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Investigation of Eletrooxidation Reaction of Some Tetrahydrobenzo[b]pyran Derivatives

Lida Fotouhi[*], *Azadeh Fatehi, Majid M. Heravi*

Department of Chemistry, School of Science, Alzahra University. P.O.Box 1993891176, Tehran, Iran
[*]E-mail: lfotouhi@alzahra.ac.ir

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The oxidation mechanism of a series of tetrahydrobenzo[b]pyran (THP) derivatives (**1-6**) has been investigated at glassy carbon electrode. The study is performed in dimethylformamide (DMF) by cyclic voltammety. All compounds exhibited two irreversible oxidation peaks in which their currents increased with increasing concentration. From the plot of current vs. square root of scan rate it was found that the electron transfer is diffusion controlled. It is suggested that the mechanism of this electrooxidation involves the transformations amine to nitro compound. The transfer coefficients for all compounds were also reported.

Keywords: tetrahydrobenzo[b]pyran, cyclic voltammetry, oxidation, amine, nitro

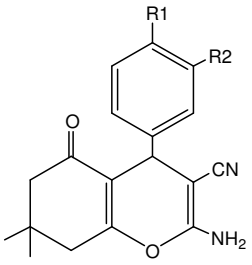
1. INTRODUCTION

In recent years, 4H-benzo[b]pyran and their derivatives have attracted strong interest due to their useful biological and pharmacological properties, such as anticoagulant, spasmolytic, diuretic, anticancer, antianaphylactin characteristics [1-3]. Some 2-amino-4H-pyrans can be employed as photoactive materials [4]. Furthermore, the 4H-pyran group is a constituent of the structures of a series of natural products [5, 6]

Recently, we reported an electrogenerated base-prompted synthesis of tetrahydrobenzo[b]pyran (THP) derivatives [7] with an amine group in their structures. Heterocyclic amines present prevalent constitutional chemotypes and underlying structural motifs in registered drugs, which renders the development of efficient procedures for their synthesis an objective of high priority from the perspective of medical and bioorganic chemistry [8, 9]. The studies undertaken so far are mostly dealing with the reduction of the nitro group by chemical and electrochemical methods leads to the subsequent formation of amines, hydroxylamines or other intermediates, including nitroso and azoxy compounds [10-13]. As far as we know there are only few reports on the oxidation of heterocyclic

amines to nitro compounds [14-16]. In order to investigate the biodegradation or biotransformation of heterocyclic amines in the future, it is necessary to show that the electrooxidation of amines follows the well-described general behavior of oxidation of amine to nitro compounds.

In continuation of our studies on electrochemical behavior of organic compound [17-21] we report herein the electrochemical behavior of some THP (Fig 1) at glassy carbon electrode in dimethylformamide.



1	R_1= OH	R_2= H
2	R_1= H	R_2= NO_2
3	R_1= Cl	R_2= H
4	R_1= CH_3	R_2= H
5	R_1= OCH_3	R_2= H
6	R_1= H	R_2= H

Figure 1. The structure of THPs.

2. EXPERIMENTAL PART

2.1. Chemical and reagents

Tetrabutylammonium perchlorate (TBAP) and N, N- dimethylformamide (DMF) were obtained from Flucka and Merck, respectively. As supporting electrolyte, 0.1 M TBAP was used. All other chemicals were of analytical reagent grade.

2.2. Instrumentation

All experiments were performed with a Metrohm model 746 VA Trace Analyzer connected to a 747 VA Stand. The working electrodes were a glassy carbon disk (GC) 2mm diameter from Metrohm. Before use, the glassy carbon electrode was sequentially polished with graded alumina powder 10μm (Merck) and then rinsed with doubly distilled water. A platinum wire from Metrohm was used as auxiliary electrode. All potentials are quoted vs. a standard Ag/AgCl / saturated KCl reference electrode (Metrohm). The scan rate (υ) in cyclic voltammetry was $100mVs^{-1}$, with the evident exception of the experiments in which the influence of this variable was studied. All voltammetric experiments were conducted at room temperature under pure argon.

A potentiostat/galvanostat system model BHP 2061-C was used for controlled potential electrolysis. The working electrode used in controlled-potential electrolysis was an assembly of four carbon rods and a large piece of platinum gauze constituted the counter electrode. The electrolysis was terminated when the electrolytic current decreased to the residual current value measured in the supporting electrolyte before the addition of the analyte.

3. RESULTS AND DISCUSSION

A typical cyclic voltammograms of **1** at various concentrations are shown in Fig 2, obtained on a glassy carbon electrode in 0.10 M TBAP in DMF. As illustrated in Fig 2, **1** was oxidized at two anodic peaks, at 1.32 and 1.60 V without any reduction peak at reverse scan, indicating that both anodic peaks were irreversible electron transfer processes. The height of both anodic peaks showed linear variation with concentration, which indicated that the electron transfer is diffusion-controlled (Fig 2, inset). With increasing concentration, peak potentials were shifted to more positive potentials due to the irreversibility of the process. All THP derivatives showed a similar voltammograms with two anodic peaks, in which their currents increased with increasing the concentration. The peak potentials of all THPs (**1-6**) are shown in the Table 1.

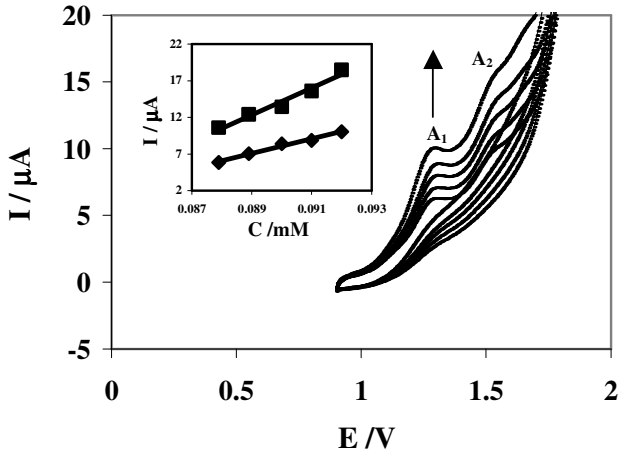


Figure 2. The cyclic voltammograms of compound **1** in 0.10 M TEAP+ DMF solutions at different concentrations; 0.088, 0.089, 0.90, 0.091, 0.092 mM, scan rate 100mVs^{-1}.

Table 1. Electrochemical data of the studied THPs (**1-6**) by cyclic voltammetric method with glassy carbon electrode.

THPs	E_{p1} (V)	E_{p2} (V)	αn (A_1)	αn (A_2)
1	1.32	1.58	0.48	0.49
2	1.23	1.50	0.47	0.44
3	1.20	1.49	0.49	0.41
4	1.22	1.47	0.43	0.48
5	1.19	1.47	0.40	0.44
6	1.24	1.54	0.34	0.37

A general study of the oxidation of amine compounds [14-16] proposes a reaction scheme in which after losing 2e, the hydroxylamine resulted, in which oxidized to nitro via 4e oxidation process. We have proposed similar behavior in our compounds [20-21].

To ascertain whether the oxidation mechanism follows the above suggested pattern, the cyclic voltammograms of **1** at various scan rates (Fig 3) have been carried out in the potential range of first and second anodic peaks. The linear dependence of current vs. $\upsilon^{1/2}$ for both peaks (Fig 3, right, inset) indicates that the oxidation of redox species are diffusion controlled. However the current function of the anodic peaks was constant for the range of the scan rate, which indicates that there was only an irreversible electron transfer without any coupled chemical reaction for both peaks (E mechanism).

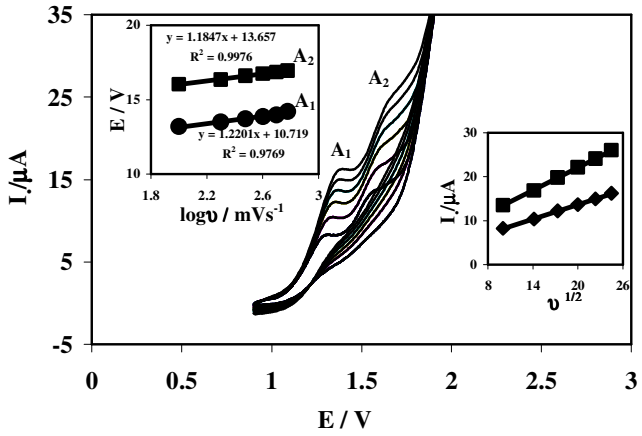


Figure 3. Cyclic voltammograms of 0.90 mM of **1** at scan rates: 100, 200, 300, 400, 500, 600 mVs^{-1}. Inset, left: Peak potential variation of both anodic peaks (A_1 and A_2) as a function of log υ. Inset, right: variation of current peaks (A_1 and A_2) vs. $\upsilon^{1/2}$.

The peak potentials were found to depend on scan rate and concentration in voltammetry of all the compounds which indicate a totally irreversible oxidation wave. In order to obtain information on the rate determining step a Tafel slope, b, was determined using the following equation valid for a totally irreversible diffusion controlled process.[22]

$$E_p = (b/2) \log \upsilon + \text{Const.}$$

Where, b is Tafel slope. The plot of E_p vs. log υ is shown in Fig 3 (inset, left). The slope of the linear plot is equal to b/2-=0.059/αn. So, b=2(0.059/αn) V. The observed values of transfer coefficients are shown in Table 1.

From the above results we have concluded that the oxidation in both anodic peaks followed the well-defined oxidation mechanism in amine compounds [14-16].

$$RNH_2 + H_2O \rightarrow RNHOH + 2H^+ + 2e$$
$$RNHOH + H_2O \rightarrow RNO_2 + 4H^+ + 4e$$

Controlled potential electrolysis was performed to provide more detailed information about the electrode process. In a typical procedure, a DMF (40 ml) solution of **1** and 0.1 M TEAP as supporting electrolyte in an undivided cell fitted with the carbon rods anode and a Pt cathode was subjected to electrolysis at 1.70 V potential. The progress of the reaction was monitored by thin layer chromatography. The resulting precipitate was filtered and dried. The product was characterized by FT-IR spectroscopy. From the FT-IR spectrum it can be seen that the THPs showed two bonds at 3394 and 3324 Cm^{-1} corresponding to amine group. While the FT-IR spectrum of electrolyzed products did not show any bond at this region and two bands due to nitro group were appeared at 1458 and 1574 Cm^{-1} which is a good indication of electrooxidation of amine to nitro group.

The cyclic voltammogram of **2** with two amine and nitro groups is shown at Fig 4. In addition to two anodic peaks at the same potential range, a reversible peak at -1.00 V (**A_3**) was appeared. Recording the cyclic voltammogram in the potential range of -1.40 to -0.70 V showed the reversible peak corresponding to one-electron reduction of nitro group to radical anion of nitro as following, which is well-defined in the most nitro compounds [10, 11, 20, 23].

$$RNO_2 + 1e \leftrightarrow RNO_2^{\cdot -}$$

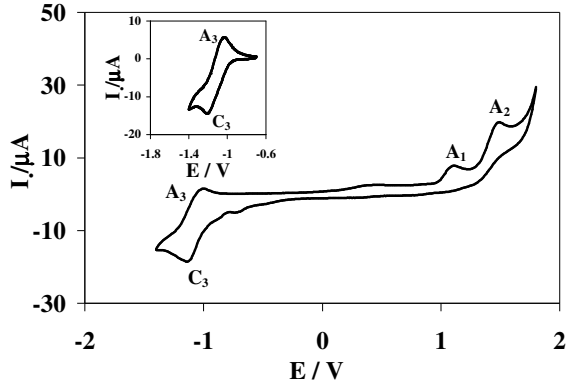


Figure 4. The cyclic voltammogram of **2** at wide range of -1.40 to 1.80 V, 0.10 M TEAP+ DMF solution, scan rate: 100 mVs^{-1}.Inset: The cyclic voltammogram of **2** at potential range -1.40 to -0.70 V.

4. CONCLUSIONS

The electrooxidation of THPs (**1-6**) in DMF follows a well-defined mechanism in the compound containing amine group. It is suggested that the mechanism of this oxidation involves the transformation of amine to nitro compound via two anodic peaks. The transfer coefficients are also given.

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