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Electrochemical Oxidation of Catechol in the Presence of Dimethyl Chloromalonate and its Digital Simulation

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Electrochemistry of catechol has been studied in the presence of dimethyl chloromalonate as a nucleophile in the aqueous solution using cyclic voltammetry and square wave voltammetry methods. The results indicate that the *o*-quinone derived from catechol participates in Michael addition reaction with dimethyl chloromalonate to form the corresponding adduct. Interestingly, the results provide linear dependence between cathodic peak current and concentration of dimethyl chloromalonate in the ranges of 5×10^{-6} - 4×10^{-4} M and 4×10^{-4} - 1.2×10^{-3} M with different slopes. Also, the cyclic voltammograms digitally simulated based on ECE mechanism and the following chemical reaction rate constant was estimated.

Key Words: Electrochemistry, Michael addition, Dimethyl chloromalonate, Catechol, Cyclic voltammetry, Square wave voltammetry.

INTRODUCTION

Quinones are the widespread compounds found in living organism performing a variety of biochemical and physiological functions. They contribute as the components of biological electron transfer chains located in the membranes of mitochondria, bacteria and chloroplasts[1]. In addition, many drugs, such as doxorubicin, daunorubicin and mitomycin C in cancer chemotherapy contain quinones[2] and some others posses antibacterial and antifungal activities[3], whereas various other quinones have found uses in industry[4].

Extensive works have already been carried out on the quinones and the electrochemical characteristics of simple and complicated quinones and their reduced forms in water or other solvents using various electrodes and supporting electrolytes have been studied[5-13].

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Previously, the electrochemical oxidation of catechols in the presence of various nucleophiles such as: 4-hydroxycoumarin, 2-thiobarbituric acid, 4-hydroxy-6-methyl-2-pyrone, 3-hydroxycoumarin, 2-thiouracil, 4,5,7-trihydroxtycoumarin, 4,7-dihydroxycounarin, 4-hydroxy-6-methyl-α-pyrone and sulfunic acid were studied[14-19]. Recently, the electrochemical behaviour of catechols in the presence of some nucleophiles such as aliphatic and aromatic amines, alcohols and 1,3-indandione[20-23] were investigated. To the best of our knowledge only few papers have been published on the electrochemical oxidation of catechol in the presence of 1,3-diketones[23-26] however, there is no any report using malonates as a nucleophile in the catechol oxidation reaction medium.

Because of importance of malonates as well-known carbon source in carbon-carbon bond formation reactions, in this work, the anodic oxidation of catechol in the presence of dimethyl chloromalonate (DMCM) in aqueous solution using cyclic voltammetry and square wave voltammetry methods is investigated.

EXPERIMENTAL

All reagents were obtained from Fluka and used without further purification. All experiments were carried out in 0.1 M phosphate buffer solution.

The voltammetric experiments were performed by an Autolab potentiostat and galvanonstat (Netherlands) coupled with a Pentium IV personal computer with a standard three electrode configuration. Glassy carbon disk (Azar electrode, Iran, diameter 2 mm) served as working electrode; a platinum wire electrode provided the counter electrode with an Ag|AgCl|KCl 3 M 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. The solutions were deoxyegenated by the bubbling nitrogen gas with purity of 99.99 %. All experiments were conducted a 298 ± 0.1 K using water thermostat circulator (polystat CC1, Hubber, Germany).

RESULTS AND DISCUSSION

The oxidation of catechol yields first the corresponding *o*-benzoquinone, which frequently undergo nucleophilic attack. The nucleophile usually reacts by a Michael (1,4-addition) reaction to from a substituted *o*-benzoquinone. 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 substituent is such that the potential for the oxidation of product is lower, the further oxidation-addition may occur. First cycle of cyclic voltammograms of 1 mM catechol in the presence of 2 mM DMCM in different pHs were compared in Fig. 1. As can be seen, in

acidic pH (*e.g.* pH = 3), because of that DMCM exists in protonated form, so has no nucleophilic characteristics and reverse peak (C_0, cathodic peak) related to reduction of *o*-benzoquinone is observed. On the other hand, in more basic solution (*e.g.* pH = 11) electrochemical behaviour of catechol become irreversible and its hydroxylation may occur. Thus, pH range of 7-10 in which an appearance of a new cathodic peak (C_1) is along with disappearance of C_0 cathodic peak, is optimum range for study of the reaction between of *o*-quinone derived from catechol oxidation and DMCM.

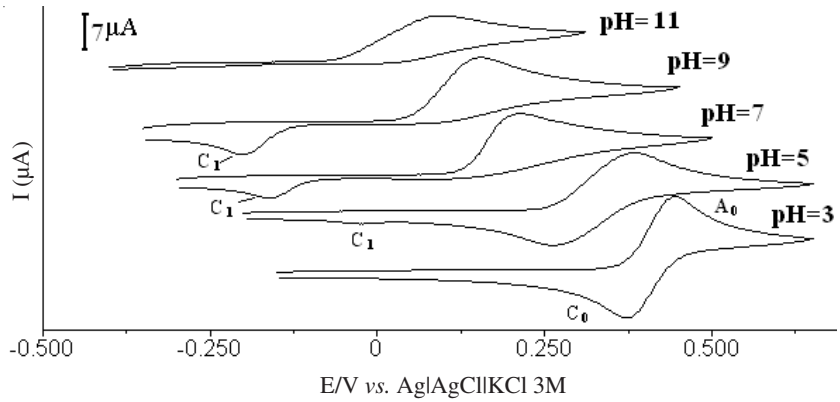


Fig. 1. Cyclic voltammograms of 1 mM catechol in the presence of 2 mM DMCM, at glassy carbon electrode, in buffered solutions with various pH values. Scan rate of potential is 50 mV s^{-1} and phosphate buffer concentration is 0.1 M

The cyclic voltammograms of catechol in the absence and presence of DMCM at scan rate of 50 mV s^{-1} in pH = 9 are shown in Fig. 2. As shown in Fig. 2a, DMCM has no electrochemical behaviour in the potential range of -0.350 V to +1.25 V *vs.* Ag|AgCl|KCl 3 M, thus, it can only act as a nucleophile in this wide potential range. For catechol, a quasi-reversible behaviour involving the anodic and cathodic peak potentials are observed at +0.146 V and +0.074 V *vs.* Ag|AgCl|KCl 3 M, respectively (Fig. 2c). It is well known that the anodic oxidation of catechols is characterized by an overall two-electron and two-proton transfer process[27], the forward peak A_0 is related to oxidation of catechol to *o*-benzoquinone and reverse peak C_0 was related to reduction of formed *o*-benzoquinone to the catechol. Upon addition of 2 mM DMCM to solution, the cathodic peak C_0 diminishes and a new cathodic peak C_1 appears in reverse scan at -0.204 V *vs.* Ag|AgCl|KCl 3 M (Fig. 2d). Also, in the second potential scan a new anodic peak appears at -0.146 V *vs.* Ag|AgCl|KCl 3 M attributed to the oxidation of formed adduct (Fig. 2e). The disappearance of C_0 peak and appearance of C_1 peak in the presence of DMCM indicates that it is due to follow up reaction of

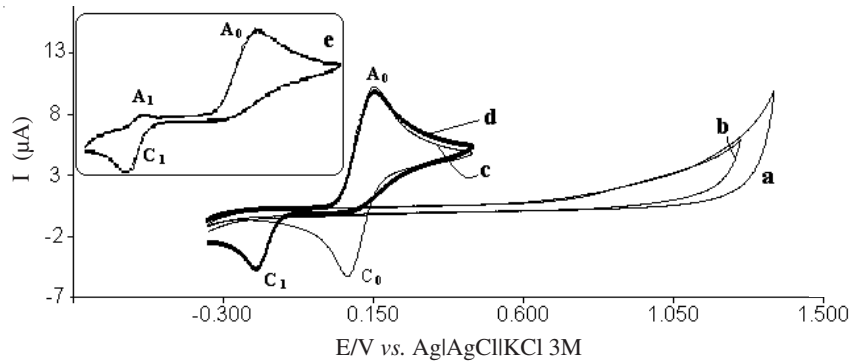
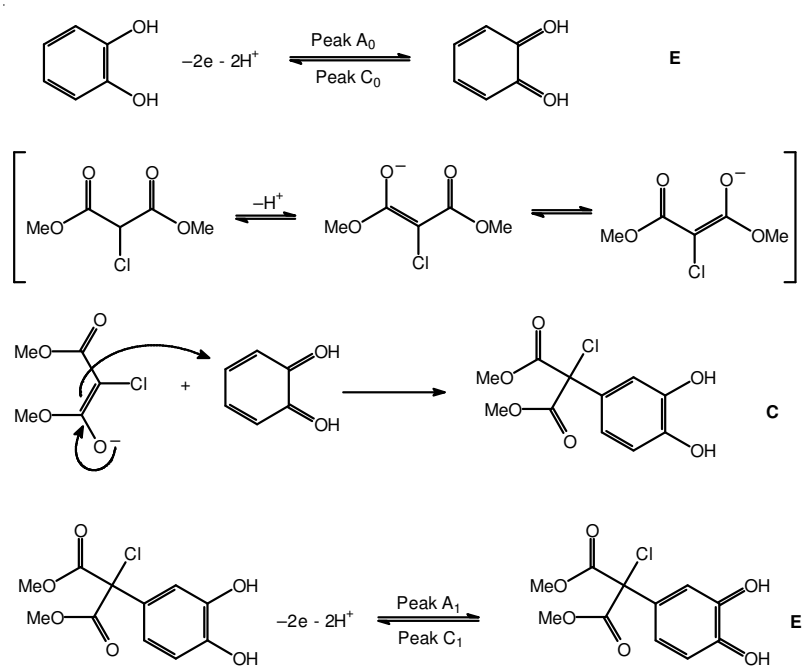


Fig. 2. Cyclic voltammograms of 1 mM catechol in the absence c) and the presence of 2 mM DMCM d) in 0.1 M phosphate buffer with pH 9 at the scan rate of 50 mV s^{-1}. e) Shows the second cycle of cyclic voltammograms of 1 mM catechol in the presence of 2 mM DMCM. Cyclic voltammograms of a) and b) represent the electrochemical behaviour of buffer and 2 mM DMCM at the surface of GC electrode, respectively

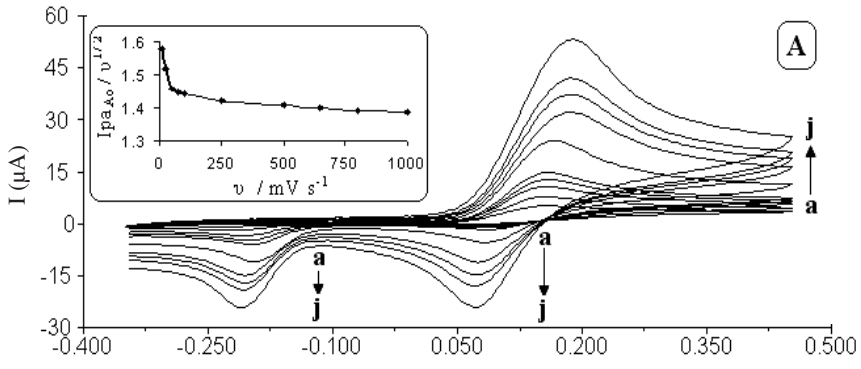
o-benzoquinone with DMCM. This observation can be explained by considering nucleophilic attack of DMCM to *o*-benzoquinone (**Scheme-I**). As stated above, electro-oxidation of catechol results in formation of *o*-benzoquinone which can be attacked by nucleophiles. The nucleophilic attack of DMCM to *o*-benzoquinone reduces the *o*-benzoquinone concentration in reaction layer, consequently the cathodic current C_0 reduces or totally disappears depending on the scale of reaction between *o*-benzoquinone and DMCM, whereas produces catechol-DMCM adduct and consequently, this produced adduct reduces and shows cathodic peak C_1. The above behaviour can be denoted by an ECE mechanism in which DMCM attacks to formed *o*-benzoquinone *via* 1,4-Michael second order addition reaction (**Scheme-I**).

The effect of scan rate was also studied on the electrochemical behaviour of catechol in the presence of DMCM. As can be seen in Fig. 3A, the cyclic voltammograms show that the cathodic peak for reduction of *o*-benzoquinone disappears in the scan rate of up to 75 mV s^{-1}. But in scan rates higher than 75 mV s^{-1}, the cathodic peak C_0 for reduction of *o*-benzoquinone begins to appear and increase. On the other hand, the value of current function $Ip(A_0) / \nu^{1/2}$ was found to be decreased with increasing the scan rate (inset of Fig. 3A). The exponential nature of the plot of current function *vs.* scan rate of potential confirms the ECE mechanism for electrode process[28]. But, the cathodic peak C_1 for reduction of catechol-DMCM adduct has different behaviour. Fig. 3B shows the plot of Ip (C_1) *vs.* scan rate. As can be seen, with increasing of scan rate, its current increases until reaches to a maximum value in scan rate of 1000 mV s^{-1} and then begins to decrease in scan rates of higher than 1000 mV s^{-1}. This complicated behaviour is the



Scheme-I

result of three different effects of scan rate on this cathodic peak. These effects can be explained as below: with increasing of scan rate, (1) concentration gradient increases, (2) time scale of reaction between catechol and DMCM decreases and therefore, concentration of formed catechol-DMCM adduct decreases and (3) probability of decomposition of catechol-DMCM adduct decreases. It is well-known that effects of (1) and (3) can increase the C_1 peak current whereas effect (2) decreases it. The value of current of C_1 peak is result of three mentioned effects of scan rate on cyclic voltammetry.



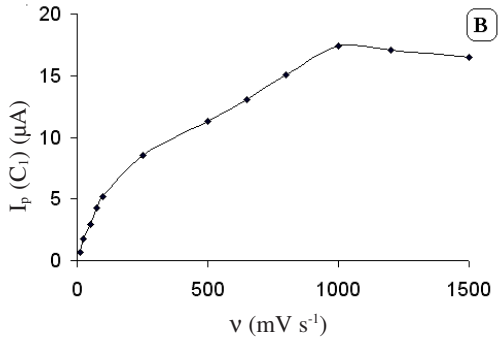


Fig. 3. Cyclic voltammograms of 1 mM catechol + 2 mM DMCM i .1 M phosphate buffer solution (pH 9) at various potential scan rates: a to j are 10, 25, 50, 75, 100, 250, 500, 650, 1000 and 1500 mV s^{-1}, respectively. Inset: Variation of peak current function for A_0 peak ($Ip(A_0)/\nu^{1/2}$) *versus* scan rate. B) Plot of $Ip(C_1)$ *versus* of potential scan rate. Data were obtained from analysis of cyclic voltammograms of Fig. 3A

All the above observations can be attributed to the reaction between the DMCM and *o*-benzoquinone produced at the surface of electrode.

Square wave voltammetry: Square wave voltammetry (SWV) was used both to obtain a peaked voltammetric response for catechol in the presence of DMCM and quantitative discussion of effect of DMCM concentration on voltammetry of catechol. In SWV, pulse amplitude of 20 mV, step potential of 5 mV and frequency of 25 Hz were used. Catechol was 0.1 mM and concentration of DMCM was changed in wide range. The results were shown in Fig. 4. As can be seen in Fig. 4A, with increasing DMCM concentration, the current of cathodic peak C_0 decreases whereas current of C_1 peak increases. This observation is in agreement with this fact that with increasing DMCM concentration, *o*-benzoquinone derived from catechol oxidation is chemically consumed in the reaction layer and consequently, catechol-DMCM adduct is produced. Decreasing the quantity of *o*-benzoquinone decreases C_0 peak current and increasing the amount of catechol-DMCM adduct enhances the C_1 peak height. Interestingly, with plotting $Ip(C_1)$ *vs.* concentration of DMCM, we found that $Ip(C_1)$ increases linearly with increasing DMCM concentration in two concentration ranges with different slopes (Fig. 4B). These concentration ranges are 5×10^{-6} - 4×10^{-4} M and 4×10^{-4} - 1.2×10^{-3} M. Limit of detection (2σ) was obtained 2.6×10^{-6} M. Thus, this finding could be considered as an electrochemically initiated reaction pathway for determination of DMCM in low concentration level, which is similar to Compton and coworker's[29,30] reports in the determination of some compounds such as amines and thiols.

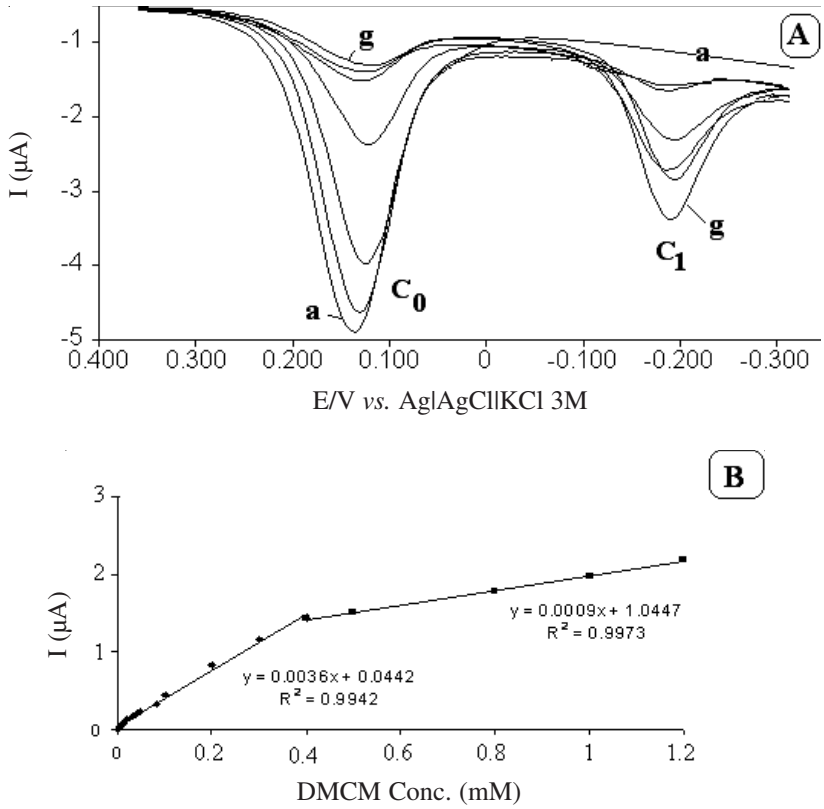
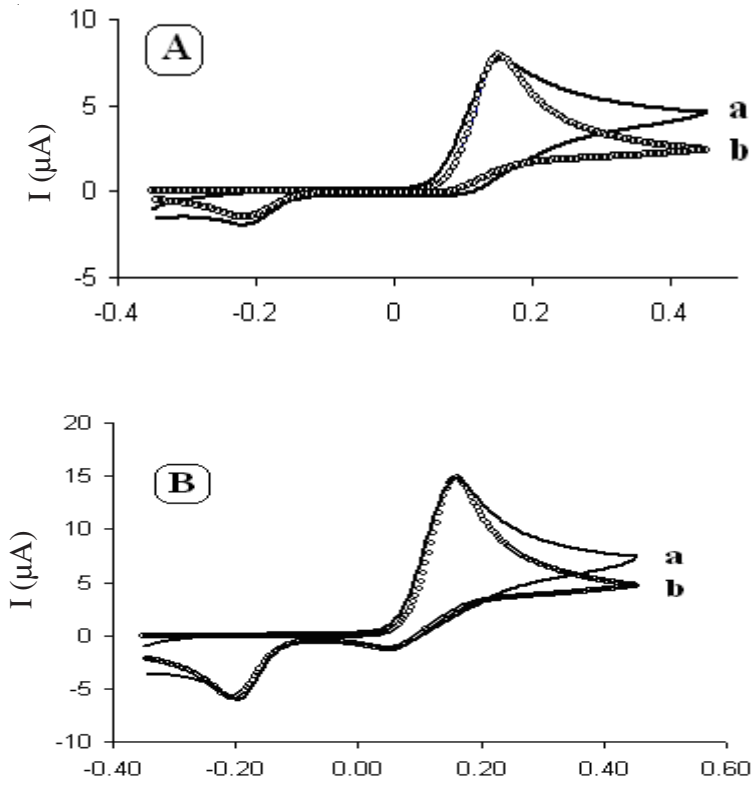


Fig. 4. (A) Square wave voltammograms of 0.1 mM of catechol in the presence of different concentration of DMCM: a) 0.0, b) 0.02, c) 0.08, d) 0.20, e) 0.50, 1.00 and g) 1.20 mM in 0.1 M phosphate buffer with pH= 9. Scan rate of potential is 50 mV s^{-1}. (B) variations of Ip(C_1) *vs.* DMCM concentration

Digital simulation: Digital simulation of cyclic voltammograms provide an opportunity both for test the ECE mechanism illustrated in **Scheme-I** and if successful, to estimate the rate of chemical reaction of *o*-benzoquinone with DMCM. To verify the reaction mechanism shown in **Scheme-I** for the electrochemical oxidation of catechol in the presence of DMCM, the cyclic voltammograms have been analyzed by digital simulation to find the best fit between experimental and simulated cyclic voltammograms.

Digital simulation carried out[31,32] using software DigiElch 3.0. The experimental results were simulated according to an ECE mechanism assuming that the concentration of DMCM (in excess) did not change as consequence of reaction, so an apparent first order rate constant for the chemical reaction between *o*-benzoquinone and DMCM was considered. The simulation was carried out assuming semi-infinite diffusion and planar geometry of

electrode and the number of electrons transferred in all steps is two. The formal potential (E°') of catechol/*o*-benzoquinone redox couple was experimentally calculated as $(E_{pc} + E_{pa})/2$ and assumed that is equal to its standard electrode potential (E°). With drawing a Tafel plot, the values of α and k° were obtained 0.55 ± 0.14 (assuming n = 2) and (5 ± 0.32) × 10^{-4} cm s^{-1}, respectively. The experimental parameters entered for digital simulation consisted of the following: Estart -0.35 V, Eswitch +0.45 V *vs.* Ag|AgCl|KCl 3 M and the surface area of electrode 3.69 × 10^{-2} cm^2. All these parameters were kept constant through out the fitting of the digitally simulated cyclic voltammograms to the experimental data. The parameters E°, k° and a are fixed and k_1 were allowed to change through the fitting process. The typical simulated cyclic voltammograms for 1 mM catechol in the presence of 2 mM DMCM in various scan rates were compared with corresponding experimental voltammograms in Fig. 5. As can be seen, the simulated voltammograms using ECE mechanism were fitted very well with the experimental voltammograms and value of (4.92 ± 0.27) × 10^2 s^{-1} was obtained for the pseudo-first order chemical reaction rate constant between the *o*-benzoquinone and DMCM.



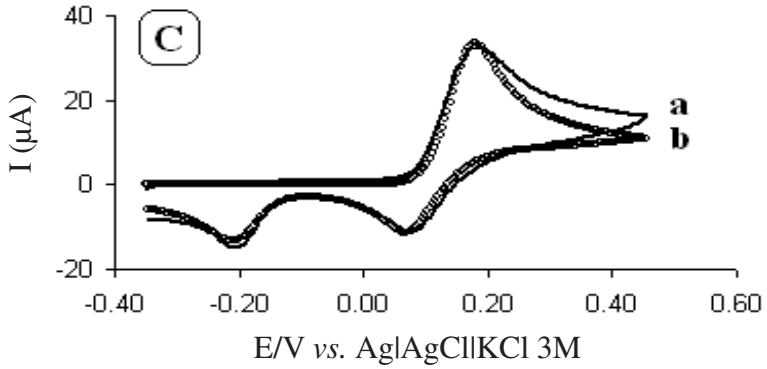


Fig. 5. Cyclic voltammograms of 1 mM catechol + 2 mM DMCM and in 0.1 M phosphate buffer solution (pH = 9) at various scan rates with corresponding simulated cyclic voltammograms. (A) 25, (B) 100 and (C) 500 mV s^{-1}, a) experimental, b) simulated

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