Mechanistic Study of Homogeneous Reactions Coupled with Electrochemical Oxidation of Catechols

D. Nematollahia,*, M. Rafieeb and L. Fotouhić

aFaculty of Chemistry, Bu-Ali-Sina University, Hamadan 65174, Iran
bDepartment of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Gavazang, Zanjan 45195-1159, Iran
cDepartment of Chemistry, School of Science, Alzahra University, P.O. Box 1993891176, Tehran, Iran

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The electrochemical oxidation of catechols was described and has shown that these compounds can be oxidized to related \( o \)-benzoquinones. The electrochemically generated \( o \)-benzoquinones are quite reactive and can be attacked by a variety of nucleophiles under various mechanistic disciplines such as \( CE \), \( EC \), \( EC' \), \( ECE \), \( ECEC \), \( ECECE \), \( ECECEC \) and trimerization, in which \( E \) represents an electron transfer at the electrode surface, and \( C \) represents a homogeneous chemical reaction. The mechanistic pathways and final products are depending on some parameters such as electron withdrawing or donating properties of nucleophile, electrolysis medium (solvent, acidity or pH) and nature of catechol.

**Keywords:** Catechol, Mechanistic study, Electrochemical oxidation, Homogeneous coupled chemical reaction, Cyclic voltammetry

**INTRODUCTION**

Electrochemistry provides very interesting and versatile means for the study of chemical reactions. Recently, the terms molecular electrochemistry or dynamic electrochemistry have been used for that part of electrochemistry that studies the mechanistic events at or near an electrode on a molecular level [1]. The majority of organic electrode reactions are characterized by the generation of a reactive intermediate at the electrode by electron transfer and subsequent reactions typical for that species. These are often assumed to occur in a homogeneous solution, and not at the electrode surface itself. The main goal of the electrochemical studies is the elucidation of the sequence of electron transfer and chemical reactions that occur near the electrode surface and their applications to electrosynthesis of organic compounds. The electrochemical generation and study of the intermediates may be advantageous because of the mild reaction conditions employed and the additional selectivity introduced in controlled-potential experiments [2].

Among the organic compounds, catechols \( (1) \) can be easily oxidized to the corresponding reactive \( o \)-benzoquinones \( (1a) \) mainly due to their low oxidation potentials. It is worth mentioning that catechols are used in a variety of applications including photography, dyeing, rubber and plastic production and pharmaceutical industry [3]. In addition, catechol derivatives play an important role in mammalian metabolism, and many compounds of this type are known to be secondary metabolites of higher plants. Also, many drugs such as doxorubicin, daunorubicin and mitomycin C which are used
in cancer chemotherapy contain quinones [4]. The catechol derivatives are a promising group of compounds which may lead to the discovery of selective acting, biodegradable agrochemicals having high human, animal and plant compatibility and, thus, worthwhile for further investigation [5]. On the other hand, because electrochemical oxidation very often parallel the cytochrom P450 catalyzed oxidation in liver microsomes, it was interesting to study the anodic oxidation catechol derivatives in different conditions [6].

In recent years our research group has been mainly focused on the electrooxidation of catechols (1) to produce o-benzoquinones (1a) as reactive intermediates in many useful homogeneous reactions. Thus, based on these valuable experiences, here we wish to present a review paper on the mechanistic study of homogeneous reactions coupled with electrochemical oxidation of catechols.

CHARACTERIZATION OF CHEMICAL REACTIONS COUPLED WITH ELECTRON TRANSFER

Among many electrochemical techniques presented for the study of chemical reactions, cyclic voltammetry has become a very popular technique for initial electrochemical studies of new systems. It is easy to apply experimentally, readily available in commercial instruments and has proven as very useful tool in obtaining information about fairly complicated electrode reactions. Cyclic voltammograms are frequently and routinely used today to define the redox properties of newly synthesized organic compounds, similar to the use of NMR spectra for structural characterization [7]. The time scale of a cyclic voltammetry experiment is determined by the scan rate, i.e., increasing scan rate decreases the experimental time scale; therefore, an important parameter in determining the effect of chemical reaction is the ratio of rate constant of chemical reaction to the scan rate, k/v, and the effect of scan rate is appeared in the cyclic voltammograms of different electrochemical mechanisms [8]. The detailed quantitative study of the chemical reactions coupled with electron transfer using diagnostic criteria has been reported by Shain and Saveant [2]. More complicated systems, involving slow heterogeneous kinetics, coupled homogeneous reactions or equilibria or more complex forms of mass transfer have been most easily treated by digital simulation.

Even more information about the reaction can be gained from electrolysis experiments at various defined potentials, for example after each peak in the cyclic voltammogram of the substrate. This type of experiment has been traditionally called as controlled potential coulometry. Cyclic voltammetric analysis can be carried out during the coulometry, and the change in concentrations of electroactive species can be followed during electrolysis by cyclic voltammetry. This combination can be a useful method for detection of intermediate(s) during coulometry [2]. From exhaustive potentiostatic electrolysis, the product(s) formed at the selected electrode potential can be isolated and structurally characterized by various analytical techniques. All of these results will often allow the defining of reaction steps.

CLASSIFICATION OF ELECTRODE REACTIONS

Most electrode reactions of interest to the organic electrochemists involve chemical reaction steps. The reaction mechanisms of electrode reactions are thus composed of at least one electron transfer step at the electrode as well as preceding and follow-up band breaking, bond forming or structural rearrangement steps. The nomenclature used to described the mechanisms is based on $E$ for an electron transfer reaction and $C$ for a chemical reaction, for example, an $EC$ mechanism consists of an electron transfer reaction ($E$) followed by a chemical reaction ($C$) [9].

THE CRUCIAL PARAMETERS ON REACTION MECHANISM OF CATECHOLS

As reported previously the electrochemical oxidation of catechol in different conditions leads to the formation of final products via various mechanisms such as $CE$, $EC'$, $EC$, $ECE$, $ECEC$ and etc. There are some determining parameters on mechanism including catechol type, nature of nucleophile, electrode potential and electrolysis medium.

Catechol is known as a polyphenol in which two hydroxyl groups are substituted onto benzene ring. The other four remaining substituents are important parameters on determining the reaction mechanism. The presence of poor