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Digital Simulation of the Cyclic Voltammetry Study of the Catechols Electrooxidation in the Presence of some Nitrogen and Carbon Nucleophiles

Jahan-Bakhsh Raoof [1,*], *Reza Ojani* [1], *Davood Nematollahi* [2], *Abolfazl Kiani* [3]

[1] Electroanalytical Chemistry Research Laboratory, Department of Analytical Chemistry, Faculty of Chemistry, Mazandaran University, Babolsar, Iran
[2] Faculty of Chemistry, University of Bu-Ali-Sina, Hamadan, Iran
[3] Department of Chemistry, Faculty of Science, University of Isfahan, Iran
[*]E-mail: j.raoof@umz.ac.ir

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The electrochemical generation of *o*-quinone from catechol and its subsequent reaction with the some nitrogen and carbon nucleophiles have been investigated using cyclic voltammetry. The results indicate that the *o*-quinone derived form the anodic oxidation of catechol participates in Michael addition reaction with active methylene compounds to form the corresponding adducts. Digital simulation analyses based on different oxidation mechanisms have been performed for the cyclic voltammograms obtained on the surface of GC electrode. The kinetic data were extracted from cyclic voltammograms with the help of digital simulation. The homogeneous and heterogeneous rate constants were estimated by comparing the experimental cyclic voltammetric responses with the digital simulated results.

Keywords: Catechol, Digital simulation, Active methylene compounds, Anodic oxidation, Nitrogen nucleophiles

1. INTRODUCTION

Electrochemical oxidation of catechols has been studied by many authors [1-3]. Electrochemical oxidation of catechols leads to the *o*-quinone as the first oxidation product. Electrochemical study on a glassy carbon electrode using cyclic voltammetry has shown that the first oxidation step involved a number of electrons per molecule equal to two which likely correspond to the formation of *o*-quinone [4]. The widespread availability and ease of oxidation of catechols in the presence of other functionalities make these compound attractive substrates for oxidative functionalization reactions. Electrooxidation of catechols and reactions of formed *o*-quinone with nucleophiles are well known and often comprise useful synthetic processes [5-9].

In direction of investigation of electrochemical behavior of catechols in the presence of nucleophiles, [10-12] we became interested in understanding and exploiting mechanism of electrooxidation of catechol in the presence of carbon and nitrogen nucleophiles using digital simulation of cyclic voltammograms.

The present study concerns the electrochemical behavior of catechol in the presence of some active methylene and nitrogen compounds as nucleophiles in order to develop its oxidation mechanism.

2. EXPERIMENTAL PART

2.1. Regents and Material

All reagents were obtained from Fluka and used without further purification.

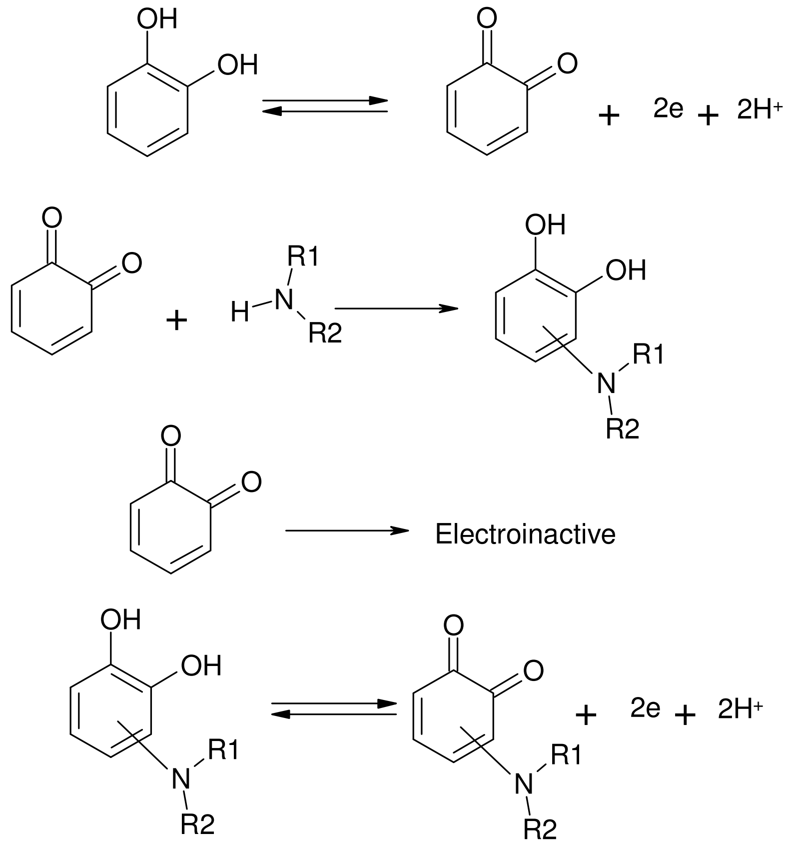
2.2. Instrumentation

The voltammetric experiments were performed using an Autolab potentiostat & galvanostat (Netherlands) coupled with a Pentium IV personal computer with a standard three electrodes configuration. Glassy carbon disk (Metrohm, diameter 1.8 mm) served as working electrode; a platinum wire electrode provided the counter electrode with an Ag│AgCl│KCl_{3M} reference electrode completing the cell assembly. The glassy carbon electrode was polished between each set of experiments with aluminum oxide powder on a polishing cloth. All experiments were conducted at 25 ±0.1 ºC using of water thermostat circulator (polystat CC1, Huber, Germany).

2.3. Digital Simulation

To verify the reaction mechanism shown in Scheme 1 for the electrochemical oxidation of catechol in the absence and presence of the nucleophiles, the cyclic voltammograms have been analyzed by a commercial digital simulation program (DigiElch) [13-15] to find the best-fit between experimental and simulated cyclic voltammograms. Several assumptions have been made to simplify the problem: (i) all the diffusion coefficients except for catechol, were kept constant as 1×10^{-5} cm^2 s^{-1}. (ii) The number of electrons transferred in all steps is two.

The simulation was carried out assuming semi-infinite diffusion and planar electrode geometry. The parameters k^o, and k were allowed to change through the fitting processes. Further refinement was accomplished by holding the best-fit parameters constant and allowing diffusion coefficient, D_O (for catechol) to vary throughout the fitting process.



Scheme 1. Proposed mechanism for electrooxidation of catechol in the presence of nitrogen nucleophiles.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltammetry of Catechol

The redox properties of a compound are readily characterized by cyclic voltammetry. Electrochemical properties of catechol were studied by cyclic voltammetry. Cyclic voltammograms of 1.0 mM catechol in aqueous solution containing phosphate buffer (pH 7.00) at various scan rate of potential along with simulation (circles) according to the E_q mechanism is shown in Fig. 1. As can be seen, there is one anodic peak (A_0) related to oxidation of catechol to *o*-quinone and one corresponding cathodic peak (C_0) related to reduction of *o*-quinone to catechol with half-wave potential, $E_{1/2}$ equal to 0.17 V vs. Ag I AgCl I KCl $_{3M}$. The peak separation potential, ΔE_p at scan rate of 50 mV s^{-1} is about 50 mV, showing a quasi-reversible behavior of a two-electron two-proton process. The simulated cyclic voltammograms based on E_q mechanism show good agreement with those obtained experimentally. The redox potentials, the standard electron transfer rate constants and the diffusion coefficients were optimized as follows:

$$E^{0'} = 0.17\,\mathrm{V}, k^{\circ} = (4 \pm 1) \times 10^{-3}, \alpha = 0.5 \text{ and } D = (4.8 \pm 0.2) \times 10^{-6}\,\mathrm{cm^2/s} \qquad (1)$$

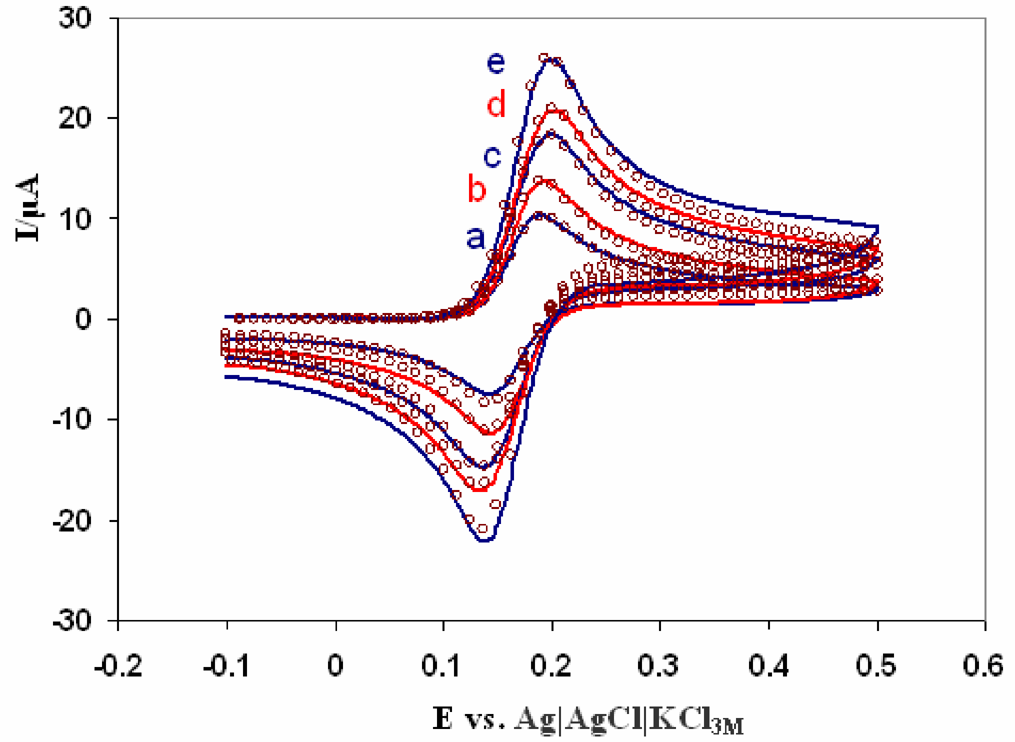


Figure 1. Experimental (line) and simulated (circles) cyclic voltammograms based on $E_qC_rC_iE_q$ mechanism of 1.0 mM catechol in phosphate buffer solution (pH 7.0) at various scan rates: (a) 50, (b) 100, (c) 150, (d) 200 and (e) 300 mV s^{-1}.

3.2. Cyclic Voltammetry of Catechol in the Presence of Nitrogen Nucleophiles

The oxidation of catechol yields *o*-quinone, which frequently undergoes nucleophilic attack. The nucleophile usually reacts by a Michael 1, 4- addition reaction to form a substituted *o*-quinone. If the substituent is such that the potential for the oxidation of product is higher, the reaction will be complete after the first oxidation-addition process. However if the constituent is such that the potential for the oxidation of product is lower, then further oxidation of the product is lower, the further oxidation and further addition may occur.

The electrochemical behavior of catechol in the presence of amines was studied using cyclic voltammetry. The typical experimental cyclic voltammograms (line) of 1.0 mM catechol in the presence of 50 mM dibutylamine at scan rate of 50 mV s^{-1} was represented in Fig. 2. Compare to cyclic voltammograms presented in Fig. 1, a new reduction peak appears at -0.14 V vs. Ag | AgCl | KCl $_{3M}$ in the presence of dibutylamine. Conversely, the reduction peak due to electrogenerated *o*-quinone species diminishes in the presence of dibutylamine. In the second scan of potential (not shown), also a new oxidation peak appears which can be attributed to the oxidation of adduct formed between the *o*-quinone and dibutylamine according to Scheme 1. The simulated cyclic voltammograms (circle) was obtained according to $E_qC_rC_iE_q$ mechanism. As is seen, a passable result was obtained in the curve fitting. However, in the simulations based on an $E_qC_iE_q$, the cathodic peak could not be well fitted to the simulation curve. For obtaining better results in curve fitting, we then employed more complex mechanisms in which the electrogenerated o-quinone is assumed to undergo a self-chemical reaction beside the chemical reaction with dibutylamine. Therefore, a much better fitting was achieved for the whole experimental data, even around the cathodic peak. In these mechanisms, protonation/ deprotonation processes are not separately described, being treated together with electron-transfer or chemical reactions in single steps. This is because such processes are generally too fast to be limiting processes in protic media. Considering the results presented, the electrogenerated *o*-quinone undergoes two reaction pathways: converting to an electro-inactive compound and electrophilic reaction with dibutylamine through a Michael 1, 4- addition reaction. A result, the curve fitting with the $E_qC_rC_iE_q$ mechanism at various scan rates is shown in Fig. 3. Table 1 shows the fitting parameters obtained with the $E_qC_rC_iE_q$ mechanism for different nitrogen nucleophiles. As is seen in Table 1, $k_{f,2}$, was enlarged in the order of dibutylamine, pipiridne, and diethylamine, showing that the chemical reaction with diethylamine occurs more readily.

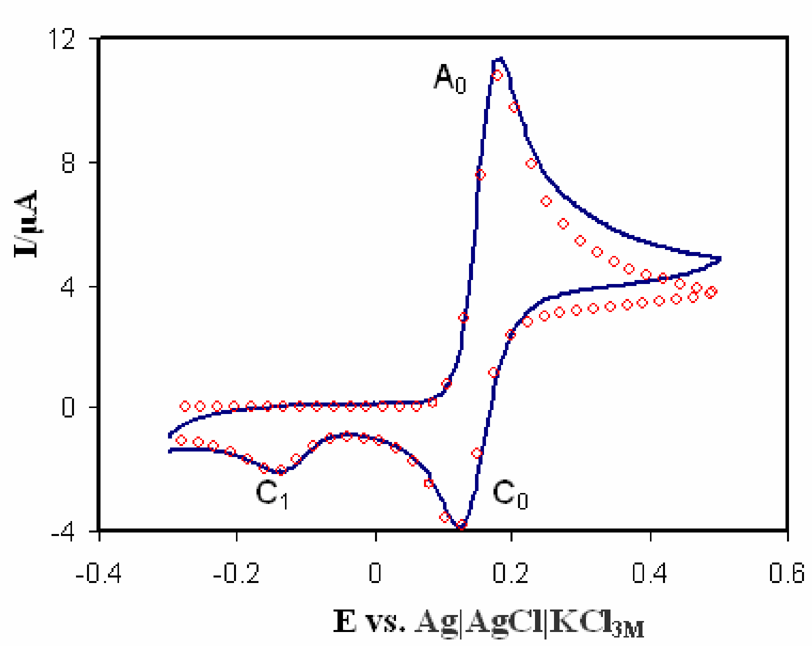


Figure 2. Experimental (line) and simulated (circles) cyclic voltammograms of 1.0 mM catechol based on $E_qC_rC_iE_q$ mechanisem in the presence of 50.0 mM dibutylamine in phosphate buffer solution (pH 7.0) at scan rate of 50 mV s^{-1}.

The above digital simulation analysis showed that the $E_qC_iE_qC_i$ mechanism gave the best fitting performance. Thus, it has been suggested that the two electron oxidation of catechol resulted in electrogenerated o-quinone which undergo two irreversible chemical reactions. Nevertheless, this does not deny possibilities of other reaction mechanisms which might involve more complicated chemical reactions such as dimmer formation [12], hydroxylation reaction [16] and so on. According to the data obtained from the fitting procedures, the rate constant for 1, 4-Michael addition reaction between nucleophiles and electrogenerated *o*-quinone is faster than the self-chemical reaction of electrogenerated *o*-quinone.

Because proton participates in redox step, the apparent redox potential of catechol, which is approximated by the average of anodic and cathodic peak potentials, should be dependent on the pH of solution. Also the nucleophilicity of amines and active methylene compounds depend on solution pH value, which makes a buffered solution necessary for carrying out experiments.

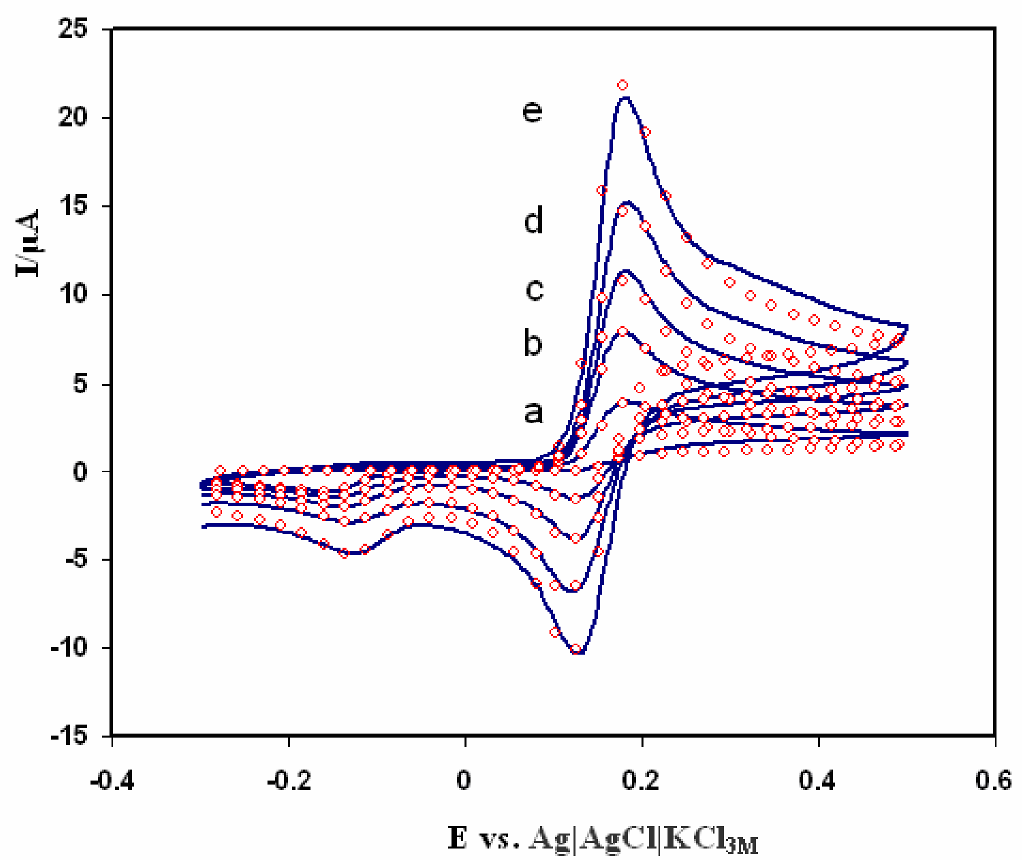


Figure 3. Experimental (line) and simulated (circles) cyclic voltammograms besed on $E_qC_rC_iE_q$ mechanism of 1.0 mM catechol in the presence of 50.0 mM dibutylamine in phosphate buffer solution (pH 7.0) at various scan rates: (a) 5, (b) 25, (c) 50, (d) 100 and (e) 200 mV s^{-1}.

Table 1. Extracted kinetics data from simulated cyclic voltammograms of catechol in the presence of nitrogen nucleophiles.

Mechanism	$k_{f,2}$ (s^{-1})	$k_{f,1}$ ($M^{-1}s^{-1}$)	k_2^o (cm s^{-1})	k_1^o (cm s^{-1})	**Nucleophile**
$E_qC_qC_iE_q$	$(5\pm1)\times10^{-3}$	(6.5 ± 0.4)	$(5\pm1)\times10^{-3}$	$(9\pm1)\times10^{-3}$	**Diethylamine**
$E_qC_qC_iE_q$	$(3.0\pm0.1)\times10^{-2}$	(4.1 ± 0.3)	$(2\pm1)\times10^{-3}$	$(9\pm2)\times10^{-3}$	**Dibutylamine**
$E_qC_qC_iE_q$	$(1.0\pm0.1)\times10^{-2}$	(5.3 ± 0.3)	$(1\pm0.1)\times10^{-2}$	$(8\pm1)\times10^{-3}$	**Pipiridine**

3.3. Electrochemical Behavior of Catechol in the Presence AMCS

We studied the electrochemical behavior of catechol in the presence of some active methylene compounds, such as diethyl malonate (DM), ethyl acetoacetate (EA) and diethyl bromomalonate (DBM), as carbon nucleophiles, by cyclic voltammetry. Because of low solubility of AMCs in the aqueous solution, we failed to obtain good results. We then changed to the medium aqueous/ Acetonitrile 9:1 (V/V). Cyclic voltammetry at various scan rates used to observe the voltammetric features of aqueous/acetonitrile (9:1 V/V solution containing pure catechol (1.0 mM, pH 7.00) and catechol in the presence of DM, EA or DBM. The typical experimental cyclic voltammograms which represent the electrochemical behavior of 1.0 mM catechol in the presence of 20.0 mM of DM recorded at various scan rates are shown in Figure 4 (line).As can be seen, the simulated voltammograms (circles) using the $E_qC_rE_qC_i$ mechanism (scheme 2) fit with the experimental voltammogram very well. In the Fig. 5, the digital simulation was performed assuming a simple reaction mechanism, i.e., a quasi-reversible electron transfer followed by a first order irreversible chemical reaction. However, the cathodic peak (C_1) could not be well fitted to the simulation curve, which usually showed a cathodic peak. For obtaining better results in curve fitting, we then employed more complex mechanisms in which an electron-transfer reaction is assumed to occur following chemical reaction ($E_qC_rE_q$). However no much better fitting was achieved for around the cathodic

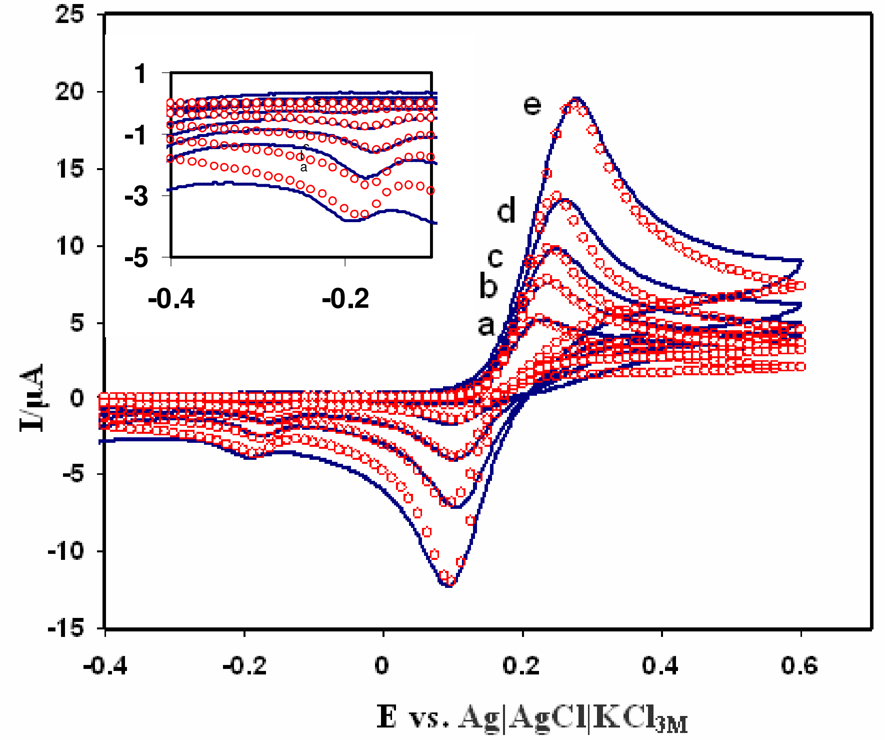


Figure 4. Experimental (line) and simulated (circles) cyclic voltammograms based on $E_qC_iE_qC_i$ mechanism of 1.0 mM catechol in Phosphate buffer + acetonitrile (10%, v/v) mixed solvent containing 20.0 mM of DBM at various scan rates: (a) 10, (b) 25, (c) 75, (d) 100 and (e) 200 mV s^{-1}. Inset: the expanded range of cyclic voltammograms.

peak, with always a larger cathodic peak current in simulation results compare to experimental ones. To obtain better results some instability in catechol-DM adducts was assumed and the digital simulation was performed considering a mechanism like EqCiEqCi. These results show that this mechanism is more suited for the electrochemical oxidation of catechol in the presence of DM. Table 2 shows the fitting parameters for the $E_qC_iE_qC_i$ mechanism.

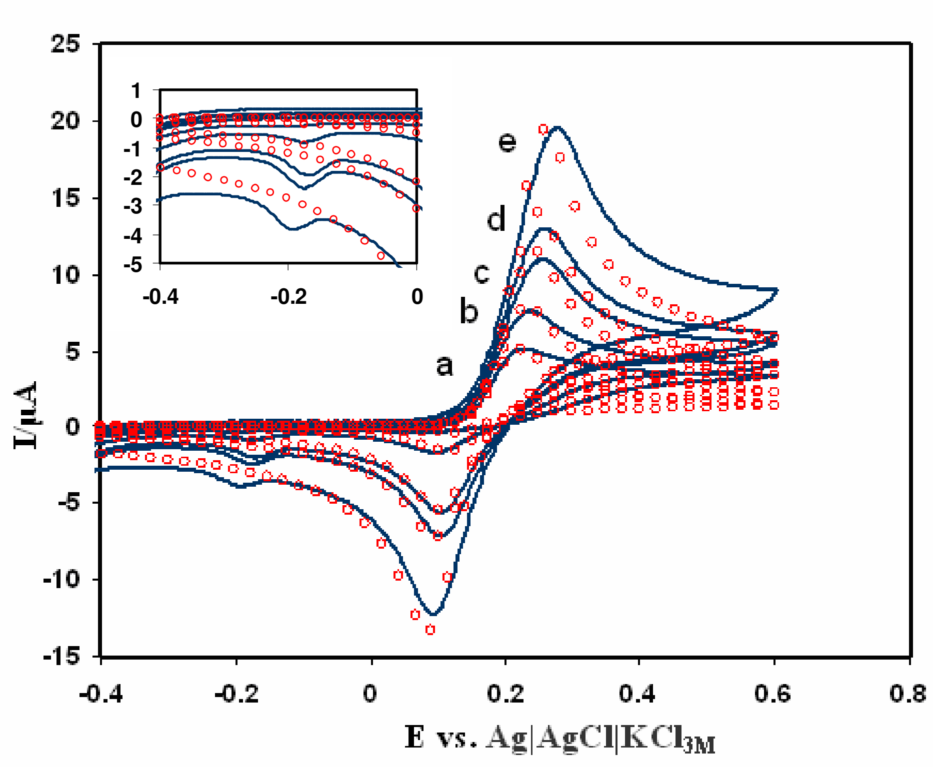
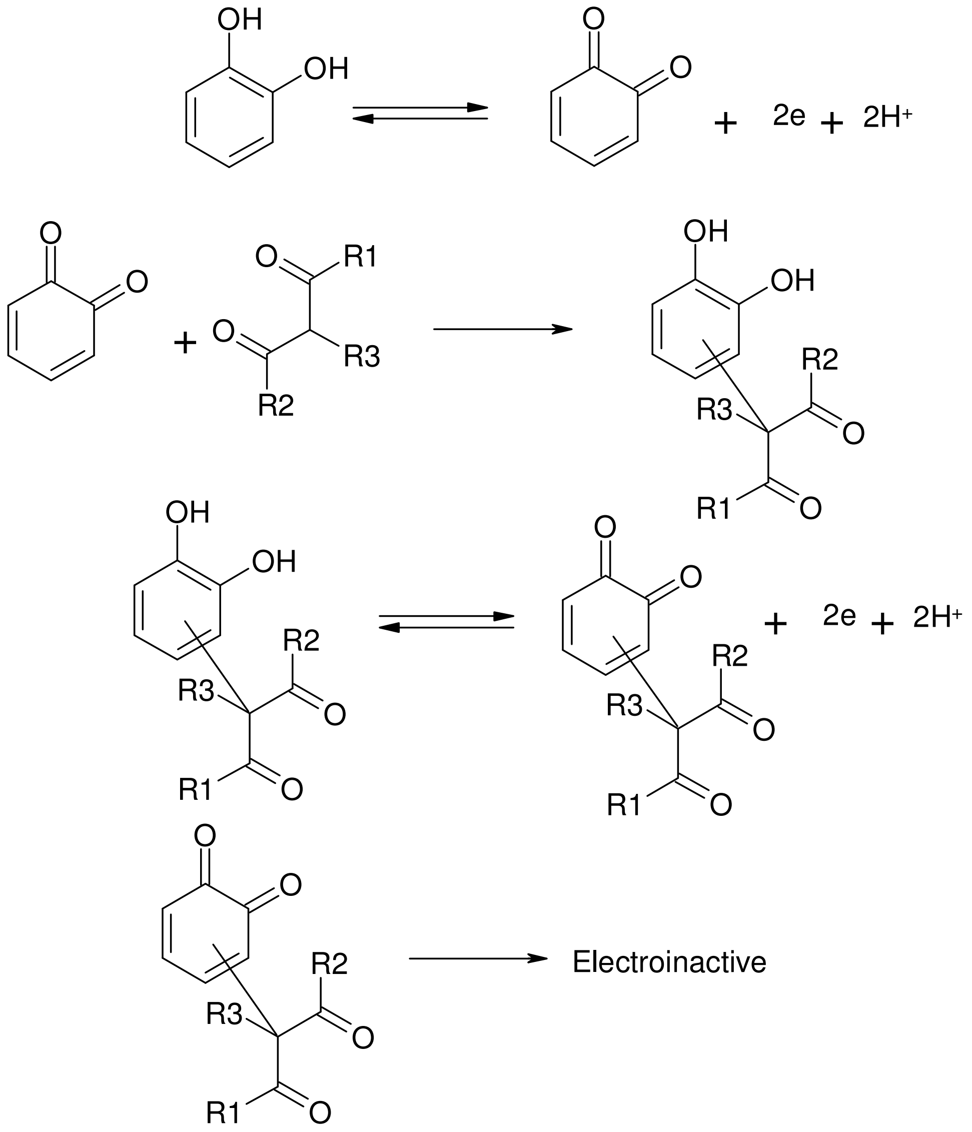


Figure 5. Experimental (line) and simulated (E_qC_i mechanism, circles) cyclic voltammograms of 1.0 mM catechol in Phosphate buffer + acetonitrile (10%, v/v) mixed solvent containing 20.0 mM of DBM at various scan rates: (a) 10, (b) 25, (c) 75, (d) 100 and (e) 200 mV s^{-1}. Inset: the expanded range of cyclic voltammograms.

Table 2. Extracted kinetics data from simulated cyclic voltammograms of catechol in the presence of carbon nucleophiles.

Mechanism	$k_{f,2}$ **(s^{-1})**	$k_{f,1}$**($M^{-1}s^{-1}$)**	k^{o}_{2} **(cm s^{-1})**	k^{o}_{1} **(cm s^{-1})**	**nucleophile**
$\mathbf{E_qC_rE_qC_i}$	$(2.2\pm0.3)\times10^{-}$	(18 ± 1)	$(1\pm0.1)\times10^{-1}$	$(7\pm1)\times10^{-4}$	**DM**
$\mathbf{E_qC_rE_qC_i}$	$(22\pm2)\times10^{-1}$	(211 ± 3)	$(1\pm0.1)\times10^{-1}$	$(7\pm1)\times10^{-4}$	**EA**
$\mathbf{E_qC_rE_qC_i}$	$(1.70.1)\times10^{-2}$	(91 ± 2)	$(3\pm0.1)\times10^{-1}$	$(1\pm0.1)\times10^{-}$	**DBM**



Scheme 2. Proposed mechanism for electrooxidation of catechol in the presence of carbon nucleophiles

4. CONCLUSIONS

The electrochemical behavior of catechol in the presence of some carbon and nitrogen nucleophiles was investigated using cyclic voltammetry. The anodic oxidation of catechol results in formation of *o*-quinone, which was attacked by carbon and nitrogen nucleophiles. The digital simulation allowed us to determine the rate constants for reaction of nucleophiles with electrogenerated o-quinone. The reactions process can be donated $E_qC_rC_iE_q$ and $E_qC_rE_qC_i$ mechanisms in the case of nitrogen and carbon nucleophiles, respectively.

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