

## Electrochemical Investigation of 4-[(2-Hydroxy-1-naphthyl)azo]benzenesulfonic Acid Sodium Salt (Orange II) at Glassy Carbon Electrode

AYÇA DEMIREL ÖZEL and ESMA KILIÇ\*

Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey

Fax: (90)(312)2232395; Tel: (90)(312)2126720

E-mail: ekilic@science.ankara.edu.tr

The electrochemical behaviour of 4-[(2-hydroxy-1-naphthyl)azo]benzenesulfonic acid sodium salt (orange II) at glassy carbon electrode in aqueous solutions was investigated. Orange II was found to give a single sharp cathodic CV peak that is found to correspond to a gain of 4 electrons per molecule. The diffusion coefficient was calculated by the aid of chronoamperometric data, the number of electrons transferred was calculated by controlled potential electrolysis and the standard rate constant for the reduction was calculated by Klinger-Kochi technique. From the electrochemical data obtained by using these techniques and thin layer chromatography in aqueous solutions of varying pH, a plausible reduction mechanism of the azo dye was proposed.

**Key Words:** Orange II, Azo dyes, Electrochemical behaviour, Voltammetry, Glassy carbon electrode, Electrochemical reduction mechanism.

### INTRODUCTION

Aromatic azo compounds are well known for their widespread applications in many areas of technology and medicine. They are especially used in industrial processes such as the production of dyes or drugs used in chemotherapy<sup>1</sup>. Azo dyes as an important class of aromatic azo compounds, belong to the most intensively investigated classes of dye-stuffs. They are used as colouring agents in foods and pharmaceuticals *etc.*<sup>2-4</sup> and are widely employed in a variety of products, such as in dyeing of textiles, cosmetics, paints, inks, plastics and paper. Thus, they are found in the wastewaters of the related industries<sup>5</sup>. Orange II, also called acid orange 7, is one of the azo dyes and it is a water-soluble molecule that has O–H···N and N=N bonds and may show photoinduced intramolecular proton-transfer (IPT) and *trans-cis* isomerization reactions. It has been reported that it exists under azoenol (AZO) and ketohydrazone (HYZ) forms (Fig. 1)<sup>5-8</sup>. In a water solution, for example, the H-atom within the O–H···N intramolecular

H-bond is shifted to the nitrogen site, making HYZ structure the most stable one (*ca.* 95 %) <sup>5,8</sup>. It poses a potential risk to human health and is even carcinogenic <sup>9-12</sup>. Furthermore, recent estimates indicate that *ca.* 12 % of the synthetic textile dyes used each year are lost to waste streams during manufacturing and processing operations and that 20 % of those losses will enter the environment through effluents from wastewater treatment plants <sup>13</sup>. As a result, Orange II can enter the body through the intake of foods and drugs that contain it as a colouring agent.

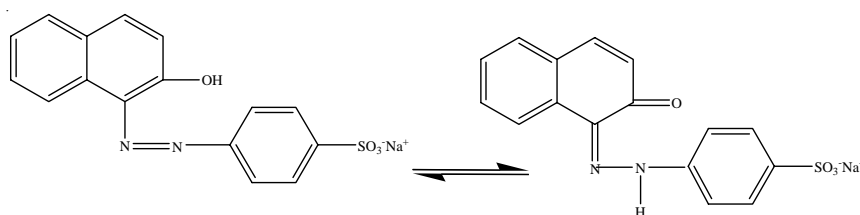


Fig. 1. Azoenol (AZO) and keto-hydrazone (HYZ) forms of Orange II

The redox chemistry of azo compounds has attracted considerable attention due to the capability of bacteria in reduction of azo compounds mainly in liver and intestine <sup>14</sup>. They are easily reduced by enzymes <sup>15-20</sup> and can also be reduced by chemical systems, such as zero-valent iron, reduced flavin adenine nucleotide and nicotinamide adenine dinucleotide under aerobic and anaerobic conditions <sup>21-23</sup>. Reduction of azo linkages may generate potentially carcinogenic aromatic amines <sup>19,24,25</sup>. Since azo compounds are generally electroactive and the bacterial cleavage of the azo compounds is a reductive process, electrochemistry provides convenient methods for studying mechanisms and kinetics of such reactions. Although much effort has been undertaken to investigate the electrochemical reduction of azo compounds, most of the studies were carried out by polarographic methods <sup>2,3,9,13,26-37</sup> and few attempts have been made to study the redox-reactions of azo compounds at solid electrodes <sup>1,14,38-43</sup>. No report has been published on electrochemical behaviour of commercial azo dye named Orange II at glassy carbon electrode in aqueous media.

This paper mainly concerns the electrochemical behaviour and redox mechanism of a 4-[(2-hydroxy-1-naphthyl)azo]benzenesulfonic acid sodium salt (Orange II) on glassy carbon electrode. The diffusion coefficient (*D*), the number of electrons transferred (*n*) and the standard heterogeneous electrochemical rate constants (*k<sub>s</sub>*) were determined by using chrono-amperometry, controlled potential electrolysis and cyclic voltammetry, respectively.

## EXPERIMENTAL

Orange II sodium salt was purchased from Fluka. All other chemicals were of analytical grade and were obtained from Merck except phosphoric acid that was purchased from Pancreac. Britton-Robinson buffer solutions (pH 2.0- 11.0) were prepared from boric acid, acetic acid and phosphoric acid and adjusted to the desired pH with 0.2 M sodium hydroxide. All solutions were prepared by deionized water.  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  redox couple was used as a reference matter in aqueous media.

Stock solutions ( $1.0 \times 10^{-3}$  M) were prepared by dissolving an exactly weighed amount of Orange II in deionized water and sample solutions ( $2.0 \times 10^{-4}$  M) were prepared by dilution of 1 mL of the stock solution to 5 mL with Britton-Robinson buffer solution of the desired pH. All measurements were carried out in pH range 2.4-11.2.

All voltammetric studies were carried out using a computer controlled electroanalysis system named BAS-100B electrochemical analyzer (USA) with cell stand of C3. A three electrode combination system was used. This consisted of a glassy carbon working electrode (GC) (BAS MF-2012, A:  $7.065 \text{ mm}^2$ ), a platinum wire auxiliary electrode (BAS MW-1034) and a Ag/AgCl reference electrode (BAS MF-2052 RE-5B). For controlled potential electrolysis studies, BAS MF-1056 bulk electrolysis cell was employed. A three electrode combination system for bulk electrolysis was consisted of reticulated vitreous carbon electrode (BAS MF-2077) as working electrode, Ag/AgCl reference electrode (BAS MF-2052 RE-5B) and coiled platinum wire auxiliary electrode (23 cm) (BAS MW-1033).

Prior to each experiment, the working electrode GC was polished with alumina polishing powder on a smooth polishing cloth, rinsed with deionized water and sonicated for about 2 min in deionized water by using Ultrasonic LC30H trademark sonication device. Deionized water was provided from human power I<sup>+</sup>, ultra pure water system.

All pH measurements were made with Thermo Orion Model 720A pH ion meter with an Orion combined glass pH electrode (912600) which had been calibrated with pH 4.13 and pH 8.20 stock buffer solutions before measurements.

**Method:** The solutions were initially deaerated with pure argon for 10 min and an additional 10 s before each scan and a continuous stream of argon was passed over the solutions throughout the experiments. All the measurements were taken at room temperature ( $21 \pm 2$  °C).

The electrochemical behaviour of the azo dye was described using cyclic voltammetry (CV), square wave voltammetry (SWV), chronoamperometry (CA) and controlled potential electrolysis. At cyclic voltammetric measurements, the potentials were scanned from + 0.5 V to various ending

potentials according to the experimental conditions and scan rates employed between 0.01 and 50 V/s.

The solutions obtained after the controlled potential electrolysis of Orange II at the potentials determined by cyclic voltammetry experiments at both pH 2.4 and pH 9.2, were employed thin layer chromatography that was carried out on silica gel 60 F<sub>254</sub> TLC aluminium sheets (Merk) with methanol as developer.

The number of electrons transferred was determined by the controlled potential electrolysis of Orange II for both pH 2.4 and pH 9.2 media in the bulk electrolysis cell. Diffusion coefficients for both acidic and basic media were calculated by Cottrell equation<sup>44</sup> in which the data obtained from chronoamperometric studies were used. The heterogenous rate constants were calculated according to Klingler-Kochi method<sup>45</sup>.

## RESULTS AND DISCUSSION

### Voltammetric studies

To elucidate the electrode reaction of Orange II, voltammograms at GC electrode over the wide pH range and with different scan rates were examined. Multicyclic voltammograms of Orange II obtained at a scan rate of 0.1 V s<sup>-1</sup> for pH 2.4 and 9.2 are shown in curves (a) and (b) of Fig. 2 as an example. On the voltammogram recorded at pH 2.4, a distinct reduction peak (A) at -0.26 V and a sharp oxidation peak (B) at around +0.32 V are discernable. At pH 9.2, the corresponding reduction and oxidation peaks are observed at -0.81 V and -0.14 V, respectively. In both cyclic voltammograms of acidic and basic solutions, a small cathodic peak denoted as C is observed during the second cycle, which is caused by the reduction of product formed on the anodic sweep of the first scan. The same phenomenon for some azo compounds is reported in literature<sup>13,41,43</sup>.

As it can be seen from Fig. 2, pH is one of the variables that commonly and strongly influence the electrochemical behaviour of this compound. The effect of pH for various azo compounds was examined and reported in literature<sup>1-3,9,13,14,26,35,41-43</sup>. So, the electrochemical behaviour of the investigated azo compound was studied as a function of pH. The pH dependence of cyclic voltammogram of Orange II obtained at pH 2.4-11.2 is given in Fig. 3. The peak potential of the cathodic wave (A) shifts towards more negative values as the pH increases in the range of 2.4-11.2 with an increase of pH while simultaneously diminishing in peak current.

As shown in Fig. 3a, there are two separate linear relationships which represent the effect of pH on the potential of the cathodic peak over the pH range 3.4-7.2 and 7.2-11.2 as below equations:

$$E_p = -65.6 - 84.1 \text{ pH} \quad (r^2 = 0.9980, \text{ pH } 3.4-7.2)$$

$$E_p = -429.4 - 34.4 \text{ pH} \quad (r^2 = 0.9622, \text{ pH } 7.2-11.2)$$

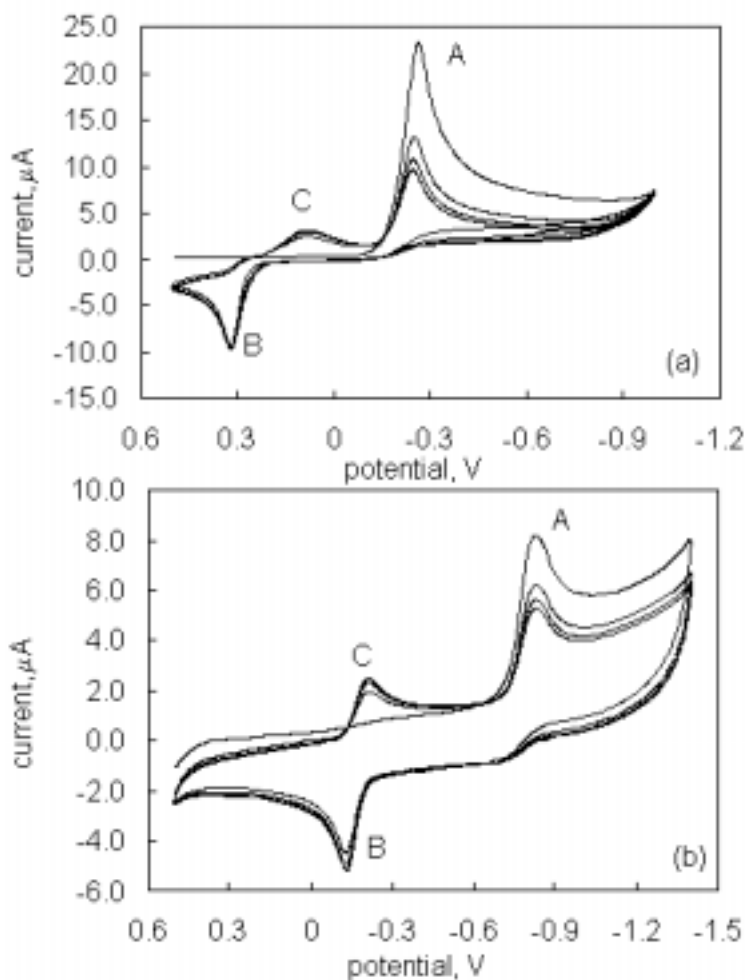


Fig. 2. The multicyclic voltammograms of  $2.00 \times 10^{-4}$  M Orange II in (a) acidic medium (pH: 2.4) and (b) basic medium (pH: 9.2) at  $0.1 \text{ Vs}^{-1}$  scan rate (8 segments)

Since the reduction of Orange II to yield an amine requires the uptake of one proton per electron<sup>1,46,47</sup> a slope of  $-59 \text{ mV/pH}$  is expected for the reduction potential as a function of pH, provided that the protonation of Orange II does not change in the investigated pH range. However, the experimental values of the slopes of the peak potential against pH curves were found to be  $84.1 \text{ mV/pH}$  for pH range 3.4-7.2 and  $34.4 \text{ mV/pH}$  for 7.2-11.2. This deviation can be explained by the different acid-base properties of the reaction products and reactants. Indeed, two aromatic amine groups are formed after the azo bond cleavage. As these amines can be protonated, the overall reaction could be described as a  $4e^-/6H^+$  process,

giving theoretical slope of 90 mV/pH which is nearly in agreement with present results for acidic medium<sup>43</sup>. However, at pH > 7, the peak potential is less dependent of pH, suggesting that in alkaline solutions, the azo group is reduced in a non-protonated form<sup>13</sup>.

The change of cathodic peak currents (peak A) with pH is given in Fig. 3b. As shown in Fig. 3b, peak currents decrease strongly around pH 3.4, shows a gradual increase up to pH 5.7 and then decreases with increasing pH. According to these results, the shift in the cathodic peak potentials to more negative values and change in the cathodic currents with increasing pH indicate that hydrogen ions are involved in electrode reaction<sup>2,13,38,48-50</sup>.

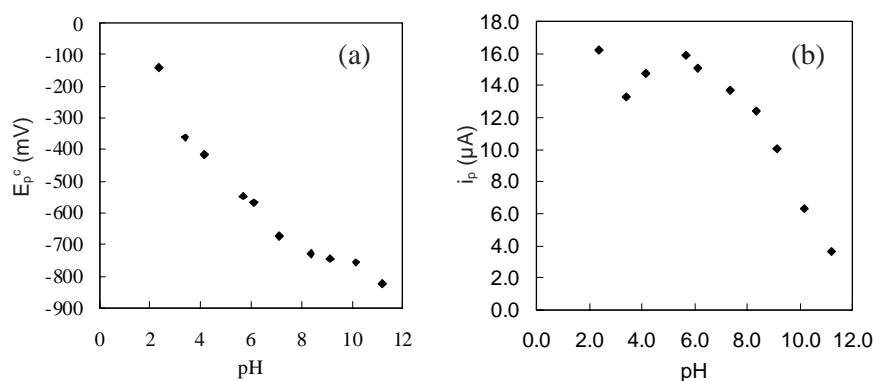


Fig. 3. Effect of pH on the (a) peak potentials and (b) peak currents obtained from differential pulse voltammetric data for  $2.00 \times 10^{-4}$  M Orange II (vs. Ag/AgCl reference electrode)

To throw light on whether adsorption is operative in the electrochemical process in question, the influence of scan rate ( $v$ ) on the cathodic peak current ( $i_p$ ) was investigated by cyclic voltammetry<sup>44</sup>. The  $\log i_p$  vs.  $\log v$  plots are given in Fig. 4 for  $2.0 \times 10^{-4}$  M Orange II. The slopes of these graphs were not > 0.5. The results indicate that the adsorption phenomenon is not dominant according to Bard and Faulkner<sup>44</sup>. The fact that no pre- and post-peaks are observed in the CV's of Orange II at high scan rates and the data obtained from CV is another indication that adsorption does not occur, to a considerable extent, on the GC electrode surface<sup>44</sup>. The peak current is proportional to  $v^{1/2}$ , indicating that the electrochemical reduction process of Orange II is diffusion controlled at pH 2.4 and 9.2 (Fig. 5).

It is known that electrochemical reactions of aromatic compounds containing hydroxy group involve a cleavage of the azo bond to form the corresponding amines in weakly acidic solutions while the reduction of unsubstituted azo compounds or azo compounds with electron withdrawing

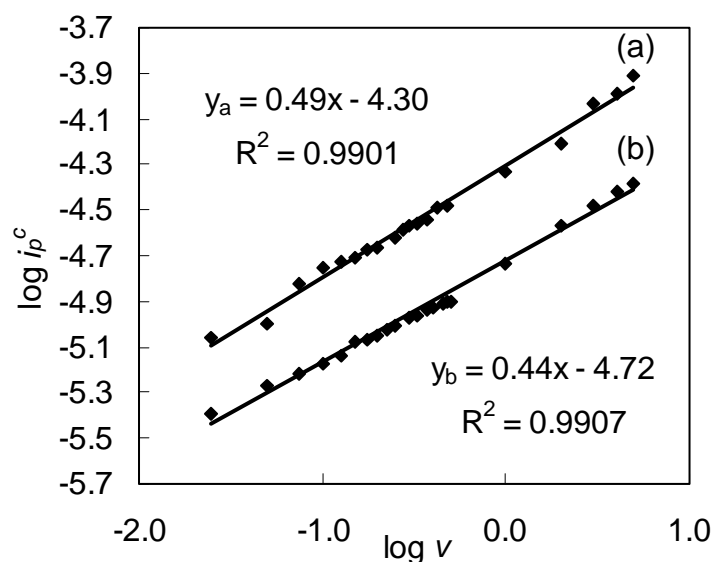


Fig. 4.  $\log i_p^c$ - $\log v$  plots of  $2.00 \times 10^{-4}$  M Orange II in (a) acidic medium (pH: 2.4) and (b) basic medium (pH: 9.2)

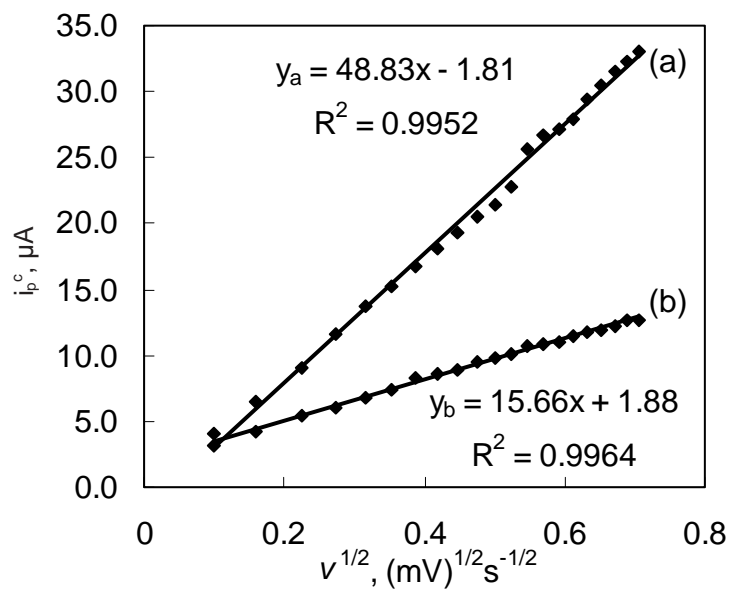


Fig. 5. Variation of cathodic peak currents with  $v^{1/2}$  for  $2.00 \times 10^{-4}$  M Orange II in (a) acidic medium (pH: 2.4) and (b) basic medium (pH: 9.2)

substituents generally gives rise to the corresponding hydrazo compounds. The cleavage of the azo bond should be a 4-electron process ( $4e^-$ ,  $4H^+$ ) while the reduction to a hydrazo compound should involve only 2-electron process ( $2e^-$ ,  $2H^+$ )<sup>1,26,27,41-43,46</sup>. To investigate this hypothesis for Orange II, the number of electrons involved in the reduction was determined by using controlled potential electrolysis which was performed at a potential more negative than the reduction peak observed and was found to be four in both acidic and basic solutions (Table-1). It is therefore reasonable to assume that Orange II studied here is reduced to the corresponding amines in both acidic and basic solutions as the previously reported studies<sup>27,35,43</sup>. From the results presented here, it is possible to deduce the principal electrochemical and chemical steps in the electrochemical reduction of Orange II. Its electrochemical reduction is an irreversible process unambiguously leading to the cleavage of the azo bond. This is in agreement with the results in literature obtained for similar azo compounds<sup>1,42,43</sup>. The diffusion coefficient values of Orange II in both acidic and basic media were calculated by using Cottrell equation and are given in Table-1.

TABLE-1  
DIFFUSION COEFFICIENTS, NUMBER OF ELECTRONS, STANDARD RATE CONSTANTS FOR HETEROGENEOUS ELECTRON TRANSFER IN ACIDIC AND BASIC MEDIA ( $c = 2.00 \times 10^{-4}$  M)\*

Media	Diffusion coefficient (D) $cm^2/s \ D \pm \frac{ts}{\sqrt{N}}$	Number of electrons transferred (n)**	Standard rate constants (ks), $cm/s, \ k_s \pm \frac{ts}{\sqrt{N}}$
Acidic	$7.49 \times 10^{-6} \pm 0.34 \times 10^{-7}$	$3.85 \pm 0.17$	$4.32 \times 10^{-6} \pm 1.08 \times 10^{-7}$
Basic	$3.06 \times 10^{-6} \pm 0.12 \times 10^{-7}$	$4.09 \pm 0.16$	$3.88 \times 10^{-6} \pm 1.23 \times 10^{-6}$

\*At 95 % confidence level, N = 4.

\*\*Obtained from controlled potential electrolysis.

According to the Klingler-Kochi method<sup>45</sup>, as the scan rate is increased,  $E_p^c$  and  $E_{p/2}^c$  change and so does the value of  $k_s$ . The  $k_s$  vs.  $v^{1/2}$  plot tends to take the form of a plateau at high scan rates. The average  $k_s$  values that are independent of  $v$  at  $21 \pm 2$  °C are also given in Table-1. These  $k_s$  values are another indication that the system is irreversible because the condition  $k_s < 0.004v^{1/2}$  is met here<sup>44</sup>.

### Studies on the reduction mechanism

On the basis of experimental data presented above together with electrochemical information about the reduction of some azo compounds<sup>1,14,41-43</sup>, it can be concluded that according to the coulometric studies, Orange II is reduced to give two corresponding amines in both acidic and basic



solutions. The possibility of coupled chemical reactions was confirmed by the plot of  $i_p^a/i_p^c$  vs.  $\log v$  in acidic medium (Fig. 6). The S-shaped curve obtained in Fig. 6 indicated the ECE mechanism for the reduction of Orange II for the charge transfer followed by an irreversible chemical reaction<sup>51</sup>. In addition, the thin layer chromatography of the electrolyzed solutions of Orange II for both acidic and basic media exhibited that same amines have been formed. The evidence of same products in both acidic and basic reaction media confirms the proposed mechanism of azo bond cleavage upon electrochemical reduction of Orange II.

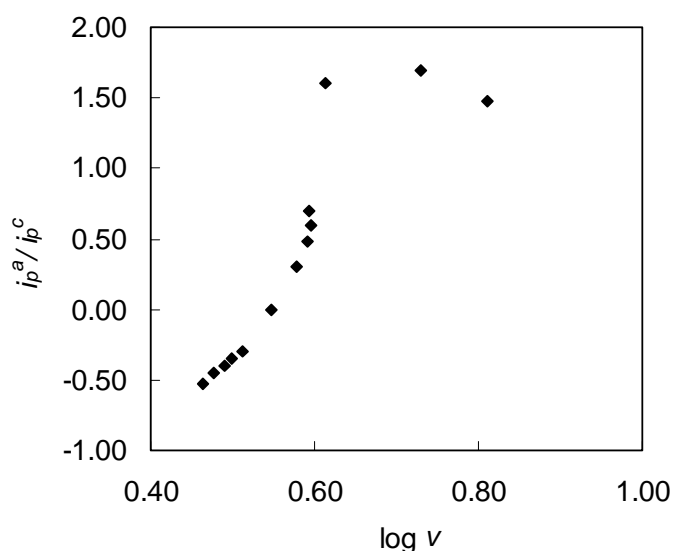
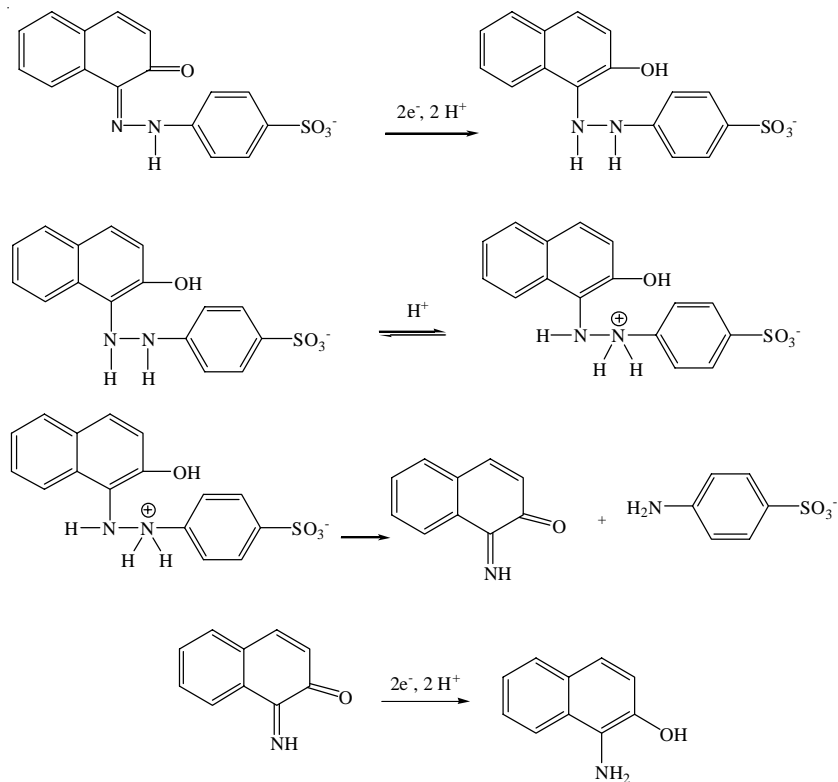


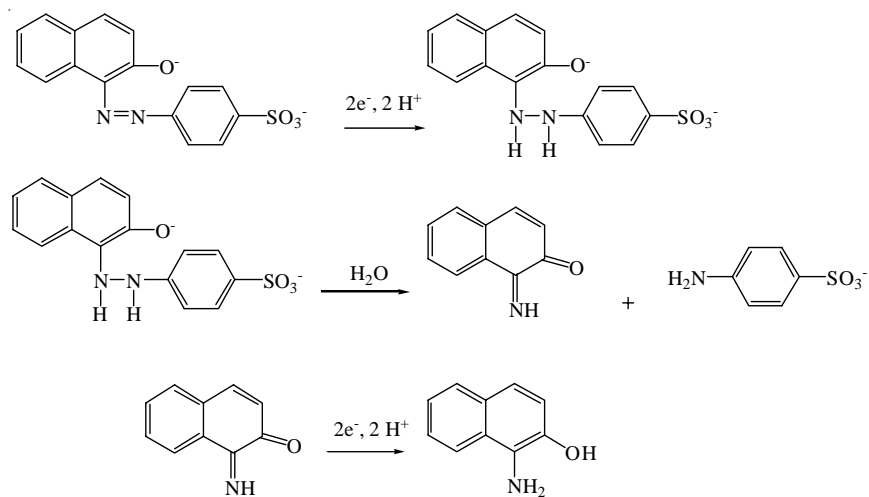
Fig. 6. Variation of  $i_p^a/i_p^c$  ratio with  $\log v$   $2.00 \times 10^{-4}$  M Orange II for acidic medium (pH: 2.4)

According to electrochemical experiments employed in this study and the reported literature results of similar compounds, the ECE mechanism in acidic and basic media can be suggested as in **Schemes I and II**.

Furthermore, taking into consideration that azo dyes need to be determined in real samples, it was observed that square wave voltammetry technique was suitable to suggest an analytical method for the determination of Orange II by using glassy carbon electrode. From the calibration graphs obtained by measuring the cathodic peak current as a function of concentration in the selected optimum pH value of 2.4, the linear concentration range was determined. It is found that Orange II could be determined with glassy carbon electrode in the concentration range of  $4.0 \times 10^{-6}$ – $8 \times 10^{-5}$  M which has a curve of  $I_p = 0.68C + 8.46$ ,  $R^2: 0.9904$ .



Scheme-I. Electrochemical reduction mechanism of Orange II in acidic medium



Scheme-II. Electrochemical reduction mechanism of Orange II in basic medium

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