

Mechanistic Study of Homogeneous Reactions Coupled with Electrochemical Oxidation of Catechols

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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*, *ECEC₂*, *ECECE*, *ECECEC*, *ECECECE* 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

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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/ν , 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

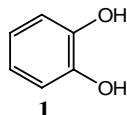
Most electrode reactions of interest to the organic electrochemists involve chemical reaction steps. The reaction mechanisms of electrode reactions are thus composed of at least one electron transfer step at the electrode as well as preceding and follow-up bond breaking, bond forming or structural rearrangement 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

leaving groups or bulky groups on the reactive positions of electrochemically generated *o*-benzoquinone, *i.e.*, C-3 and C-4, inhibit or slowdown the coupled chemical reactions.



Because of high reactivity of *o*-benzoquinone, the most coupled chemical reactions are following nucleophilic attacks and, thus, the nature of nucleophile plays an important role in these reactions. The nucleophilic attacks that lead to the formation of catechol derivatives with more or less positive oxidation potentials are followed by more *E* steps and *C* steps depends on the structure of intermediates by *EC* reaction and even more *E* and *C* steps.

All of the chemical and electrochemical reactions of catechol derivatives are depend on the nature of solvent and reaction media, specially, pH of solution. The oxidation potential of catechol, reactivity of nucleophile, reactivity of catechol and produced quinone are strongly pH dependent.

Solubility of final product or intermediate as well as the other reaction conditions is also important. For example low solubility or insolubility of intermediate inhibits the following chemical reactions.

EC MECHANISM

This mechanism contains one electron transfer step followed by a coupled chemical reaction. In this mechanism, catechols (**1**) is oxidized in a two-electron process to the related *o*-benzoquinone (**1a**) (*E* step). In the next step, the electrochemically generated *o*-benzoquinone (**1a**) as a reactive Michael acceptor participates in a chemical reaction (*C* step) to form the final product. The over-oxidation of the product is precluded by the presence of electron-withdrawing groups on the final product or formation of insoluble products (Scheme 1).

The irreversible bond formation is the most common following coupled chemical reaction in *EC* mechanism. The *EC* mechanisms in this review are classified according to the type of bond formation C-C, C-S, C-N and C-P between electrochemically generated *o*-benzoquinone and the nucleophile.

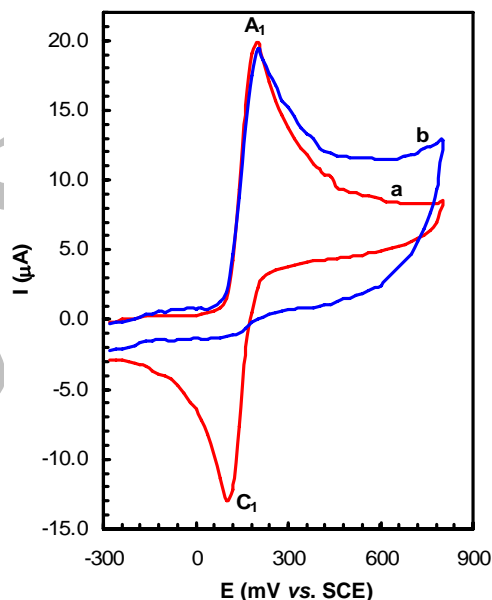
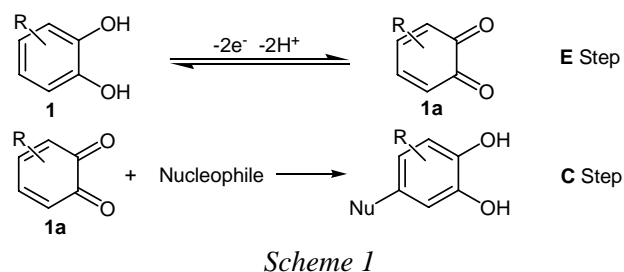
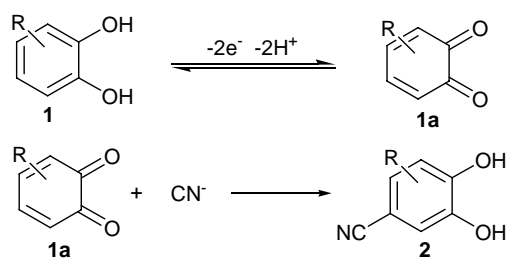


Fig. 1. Cyclic voltammograms of 1 mM catechol in the absence (a) in the presence of 1 mM cyanide ion (b), at glassy carbon electrode, in phosphate buffer solution of pH 7.0 at a scan rate of 100 mV s⁻¹.

C-C Bond Formation

Figure 1, curve a, shows the cyclic voltammogram recorded for catechol (**1**) in aqueous solution containing phosphate buffer of pH 7.0. The voltammogram shows an anodic peak (*A*₁) in the positive-going scan and a cathodic counterpart peak (*C*₁) in the negative-going scan corresponding to the transformation of catechol (**1**) to *o*-benzoquinone (**1a**) and vice-versa within a quasi-reversible two-electron process. Figure 1, curve b, shows the cyclic voltammogram obtained for a solution of catechol (**1**) in the presence of cyanide ion in the same conditions. The existence of an *EC* mechanism (Scheme 2) is supported by the following evidences: (a) Disappearing of peak *C*₁ current during the reverse scan. This could be indicative of the fact that



Scheme 2

electrochemically generated *o*-benzoquinone (1a) is removed by chemical reaction with cyanide ion. (b) Appearance of cathodic peak C_1 in higher sweep rates, or dependence of the peak current ratio (I_{pC1}/I_{pA1}) on the potential sweep rate. (c) Consumption of two electrons per molecule of catechol [10].

The presence of electron-withdrawing substituent (nitrile group) on catechol ring circumvented the next oxidation step in controlled potential conditions. Table 1 shows other C-C

Table 1. The Structure of Final Products in Electrochemical Oxidation of Catechols in the Presence of CH Acid Nucleophiles *via EC* Mechanism

Nucleophile	Product	Ref.
CN^-		[10]
		[11]
		[12]
		[13]
		[14]
		[15]
		[16]
		[16]

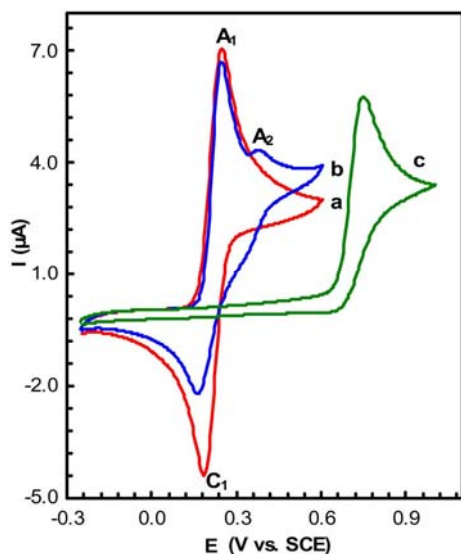


Fig. 2. Cyclic voltammograms of 1 mM catechol in the absence (a), in the presence of nitrite ion (b) and 2 mM nitrite ion at glassy carbon electrode (c), in phosphate buffer solution of pH 6.5 at a scan rate of 10 mV s^{-1} .

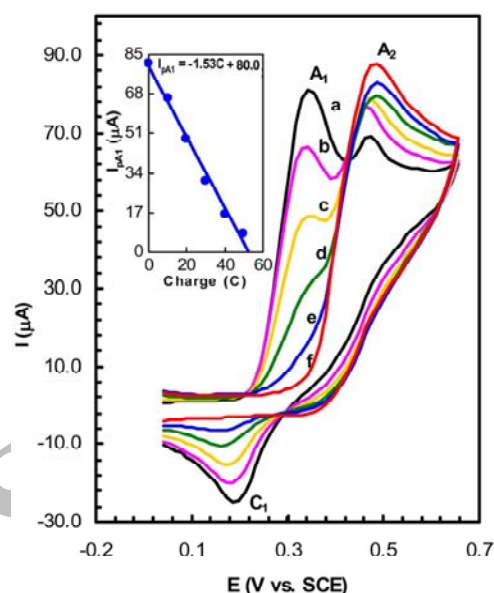
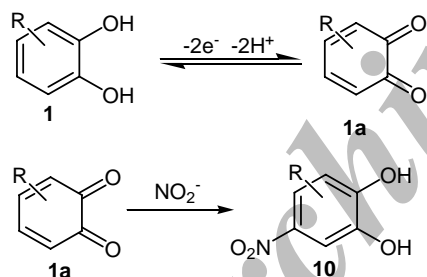


Fig. 3. Cyclic voltammograms of 0.25 mmol catechol in the presence of 0.25 mmol nitrite ion, at glassy carbon electrode in 0.15 M phosphate buffer solution of pH 6.5 during controlled potential coulometry at 0.25 V vs. SCE, after consumption of 0 (a), 10 (b), 20 (c), 30 (d), 40 (e) and 50 (f) C. Inset shows the variation of peak current (I_{pA1}) with charge consumed. Scan rate, 100 mV s^{-1} .



Scheme 3

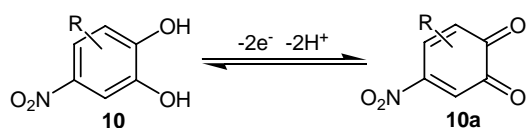
bond formation proposed for anodic oxidation of catechols in the presence of 1,3-indandione (**3**) [11], 2-phenyl-1,3-indandione (**4**) [12], 2-acetylcyclohexanone (**5**) [13], 2-acetylcyclopentanone (**6**) [13,14], indole (**7**) [15], 6-aminouracil (**8**) and 6-amino-1,3-dimethyluracil (**9**) [16].

C-N Bond Formation

Electrochemical nitration of catechols (**1**) has been studied in the presence of nitrite ion as a nucleophile in aqueous solution (Fig. 2) [17]. The results indicate the participation of produced *o*-benzoquinones (**1a**) in a Michael nitrocatechols (**10**). Considering the predominance of an *EC* mechanism, the observed homogeneous rate constants of

nitration reaction were estimated by comparing the experimental cyclic voltammograms with the digital simulated results. In spite of the fact that the nitration of aromatic compounds mostly performed based on their nucleophilicity, in published work, the nitration of catechols (**1**) has been reported based on the electrophilicity of electrochemically generated *o*-benzoquinones (**1a**) (Scheme 3) [17].

This is a good example of conversion of a nucleophile to electrophile *via* an electrochemical process. Since oxidation potential of nitrocatechol (**10**) is more than that of catechol (**1**), the further oxidation of product is precluded. Controlled-potential coulometry and voltammetric analysis during the electrolysis show the progressive formation of new anodic peak (A_2) parallel to the disappearance of the first anodic peak (A_1) with consumption of $2e^-$ per molecule of catechol (**1**), which is in support of the occurrence of an *EC* mechanism (Fig. 3). In this figure, peak A_2 pertain to the oxidation of



nitrocatechol (**10**) to the nitro-*o*-benzoquinone (**10a**) which takes place at more positive potentials (Scheme 4).

C-S Bond Formation

Electrochemical oxidation of catechols has been studied in the presence of various SH acid nucleophiles such as 2-mercaptopyridine (**11**) [18], 2-mercaptobenzoxazole (**12**) [19], 3-mercapto-1,2,4-triazole (**13**) [20], 4-mercaptocoumarin (**14**) [21], 4-amino-3-methyl-5-mercapto-1,2,4-triazole (**15**) [22], 1-phenyl-5-mercaptotetrazole (**16**) [23], 2-mercapto-4(3H)-quinazolinone (**17**) [24], 2-thiazoline-2-thiol (**18**) [25] and 6-mercaptapurine (**19**) [26], using cyclic voltammetry and controlled-potential coulometry, which result in the C-S bond formation. The results revealed that the quinones derived from

catechols participate in a Michael type addition reaction *via* an *EC* mechanism converted to the corresponding catechol derivatives. The electrochemical synthesis of various thiocatechol products (Table 2) has been successfully performed at a carbon rod electrode and in an undivided cell with good yields and high purity [18-26].

The sulfone derivatives of catechol (**21**) are also obtained through the Michael type addition of benzenesulfonic acids (**20**) to anodically generated *o*-benzoquinones (Scheme 5) [27-33].

C-P Bond Formation

Some new C-phosphoniumquinol betaine compounds (**23**) were synthesized from a conjugated addition reaction of triphenylphosphine (**22**) to the electrochemically generated *o*-benzoquinone *via* an *EC* mechanism (Scheme 6) [34].

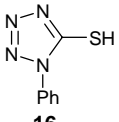
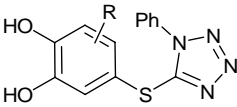
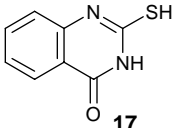
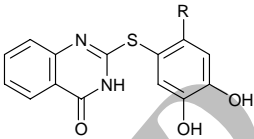
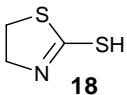
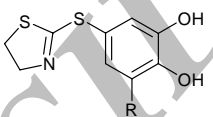
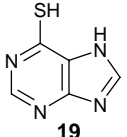
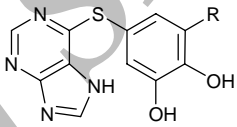
ECC, ECCC and ECCCC Mechanisms

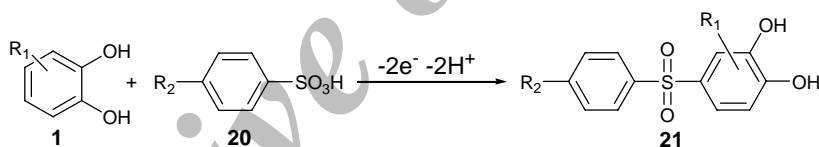
In some *EC* mechanisms, the electro-generated *o*-

Table 2. The Structure of Final Products in Electrochemical Oxidation of Catechols in the Presence of SH Acid Nucleophiles *via EC* Mechanism

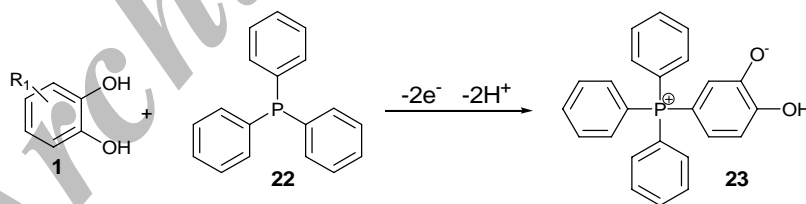
Nucleophile	Product	Ref.
		[18]
		[19]
		[20]
		[21]
		[22]

Table 2. Continued

 16	 [23]
 17	 [24]
 18	 [25]
 19	 [26]



Scheme 5



Scheme 6

benzoquinone may participate in more than one coupled chemical reactions such as *ECC*, *ECCC* etc. These mechanisms show a similar electrochemical behavior as *EC* mechanism. Figure 4 shows the voltammetric results for a typical *ECC* mechanism (Scheme 7) of electrochemical oxidation of catechol in the presence of 1,3-cyclopentadiene (**24**) [35]. In contrast to previous works, in this case the electro-generated *o*-benzoquinone (**1a**) is used as a dienophile. Decreasing the height of cathodic peak in the presence of the 1,3-cyclopentadiene as a diene indicates the reactivity of

electro-generated *o*-benzoquinone towards the cyclopentadiene (Fig. 4). The increasing cathodic to anodic peak current ratio (I_{pc}/I_{pa}) in high scan rate, as well as consumption of $2e^-$ per each molecule of catechol at constant potential coulometry (Fig. 5, curves I and II) are also good indications of an *EC* mechanism.

According to the obtained results, it seems that the [4 + 2] cycloaddition reaction of 1,3-cyclopentadiene (**24**) to *o*-benzoquinones (**1a**) (Scheme 7, Eq. (2)) is faster than the other secondary reactions, leading to the intermediate (**25**). During

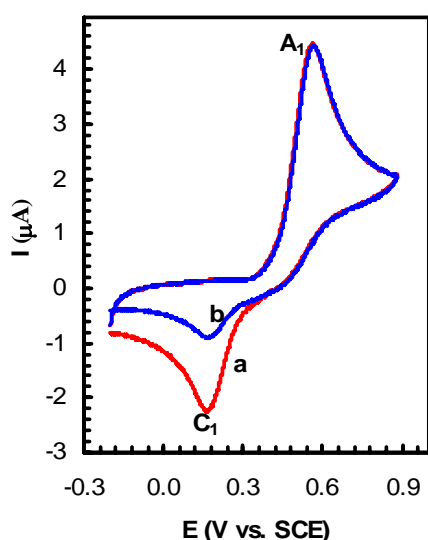
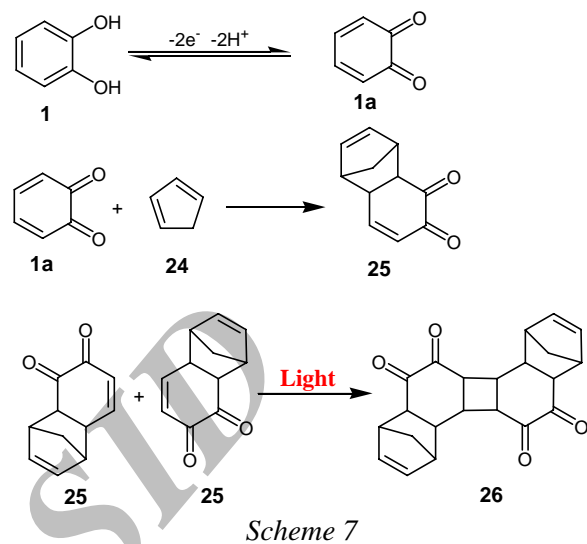


Fig. 4. Cyclic voltammograms of 1 mM catechol (**1**) in the absence (a) and presence of 3 mM 1,3-cyclopentadiene (**24**), in an ethanol/water (40/60 v/v) mixture containing 0.30 M lithium perchlorate as supporting electrolyte and 0.1 M acetic acid at glassy carbon electrode.



the electrolysis process and in the presence of room light, compound (**25**) is unstable and in the [2+2] cycloaddition reaction (Scheme 7, Eq. (3)) converts to novel symmetric dimer (**26**) in good yield. This reaction is stopped in the absence of light.

The electrochemical oxidation of catechols (**1**) in the presence of ethyl-2-chloroacetoacetate (**27**) and 2-chloro-5,5-

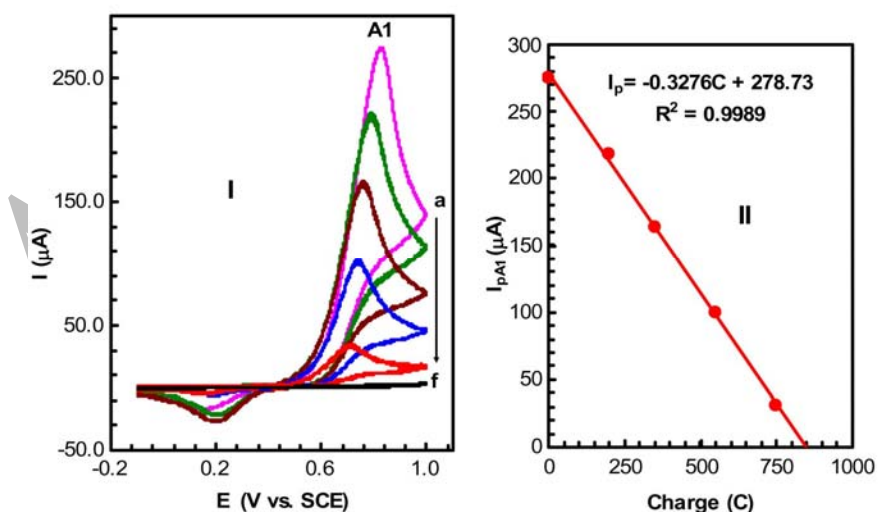
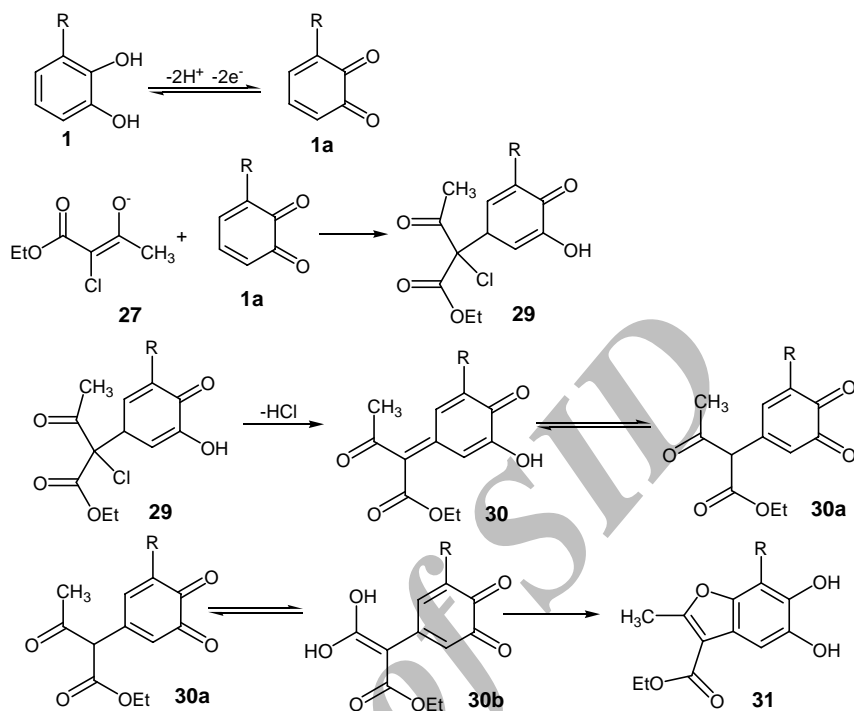
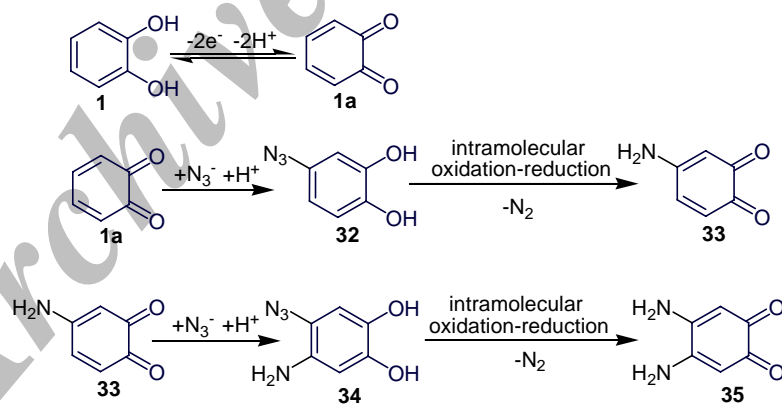


Fig. 5. (I) Cyclic voltammograms of 4.0 mmol catechol (**1**) in the presence of 16.0 mM 1,3-cyclopentadiene (**24**), in an ethanol/water (80/20) mixture containing 0.30 M lithium perchlorate as supporting electrolyte and 0.1 M acetic acid at glassy carbon electrode during controlled-potential coulometry at 0.80 V vs. SCE, after the consumption of 0 (a), 200 (b), 350 (c), 550 (d), 750 (e) and 850 (f) C of charge. (II) Variation of peak current (I_{pA1}) vs. charge consumed at a scan rate of 20 mV s^{-1} .

Mechanistic Study of Homogeneous Reactions



Scheme 8



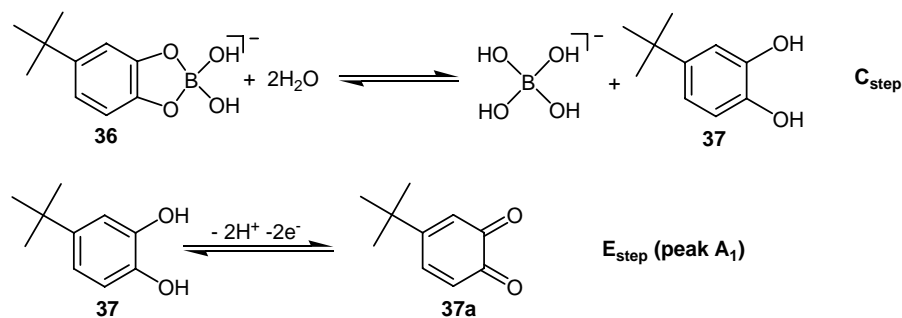
Scheme 9

dimethyl-1,3-cyclohexanedione (**28**) are examples of *ECCC* mechanism resulting in both C-C and C-O bond formation[36,37] (Scheme 8).

An efficient method for the synthesis of diamino-*o*-benzoquinone (**35**) based on the Michael-type reaction of electrochemically generated *o*-benzoquinone with azide ion with an *ECCCC* mechanism has been reported (Scheme 9) [38].

CE MECHANISM

Among the coupled homogeneous reactions, *CE* is an infrequent mechanism within individual *I-E* curves. Catechols with two hydroxyl groups in *ortho* position as electron donor are capable of forming a 1:1 complex with some electron-pair acceptors such as boric acid *via* a *CE* mechanism (Scheme 10) [39].



Scheme 10

The cyclic voltammogram of catechol derivatives in 0.1 M boric acid buffer of pH 9.2 shows an anodic sigmoidal shaped curve (A_1), corresponding to the oxidation of free catechol derivatives dissociated from boric acid complex to their *o*-benzoquinone and a new anodic peak (A_2) at more positive potential, due to the oxidation of catechol in the form of catechol-boric acid complex (Fig. 6).

EC' MECHANISM

EC' as an electrocatalytic reaction is a special type of EC processes. In the catalytic reaction, fast and reversible couple catechol/*o*-benzoquinone serves as a mediator for the oxidation of the substrates. The electrooxidation of NADH at a coumestan derivatives modified carbon paste electrode is a typical example of catalytic mechanism (EC'). The catalysis comes out as an increase in the mediator wave accompanied by the loss of reversibility. The anodic current height of coumestan (8,9-dihydroxy-6*H*-benzofuro[3,2-*c*]chromen-6-one) (**38**) in a chemically modified carbon paste electrode increased in the presence of NADH (Fig. 7) [40]. NADH diffuses toward electrode surface and reduces the coumestan_{ox} (**39**) to coumestan (**38**) while the simultaneous oxidation of regenerated coumestan (**38**) causes an increase in anodic current (Scheme 11).

There are some reports on electrocatalytic determination of NADH, hydrazine and hydroxylamine by catechol derivatives modified electrodes [41-45].

ORTHO-BENZOQUINHYDRONE FORMATION

There is only one report in which electro-generated

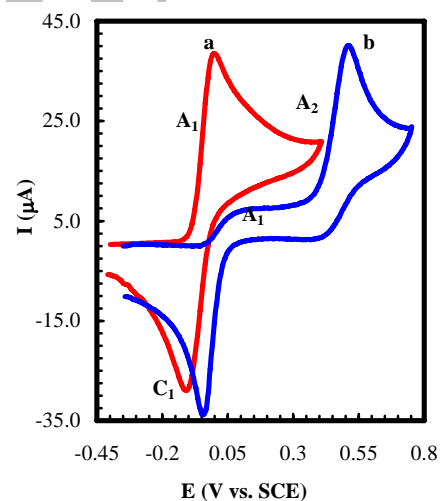


Fig. 6. Cyclic voltammograms of 1 mM 4-*tert*-butylcatechol in the absence (a) and presence of 0.1 M boric acid buffer of pH 9.2 (b) with different switching potentials, at a glassy carbon electrode. Scan rate 120 mV s^{-1} .

3,5-di-*tert*-butyl-1,2-benzoquinone (**40a**) participates in non-covalently linked interaction with 3,5-di-*tert*-butylcatechol (**40**) converted to an *ortho*-benzoquinhydrone complex (**41**) (Scheme 12) [46].

This is a unique example for the effect of solubility on the reaction mechanism. The final oxidation product is dependent on the ratio of organic solvent in mixture. In ethanol enriched solutions (*ca.*, ethanol/water (80/20) or more), the final product is 3,5-di-*tert*-butyl-1,2-benzoquinone (**40a**) which will be obtained after consumption of $2e^-$ per each molecule of 3,5-di-*tert*-butylcatechol (**40**), whereas in ethanol/water

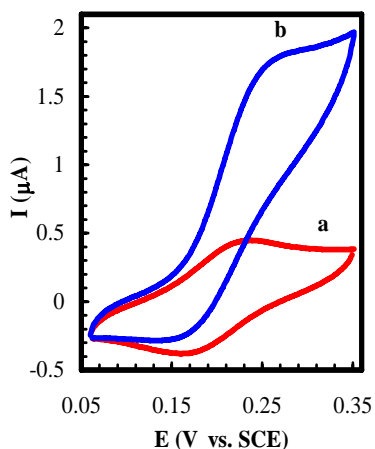


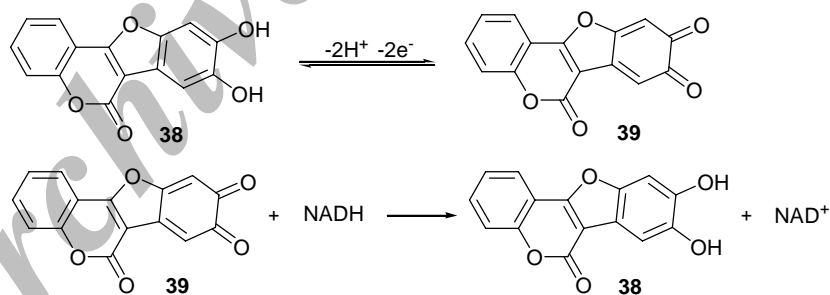
Fig. 7. Cyclic voltammograms of a coumestan modified carbon paste electrode at 20 mV s^{-1} in 0.1 M phosphate buffer of pH 7.0 in the absence (a) and in the presence of 0.4 mM NADH (b).

(20/80) or less, the main product is an *ortho*-benzoquinhydrone (**41**) type complex with consumption of $1e^-$ per molecule of catechol (**40**).

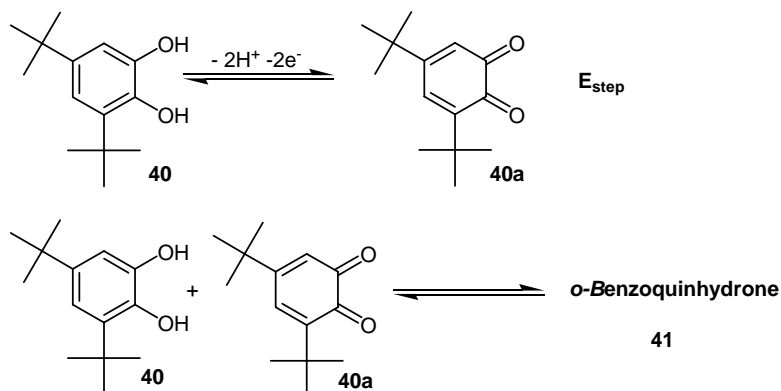
ECE MECHANISM

When the product of the following chemical reaction is electroactive at potentials of the catechol/*o*-benzoquinone electron transfer reaction, a second electron transfer reaction can take place.

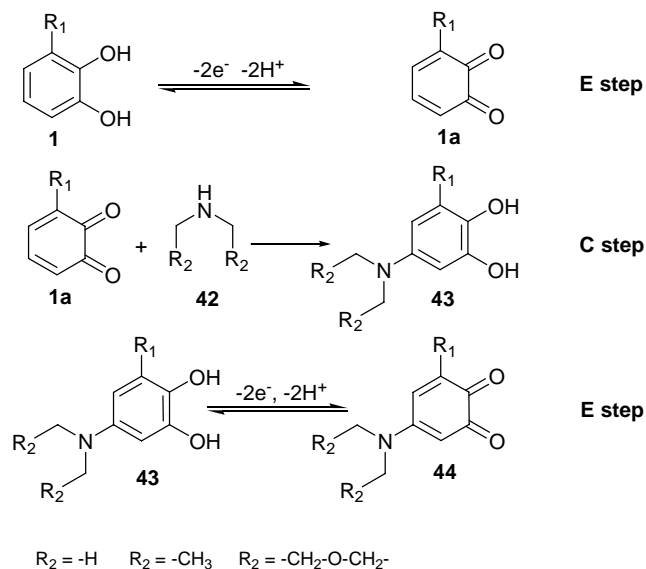
Electrochemical oxidation of catechols (**1**) in the presence of secondary amines such as dimethylamine (**42a**) ($R_2 = -H$), diethylamine (**42b**) ($R_2 = -CH_3$) and morpholine (**42c**) ($R_2 = -CH_2-O-CH_2-$) is a typical example of *ECE* mechanism (Scheme 13) [47]. Figure 8 shows increasing anodic peak current (A_1), decreasing height of cathodic peak (C_1) and appearance of a new redox couple (A_2/C_2) in multi scan voltammetry of catechol (**1**) in the presence of morpholine (**42c**). During controlled-potential coulometry and consumption of $4e^-$ per molecule of catechol (**1**), proportional to the advancement of coulometry and parallel to the decrease in height of anodic peak A_1 and cathodic peak C_1 , the height of A_2 and C_2 is increased (Fig. 9). According to Scheme 13, the 1,4-(Michael type) addition reaction of nucleophiles (**42**)



Scheme 11



Scheme 12



Scheme 13

to *o*-benzoquinone (**1a**) leads to the formation of an intermediate (**43**), followed by its oxidation in a second electron transfer step. Oxidation of this intermediate (**43**) is easier than the oxidation of parent starting molecule by virtue of the presence of electron-donating amine group.

C-C Bond Formation

Electrochemically generated 4-substituted *o*-benzoquinone

(**1a**) reacts with Meldrum's acid (**45**) to form intermediate (**46**). The oxidation of (**46**) is easier than that of catechol (**1**) because of the presence of Meldrum's acid group with electron-donating character on the catechol ring. In this

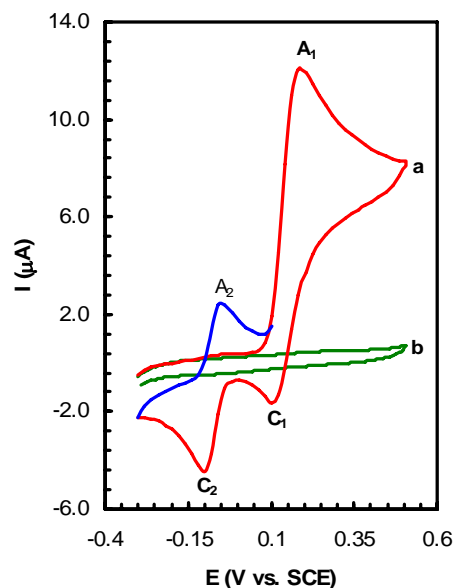


Fig. 8. Cyclic voltammograms of 1 mM catechol in the presence of 10 mM morpholine (**42c**) (first and second cycles) (a), and 10 mM morpholine (**42c**) in the absence of catechol (**1**) in 0.2 M phosphate buffer of pH 7.2 (b) at a scan rate 50 mV s⁻¹.

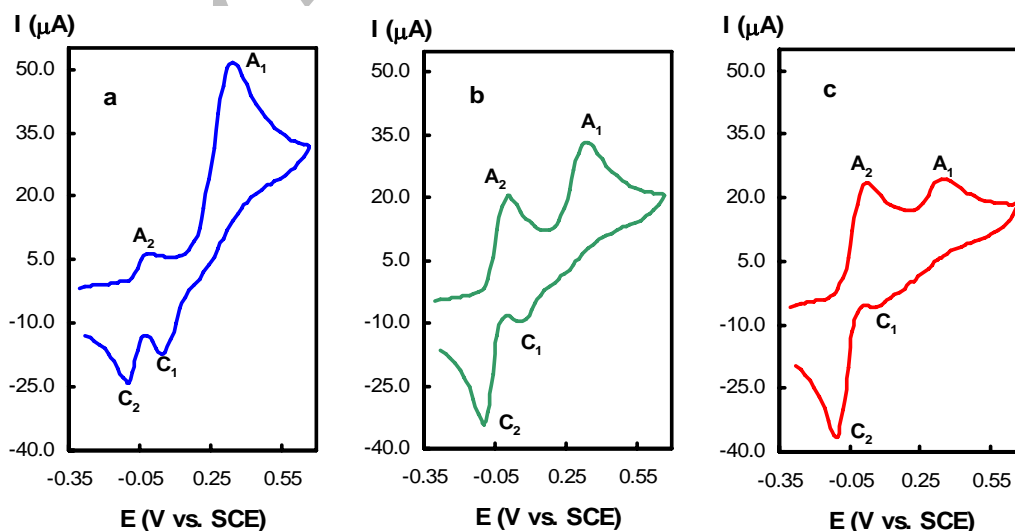
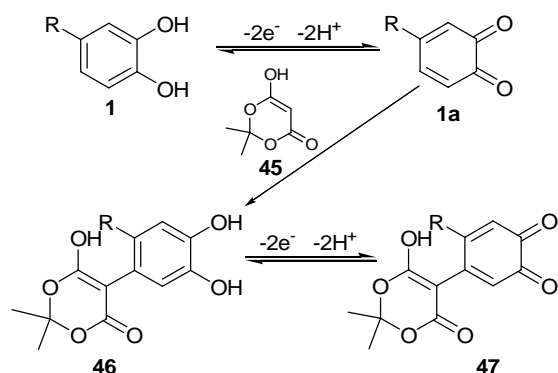


Fig. 9. Cyclic voltammogram of 5 mM catechol (**1**) in the presence of 50 mM morpholine (**42c**), during controlled potential coulometry at 0.4 V vs. SCE, in 0.2 M phosphate buffer of pH 7.2.



Scheme 14

condition, intermediate (**46**) undergoes a second oxidation process to final product (**47**) (Scheme 14) [48].

Also the electrochemical oxidation of 4-*tert*-butylcatechol (**37**) in the presence of 4-hydroxy-6-methyl-2-pyrone (**48**) *via* the same mechanism leads to formation of functionalized *o*-benzoquinone (**49**) (Scheme 15) [49].

C-N Bond Formation

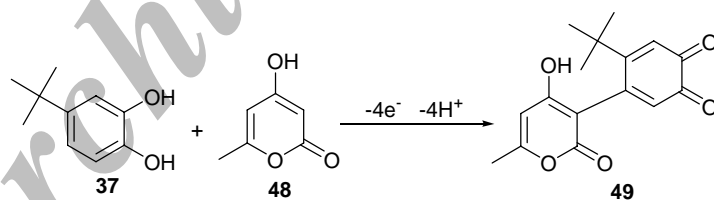
The most well known *ECE* reaction is the oxidation of catecholamines (**50**) in neutral or mild basic conditions. Catecholamines (**50**) can be oxidized electrochemically to

their *o*-benzoquinones (**50a**) that are quite reactive and can be attacked by the side chain amino group *via* intramolecular Michael-type addition reactions [50]. The cyclization reaction is followed by a second electron transfer oxidation to form the corresponding *o*-quinone derivatives (**51a**) (Scheme 16).

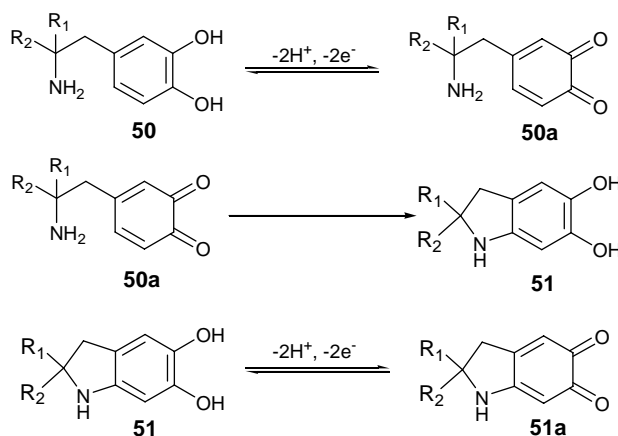
The kinetics of the reaction of electrogenerated two-electron oxidation product with the side chain amine group were studied by digital simulation under *ECE* mechanism and the effect of pH on the oxidation pathway of catecholamine has also been discussed [50].

In this direction, the electrochemical oxidation of some catecholamines has been studied in the presence of 4-aminobenzoic acid. Variation in the cathodic peaks due to the competition between intramolecular and intermolecular Michael-type addition reaction has been studied at various pH values, and the best conditions for the reaction with 4-aminobenzoic acid was obtained. The observed homogeneous rate constants were estimated by comparing the experimental cyclic voltammetric responses with the digital simulated results based on *ECE* mechanism. The rate constants were calculated using microscopic acidic dissociation constant of ammonium group in 4-aminobenzoic acid [51].

The electrooxidation of catechols (**1**) has been studied in



Scheme 15



Scheme 16

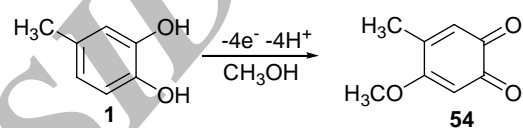
the presence of dibenzylamine (**52**) using spectroelectrochemical and electrochemical methods [52,53]. The *o*-benzoquinones derived from catechols participate in Michael-type addition reactions with dibenzylamine (**52**) to form the corresponding mono amino-substituted *o*-benzoquinones (**53**) (Scheme 17).

Time-dependent absorption spectra of the mixture of catechol and dibenzylamine were collected during a controlled-potential coulometry experiment (Fig. 10) The spectra showed that, during charge consumption of $4e^-$ per molecule of catechol (**1**), an absorption peak with λ_{max} at 500 nm appeared which belongs to the aminoquinone produced.

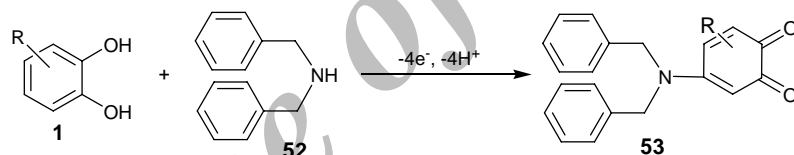
Oxidation of catechols (**1**) in the presence of sulfanilic acid [54] and some secondary amines such as dibutylamine, diethylamine [55] and some azacrown ethers [56] with the same mechanism has also been reported.

C-O Bond Formation

The results of electrochemical oxidation of 4-methylcatechol (**1**) in methanol indicate that this compound undergo methoxylation reaction according to an *ECE* mechanism to form the related methoxyquinone (**54**) [57,58] (Scheme 18). The electrochemical syntheses of final product have been successfully performed in methanol in the presence of sodium acetate as supporting electrolyte with good yield.



Scheme 18



Scheme 17

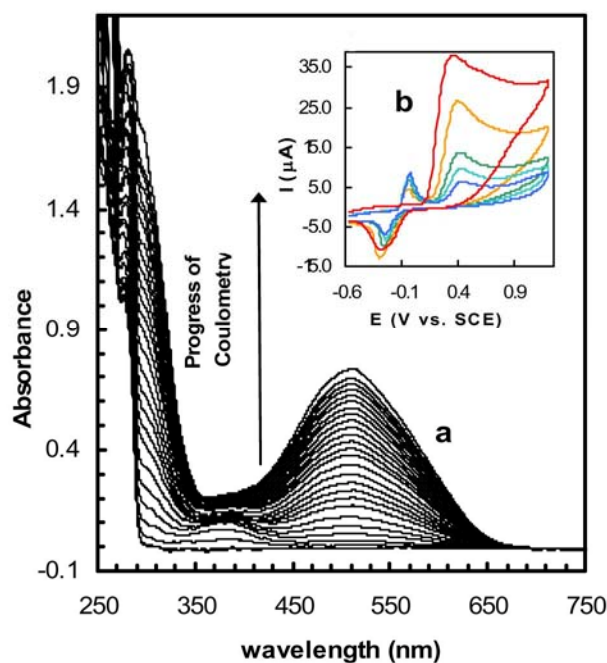


Fig. 10. (a) Absorption spectra and (b) cyclic voltammograms of the mixture of catechol (**1**) and dibenzylamine (**52**) during controlled-potential coulometry at 1.0 V vs. SCE. Time intervals, 300 s; scan rate, 50 mV s⁻¹.

ECEC MECHANISM

This type of mechanism occurs very often, in electrochemical oxidation of catechols (**1**) in the presence of bidentate nucleophiles (bis-donors). In this mechanism, the perturbation of anodic peak is the same as *ECE* mechanism; however, in the reverse scan, the current of second cathodic peak is less than that predicted for *ECE* mechanism (for example, C_2 in Fig. 8). This peak is not observed at higher k_2 and/or lower scan rates (where k_2 is homogeneous rate constant for second chemical reaction). Under these conditions, the cyclic voltammogram in reverse scan shows an *EC* characteristic.

Electrochemical oxidation of catechols (**1**) in the presence of dimedone (**55**) is a typical example of *ECEC* mechanism with fast intramolecular Michael addition reaction (large k_2). Figure 11, (curve b) shows the cyclic voltammogram obtained for catechol (**1**) in the presence of dimedone (**55**). The voltammogram exhibits an increase in anodic peak A_1 , and the cathodic counterpart of the anodic peak A_1 nearly disappears. This peak (C_1) appeared at higher scan rates, and proportional to the augmentation of potential scan rate, its height is increased (Fig. 12). The reaction mechanism includes the oxidation of catechol (**1**), intermolecular Michael addition reaction and formation of adduct (**56**), oxidation of adduct (**56**) and intramolecular Michael addition reaction, respectively (Scheme 19) [59-61].

Electrochemical oxidation of catechols (**1**) in the presence of cyanoacetone (**58**) is another example of *ECEC* mechanism with slow intramolecular Michael addition reaction (Scheme 20) [62]. Figure 13, shows the cyclic voltammograms of catechol (**1**) in the presence of cyanoacetone (**58**) at various scan rates.

According to the presented mechanism, the Michael addition reaction of anion of cyanoacetone (**58**) to *o*-benzoquinone (**1a**) leads to the formation of intermediate (**59**). The oxidation of **59** is easier than the parent-starting molecule (**1**) by virtue of the presence of negative charge and electron-donating effect of the linked nucleophile. In the next step, the oxidized intermediate (**59a**) participates in a slow intramolecular Michael addition to form the final product (**60**). As shown in Fig. 13, when intermolecular Michael addition reaction is fast and intramolecular Michael addition reaction is slow (large k_1 and small k_2), the second cathodic peak (C_2) is

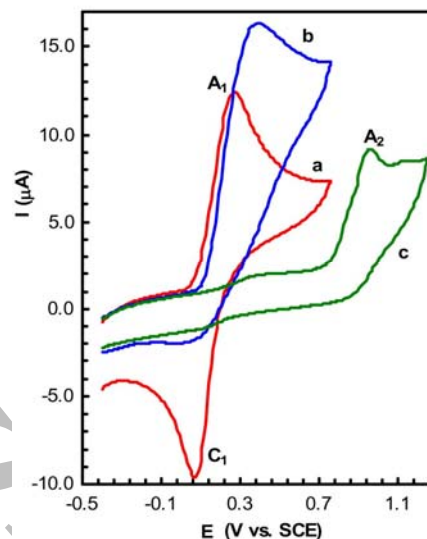


Fig. 11. Cyclic voltammograms of 1 mM catechol (**1**) in the absence (a), in the presence of 1 mM dimedone (**55**) (b) and 1 mM dimedone (**55**) in the absence of catechol (**1**) (c) at glassy carbon electrode in aqueous solution. Supporting electrolyte, 0.15 M sodium acetate; scan rate, 100 mV s^{-1} .

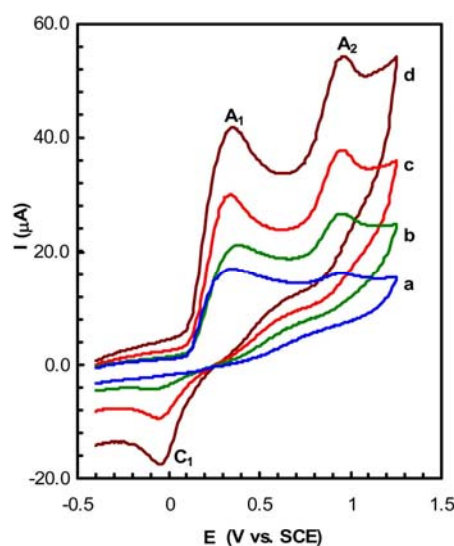
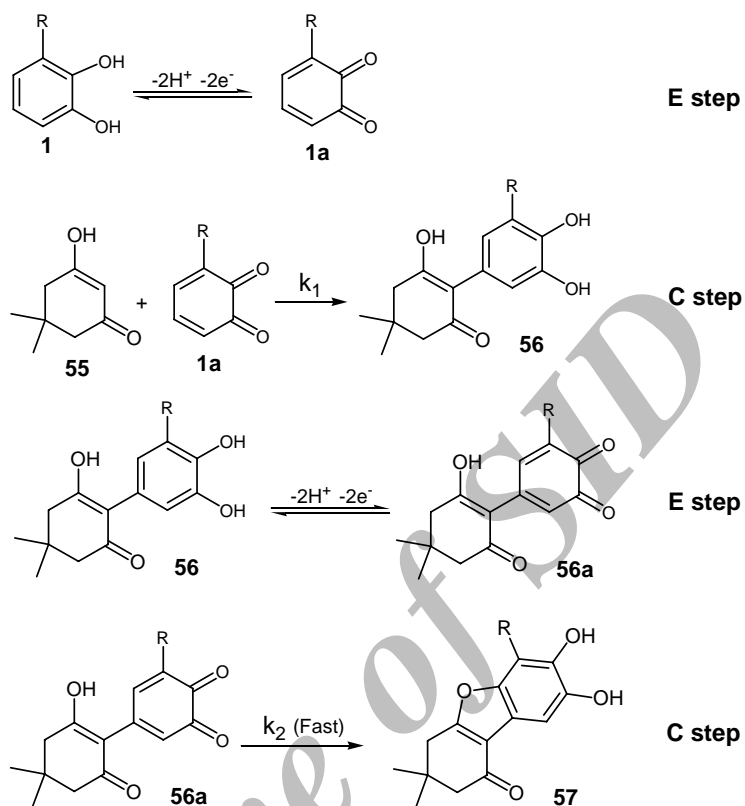
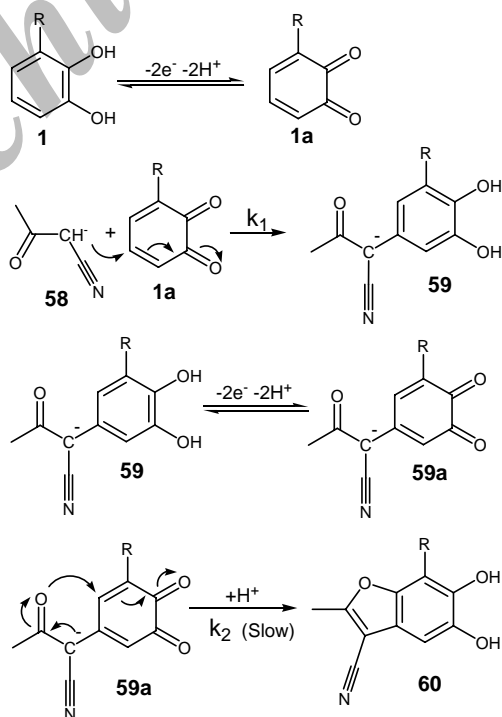


Fig. 12. Typical voltammograms of 1 mM catechol (**1**) in water in the presence of 1 mM dimedone (**55**) (0.15 M sodium acetate) at scan rates from 100 (a), 250 (b), 500 (c) and 1000 mV s^{-1} (d).



Scheme 19



Scheme 20

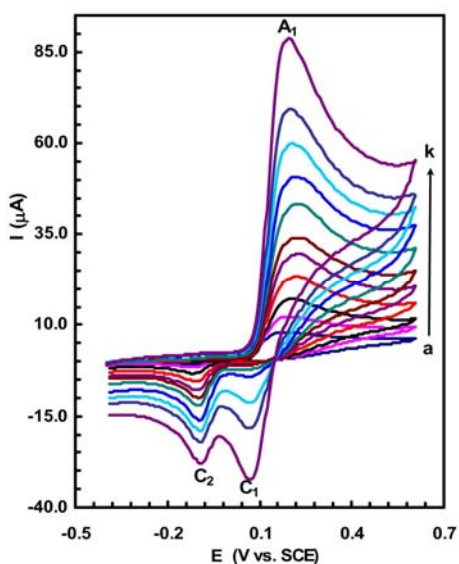


Fig. 13. Cyclic voltammograms of 1 mM catechol (**1**) in the presence of 1 mM cyanoacetone (**58**) at glassy carbon electrode, in 0.2 M phosphate buffer of pH 6.7. Scan rates from a to k are 10, 25, 50, 100, 170, 250, 400, 600, 1000, 1600 and 2500 mV s^{-1} .

observed as a well defined peak.

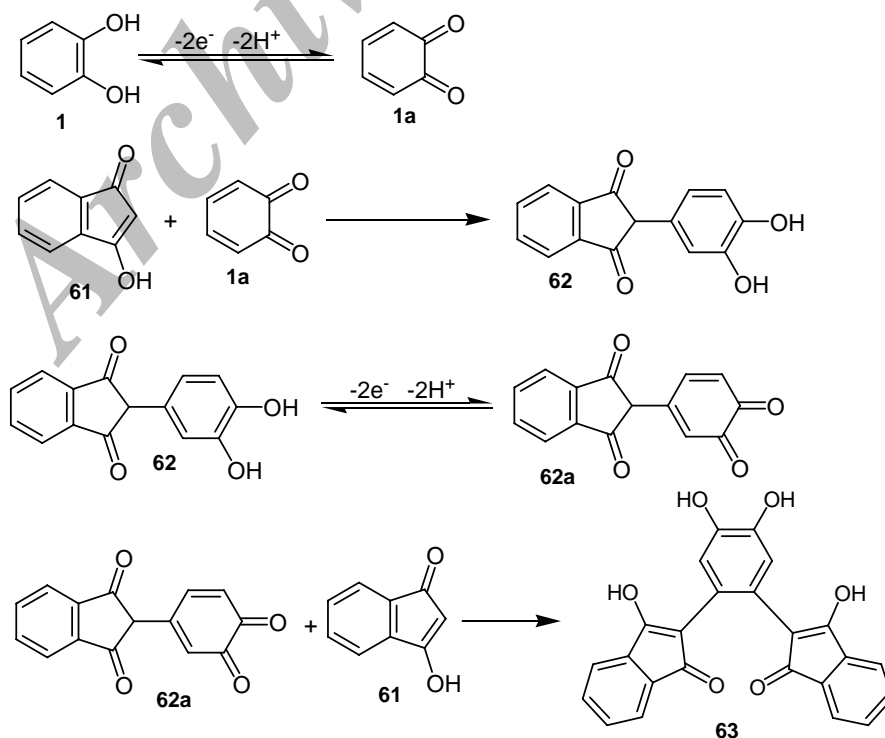
C-C C-C Bond Formation

Electrochemical oxidation of catechol (**1**) in water-acetonitrile mixture (16% v/v) containing acetate buffer (pH = 4.8) in the presence of 1,3-indandione (**61**) as nucleophile is an example of *ECEC* mechanism with two successive C-C bond formation [63]. Diagnostic criteria of cyclic voltammetry including the consumption of four electrons per molecule of catechol (**1**) and the mass spectrum of isolated product ($m/z = 398$) indicates that the reaction mechanism of electrooxidation of catechol (**1**) in the presence of (**61**) contains two successive *EC* (*ECEC*) (Scheme 21).

A same result was obtained in electrochemical oxidation of 4-methylcatechol (**1a**) in the presence of barbituric acid derivatives as nucleophiles [64].

C-C C-O Bond Formation

Benzofurans and their analogues constitute a major group of naturally-occurring compounds that are of particular interest because of their biological activity and their role in



Scheme 21

plant defense systems [65,66]. Several methodologies are available for the synthesis of simple benzofurans [67], but less attention has been given to the synthesis of hydroxylated benzofurans. Electrochemical oxidation of catechols (**1**) in the presence of cyclic and open chain β -diketones such as dimedone (**55**) [61], acetylacetone (**64**) [68-70], 3-hydroxy-1*H*-phenalen-1-one (**65**) [71,72], dibenzoylmethane (**66**) [73] and benzoylacetone (**67**) [74], cyclic and open chain β -ketoesters, such as 4-hydroxycoumarin (**68**) [59,60,75-77], 4-hydroxy-6-methyl-2-pyrone (**69**) [49,78] and alkylacetoacetate (**70**) [79], dialkylmalonates (**71**) [70], barbituric acid derivatives (**72**) [80], 4,6-dihydroxy-2-methylpyrimidine (**73**) [81], 4-hydroxy-1-methyl-2(1*H*)-quinolone (**74**) [82-84] and 2-hydroxy-1,4-naphthoquinone (**75**) [85] introduced an easy and one-pot electrochemical method for the synthesis of hydroxylated benzofurans (see Table 3) *via ECEC* mechanism (Scheme 22), in high yield and purity, using environmentally friendly method with high atom economy.

Table 3. The Structure of Final Products in Electrochemical Oxidation of Catechols in the Presence of C-H Acid Nucleophiles *via ECEC* Mechanism

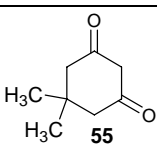
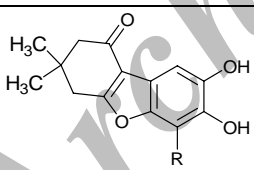
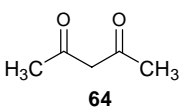
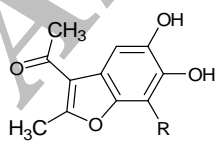
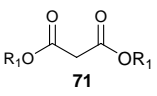
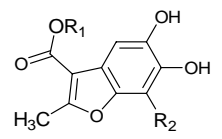
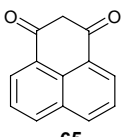
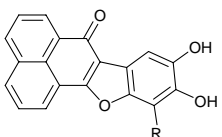
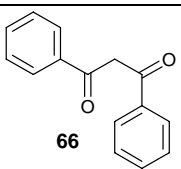
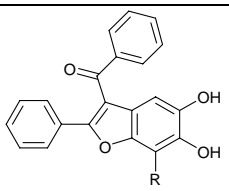
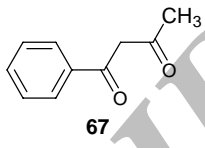
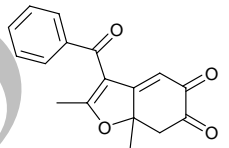
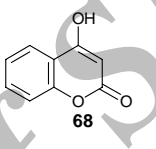
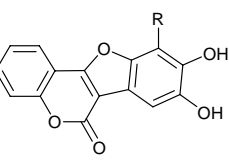
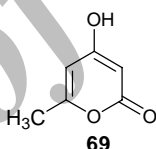
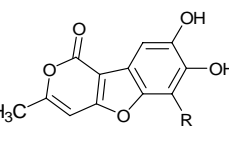
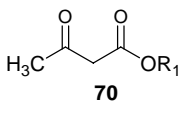
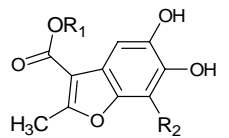
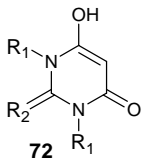
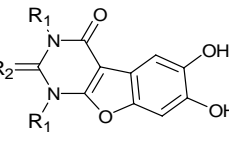
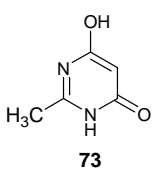
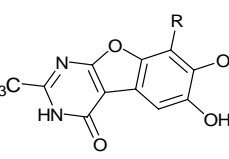
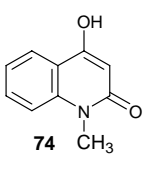
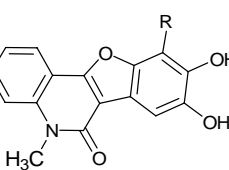
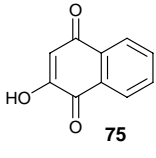
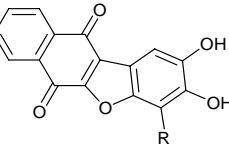
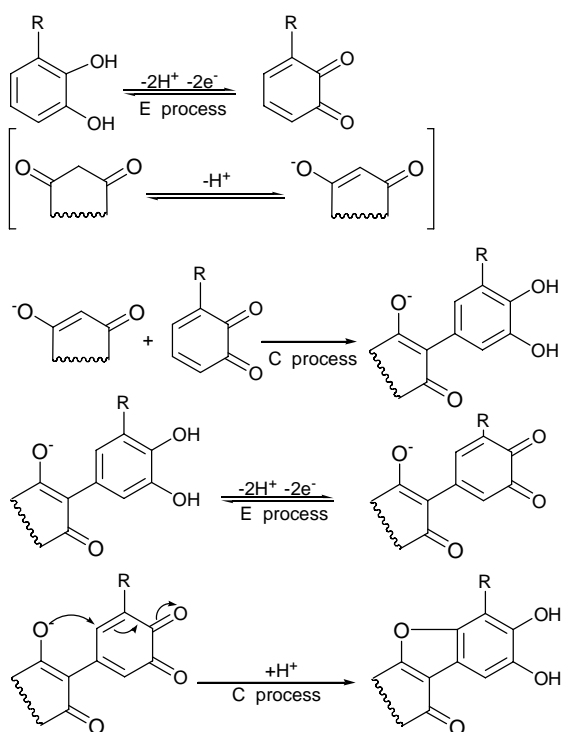
Nucleophile	Product	Ref.
		[61]
		[68-70]
		[70]
		[71,72]

Table 3. Continued

		[73]
		[74]
		[59,60,75-77]
		[49,78]
		[79]
		[80]
		[81]
		[82-84]
		[85]

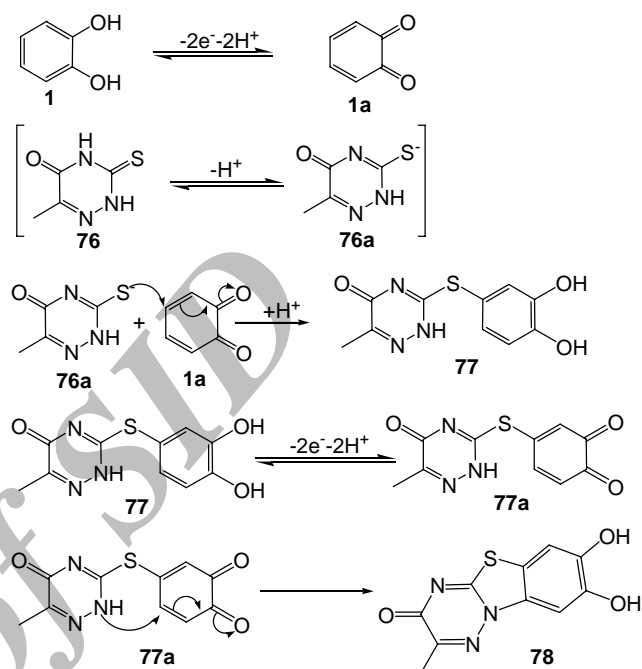


Scheme 22

C-N C-S Bond Formation

It is reported that 7*H*-thiazolo[3,2-*b*]-1,2,4-triazin-7-ones are anti-inflammatory agents with immunomodulating properties [86]. Also, it is reported that a part of the anti-inflammatory effects of these compounds is most probably related to their antioxidative activity [86]. Therefore, it is probable that attachment of a catechol (**1**) to a thiazolo-triazine might cause an enhancement of its antioxidative activity. This is motive for electrochemical oxidation of catechols (**1**) in the presence of 6-methyl-1,2,4-triazine-3-thion-5-one (**76**) as a bidentate nucleophile with S and N donors. The reaction mechanism is an *ECEC* mechanism with S-C intermolecular and N-C intramolecular Michael type addition reactions, respectively (Scheme 23) [87,88].

Electrochemical oxidation of catechols (**1**) in water containing phosphate buffer (pH = 7.0) in the presence of 4-amino-6-methyl-1,2,4-triazine-3-thion-5-one (**79**) [89], 4-amino-3-thio-1,2,4-triazole (**80**) [90] and 2-thiouracil (**81**) [91] as nucleophiles are other examples of an *ECEC* mechanism with C-S and C-N bond formation (see Table 4). Also the oxidation of C-3 substituted catechols in the presence of 2-



Scheme 23

Table 4. The Structure of Final Products in Electrochemical Oxidation of Catechols in the Presence of S-H Acid Nucleophiles via *ECEC* Mechanism

Nucleophile	Product	Ref.
		[88]
		[89]
		[90]
		[24]

mercapto-4-(3*H*)-quinazolinone (**17**) proceeds *via* an *ECEC* mechanism [24].

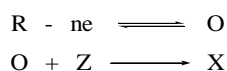
C-S C-S Bond Formation

Electrochemical oxidation of catechol (**1**) in aqueous solution in the presence of 1-methyl-1*H*-imidazole-2-thiol (**82**) as a mono-dentate nucleophile with S donor atom is an example of *ECEC* mechanism with two successive C-S bond formations (Scheme 24) [92].

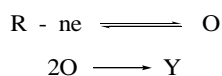
The same results obtained in electrochemical oxidation of catechols (**1**) in the presence of pyrimidine-2-thiol derivatives (**85**) as nucleophiles (Scheme 25) [93-96].

*ECEC*₂ MECHANISM

In *EC* process, the product of the electrode reaction reacts to produce a species that is not electroactive at potentials where the oxidation of R is occurring [97].

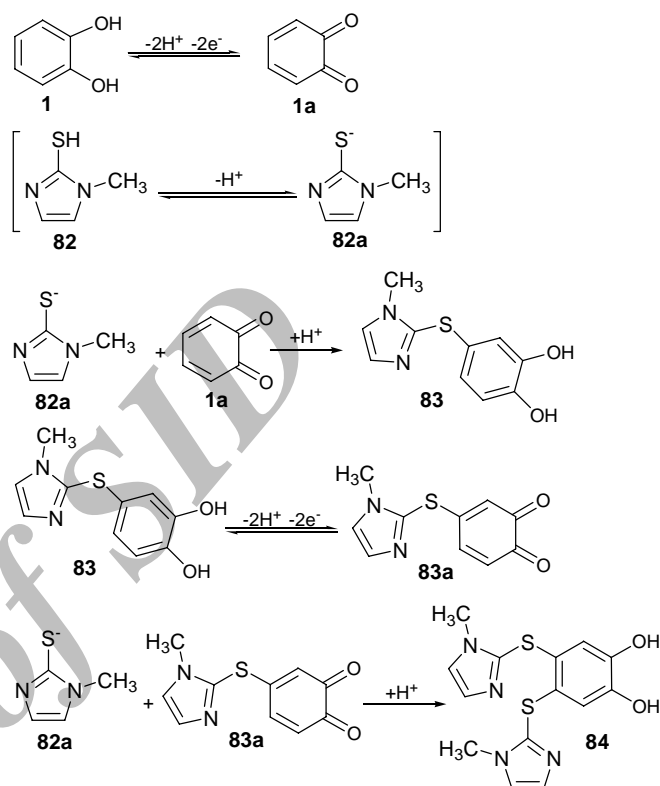


A special type of *EC* process involves dimerization reaction of O. In this case, the chemical reaction following the electron transfer is a second-order reaction, and designated as an *EC*₂ reaction.

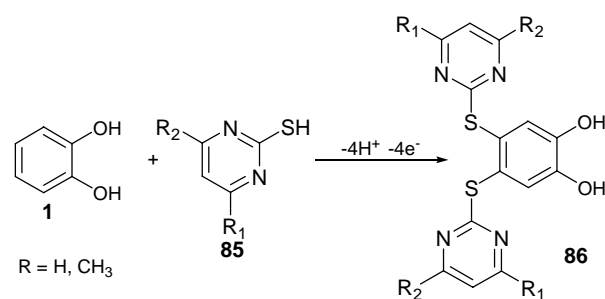


Electrochemical oxidation of catechols (**1**) in the presence of barbituric acid (**87a**), 1,3-dimethylbarbituric acid (**87b**) and 1,3-diethyl-2-thiobarbituric (**87c**) is an example of *ECEC*₂ mechanism, in which the starting materials are converted to dispiropyrimidine derivatives (**89**). The electrochemical synthesis of products has been successfully performed in an undivided cell in good yield and purity. The reaction mechanism for the anodic oxidation of catechols (**1**) in the presence of nucleophiles (**87**) is presented in Scheme 26 [98,99].

Because of the presence of a *tert*-butyl group in a reactive site of catechol, the electrochemical oxidation of 4-*tert*-



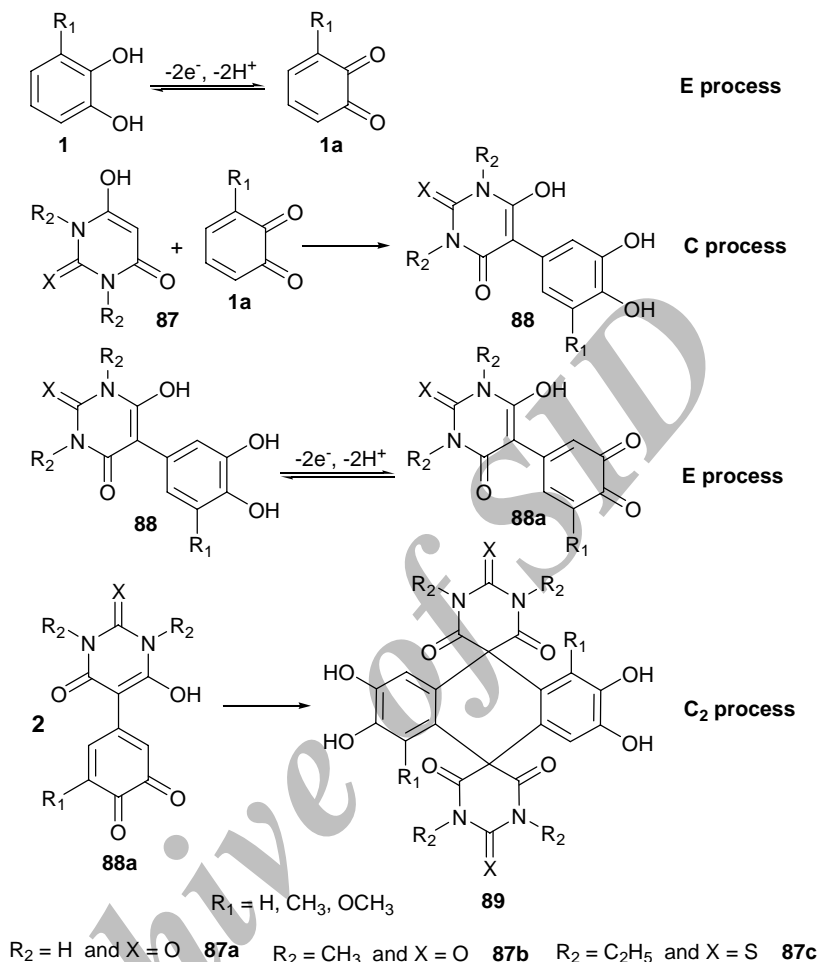
Scheme 24



Scheme 25

butylcatechol (**37**) in the presence of 1,3-dimethylbarbituric acid (**87b**) and 1,3-diethyl-2-thiobarbituric acid (**87c**) leads to formation of corresponding spiroypyrimidine derivatives (**92**), *via* a different type of *ECEC*₂ mechanism [100]. Contrary to previous *ECEC* and *ECEC*₂ mechanisms, in this case, the apparent number of transferred electrons is 3e⁻ per molecule of 4-*tert*-butylcatechol (**37**). The overoxidation of the final product was circumvented during the preparative reaction because of their insolubility in aqueous media (Scheme 27).

Mechanistic Study of Homogeneous Reactions



Scheme 26

Electrochemical oxidation of catechol (**1**) in the presence of chloranilic acid (**93**) as a nucleophile led to the formation of new benzodifurans as final product through a novel mechanism (Scheme 28) [101].

ECECE MECHANISM

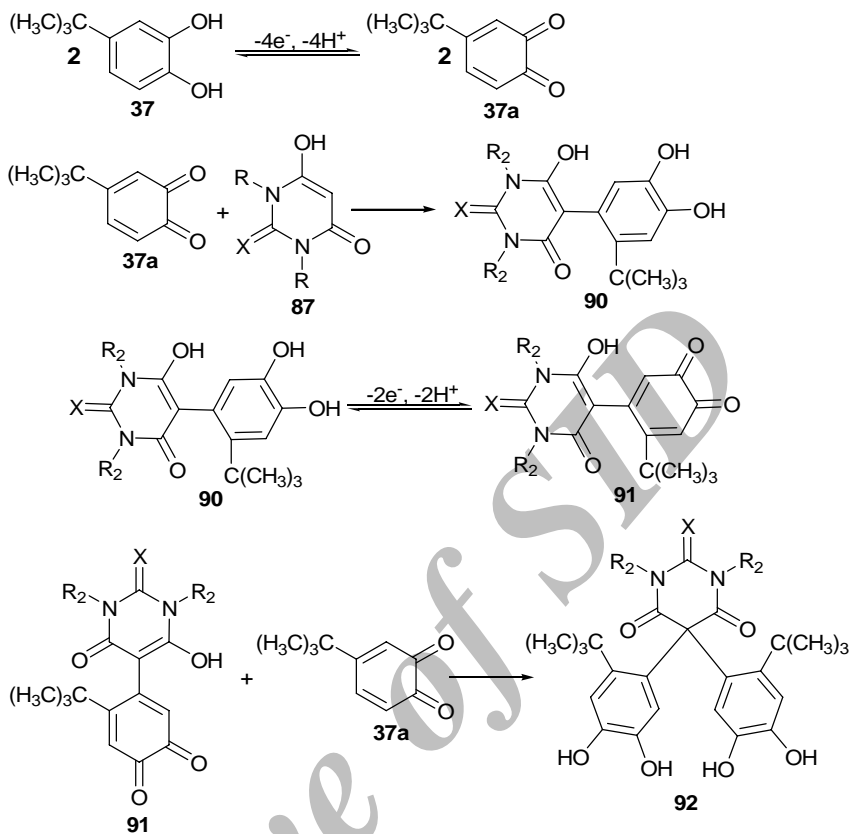
C-O C-O Bond Formation

Electrochemical oxidation of catechol in methanol shows an *ECECE* mechanism. Cyclic voltammogram of catechol in methanol containing sodium acetate as supporting electrolyte shows one anodic peak (A_1) as well as three cathodic peaks (C_1 , C_2 and C_3) in the reverse scan (Fig. 14) [102]. In this condition, the peak current ratios I_{pC1}/I_{pA1} , I_{pC1}/I_{pC2} and

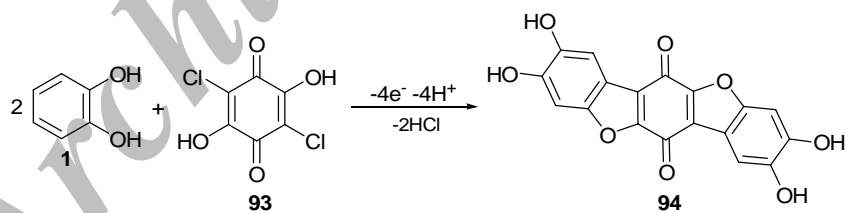
I_{pC1}/I_{pC3} strongly depend on the potential sweep rate, and increase with increasing sweep rate. For example, for a sweep rate of 600 mV s^{-1} or greater, only peak C_1 is observed and the other cathodic peaks (C_2 and C_3) disappear.

Diagnostic criteria of cyclic voltammetry including consumption of six electrons per molecule of catechol (**1**) and the spectroscopic data of isolated product indicate that the reaction mechanism of electrooxidation of catechol (**1**) in methanol is of *ECECE* type (Scheme 29).

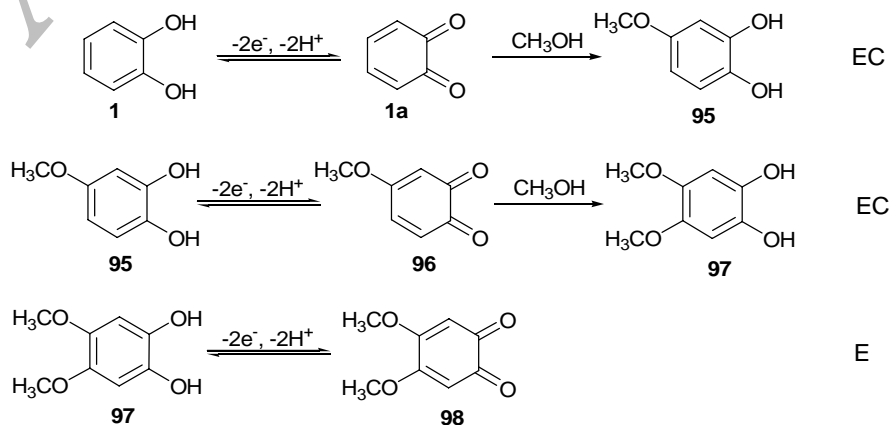
According to the proposed mechanism the Michael type addition reaction of methanol to *o*-benzoquinone **1a** leads to the formation of methoxylated catechol **95**. The oxidation of compound **95** is easier than that of catechol **1** by virtue of the presence of an electron-donating group and so it is oxidized to



Scheme 27



Scheme 28



Scheme 29

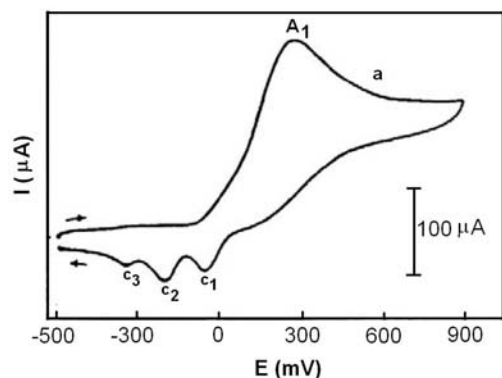


Fig. 14. Cyclic voltammogram of 1 mM catechol (**1**) in methanol containing 0.15 M NaCH₃COOH, at glassy carbon electrode. Scan rate, 50 mV s⁻¹.

o-benzoquinone **96**. In the next step, *o*-benzoquinone **96** is converted to intermediate **97**, via another Michael type reaction. Further oxidation converts intermediate **97** into the final product **98**. Accordingly, the anodic peak A₁ pertains to the oxidation of catechol **1** to the *o*-benzoquinone **1a**. Obviously, the cathodic peak C₁ corresponds to the reduction of the *o*-benzoquinone **1a**. The cathodic peaks C₂ and C₃ are correspond to the reduction of the *o*-benzoquinones **96** and **98**, respectively. The same result was obtained in electrochemical oxidation of catechol (**1** in ethanol [103].

C-N C-N Bond Formation

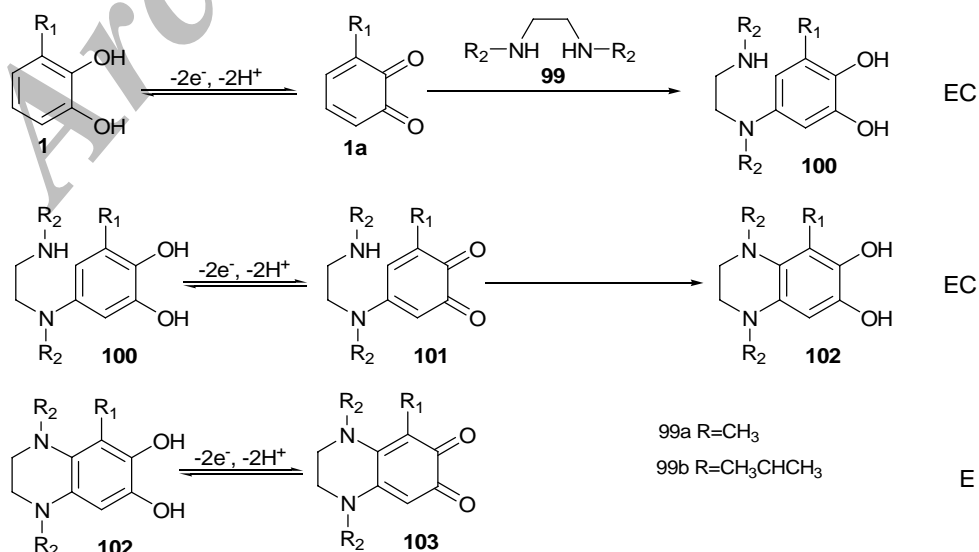
Quinoxalinedione derivatives have been used extensively as pharmaceutical agents for the treatment of different diseases [104-106]. This is a reason for the study of electrochemical oxidation of catechols (**1**) in the presence of *N,N*-dimethylethylenediamine (**99a**) and *N,N'*-diisopropylethylenediamine (**99b**) as bidentate nucleophiles with two N donors. The reaction mechanism is an *ECECE* via two inter and intramolecular N-C Michael-type addition reactions (Scheme 30) [107,108].

These works have led to the development of facile and environmentally friendly electrochemical method for synthesis of some new quinoxalinedione derivatives (**103**).

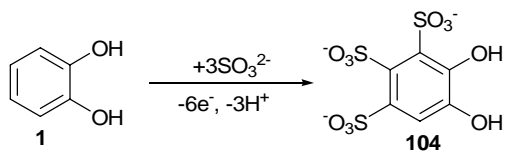
ECECEC MECHANISM

Electrochemical oxidation of catechol (**1**) in the presence of sulfite ion in aqueous phosphate buffer, pH 6.0, shows an *ECECEC* mechanism. This mechanism has been supported using diagnostic criteria of cyclic voltammetry and consumption of six electrons per molecule of catechol (**1**). According to this mechanism, catechol (**1**) during three successive *EC* process converts to trisulphonated catechol (**104**). The overall reaction mechanism is shown in Scheme 31 [109].

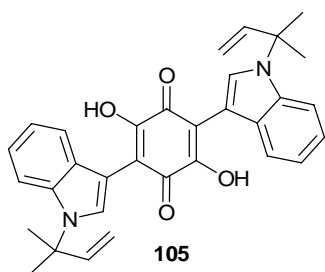
In published work, the experimental and theoretical



Scheme 30



Scheme 31



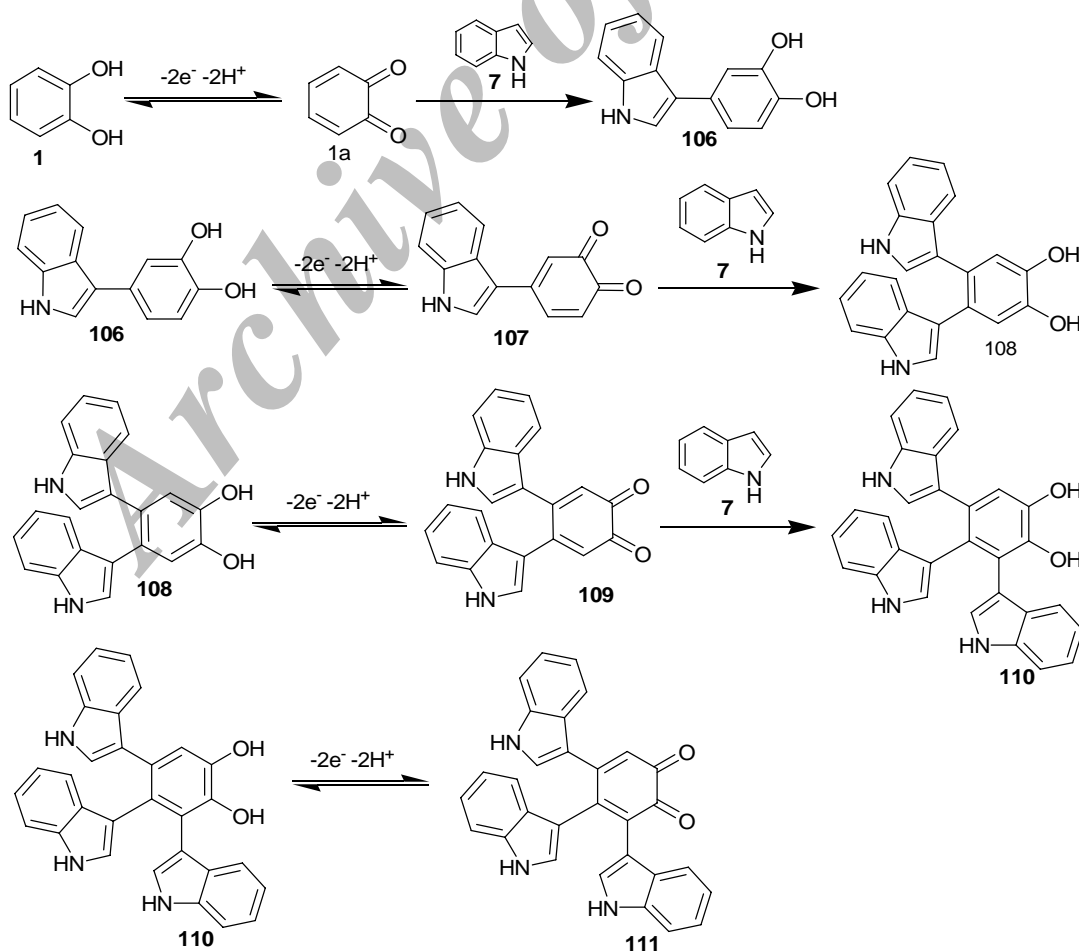
Asterriquinone A1

electrochemical methods, especially cyclic voltammetry, have been used to present new data on electrochemical sulphonation of catechol (**1**).

ECECECE MECHANISM

It is recognized that the 3-indolylbenzoquinone fragment is a core structure in a number of biologically active natural products such as asterriquinones [110]. The asterriquinones (**105**) exhibit a wide spectrum of biological activities including antitumor properties, and are inhibitors of HIV reverse transcriptase [111]. Thus, the electrochemical oxidation of catechol (**1**) has been studied in the presence of indole (**7**) as the nucleophile in a water/acetonitrile (50:50) mixture using cyclic voltammetry and controlled-potential coulometry.

The results revealed that the quinone derived from the oxidation of catechol (**1**) participates in Michael addition reactions with indole (**7**), via a novel ECECECE mechanism, converting it to the trisindolyl-*o*-quinone (**111**) (Scheme 32) [112].



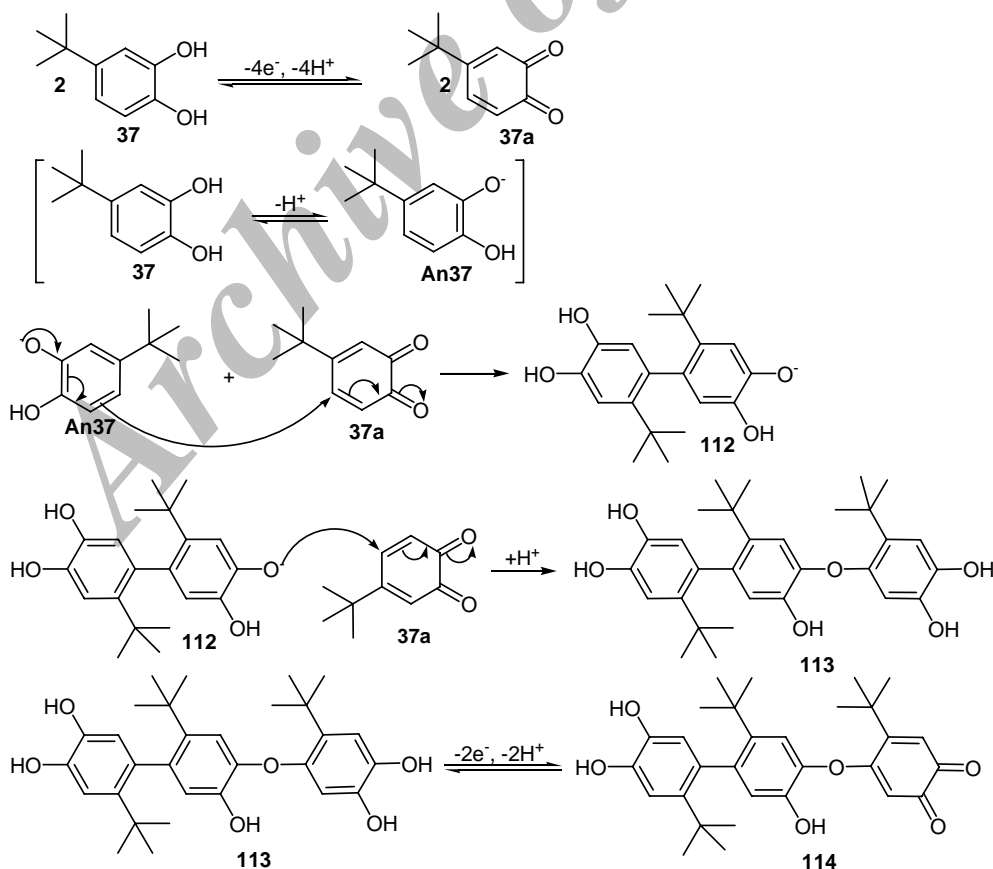
Scheme 32

Diagnostic criteria of cyclic voltammetry including the consumption of eight electrons per molecule of catechol **1**, and the mass spectra of the isolated products, confirmed the proposed mechanism (Scheme 32). According to the presented mechanism, it seems that the Michael addition reaction of **7** to *o*-benzoquinone **1a** leads to intermediate **106**. The oxidation of this compound **106** is easier than the oxidation of catechol **1** by virtue of the presence of an electron-donating group. In the next step, *o*-benzoquinone **107**, via a Michael reaction, is converted to intermediate **108**. Another oxidation and Michael addition transforms the intermediate **108** to intermediate **110**. Further oxidation converts the intermediate **110** into the final product **111**.

TRIMERIZATION MECHANISM

The electrochemical trimerization of 4-*tert*-butylcatechol (**37**) is described [113] and its mechanism has been studied in

aqueous solution using cyclic voltammetry, controlled-potential coulometry and has been confirmed by the spectroscopic data (Scheme 33). According to the voltammetric results, in electrooxidation of 4-*tert*-butylcatechol the ratio of cathodic peak current to anodic peak current (I_{pC1}/I_{pA1}) is dependent to 4-*tert*-butylcatechol concentration, potential scan rate, solution pH and temperature. This ratio decrease with (i) increasing 4-*tert*-butylcatechol concentration, (ii) decreasing potential scan rate, (iii) increasing pH and (iv) increasing temperature. Controlled-potential coulometry at E_{pA1} gave an n value of about 2 and cyclic voltammetric analysis carried out during the electrolysis shows the progressive formation of new anodic (A_2) and cathodic (C_2) peaks, parallel to the disappearance of A_1 and C_1 peaks (Fig. 15). The peaks A_2 and C_2 are related to the transformation of (**113**) to the related *o*-quinone (**114**) and vice-versa [113].



Scheme 33

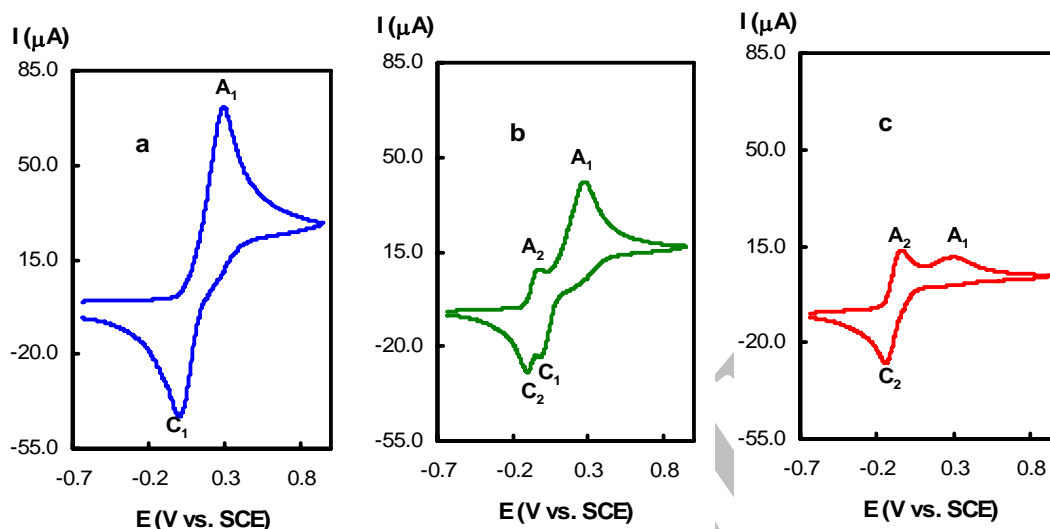


Fig. 15. Cyclic voltammograms of 1 mmol 4-*tert*-butylcatechol (**37**) in 0.15 M sodium acetate at glassy carbon electrode during controlled-potential coulometry at 0.40 V vs. SCE, after consumption of: 0 (a), 0.98 (b) and 1.71 F mol⁻¹. (c) Scan rate 50 mV s⁻¹.

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