethanol and used as working solution.

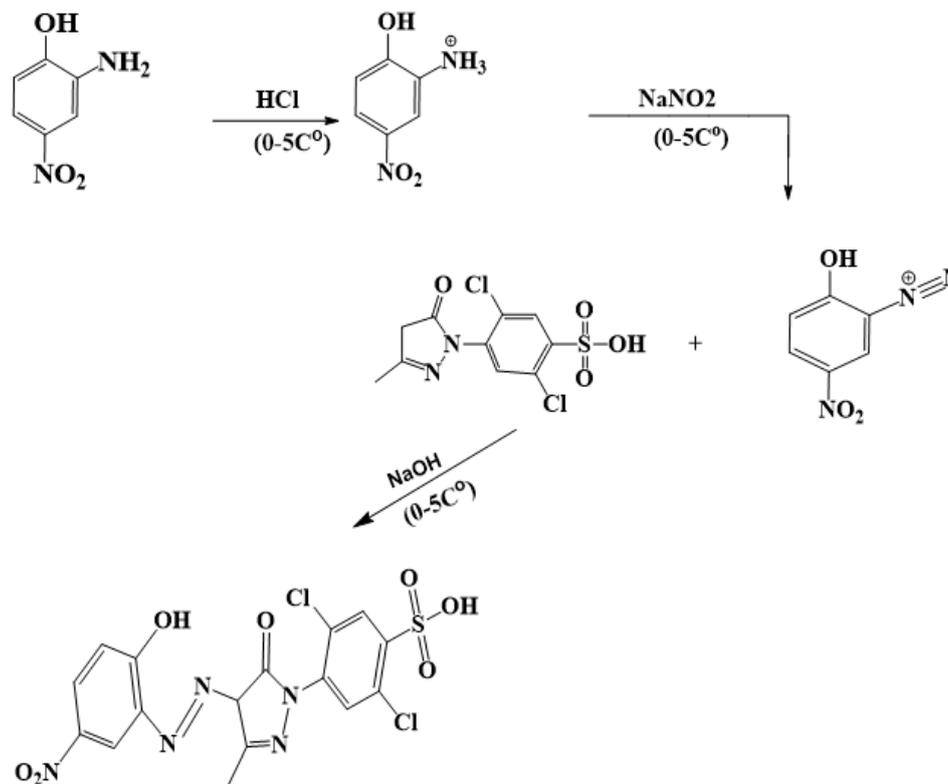
Procedure of Polarographic Measurements

2.0 mL of the stock solution of the 2HNAP reagent solution 1x10⁻³ M in ethanol, 8.0 mL of the buffer solution with required pH (4.0-10) were mixed completely. The polarogram was recorded after stripping the dissolved O₂ by passing dry and pure N₂ gas through the solution about 10 minutes.

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Synthesis of 2-HNAP

The reagents and solvents were of analytical grade and used without further purification. 2-amino-4-nitrophenol (0.0072mole) 1.0000 g was diazotized by dissolving it in 25ml ethanol then 5ml of HCl was added keeping the temperature at 0-5°C and then adding NaNO₂ solution gradually and left the solution about 15min. The diazonium salt was spontaneously added slowly drop wise to a well cooled alkaline solution of coupling agent 2,5-dichloro-4-sulfophenyl-3-methyl-5-pyrazolone 2.2752g, the mixture was allowed to stand for 1 h. The dark colored mixture was neutralized with HCl and the solid precipitate was filtered off and washed several times with (1:1) (ethanol: water) mixture then recrystallised from boiling ethanol and left to dry. Scheme .1.



Scheme 1: Preparation of reagent 2HNAP

RESULTS AND DISCUSSION

Heterocyclic azo pyrazolone dyes are essential in various fields of chemistry due to their biological activities. As well as to their biological activities, their sensor and photochromic properties have guide to their purpose in diverse areas. The found of polar hydroxyl groups promoted the molecular stabilized the compounds. In addition contain interesting groups for electrochemical studies.

Spectral data of the 2HNAP azo reagent

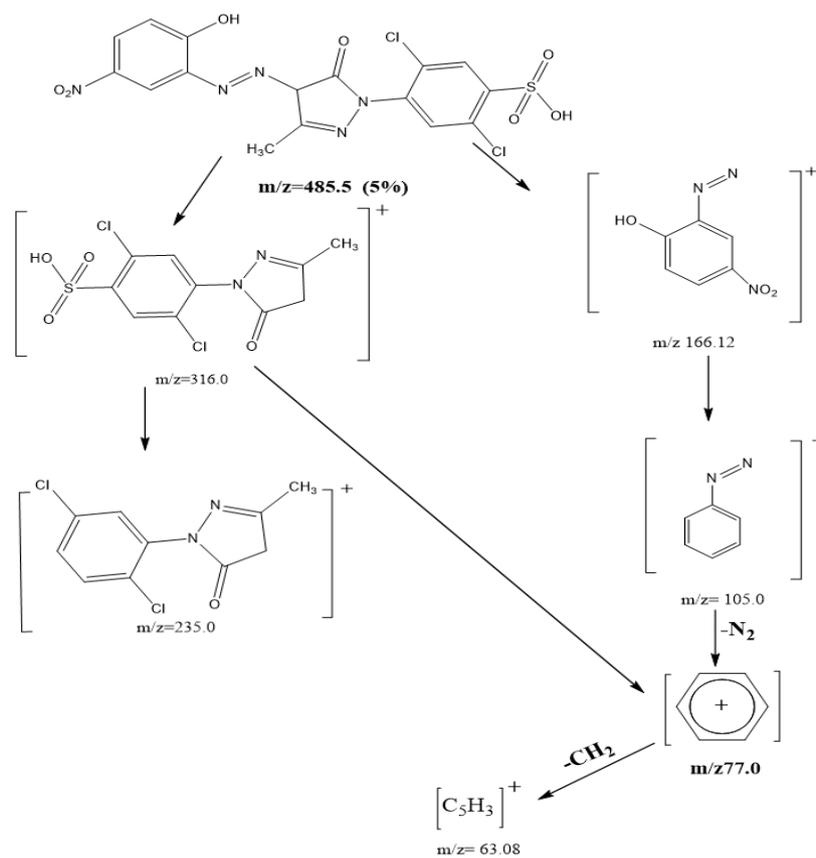
[C₁₆H₁₀Cl₂N₅O₇S]; dark orange, yield; 85%, mp.= 298 C

FT-IR, ¹H-NMR and Mass Spectroscopy

The IR spectrum of the 2HNAP dye was carried out in the range 4000-400 cm⁻¹. The ν C=N of pyrazole ring display a sharp band at 1625 cm⁻¹. Also, the reagent two bands at 1165 and 1346 cm⁻¹ attributed to ν sym and asym (SO₂) stretching vibrations respectively. The vibration bands at 3433, 3093 and 2870 cm⁻¹ ascribed to (OH) and (Ar-H, C-H) respectively. IR showed band at 1660 cm⁻¹ assigned to ν C=O and weak band at 1479 cm⁻¹ correspond to the N=N due to nonpolar nature of band.[15]. The band at 2870 cm⁻¹ exhibited the existence of N--3-H-O intramolecular hydrogen bonds [16].

The ¹H-NMR spectrum of the 2HNAP showed signal at 13.22 ppm corresponding to OH proton. The solvent and CH₃ protons attached to the pyrazole were found as singlets at 2.5 and 2,3 ppm for 2HNAP reagent respectively. Multiplet signals at 7.2-7.9 ppm assigned to 5 aromatic protons.

Mass spectrum presented molecular ion peak at m/z= 485.5 corresponding the molecular weight confirming the molecular formula of the 2HNAP dye. The fragmentation model was exhibited in Scheme.2. Fig.1



Scheme 2: Fragmentation model of the 2HNAP reagent

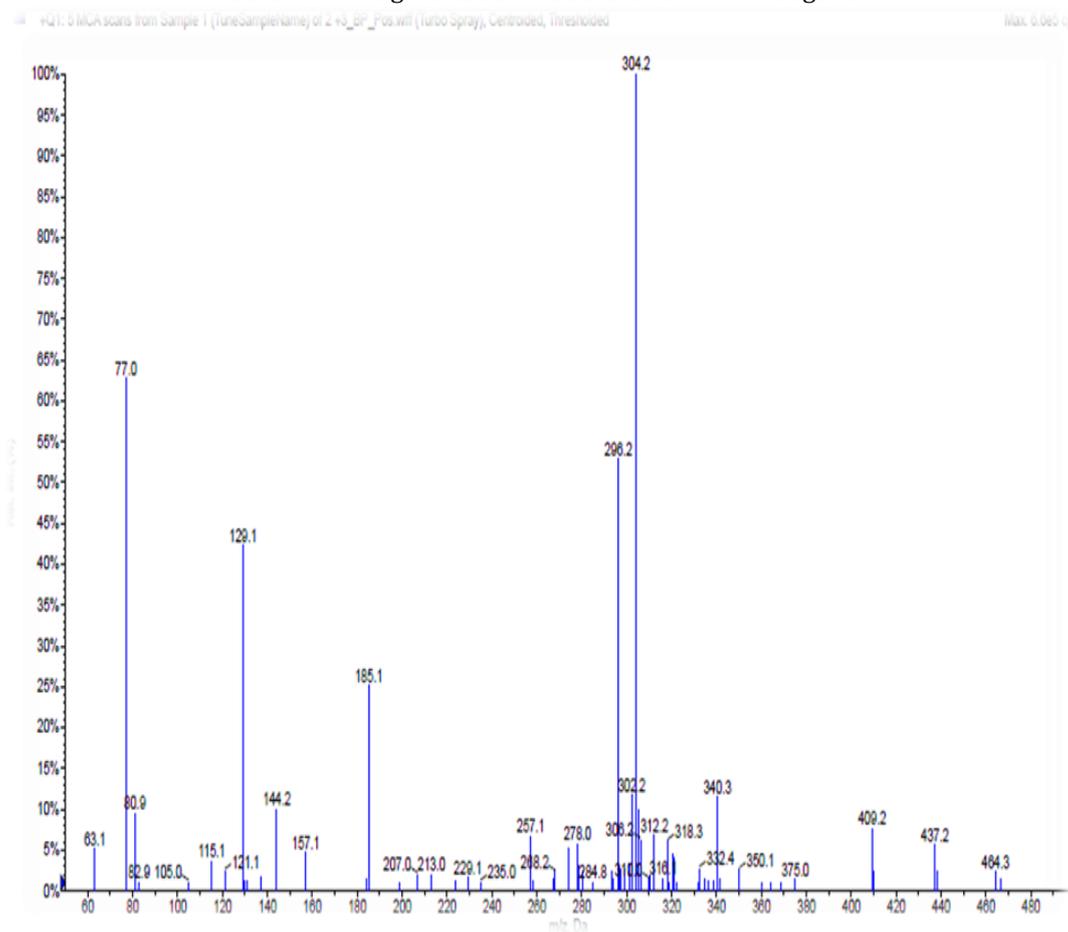


Figure 1: Mass spectrum of the 2HNAP reagent

Electro Chemical of the Reagent 2HNAP

The oxidation characteristics of 2HNAP was studied using a mercury electrode by differential pulse polarography in the potential range.

The effect of various parameters on the electrochemical behavior of the reagent 2HNAP was studied and the conditions were optimized.

Effect of Mercury Drop Size

The effect of mercury drop size on the diffusion current to reagent and its complex was studied and according to the results the effect was observed in the diffusion current with in mercury drop size range from 3.0-9.0 mm². Thus, a mercury drop size of 9.0 mm² was chosen for the procedure Table. 1.

Table 1: Effect of drop size on the signal of differential pulse polarography for 2HNAP

Drop size	E _{1/2} V	id A
4	0.331	1.4e-006
5	0.331	1.49e-006
6	0.331	1.56e-006
7	0.331	1.58e-006
8	0.363	1.66e-006
9	0.365	1.72e-006

Effect of Deposition Time (D.t)

The deposition time on the diffusion current system shows a maximal diffusion current at deposition time ranging from (20 to 80 sec). Thus a deposition time of 40 sec was chosen for the procedure Table.2.

Table 2: Effect of deposition time on the signal of differential pulse polarography for 2HNAP

Deposition time /sec	E _{1/2} V	id A
20	0.331	1.4e-006
30	0.331	1.76e-006
40	0.331	1.81e-006
50	0.333	1.71e-006
60	0.333	1.73e-006
70	0.333	1.75e-006
80	0.333	1.73e-006

The results of other factors effect such as pulse amplitude, pulse time, voltage step and voltage step time are given in Table.3

Table 3: Analytical characteristics of differential pulse polarography for 2HNAP at different pH

Optimal conditions	values
Drop size	9.0 mm ²
Deposition time	40 sec
Voltage step	0.002 V
Equilibration time	10 sec
Voltage step time	00.1 sec
Pulse amplitude	0.015 V
Pulse time	0.006 sec
Initial potential	-1.00 V
Final potential	2.00 V

Effect of pH

The effect of pH on the electrochemical oxidation of was studied by differential pulse polarography in buffer supporting electrolyte in range of pH 4.0-10.0.

The oxidation of 2-HNAP was shifted to a less positive potential with increasing Fig. 3 . The slope line, for E peak versus pH Fig.2. indicated an equal number of protons and electrons involved in the electrochemical oxidation mechanism. For electrolytes with pH more than 8.0, the oxidation of 2-HNAP was in agreement with the chemical deprotonation of the molecule [17]

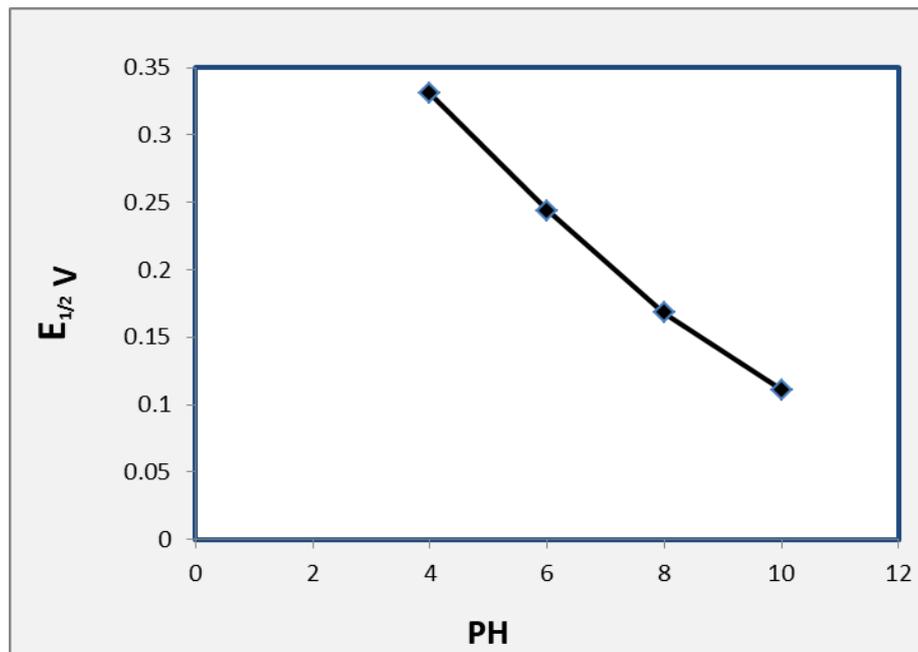
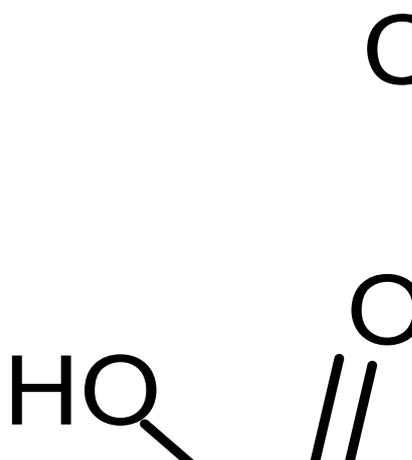


Figure 2: The effect of pH on the electrochemical oxidation of 2HNAP

Mechanism of Electrooxidation for 2HNAP Azo Dye

The oxidation of 2HNAP process for pH 8.0 Fig.3 includes the transport of one electron and one proton leading to the formation of an oxidation product that submits a two electrons and two protons reversible redox reaction. Scheme. 3.



Scheme 3: Mechanism of electrooxidation for 2HNAP azo dye at a mercury electrode

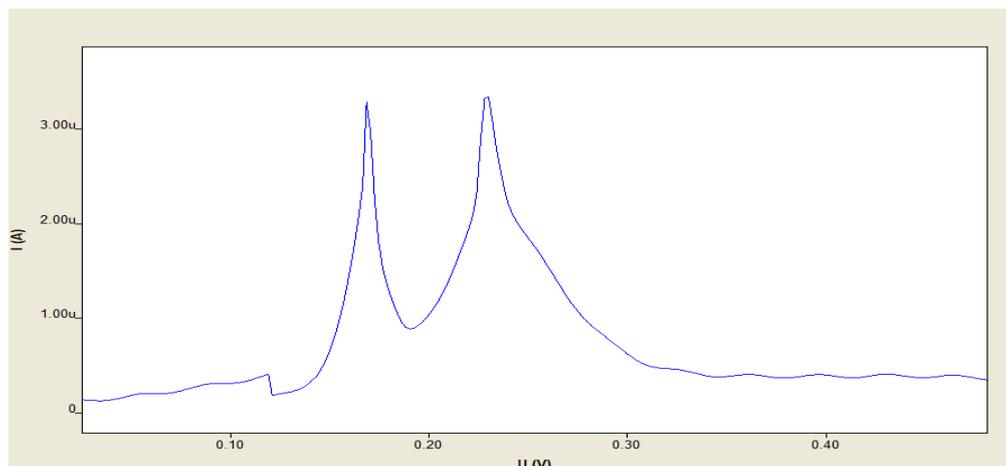


Figure 4: A typical differential pulse polarogram of 1×10^{-3} M of 2HNAP at pH=8

The oxidation of 2HNAP occur at the hydroxyl group of the adjacent of azo group producing a thermodynamically unstable phenoxyl radical in various isomeric status [18]

Then a decrease in the electron density on electroactive functional group produce to a simple reduction approach. At higher pH values, the reduction was supposed to take place in a shape of deprotonization of hydroxyl group.[19,20]

CONCLUSION

The polarographic behavior of novel 2-hydroxy-5-nitrophenyl azo1-(2,5-dichloro-4- sulfophenyl)-3-methyl-5-pyrazolone (2HNAP) was reported in this work. The differential pulse polarography behavior studied at a mercury drop electrode to derive electrooxidation mechanism.

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