

1-1-2016

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ÖZTÜRK, FUNDA; YAZAN, ZEHRA; OLMEZ, OZNUR; KILIÇ, EMİNE; and KILIÇ, ESMA (2016)
"Electrochemical investigation of 2-[8-hydroxyquinoline-5-yl)azo]benzo[cinnoline] on a platinum
electrode in dimethylsulfoxide," *Turkish Journal of Chemistry*. Vol. 40: No. 4, Article 7. <https://doi.org/10.3906/kim-1509-38>

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Electrochemical investigation of 2-[8-hydroxyquinoline-5-yl)azo]benzo[c]cinnoline on a platinum electrode in dimethylsulfoxide

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Received: 17.09.2015

Accepted/Published Online: 16.01.2016

Final Version: 21.06.2016

Abstract: 2-[8-hydroxyquinoline-5-yl)azo]benzo[c]cinnoline was synthesized for the first time and shown to possess electrochromic characteristic, i.e. changing color during the forward and back electrolysis at -1.35 V and 0.00 V, respectively, in DMSO medium. Therefore, the electrochemical investigation of this compound appears to be worthwhile.

The electrochemical reduction of 2-[8-hydroxyquinoline-5-yl)azo]benzo[c]cinnoline was investigated by cyclic voltammetry, controlled potential electrolysis, and chronoamperometry techniques in the presence of 0.10 mol L⁻¹ tetrabutylammonium tetrafluoroborate in dimethyl sulfoxide at platinum electrode. 2-[8-Hydroxyquinoline-5-yl)azo]benzo[c]cinnoline displays three sharp cathodic peaks and three anodic peaks in the cyclic voltammogram. The diffusion coefficients and the number of electrons transferred were calculated by using an ultramicroelectrode and platinum electrode. The number of transferred electrons was found to be one for each peak. The standard heterogeneous rate constant for reduction was calculated by the Klingler–Kochi technique. The electrochemical reduction mechanism of 2-[8-hydroxyquinoline-5-yl)azo]benzo[c]cinnoline was also investigated by using various electrochemical techniques, such as bulk electrolysis, and spectroscopic methods, like electron spin resonance spectroscopy. Bulk electrolysis results also provided evidence for each peak belonging to reduction of one electron, two of which were confirmed by electron spin resonance spectroscopy. This new chemical is found to be an electrochromic substance.

Key words: Azobenzene, azo dyes, benzo[c]cinnoline, electrochromic compounds, radical

1. Introduction

Azo dyes are a class of organic compounds widely used in the manufacture of dyes as chromophoric reagents,¹ and they were recently used in photochromic materials,² nonlinear optics,³ sensors,⁴ and photosensitizers.⁵ Their applications in the dye industry are described in detail by Zolinger.⁶ Furthermore, 8-hydroxyquinoline and its metallo-derivatives have been reported to possess activity against some bacteria.⁷ Therefore, a dye that has an azo-type structure adjoining the cinnoline heterocycle and 8-hydroxyquinoline could potentially be mordant-sensitive and could also be used as a pesticide because 8-hydroxyquinoline is an excellent chelating agent.⁸ As several azo dyes are reported to have genotoxic or ecotoxic properties,⁹ it is crucial to develop sensitive and accurate analytical methods for their quantification. Such a method would also be useful in research aimed at elucidating the mutagenic and other biological activities of cinnolines. The electrochemistry of azo compounds would also contribute to a better understanding of their reduction mechanisms in bacteria

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in the liver and the intestines.¹⁰ Therefore, the study of the surface electrochemical reduction mechanism of azo compounds may provide information on metabolic reactions of these compounds in biological systems. Given their widespread use, investigations of the chemical, physical, and redox properties of azo compounds remain important. The chemical and biological activity of azo dyes would vary in different media. A good knowledge of the electrochemical behavior of azo dye in dimethyl sulfoxide (DMSO) is, therefore, of considerable interest. Accordingly, knowledge of the electrochemical reduction of azo dyes is a prerequisite to understand their mechanism in both chemical and biological processes.

The reduction of azo dyes has been investigated successfully by electrochemical techniques.^{11–20} There are many studies on the electrochemical reduction of azo and benzo[*c*]cinnoline (BCC) compounds in both aqueous and nonaqueous media at mercury electrodes.^{11–16,18–20} In nonaqueous media like dimethylformamide (DMF), the electrochemical reaction of cis-azo benzene occurs in one-electron step.²¹ Geske and Padmanabhan reported that BCC was reduced to anion radical in DMF at a hanging mercury electrode by electron spin resonance (ESR) spectroscopy.²² Herlem and Amerongen presented results of a similar study of BCC and derivatives due to the formation of radical anion.²³ However, a survey of the literature reveals that not much work has been performed on the electrochemical behavior of azo dyes based on 8-hydroxyquinoline or BCC in DMSO media at platinum (Pt) electrodes.

Therefore, it would be worthwhile to elucidate the electrochemical reduction of azo dye containing 8-hydroxyquinoline and BCC groups. This study presents an investigation on the electrochemical behavior of 2-[(8-hydroxyquinoline-5-yl)azo]benzo[*c*]cinnoline (OHQAB) in DMSO at a Pt electrode. The same compound was previously synthesized to investigate its electrochemical properties in aqueous media²⁴ (the compound was referred to as HQAB therein²⁴). This work is meant to be an alternative to our previous publication that describes the voltammetric determination of OHQAB in DMSO – H₂O medium. Indeed, switching the medium from the aqueous mixture to pure DMSO causes the mechanism of the electrochemical reduction entirely, as will be discussed later. Similar to the previous work, the number of electrons transferred (n), the diffusion coefficient (D), and standard heterogeneous electrochemical rate constants (k_s) were determined by using cyclic voltammetry (CV), controlled potential electrolysis (CPE), and chronoamperometry (CA). In addition, ESR and ultramicroelectrode (UME) studies were carried out to clarify the reduction mechanism further. Adsorption properties of OHQAB on the Pt electrode's surface, and the mechanism were investigated using CV, bulk electrolysis (BE), CA, and electron spin resonance spectroscopy (ESR). The electrochemical behavior of azobenzene (AZB) and BCC were also investigated under the same conditions OHQAB was investigated. The structure of OHQAB is shown in Figure 1a, BCC in Figure 1b, and AZB in Figure 1c.

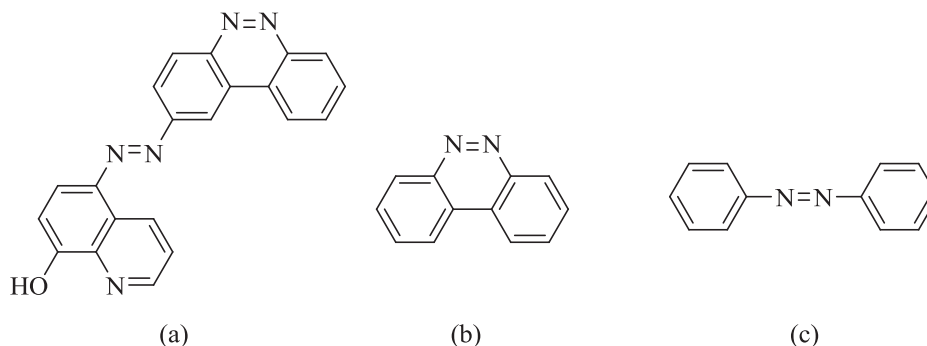


Figure 1. The molecule structures of (a) OHQAB, (b) BCC, (c) AZB.

2. Results and discussion

2.1. Cyclic voltammetric studies

Cyclic voltammograms of the solutions containing 1.0×10^{-3} mol L⁻¹ OHQAB, AZB, and BCC at a scan rate of 0.1 V s⁻¹ are obtained (Figure 2). The reduction of OHQAB in DMSO containing TBATFB proceeds in three steps. The three cathodic peaks (i_p^c) are at about -1.06 V, at -1.62 V, and at -2.00 V and the three anodic peaks are at about -0.92 V, -1.54 V, and -1.88 V, respectively.

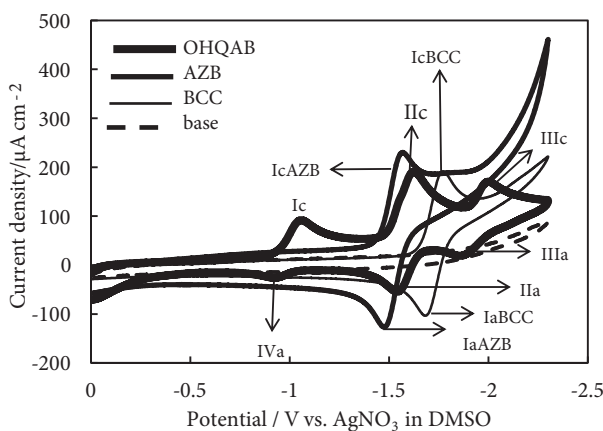


Figure 2. Cyclic voltammograms of 1.0×10^{-3} mol L⁻¹ OHQAB, AZB, and BCC (the medium: DMSO containing 0.10 mol L⁻¹ TBATFB, scan rate: 0.1 V s⁻¹, electrodes: platinum as the working electrode, Ag/Ag⁺ containing AgNO₃ in DMSO/TBATFB as the reference electrode, and Pt wire as the auxiliary electrode).

Apparently, the reduction mechanism of OHQAB in DMSO is drastically different from that in aqueous medium.²⁴ The lack of electrochromic effect in aqueous medium is obviously due to different reduction products in the presence of protons. In DMSO medium, it is probable that no protons are involved in the reduction steps. To identify the electrochemical reductions responsible for the voltammetric peaks, to major chemical entities constituting the title compound (AZB and BCC) were also investigated in DMSO medium for comparison. For AZB, cathodic and anodic peaks were observed at -1.57 V and -1.48 V, whereas for BCC, the cathodic peak was at -1.77 V and the anodic one at -1.69 V (Table 1).

Table 1. Electrochemical parameters of OHQAB, AZB, and BCC.

	1st peak				2nd peak				3rd peak			
	Ep,c (V)	ip,c (μA)	Ep,a (V)	Ip,a (μA)	Ep,c (V)	ip,c (μA)	Ep,a (V)	Ip,a (μA)	Ep,c (V)	ip,c (μA)	Ep,a (V)	Ip,a (μA)
OHQAB	-1.06	1.16	-0.92	0.27	-1.62	2.10	-1.54	1.36	-2.00	0.95	-1.88	0.67
AZB	-1.57	2.09	-1.48	2.97								
BCC	-1.77	2.10	-1.69	2.67								

These voltammograms were used to determine whether the electrochemical reduction reactions are reversible, quasireversible, or irreversible. For matching the anodic and cathodic peaks in Figure 2, reverse scans after all of the cathodic peaks were done (Figure 3). After the first cathodic peak (I_c), no anodic peak was observed for OHQAB when the switching potential scan was done. However, after the second cathodic peak (II_c), one anodic peak (II_a) was observed after the switching potential scan. After the third cathodic peak,

when the scan was switched, the anodic peaks IV_a and III_a were observed in addition to the anodic peak II_a (Figure 3).

The first anodic peak (IV_a) is probably not related to the first reduction peak, and the first anodic peak may belong to a product obtained as a result of more negative reduction of OHQAB and so the first reduction is not reversible. In addition, this hypothesis was supported by the voltammograms obtained with the CV experiments conducted at different scanning rates (Figure 4). When the scanning rate was increased, the reduction was not reversible due to the shifting of the peak potentials toward more negative values. In addition, in order to find out whether the reduction reactions of OHQAB are reversible or not, the change in $i_p^c/v^{1/2}$ versus scan rate (v) was examined.²⁷ The decrease in the values of $i_p^c/v^{1/2}$ with the values of v infers that the reduction reactions are not reversible.

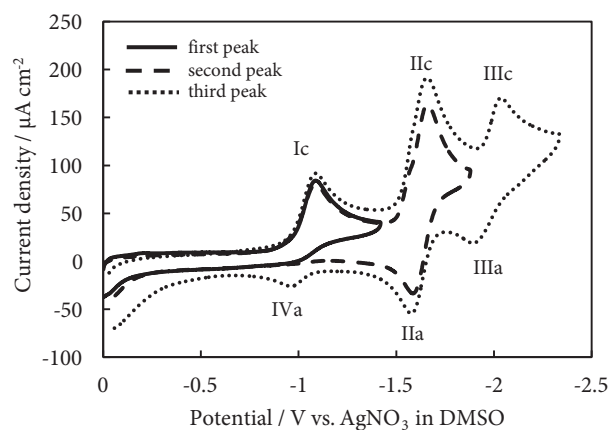


Figure 3. Cyclic voltammograms of 1.0×10^{-3} mol L^{-1} OHQAB at different switching potential scans (the medium: DMSO containing 0.10 mol L^{-1} TBATFB, scan rate: 0.1 V s^{-1} , electrodes: platinum as the working electrode, Ag/Ag^+ containing $AgNO_3$ in DMSO/TBATFB as the reference electrode, and Pt wire as the auxiliary electrode).

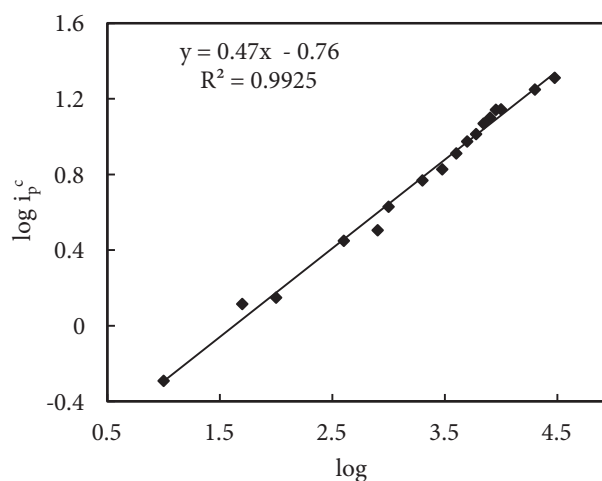


Figure 4. Influence of potential scan rate on both cathodic peak current and cathodic peak potential of 1.0×10^{-3} mol L^{-1} OHQAB (the medium: DMSO containing 0.10 mol L^{-1} TBATFB, scan rate: 0.1 V s^{-1} , electrodes: platinum as the working electrode, Ag/Ag^+ containing $AgNO_3$ in DMSO/TBATFB as the reference electrode, and Pt wire as the auxiliary electrode).

To throw light on whether adsorption is operative in the electrochemical process in question, we used CV.²⁸ The $\log i_p^c$ vs. $\log v$ is presented in Figure 5 for OHQAB. The slope of the graph is 0.47. This result indicates that the adsorption phenomenon is not dominant. The fact that no pre- or postpeaks are observed in the cyclic voltammograms of OHQAB at high scan rates is another indication that adsorption does not occur, to a considerable extent, on the electrode surface.²⁹ The linearity of i_p^c vs. $v^{1/2}$ graphs indicates that the reactions are diffusion controlled.²⁸

2.2. Calculation of n , D , and k_s values

The most important experimental data in determining the electrochemical reaction mechanism of compound on the electrode surface were the n values in each reduction step. There are various electrochemical methods used for this purpose. One of them is the constant potential coulometric method. Electrolysis was performed

for about an hour for each peak. n was calculated according to the $Q = nFN$ equation (Table 2). In order to determine whether the electrolysis was completed or not, the voltammograms were taken before and after the electrolysis. After the electrolysis, the disappearance of the peaks indicated that the electrolysis was completed.

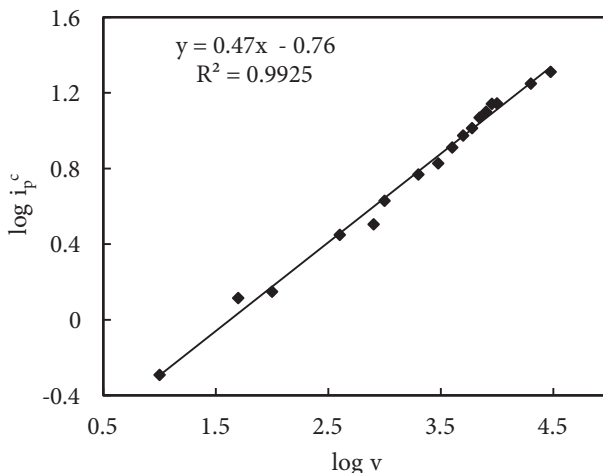


Figure 5. $\log i_p^c - \log v$ plots of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ OHQAB (the medium: DMSO containing 0.10 mol L^{-1} TBATFB, scan rate: 0.1 V s^{-1} , electrodes: platinum as the working electrode, Ag/Ag^+ containing AgNO_3 in DMSO/TBATFB as the reference electrode, and Pt wire as the auxiliary electrode).

Table 2. n , D , and k_s for heterogeneous electron transfer ($C = 1.0 \times 10^{-3} \text{ mol L}^{-1}$) in 0.10 mol L^{-1} TBATFB/DMSO for OHQAB.

n	UME	I _c	0.60 ± 0.08
		II _c	1.06 ± 0.05
		III _c	1.02 ± 0.25
	BE	I _c	0.70 ± 0.15
		II _c	1.26 ± 0.19
		III _c	1.01 ± 0.30
$D \text{ cm}^2 \text{ s}^{-1}$		I _c	$3.80 \times 10^{-6} \pm 1.31 \times 10^{-6}$
$k_s \text{ cm s}^{-1}$		I _c	$3.96 \times 10^{-2} \pm 3.54 \times 10^{-5}$
		II _c	$0.14 \pm 7.06 \times 10^{-4}$
		III _c	$0.14 \pm 7.91 \times 10^{-5}$

n and D of the compound were calculated by the method developed by Baranski et al.²⁵ Chronoamperometric measurements were achieved at a normal size Pt electrode and CV experiments were done at an UME for $1 \times 10^{-3} \text{ mol L}^{-1}$ OHQAB, AZB, BCC, and ferrocene solutions. n and D were calculated using the following equations:

$$n = \frac{n_s S^2 i_s C_s}{S^2 i C} \quad (1)$$

$$D = \frac{D_s S_s t^2}{S^2 i C} \quad (2)$$

Here i is limiting steady-state current, C is the concentration, and S is the slope of the chronoamperometric i vs. $t^{-1/2}$ plot. The same values of n_s , D_s , and C_s obtained from the ferrocene-ferrocenium couple were

used. The experimental values of n and D for OHQAB are presented in Table 2. In order to determine the limiting steady-state currents for compounds, CV was also used. n during the reduction of OHQAB was also determined by BE.

n calculated with the use of the UME was in good accordance with the number of electrons determined from BE (Table 2). Both methods indicate that one electron is transferred at each reduction step.

The values of the diffusion coefficients are presented in Table 2. The fact that the diffusion coefficients of all the compounds are similar proves that they diffuse to the electrode surface in a similar manner due to their closely related structures.

The heterogeneous electron transfer k_s values are found from cyclic voltammograms at different scan rates. In general, as the scan rate is increased, E_p^c and the peak width values, $E_{p1/2}$, show a variation with 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 (Figure 6). The average k_s values, which are independent of v , are tabulated in Table 2. The value of k_s for the first peak (I_c) is another indication that the system is quasireversible, because the condition $2.0 \times 10^{-5} v^{1/2} < k_s < 0.3 v^{1/2}$ is fulfilled (Figure 6a).²⁸ For the second and third peaks, the k_s values showed that the reduction mechanism related to the second and third reduction steps is close to being reversible (Figures 6b and 6c)

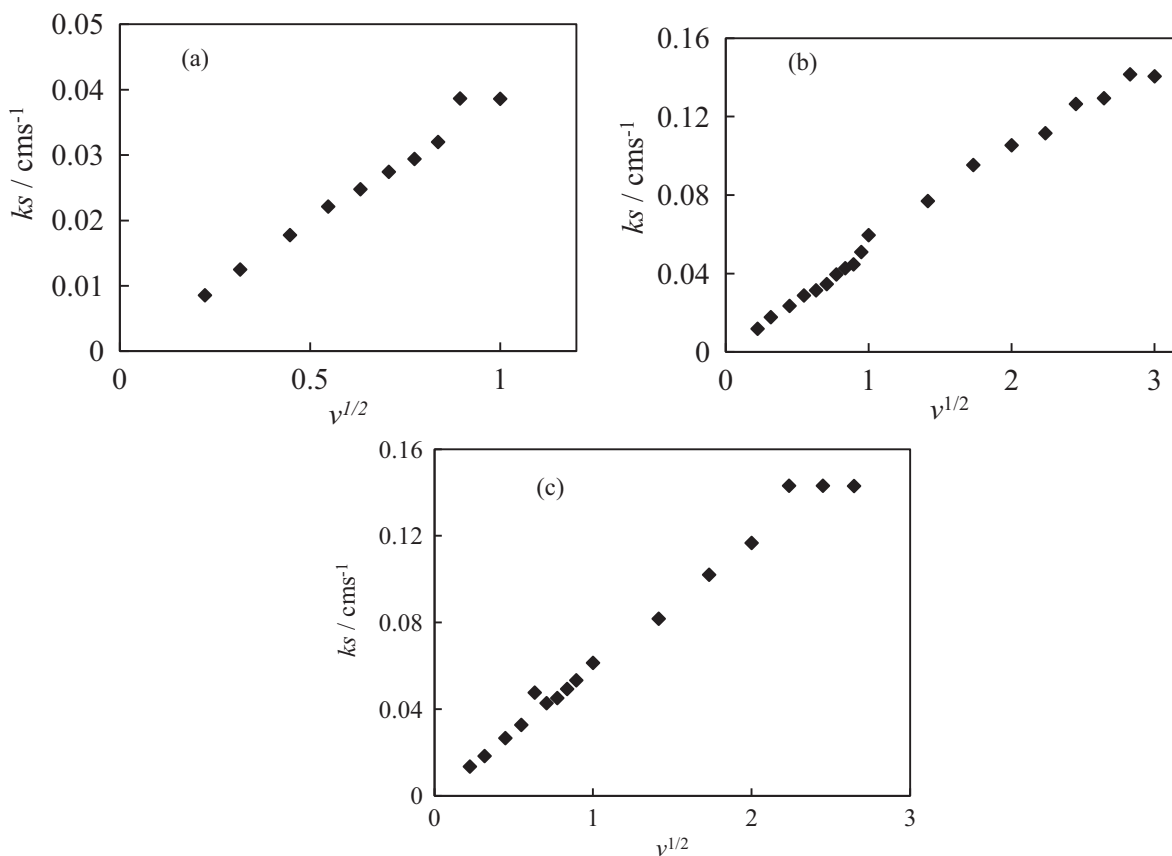


Figure 6. k_s versus $v^{1/2}$ graph of OHQAB (a) first peak, (b) second peak, (c) third peak.

2.3. Calibration graph of OHQAB dye

As this compound is very likely to find various fields of use, an investigation on the possible methods of quantitative analysis for this compound appears to be worthwhile. From the analytical point of view, the best developed and most easily evaluated peaks were obtained in the DMSO solvent. The second peak is the most suitable peak for detection of OHQAB since it is the highest and sharpest peak. The applicability of square wave voltammetry (SWV) and differential pulse voltammetry (DPV) procedures as analytical methods for the determination of OHQAB was examined by measuring the cathodic peak current density as a function of the concentration of OHQAB. The linear concentration range was determined from the calibration graph obtained by measuring the cathodic peak current density as a function of concentration (Figure 7). The result obtained by SWV method is more sensitive than the result obtained by DPV. It is concluded that OHQAB could be determined by platinum electrode in the concentration range of $1.0 \times 10^{-4} \text{ mol L}^{-1} - 8.0 \times 10^{-4} \text{ mol L}^{-1}$.

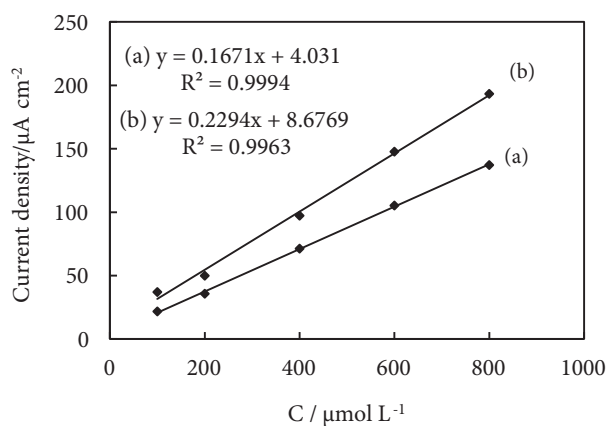


Figure 7. Calibration graph of OHQAB a: DPV and b: SWV.

2.4. Studies on the reaction mechanism

2.4.1. ESR studies

As a result of the BE, it was observed that each peak belonged to the reduction of one electron (Table 2). After the first reduction step, no ESR signal was observed. According to this result, the underlying process is expected to be an electron transfer followed by a chemical reaction.³⁰ The accompanying chemical reaction might be a protonation, dimerization, or polymerization reaction. The solution obtained as a result of BE performed in the first reduction potential of OHQAB was again electrolyzed in the peak potential of the second electrochemical reduction. Finding the transferred electron number as one (Table 2) in the second electrochemical reduction step of OHQAB infers a radical formation. With this purpose, the ESR spectrum of the solution obtained after electrolysis was recorded and a strong signal of 3482 Gauss was observed (Figure 8a). Therefore, it is concluded that a free radical might be formed in this step.³¹

The solution obtained as a result of BE performed in the second reduction potential of OHQAB was again electrolyzed in the third electrochemical reduction of peak potential. n was found to be one (Table 2). The ESR spectrum was recorded and a strong signal of 3484 Gauss was observed (Figure 8b). These radicals are observed to be stable for at least 12 h at room temperature and under daylight.

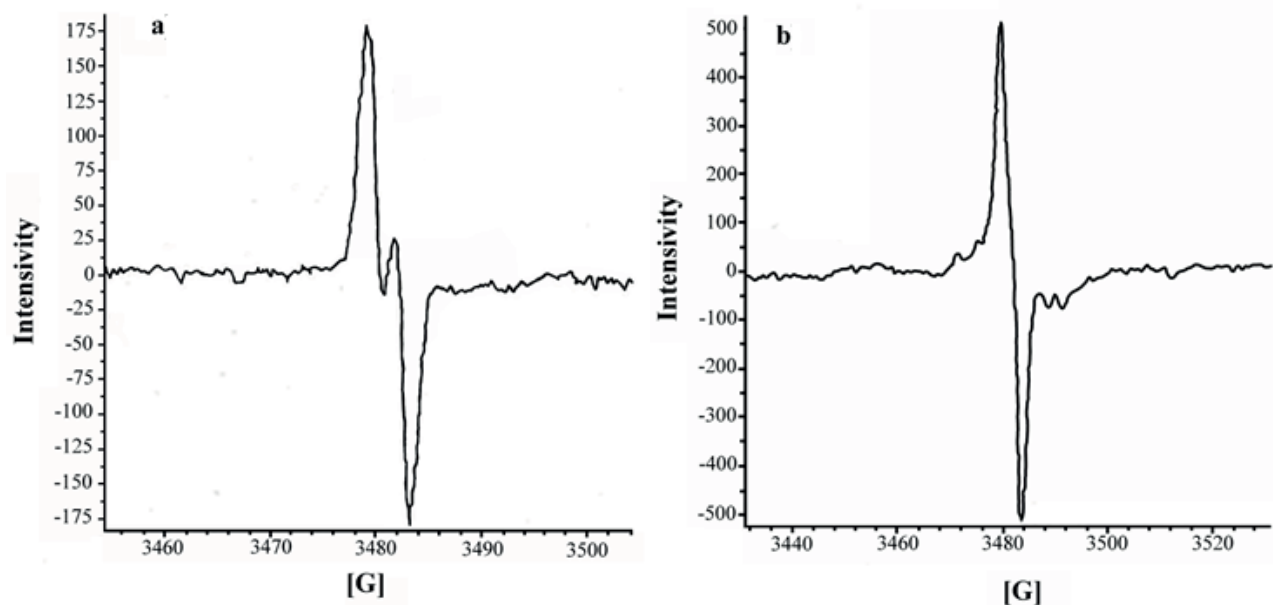


Figure 8. The ESR spectra were recorded after the BE at a: -1.80 V and b: -2.35 V potentials (the medium: DMSO containing 0.10 mol L^{-1} TBATFB, scan rate: 0.1 V s^{-1} , electrodes: platinum as the working electrode, Ag^+/Ag containing AgNO_3 in DMSO/TBATFB as the reference electrode, and Pt wire as the auxiliary electrode).

2.4.2. CV studies

In order to prove whether there was a homogeneous chemical reaction or not after the electron transfer step in the first reduction reaction, the criterion of $i_p^c/v^{1/2}$ vs. v was examined. For the first cathodic peak, the current function ($i_p^c/v^{1/2}$ C) values were plotted against the scan rate (v) and checked for their agreement with the Nicholson–Shain criteria.²⁷ The current function's exponential decrease towards the higher scan rates is an indication that the electron transfer is followed by a chemical reaction such as protonation.

The cyclic voltammogram of OHQAB is given in Figure 2. This figure has an anodic peak (II_a) corresponding the second reduction peak (II_c) of OHQAB close to reversibility. This shows that there might be a radical formation in the electrode reaction.³¹

The ratio i_p^a/i_p^c of the second reduction peak of OHQAB being lower than one and its being constant with the increase in the scan rate show that there was no chemical step afterwards.²⁷

n related to the first reduction peak of OHQAB was calculated to be 0.8 by BE and 1.1 by UME.

The mode of electrolytic reduction in DMSO is obviously not similar to that reported for the same compound in DMSO-water medium.²⁴ This is the expected outcome as the aqueous medium is a good source of protons and with protons different routes are possible.

2.4.3. The proposed mechanism

The first reduction peak of OHQAB indicates that the reaction is due to a fast reaction involving a radical anion (Eq. (3)).



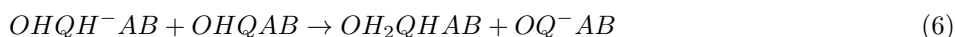
The radical produced after the transfer of the first electron takes a proton from the unreduced species and thus causes OHQAB to turn into its conjugate base, $[OQ]^- AB$ (Eq. (4) and Figure 8a).



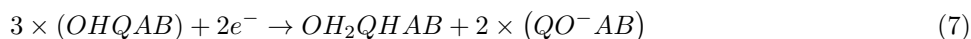
The transfer of a second electron to the protonated radical causes the formation of the anion (Eq. (5) and Figure 8b).



This anion in turns takes a proton from OHQAB (Eq. (6)).

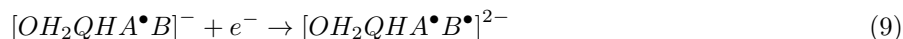
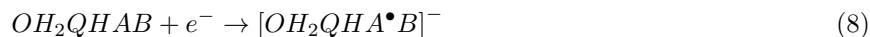


The final product in the first reduction step, OH_2QHAB , is eventually formed together with the conjugate base of the starting compound.



In order to find out of which electroactive groups in the molecule are reduced in the second and third reductions, the cyclic voltammograms of OHQAB were used (Figure 2). Figure 2 shows the corresponding reduction and oxidation cyclic voltammograms of AZB, BCC, and OHQAB. While the second peak of OHQAB corresponds to the one electron reduction of AZB (Eq. (8)), the third peak of OHQAB corresponds to the one electron reduction of BCC (Eq. (9)).

The following reaction mechanism was suggested for the second and third reduction of OHQAB according to the results:



These mechanisms were supported by the ESR data (Figures 6a and 6b) and cyclic voltammograms of AZB and BCC (Figure 2).

During the BE of OHQAB at -1.35 V after the first reduction peak, the orange color of the original solution turns green first and blue at the end. Back-electrolysis of the same solution at 0.00 V potential ended up with a brownish orange color. Although the first reduction peak at -1.06 V is not reversible, the BE at -1.35 V and then back at 0.00 V is reversible. This may be attributed to the fact that during the CV process the concentration of the reduced form is so small that the reduced form is not adsorbed on the electrode surface to produce an observable signal. On the other hand, BE at -1.35 V converts the starting material to the anionic radical $[OHQ]^\bullet AB$ and during the back electrolysis at 0.00 V there is plenty of the anionic radical to adhere to the electrode surface. With the potential fixed at -1.80 V after the second peak, the BE of the solution pretreated at the first peak potential ends up with a greenish blue (turquoise) color. The back electrolysis of this product at -1.35 V causes the color of the solution to return to blue, which is a sign that the second step is also reversible. The BE at -2.30 V changes the color to brown. Back electrolysis at 0.00 V changes the color to brownish orange. These electrolysis experiments were repeated ten times with the same OHQAB solution and the same color changes were observed in all of the experiments.

We think that the work would have been completed much better if the products of each step had been isolated and identified to prove the mechanism suggested. Indeed, we did carry out BE at the potential of each reduction peak. Unfortunately, the solvent, DMSO, used as the electrolysis medium proved to be a major obstacle in the isolation of the reduction products, possibly due to their radical nature. Therefore, we could only provide ESR spectra of the products that are obtainable from the intact electrolysis mixture. The findings indicate that OHQAB may have a prospect of electrochromic use.

This work demonstrated that OHQAB has three reduction and three oxidation peaks at a Pt electrode in DMSO. The electrochemical reduction occurs through 3 reduction steps each by one electron. In order to test the validity of the proposed mechanism controlled-potential preparative electrolysis was carried out at the potentials of each reduction peak for OHQAB. The isolated products were characterized with ESR spectroscopy. The resulting spectra showed that a free radical was formed in both the second and third reduction steps. This was taken as further evidence for the proposed mechanism. All electrochemical findings indicate that OHQAB may have a prospect of electrochromic use in future if it finds use as a dye.

3. Experimental

3.1. Reagents and solutions

The DMSO used was an absolutely dry (water $\leq 0.01\%$) batch of Fluka (41648) kept on beads of a molecular sieve (4 Å). The supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBATFB), was purchased from Fluka (21,796 – 4) and was used without purification. All of the other chemicals were reagent grade and were used without further purification. 1×10^{-3} mol L⁻¹ solution for the voltammetric studies was prepared by dissolving an appropriate amount of solid OHQAB in DMSO containing 0.1 mol L⁻¹ TBATFB.

3.2. Apparatus

Voltammetric measurements were made with BAS100B/W Electrochemical Analyzer with a cell stand of C3. A Pt electrode (BAS MF – 2013) and 100 μ m UME (BAS MF – 2150) were used as working electrodes. The electrodes were polished before each use with an alumina polishing powder. A Pt wire (BAS MW – 1034) was used as the auxiliary electrode. The reference electrode was a silver wire in contact with 0.1 mol L⁻¹ AgNO₃ in DMSO. All solutions were deaerated for 10 min with pure argon. ESR spectra were recorded in the X band (9–10 GHz) using a Bruker spectrometer with a rectangular cavity and 50-kHz field modulation. The measurement was performed using a 2-mm quartz tube.

The IR spectrum was recorded on a Mattson 1000 FTIR spectrometer in a KBr disc; microanalysis was carried out by the microanalytical service of the Scientific and Technological Research Council of Turkey (TÜBİTAK), and the electron impact (EI) spectrum was obtained on the PLATFORM II LC – MS spectrometer.

3.3. Polishing and cleaning of Pt electrode

Prior to each experiment the platinum electrode was polished successively in 1 μ m, 0.3 μ m, and 0.05 μ m alumina slurries made with dry Buehler alumina on a smooth polishing cloth rinsed with deionized water. The polished Pt electrode was sonicated in a mixture of 50:50 (v/v) methanol/DMSO before each use.

4. Method

n and D were determined by the UME CV technique of Baranski.²⁵ The k_s values were calculated according to the Klingler–Kochi method.²⁶

4.1. Electrolyses and product analysis

For CPE studies, a BAS MF – 1056 BE cell was utilized. The three-electrode combination system for BE consisted of a reticulated vitreous carbon electrode (BAS MF – 2077) as the working electrode, a Ag/AgNO₃ electrode as the reference electrode (BAS MF – 2052 RE – 5B), and a coiled Pt wire as the auxiliary electrode (23 cm) (BAS MW – 1033); 0.1 g of OHQAB was added to the catholyte (25 mL of DMSO/0.1 mol L⁻¹ TBATFB) and then the potentials were set at –1.35 V, –1.80 V, and –2.35 V, respectively. Useful information is gained from the ESR spectra of the products. The formation of radical ions is observed with ESR spectra.

Acknowledgments

We gratefully acknowledge the financial support of TR Prime Ministry State Planning Organization (Project No: 98 – K – 120830) and Ankara University Research Fund (Project No: 20050705094).

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