Cyclic Voltammetric and Electrochemical Simulation on the Electro-Oxidation of Catechol in the Absence of Any Nucleophile: Original Research

Tekalign Kasa

Madda Walabu University, College of Natural and Computational Science, Department of Chemistry

Abstract

Electro-oxidation of catechol has been investigated in the absence of nucleophile. The studies were made using cyclic voltammetry on a glassy carbon electrode in aqueous solution containing phosphate buffer solution as supporting electrolyte. The electro-oxidation of catechol produces a very reactive intermediate, o-benzoquinone, which subsequently reacts with any nucleophile in 1, 4-Michael addition reaction to form the corresponding catechol derivative product. The main purpose of this investigation was to carry out a quantitative study of the electro-oxidation of catechol in aqueous solution and the kinetic data were extracted from cyclic voltammograms with the help of digital simulation software.

Keywords: Cyclic voltammetry, Catechol, benzoquinone

INTRODUCTION

Electrochemistry provides very interesting and versatile means for the study of chemical reactions. 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. 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 its applications to electro-synthesis of organic compounds. Among the organic compounds, catechol can be easily oxidized to the corresponding reactive o-benzoquinone mainly due to its low oxidation potential [1]. Catechol has the molecular formula of $C_6H_6O_2$ and structure which is shown in the scheme 1 below.
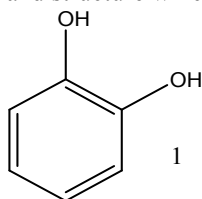
Catechol

Scheme -1 Structure of catechol

Catechol is well known in biological systems often as a reactive center of electron transfer in the structure of many natural compounds and biologically reactive molecules capable of exhibiting both anti- and pro-oxidant behavior [2]. Catechol has a great importance in both biological and environmental analysis because of its excellent electrochemical activity and it can be used for the characterization of different analytical methods. It is used in a variety of applications including photography, dying, agrochemicals, rubber, plastic production antiseptic, dyestuffs, electroplating, specialty inks, antioxidants and light stabilizers, in organic synthesis, pharmaceutical industry, antibiotics, and flavor compounds such as vanillin, precursors are essential; they are the starting material for the production of the desired compound [1, 3-6]. The electrochemical oxidation of catechol in aqueous solutions shows that catechol undergoes 1, 4-Michael addition reactions according to the so-called EC mechanism with the consumption of 2 electrons per molecule of catechol, and a conversion to catechol derivatives [7]. The purpose of the investigation was to carry out a quantitative study of the electro-oxidation of catechol in aqueous solution.

EXPERIMENTAL PARTS
CHEMICALS

The chemicals used were catechol (BDH Poole, England), HCl (Riedel-deHaen, Germany), NaOH (BDH Poole, England), sodium dihydrogen phosphate ($NaH_2PO_4.2H_2O$, Riedel-deHaen, Germany) and disodium hydrogen phosphate ($Na_2HPO_4.2H_2O$, Techno Pharmchem, India).

INSTRUMENTATION

The cyclic voltammetry apparatus used was BAS 100A electrochemical analyzer [Bio-analytical systems (BAS), USA], coupled to a Dell computer (Pentium 4). A JENWAY 3510 pH Meter (Barloworld Scientific Ltd, Dun mow, Essex, U.K.) and Electronic Balance (Model: LA 204) were used. The three electrodes used in the

voltammetry experiments were the glassy carbon electrode (3mm diameter) as working electrode, platinum wire as an auxiliary electrode and Ag/AgCl (3MKCl) as reference electrode, all from BAS. The working electrode (glassy carbon electrode) (GCE) was polished in each set of experiments with aluminum oxide powder (0.3μm) on a polishing cloth and followed by distilled water and were carried out at room temperature.

ELECTROCHEMICAL DIGITAL SIMULATION

Digital simulation is a useful method in evaluation of complicated electrode reactions and used to visualize and verify electrochemical mechanisms and also used to determine the normalized current-overvoltage curves for reversible as well as for quasi-reversible reactions [8-9]. By the development of simulation software, cyclic voltammetry has become a very powerful technique [10]. The experimental parameters entered for digital simulation consisted of the following; E_{start} = −0.2 V, E_{switch} = 0.8 V and T = 298 K. The concentration of catechol was 1mM. The transfer coefficient (α) was assumed to be 0.5. The heterogeneous rate constant (k^o) for the electrochemical oxidation of catechol to o-benzoquinone was estimated based on an E- mechanism of the simulation [11]. The best simulation fits were obtained for the E_rC_i mechanism.

RESULT AND DISCUSSION
CYCLIC VOLTAMMETRY OF CATECHOL

The number of electrons and protons involved in the oxidation of catechol can be determined from the separation peak potentials and from plots of $E^{o'}$ vs pH and E_{pa} vs pH respectively. The formal potential ($E^{o'}$), which is approximated by the midpoint potential (E_{mid}) between the anodic and cathodic peaks is given by;

$$E^{o\prime} = E^o_{pH_o} - \left(\frac{2.303mRT}{nF}\right)pH$$

Where, E^o_{pH0} is the formal potential at pH_0, and R, T, and F have their usual meanings and n and m are number of electron and proton respectively. The values of $E^{o'}$ evaluated from the midpoint potential between the anodic and cathodic peaks, (E_{mid}).

Both $E^{o'}$ and E_{pa} were shifted to negative potentials with the slope of 62 mV/pH with the correlation function R (R = -0.999601) and 63.3 mV/pH with the correlation function R (R = -0.999004) respectively. In all cases, the slopes are in good agreement with the theoretical slope ($2.303mRT/nF$) of 59 mV/pH with $m \approx 2$ and n = 2, where n and m are number of electron and proton respectively [12].

EFFECT OF pH

On increasing the pH of supporting electrolyte both the anodic and cathodic peak potentials shifted towards more negative potential [13] as shown in the Figure 1. This is expected because of the participation of proton in the oxidation reactions and these shifts of potential indicate that the electron transfer process from catechol to o-benzoquinone occurs at glassy carbon electrode easily at higher pH than at lower pH. The electrooxidation of catechol was found to be pH dependent. In acidic and neutral media catechol showed a well-developed quasi-reversible wave as indicated in Figure 1 below. Under these conditions, a peak current ratio $|i_{pc}/i_{pa}|$ of nearly unity can be considered as a criterion for the stability of o-benzoquinone produced at the surface of the electrode under the experimental conditions. In basic solutions, the peak current ratio is less than unity and decreases with increasing pH. These shifts can be associated to the coupling of the anionic or dianionic forms of catechol with o-benzoquinones (dimerization reactions) [2].
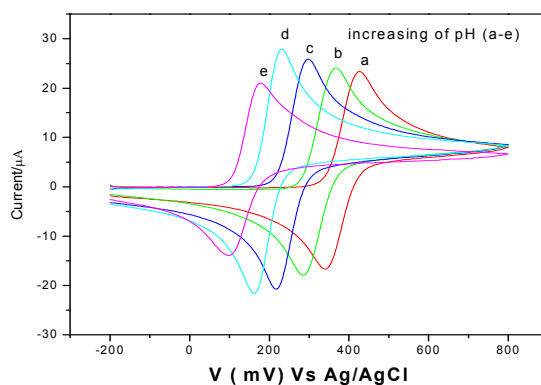

Figure 1: Typical cyclic voltammograms for 1 mM catechol at various pHs a) 4, b) 5, c) 6, d) 7 and e) 8 at a scan rate of 50 mV/s.

Figure 2 below shows that the anodic peak current increases as the pH increases and reaches the highest peak at (pH = 7) and then decreases. The highest anodic peak current (at pH = 7) was taken as the optimum pH
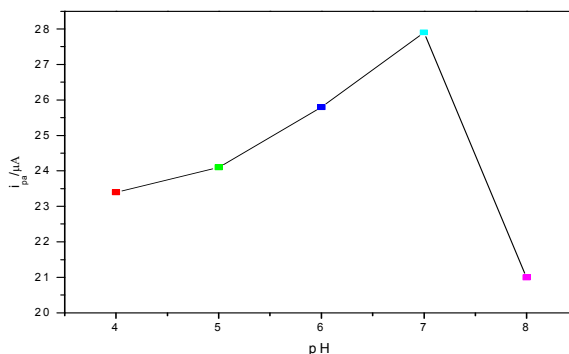
for the electrooxidation of catechol.

Figure 2: i_{pa} as a function of pH for 1 mM catechol at a scan rate of 50 mV/s.

EFFECT OF SCAN RATE

As shown in Figure 3, when the scan rate increases, both the anodic and cathodic peaks increase; the anodic peak shifts towards less positive potentials while the cathodic peak shifts towards more positive potentials. Overall, the current ratios are almost unity and the peak separation between the anodic and cathodic peak potential at scan rate of 50 mV/s is 69 mV/n which is greater than 59 mV/n and it is one of the indications that the system is a quasi-reversible process. A peak current ratio $|i_{pc}/i_{pa}|$ of nearly unity, particularly during the repetitive recycling of potential, can be considered as criteria for the stability of o-benzoquinone produced at the surface of electrode under the experimental conditions. It means that any hydroxylation or dimerization reactions are very slow which was observed in the time-scale of cyclic voltammetry [2, 14, 15].
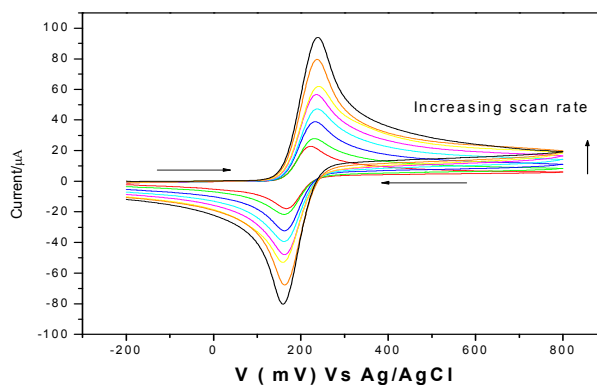

Figure 3: Cyclic voltammograms of 1mM catechol at scan rates of; 30, 50,100,150, 200,250, 300 and 400mV/s at phosphate buffer solution of pH=7.

DETERMINATION OF HETEROGENEOUS RATE CONSTANT (k^o) AT VARIOUS SCAN RATES
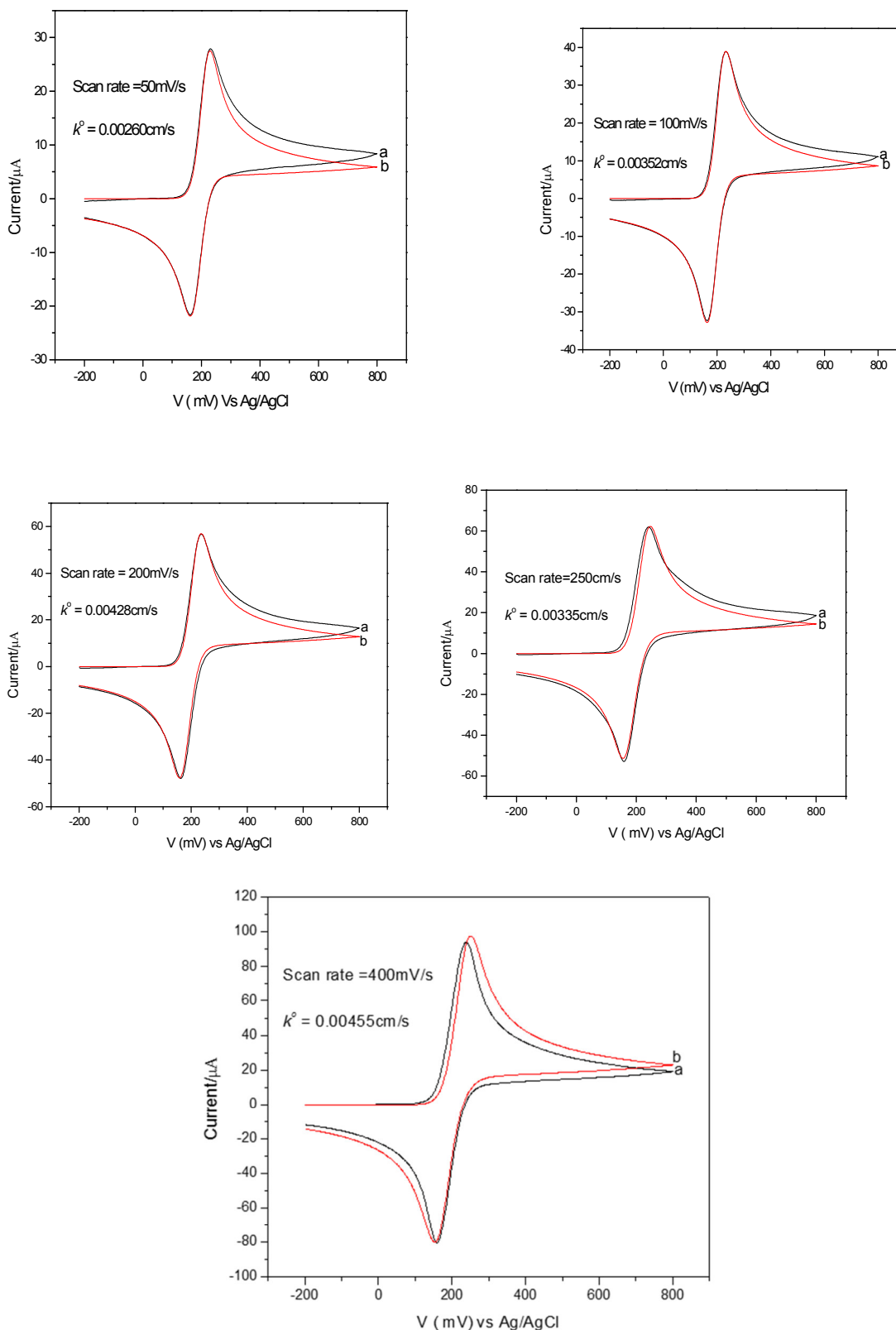

Figure 4: Typical cyclic voltammograms of 1mM catechol at various scan rates at pHs 7. (a) Experimental; (b) simulated.

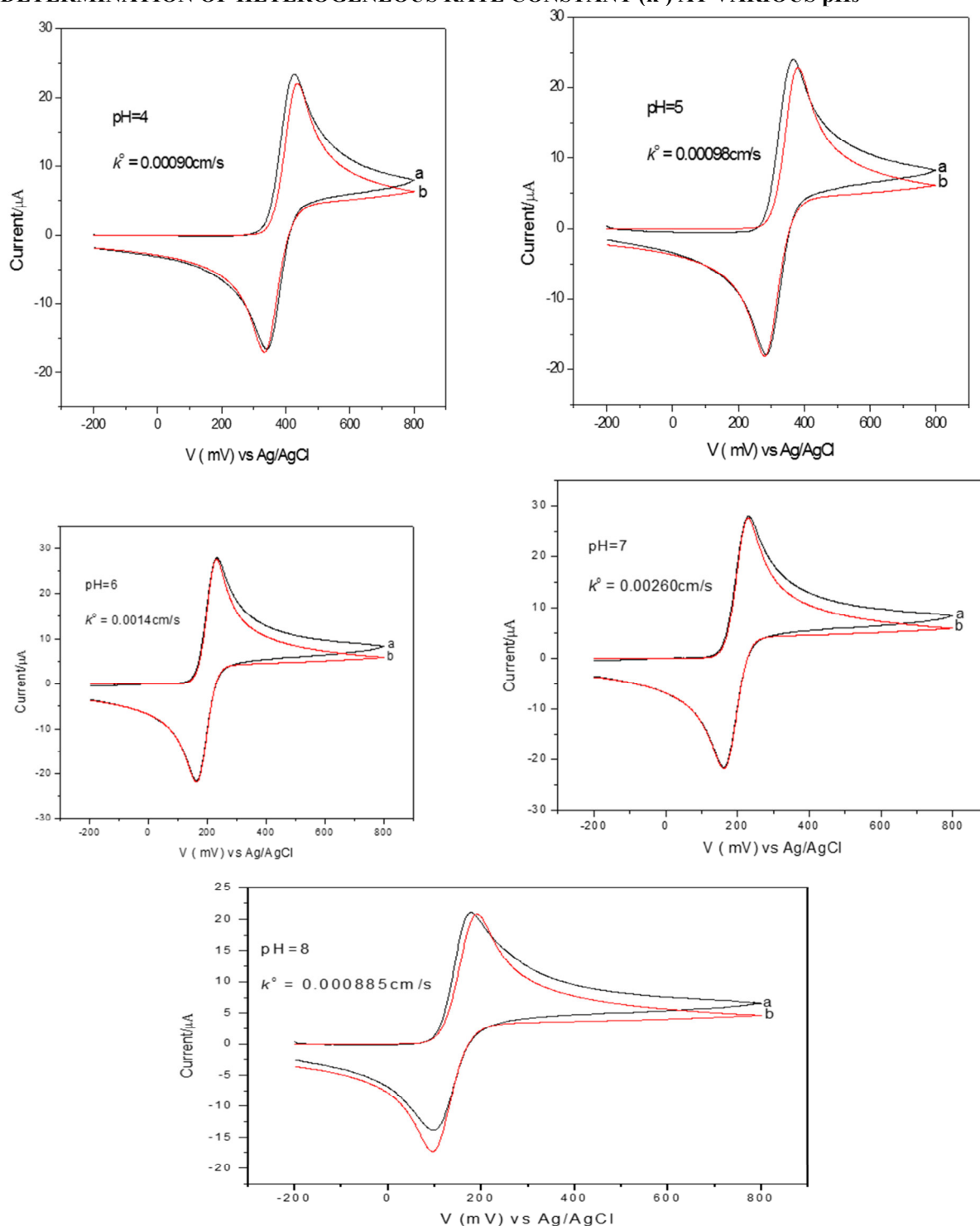## DETERMINATION OF HETEROGENEOUS RATE CONSTANT (k⁰) AT VARIOUS pHs

Figure 5: Typical cyclic voltammograms of 1mM catechol at various pHs at a scan rate of 50 mV/s. (a) experimental; (b) simulated.
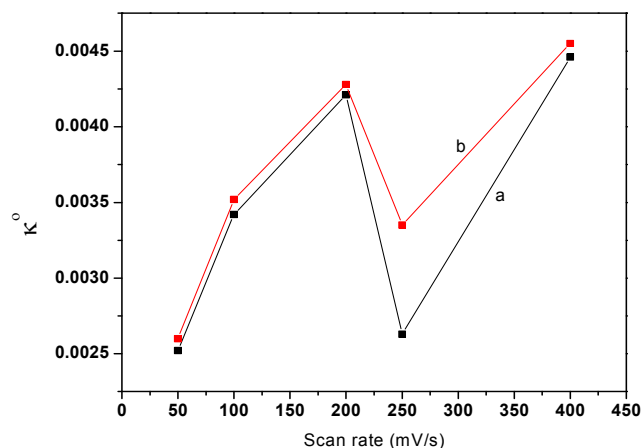
Figure 6: Variation of experimental (a) and simulated (b) heterogeneous rate constant (k^o) as the function scan rate at pH 7.
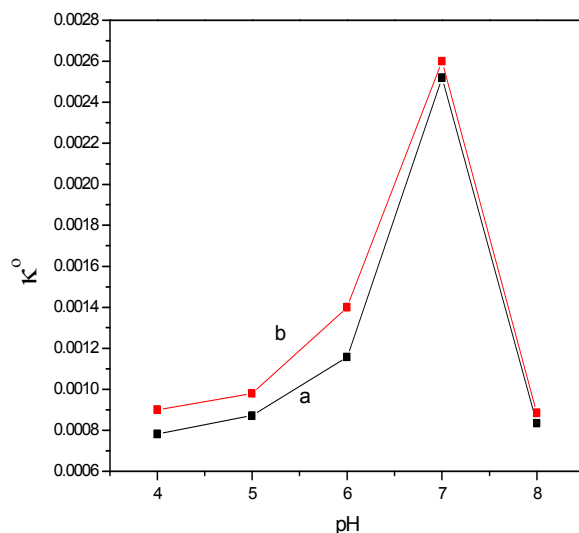

Figure 7: Variation of experimental (a) and simulated (b) heterogeneous rate constant (k^o) as the function pH at 50 mV/s.

As can be seen from the data in Figure 6 and 7, there is a good correlation between the heterogeneous rate constant (k^o) calculated using the Nicholson and Shain method and the heterogeneous rate constant (k^o) obtained using digital simulation at various scan rates and pHs.

CONCLUSIONS

The results of the study show that catechol is oxidized in aqueous phosphate buffer solution to a very reactive intermediate *o*-benzoquinone. The oxidation of catechol in the absence of nucleophile showed properties of a quasi-reversible two-electron two-proton process. The kinetic parameters for the electrooxidation of catechol in the absence of nucleophile at different scan rates and pHs were studied using cyclic voltammetry and electrochemical digital simulation.

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