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Anodic Oxidation of Catechol in Presence of Some Active Methylene Compounds

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The electrochemical generation of *o*-benzoquinone from catechol and its subsequent reaction with the some active methylene compounds such as diethyl malonate, ethyl acetoacetate and diethyl bromomalonate have been investigated using cyclic voltammetry. The results indicate that the *o*-benzoquinone derived form the anodic oxidation of catechol participates in Michael addition reaction with active methylene compounds as nucleophiles to form the corresponding adducts. The rate of Michael addition reaction showed dependence on applied active methylene compounds. While, the electrochemical behaviour of catechol in the presence of diethyl bromomalonate could be described by an ECE mechanism, in the presence of diethyl malonate and ethyl acetoacetate.

Key Words: Catechol, *o*-Benzoquinone, Active methylene compounds, Anodic oxidation.

INTRODUCTION

The efficient formation of carbon-carbon bonds with good selectivity is still a synthetic challenge in organic chemistry. On this issue during the last decade, a unique reactivity and remarkable selectivity has been exhibited on removing organic solvents in carbon-carbon bond forming reactions, which is an important drive towards the development of environmentally benign chemical technologies. In addition, organic solvents are high on the lists of toxic or otherwise damaging compounds, because of the large volumes used in industry and the difficulties in containing volatile compounds. Replacement reaction media include ionic liquids[1-3], supercritical fluids[4-7], water[8-13] and solvent-free conditions[14-16].

On the other hand, there has been a growing interest in the study of reactions between electrogeneretad quinones from oxidation of poly-hydroxyphenols and some nucleophiles in recent years[17]. Among them, the catechol has acquired an increasing interest, not only to be a model molecule for

bi-phenolic compounds such as dopamine and l-dopa, but also have important physiological functions and some pharmacological activities.

It has been shown that *o*- and *p*-diphenols can be oxidized electrochemically to *o*- and *p*-quinones, respectively. The quinones formed are quite reactive and can be attacked by a variety of nucleophiles through a 1,4-Michael addition reaction[18]. This reaction has been utilized for spectrophotometric determination of some *o*-quinones[19,20].

Recently, the Michael addition reaction of diethylamine and dibutylamine with electrogenerated *o*-quinone were reported[21-23]. Michael addition reactions represent one of the most important carbon-carbon bond forming reactions in modern synthetic organic chemistry[24].

To the best of our knowledge, less common is carbon-carbon bond forming reaction arising from addition of carbon nucleophiles to oxidized catechol and such reactions have great synthetic potential. Extending our interest in research on electrochemical oxidation of catechols in the presence of nitrogen nucleophiles[21,22] and due to the broad applicability of C-C bond formation reactions in organic synthesis, the authors became interested in understanding and exploiting oxidative carbon-carbon bond forming reaction of catechols. This paper characterizes the electrochemical behaviour of catechol in the presence of some active methylene compounds (AMCs) such as diethyl malonate (DM), diethyl bromomalonate (DBM) and ethyl acetoacetate (EA) as sources of carbon nuclephiles. The structure of applied AMCs is presented in Fig. 1.

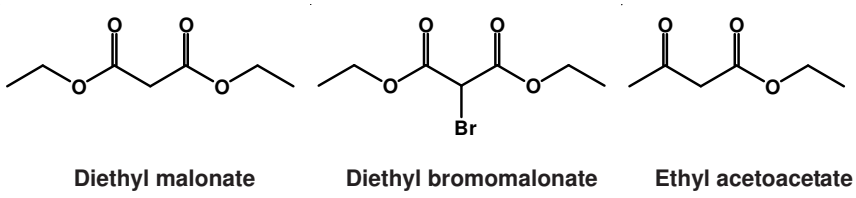


Fig. 1. Structure of different active methylene compounds (AMCs)

EXPERIMENTAL

All reagents were obtained from Fluka and used without further purification. All experiments were carried out in water (0.15 M acetate buffer)/ acetonitrile (9:1 v/v).

The voltammetric experiments were performed using a potentiostat & galvanostat (model Autolab, PGSTAT30, Eco Chemie, 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).

RESULTS AND DISCUSSION

Effect of pH: The influence of pH on the electrochemical behaviour of catechol both in the absence and presence of DBM was studied through the examining the electrode response in solution buffered between pH 3 and 8 using cyclic voltammetry method. Cyclic voltammograms of 1 M catechol in the presence of 10 mM DBM at pH 3 to 8 are compared in Fig. 2. The results show that in acidic solution (*e.g.* pH 2), catechol gave a well developed quasi-reversible wave both in the absence (is not shown) and presence of DBM (Fig. 2a). The peak separation was about 150 mV at 50 mV s^{-1} which is larger than the theoretical value of 30 mV for a two-electron, two-proton transfer reversible process. This behaviour shows that there is no any reaction between formed *o*-benzoquinone and DBM, which can be attributed to this fact that at these pHs (such as 2), the nucleophilic property of methylene groups is removed. The corresponding *o*-benzoquinone can also undergo a hydroxylation reaction in prolonged coulometric oxidation of catechol, but in acidic media this reaction is too slow to be employed in the time scale of cyclic voltammetry[25]. Because proton participates in redox step, the apparent redox potential, which is approximated by the average of anodic and cathodic peak potentials, should be dependent on the solution pH. In fact, as the pH was increased, $E_{½}$ shifted to negative potential as seen in Fig. 2. This behaviour is in agreement with that reported[25,26] by other research groups for catechol and its derivatives. In the pH ≥ 6, the formed *o*-benzoquinone undergoes a nucleophilic attack by the DBM through a 1,4-Michael addition reaction. Whereas, in the higher pH range (*e.g.* pH 9), the cyclic voltammograms of catechol show irreversible behaviour. It was thus suggested that the oxidation of catechol followed by an irreversible chemical reaction with hydroxyl ion, especially in alkaline solutions. As can be seen, increasing the pH clearly improves the following chemical reaction of *o*-benzoquinone with DBM but an operational limit (irreversibility of catechol) is reached once neutral condition prevails. Thus, pH 7 was used throughout the experiment to avoid this problem.

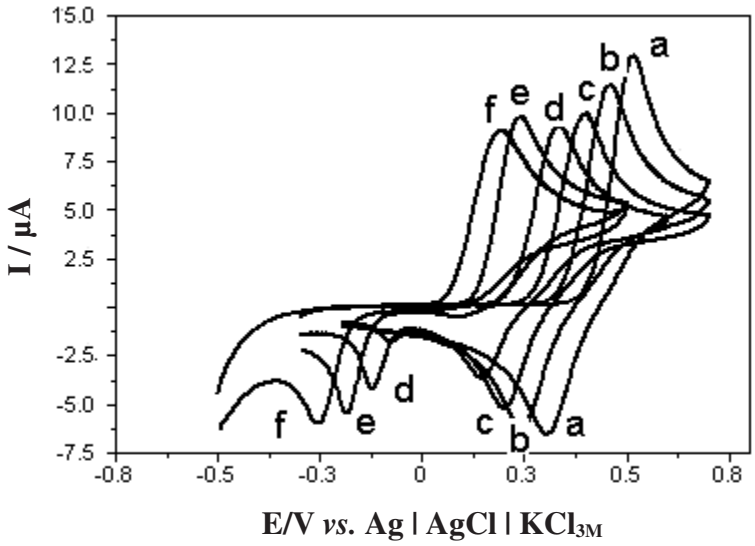
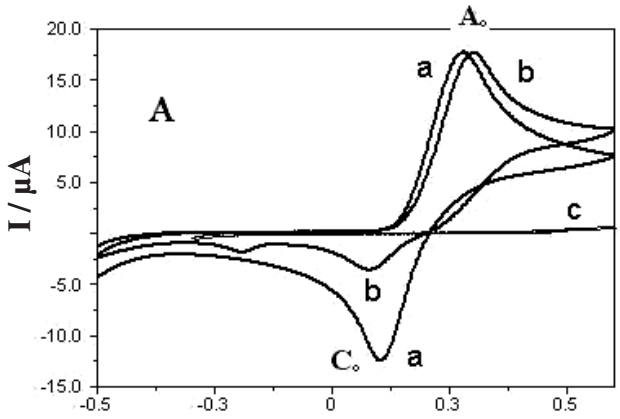


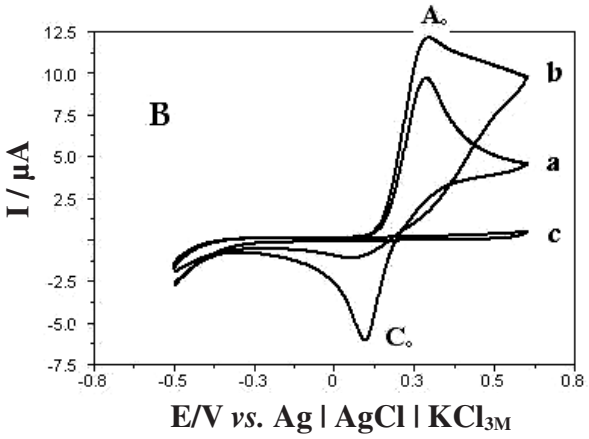
Fig. 2. Cyclic voltammograms of 1 mM catechol in the presence of 10 mM DBM at various pHs. (a) 3, (b) 4, (c) 5, (d) 6, (e) 7 and (f) 8. Scan rate of potential is 50 mV s^{-1} in water (phosphate 0.1 M)/acetonitrile (9:1)

Electrochemical behaviour of catechol in the presence AMCs: The oxidation of catechol yields first the corresponding *o*-benzoquinone, which frequently undergo nucleophilic attack. The nucleophile usually reacts by a 1,4-Michael addition reaction to form 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 and further addition may occur[17].

The electrochemical behaviour of catechol was studied in the presence of some AMCs such as DM, EA and DBM by cyclic voltammetry. Cyclic voltammetry at scan rate of 50 mV s^{-1} was used to observe the voltammetric features of both aqueous/acetonitrile (9:1 v/v) solution containing pure catechol (1 mM, pH 7) and catechol in the presence of DM, EA or DBM. The typical cyclic voltammograms which represent the electrochemical behaviour of catechol in the absence and presence of these AMCs is shown in Fig. 3. Fig. 3A (a) shows the cyclic voltammogram obtained for 2 mM catechol in the absence of DM indicating a quasi-reversible behaviour for catechol. The peak current ratio $I_p(A_0)/I_p(C_0)$ of unity indicates the formed *o*-benzoquinone at the surface of electrode is stable towards following chemical reaction at time scale of experiment. Upon addition of 65 mM DM, the cathodic peak C_0 diminishes showing that the formed *o*-benzoquinone is removed from the reaction layer in this condition (Fig. 3A (b)). It should

be noted that to see this behaviour, addition a large amount of DM is necessary and catechol shows similar voltammetric features in the absence and the presence of lower concentration of DM. The electrochemical behaviour of catechol in the presence of EA also was studied. Fig. 3B shows obtained cyclic voltammograms for 1 mM catechol in the absence (a) and presence (b) of EA. Upon addition of 20 mM EA, the cathodic peak C_0 is disappeared and anodic peak A_0 is increased, indicating an EC mechanism. As can be seen in this case, again the concentration of EA is high. As it will be indicated, presence of EA at concentration less than 10 mM makes no change in voltammetric behaviour of catechol. The increase in the oxidation peak height is attributed to solution electron transfer between *o*-benzoquninone and catechol-EA adducts or anodic oxidation of catechol-EA adduct that have arisen through the electrochemically initiated reaction. Similar behaviour was observed for oxidation of catechol in the presence of hydrogen sulfide[28].





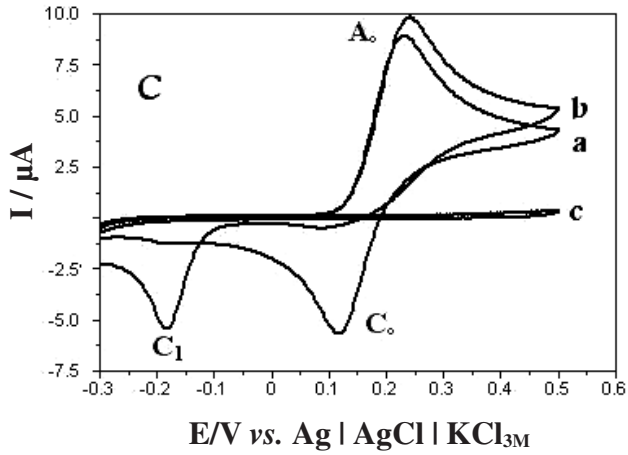


Fig. 3. Cyclic voltammograms of catechol in the absence (a) and presence (b) of active methylene compounds. (A) catechol (2 mM) and DM (65 mM), (B) catechol (1 mM) and EA (20 mM) and (C) catechol (1 mM) and DBM (10 mM) at scan rate of 50 mV s^{-1} at the surface of GC. Voltammogram (c) in all figures represents the background voltammograms. Solution condition is same as Fig. 2 at pH 7

This behaviour could be result of low acidic characteristic of C-H bond in DM and EA, which makes these AMCs poor nucleophiles. In this line, it was decided to use an AMC with more acidity characteristic such as DBM. Fig. 3C shows representative cyclic voltammograms of 1 mM catechol in the absence (a) and presence (b) of 10 mM DBM. As can be seen the cathodic peak C_0 is disappeared upon the addition of 10 mM DBM. Two significant differences are, however obvious when comparing this cyclic voltammogram with that obtained for catechol in the presence of DM and EA. First of all, less concentration of AMC is necessary to nucleophilic attack of AMC towards *o*-benzoquinone occurred in a measurable scale. Second a new cathodic peak C_1 is appeared in reverse scan of potential, indication an ECE mechanism despite of EC mechanism for anodic oxidation of DM and EA. The cyclic voltammograms c in Fig. 3, in all cases represents the electrochemical behaviour of corresponding AMC in buffered solution at the surface of GC electrode in the used range of potential. As can be seen, all these AMCs are electro-inactive in this range of potential.

The effect of AMCs concentration on electrochemical behaviour of catechol was studied. Fig. 4 shows obtained cyclic voltammogram of 2 mM catechol in the presence of various concentrations of DM (Fig. 4A), EA (Fig. 4B) and DBM (Fig. 4C). As can be seen, increasing the concentration of AMCs in all case results in a decrease in cathodic peak current C_0, which demonstrate, upon increasing the concentration of AMC more *o*-benzoquinone

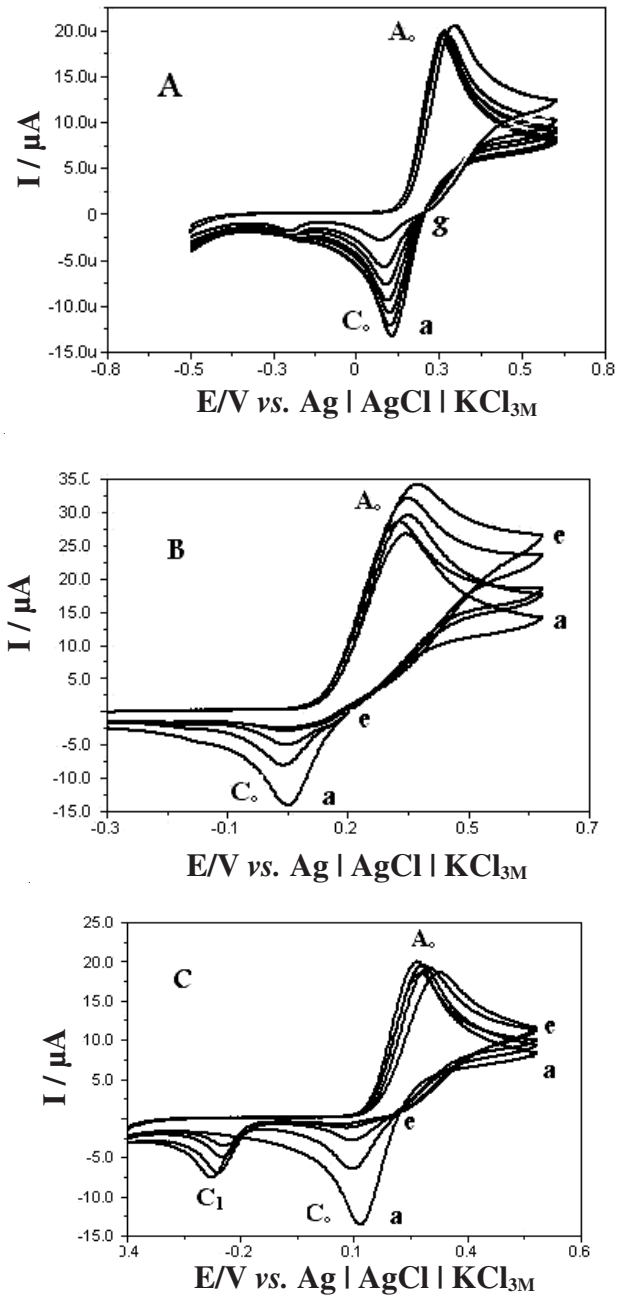
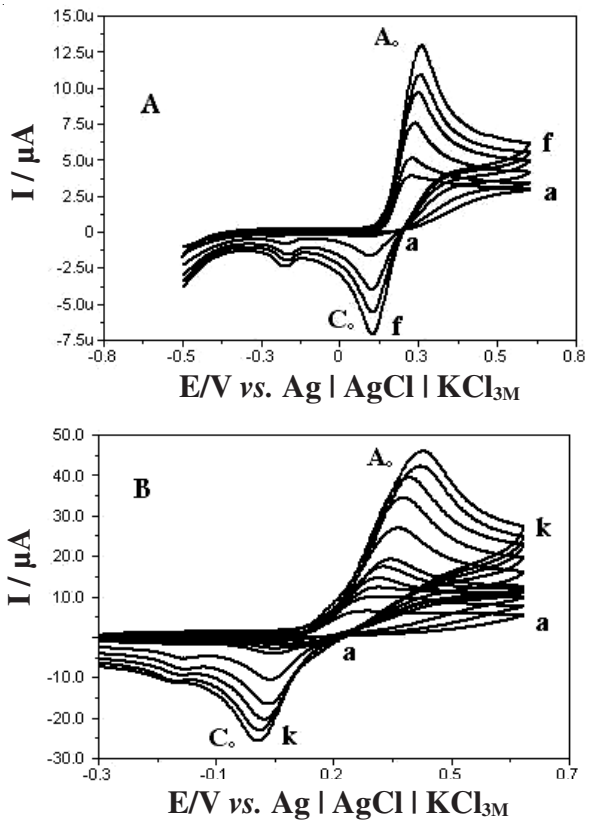


Fig. 4. Cyclic voltammograms of 2 mM catechol in the presence of various concentrations of different active methylene compounds: (A) DM (a-g) 0, 3, 5, 8, 11, 17 and 32 mM. (B) EA (a-e) 2, 4, 8, 12, 16 mM and (C) DBM (a-e) 0, 2, 4, 6, 8 mM. Scan rate of 50 mV s^{-1} at the surface of GC. Solution condition is same as Fig. 2 at pH 7

is removed from reaction layer. However, there is a difference between electrochemical behaviour of catechol in the presence of different AMCs *i.e.*, the concentration of each AMC which is necessary to remove the cathodic peak C_0. As can be seen, the order of required concentration of these AMCs is [DM] > [EA] > [DBM]. This order indicates that DBM and EA are better nucleophiles than DM, while the DBM is the best nucleophile among them.

The effect of scan rate was also studied on electrochemical behaviour of catechol in the presence of AMCs. Fig. 5 shows typical cyclic voltammograms obtained for 1 mM of catechol in the presence of 20 mM DM (A), 20 mM EA (B) and 10 mM DBM (C) at various scan rates of potential. As can be seen the cathodic peaks for reduction of *o*-benzoquinone are disappeared in the scan rates of 10, 25 and 50 mV s^{-1} in the case of DM, EA and DBM, respectively. By increasing the scan rate, the cathodic peak for reduction of *o*-benzoquinone begins to appear and increase. On the other hand, the value of current function, $I_p(A_0)/v^{1/2}$ was found to be decrease with increasing of scan rate of potential. All above observation can be



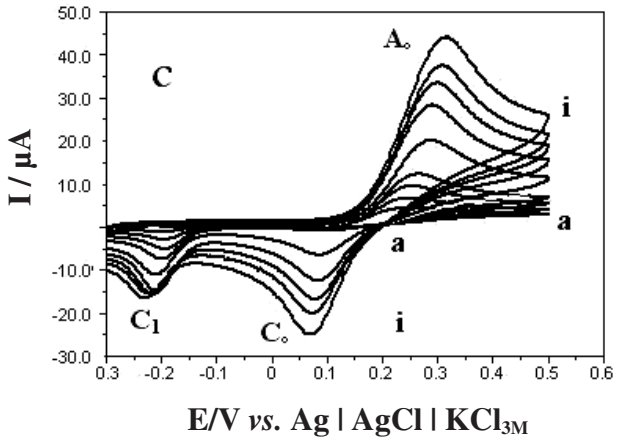


Fig. 5. Cyclic voltammograms of 1 mM catechol in the presence of different active methylene compounds; (A) DM 20 mM at scan rate of (a-f) 5, 10, 25, 50, 75 and 100 m Vs^{-1}. (B) EA 20 mM, scane rates (a-k)10, 25, 50,100, 150, 200, 400, 600, 800, 1000, 1200 mV s^{-1} and (C) DBM 10 mM at scan rates of (a-i) 10, 25, 50, 100, 300, 500, 700, 900, 1200 mV s^{-1}

attributed to the reaction between the AMC and *o*-benzoquinone species produced at the surface of electrode, with the new cathodic peak being attributed to the reduction of the newly formed *o*-benzoquinone-DBM adduct (peak C_1 in Fig. 5C).

Square wave voltammetry was used for representation of reaction between the electrochemically generated *o*-benzoquinone from catechol and DBM. The voltammetric scan is carried out at the potential more positive than that required for oxidation of catechol to produce its quinonic compound. The square wave voltammetric response of the oxidized form of 1 mM of catechol in the presence of various concentrations of DBM is shown in Fig. 6. As can be seen, two cathodic peaks (C_0 with E_p = 0.13 V and C_1 with E_p = -0.22 V *vs.* Ag|AgCl|KCl_{3M}) were obtained, which can be attributed to the reduction of *o*-benzoquinone species (C_0) and catechol-DBM adduct (C_1), respectively. As can be seen, upon increasing the concentration of DBM from 0 to 8 mM, the cathodic peak current of C_0 decreased and the cathodic peak current of C_1 increased. Also in the absence of DBM only cathodic peak C_0 was appeared. When the DBM concentration increases, more nucleophilic attack occur, consequently more catechol-DBM adducts is produced. Therefore, the concentration of *o*-benzoquinone decrease and the concentration of catechol-DBM adduct increase at the surface of electrode.

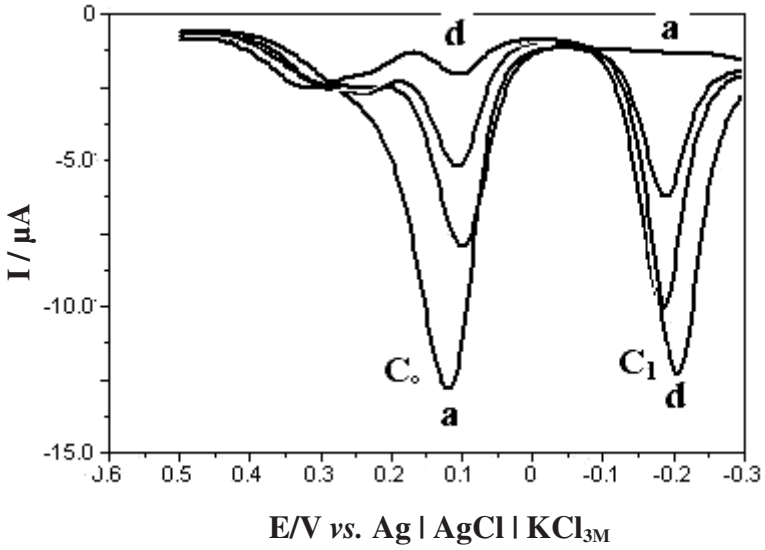


Fig. 6. Square wave voltammograms of 1 mM of catechol in the presence of various concentrations of diethylbromomalonate: a) 0, (b) 2, (c) 4 and (d) 8 mM. Solution condition is same as Fig. 2

Conclusion

The electrochemical behaviour of catechol in the absence and presence of some active methylene compounds (AMCs) such as diethyl malonate, ethyl acetoacetat and diethyl bromomalonate was investigated using cyclic voltammetry and square wave voltammetry methods. The anodic oxidation of catechol results in formation of *o*-benzoquinone, which was attacked by carbon nucleophiles. In the absence of any of these active methylene compounds, catechol shows a quasi-reversible behaviour. When diethylmalonate, ethyl acetoacetate or diethyl bromomalonate added to the solution of catechol a nucleophilic attack towards *o*-benzoquinone occurred by these carbon nucleophiles. The reactions process can be donated EC and ECE mechanism in the case of diethylmalonate or ethyl acetoacetate and diethyl bromomalonate, respectively.

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