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Electrooxidation of Catechols in the Presence of Sulfite: Presentation of a Facile and Green Method for Aromatic Sulfonation

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Electrochemical oxidation of catechols (**1a-e**) has been studied in the presence of sulfite ion (**3**) as nucleophile in aqueous solution, using cyclic voltammetry and controlled-potential coulometry. The results indicate the participation of catechols (**1a-e**) in Michael reaction with **3** to form the corresponding sulphonated derivatives. Based on ECE, ECEC or ECECEC mechanism, the homogeneous rate constants were estimated by comparing the experimental cyclic voltammetric responses with the digital simulated results.

Keywords: Catechol, Sulfite, Michael addition, Sulfonation

1. INTRODUCTION

Sulphation plays a critical role modulating the biological activity, and facilitating the elimination, of potent endogenous chemicals including steroids, thyroid hormones, and catechols, and also many synthetic chemicals or xenobiotics [1]. Sulphation is conjugation reaction by which a wide variety of substances are converted into sulphate conjugates, by sulphotransferases (SULTs) Sulphotransferases represent an important family of phase II enzymes capable of transferring sulfate groups [2]. Since many drugs and toxic compounds contain acceptor groups for these conjugation reactions, and because usually the biological effects of the substrates disappear after the conjugation, they are considered to be 'detoxifying reactions [3]. In direction of more investigation of sulphonation chemistry, we used the experimental and theoretical electrochemical methods, especially cyclic voltammetry, to present new data on electrochemical sulphation of catechol and its derivatives as natural catecholamines building blok [4].

2. EXPERIMENTAL PART

2.1. Apparatus

Cyclic voltammetry, controlled-potential coulometry and preparative electrolysis were performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (2 mm^2 area) and platinum wire was used as the counter electrode. The working electrode used in controlled-potential coulometry was an assembly of four carbon rods (31 cm^2) and a large platinum gauze constituted the counter electrode. The working electrode potentials were measured versus SCE (all electrodes from AZAR Electrodes).

2.2. Reagents

All chemicals (catechols and sodium sulfite) were reagent- grade materials from Aldrich and phosphoric acid, acetic acid, ammonia, etc. were of pro-analysis grade from E. Merck. These chemicals were used without further purification.

The homogeneous rate constants were estimated by analyzing the cyclic voltammetric responses using the DigiElch simulation software [5].

3. RESULTS AND DISCUSSION

Cyclic voltammetry of 1.0 mM of 4-*tert*-butylcatechol (**1a**) in aqueous solution containing 0.2 M phosphate buffer (pH 6.0), shows one anodic (A_1) and corresponding cathodic peak (C_1), which corresponds to the transformation of 4-*tert*-butylcatechol (**1a**) to *o*-benzoquinone (**2a**) and vice versa within a quasi-reversible two-electron process (Figure 1, curve a). A peak current ratio (I_{C1p} /I_{A1p}) of nearly unity, particularly during the recycling of potential, can be considered as criteria for the stability of *o*-quinone produced at the surface of electrode under the experimental conditions. In other word, any hydroxylation [6-9] or dimerization [10, 11] reactions are too slow to be observed in the time scale of cyclic voltammetry. The oxidation of 4-*tert*-butylcatechol (**1a**) in the presence of sulfite (**3**) as nucleophile in aqueous solution containing 0.2 M phosphate buffer (pH 6.0), was studied in some details. Figure 1 (curve b) shows the cyclic voltammogram obtained for a 1.0 mM solution of **1a** in the presence of 1.0 mM of sulfite ion (**3**). The voltammogram exhibits a significant decreasing in cathodic peak. In this figure 1, curve c is the voltammogram of sulfite.

Furthermore, it is seen that proportional to the augmentation of sulfite concentration ratio to 4-*tert*-butylcatechol, the height of C_1 peak increases (Figure 2 curves a–d). A similar situation is observed when the potential sweep rate increases. A plot of peak current ratio (I_{C1p} /I_{A1p}) versus scan rate for a mixture of 4-*tert*-butylcatechol and sulfite (**3**) confirms the reactivity of **2a** towards sulfite (**3**), appearing as an increase in the height of the cathodic peak C_1 at higher scan rates. On the other hand, the current function for A_1 peak (I_{A1p} /$v^{1/2}$), decreases with increasing the scan rate and such a behavior is adopted as indicative of ECE mechanism which the second E is performed in more positive potential [12](Scheme 1).

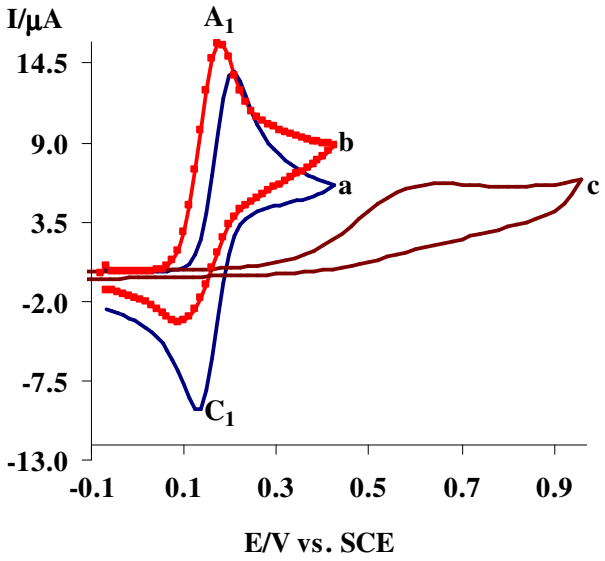


Figure 1. Cyclic voltammograms of 1.0 mM 4-*tert*-butylcatechol: (a) in the absence, (b) in the presence of 1.0 mM sodium sulfite (c) 1.0 mM sodium sulfite in the absence of 4-*tert*-butylcatechol at a glassy carbon electrode in phosphate buffer solution (0.2 M, pH= 6.0) Scan rate: 100 mVs^{-1}.

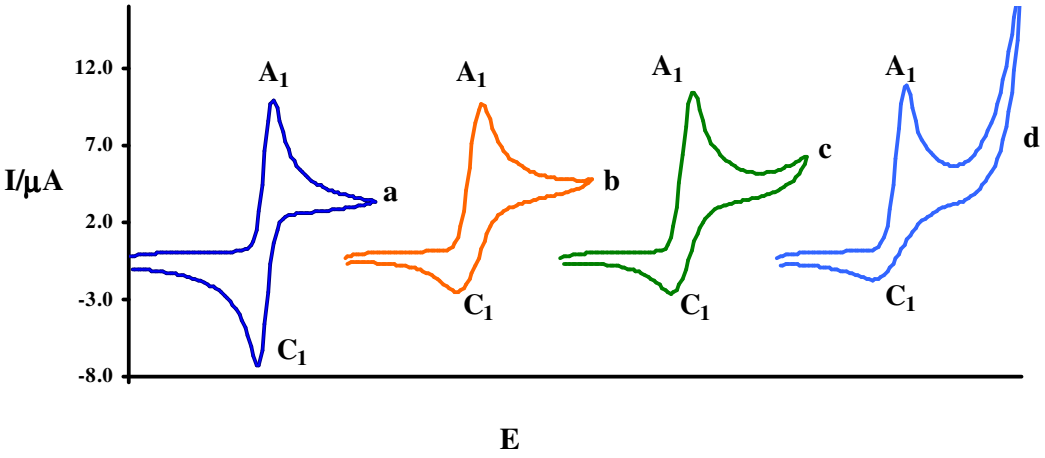


Figure 2. Typical voltammograms of 1.0 mM 4-*tert*-butylcatechol in the presence of 0.0 (a), 1.0 (b), 2.0 (c) and 5.0 (d) mM sodium sulfite at a glassy carbon electrode in phosphate buffer solution (0.2 M, pH= 6.0). Scan rate: 50 mVs^{-1}.

In the case of 4-methylcatechol the result is the same as the 4-*tert*-butylcatechol. Figure 3 shows the cyclic voltammograms of catechol 1.0 mM in the presence of various concentrations of sulfite ion. The existence of four anodic peaks (A_1, A_2, A_3 and A_4) and also the result of controlled-potential coulometry (discussed below) let us to propose an ECECEC mechanism that is shown in Scheme 2. Such cyclic voltammetry are also obtained for 3,4-dihydroxybenzoic acid and 3,4-dihydroxybenzonitrile in the presence of sulfite ion.

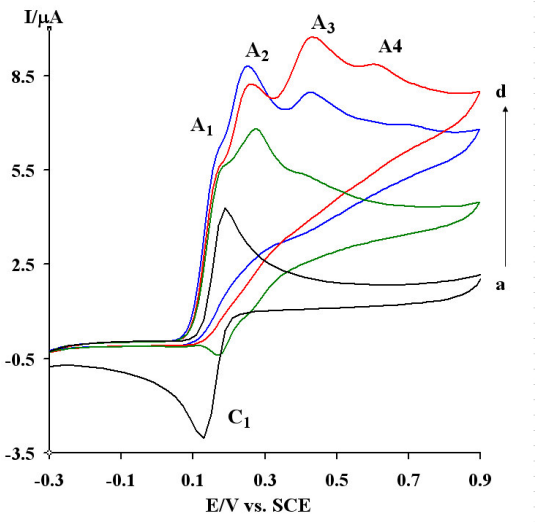


Figure 3. Typical voltammograms of 1.0 mM catechol in the presence of 0.0 (a), 1.0 (b), 2.0 (c) and 5.0 (d) mM sodium sulfite at a glassy carbon electrode in phosphate buffer solution (0.2 M, pH= 6.0). Scan rate: 10 mVs^{-1}.

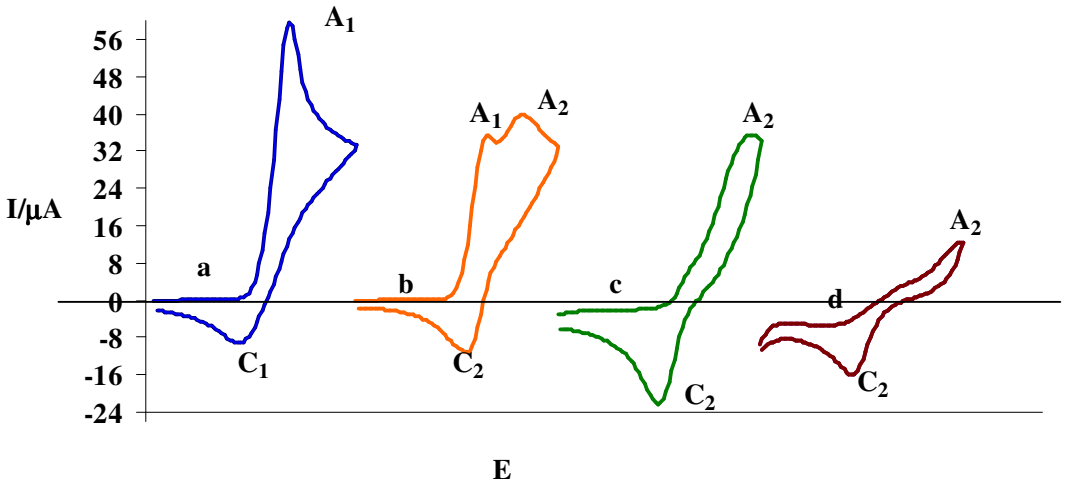
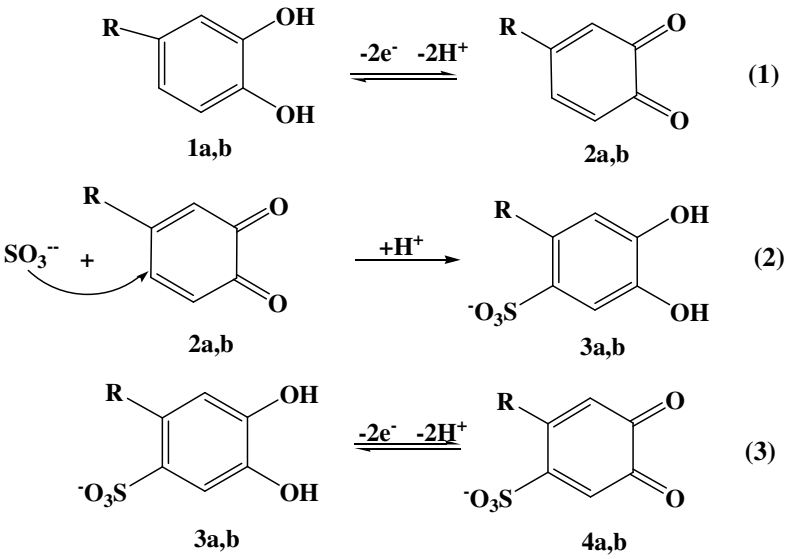


Figure 4. Cyclic voltammogram of 0.25 mmol 4-*tert*-butylcatechol in the presence of 1.25 mmol sodium sulfite at a glassy carbon electrode during controlled potential coulometry after consumption of: (a) 0, (b) 20, (c) 48, (d) 96 C. Scan rate: 25 mVs^{-1}.

Controlled-potential coulometry was performed in aqueous solution containing 0.25 mM of **1a** and 1.25 mM of sulfite (**3**) at 0.22 V versus SCE. The monitoring of electrolysis progress was carried out by cyclic voltammetry (Figure 4). It is shown that, proportional to the advancement of coulometry, the height of anodic peak A_1 and cathodic peak C_1 decrease and a new anodic peak (A_2) at the more positive potentials (0.33 V vs. SCE) appears. The A_1 disappear completely after consumption of 48

coulomb of electricity. Then the oxidation potential is increased to potential of A_2. After total consumption of 96 C of electricity at 0.33 V vs. SCE potential, all anodic and cathodic peaks disappear. The related calculations show that the anodic (A_1 and A_2) and cathodic (C_1) peaks disappear when the charge consumption becomes about $4e^-$ per molecule of **1a**. The obtained cyclic voltammogram of the reaction solution after total consumption of 96 C of electricity shows a negative current at starting potential (-0.3 V vs. SCE). On the other hand the color of solution is changed to orange at the end of coulometry, that both observations are evidences to oxidized form (quinone) of product.

These observations allow us to propose the pathway in Scheme 1 for the electrooxidation of **1a** in the presence of sulfite (**3**).

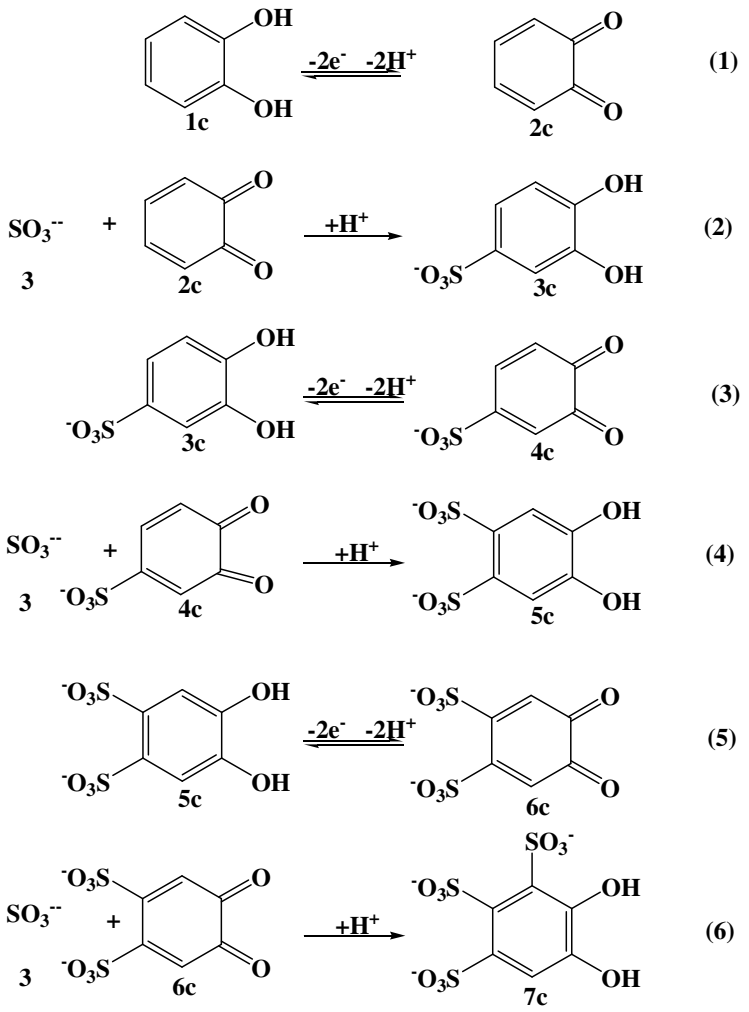


R= *t*-Bu 1a, 2a, 3a, 4a,
R= Me 1b, 2b, 3b, 4b

Scheme 1

Based on these results, the anodic peak (A_2) is corresponded to oxidation of **3a**. The result for 4-methylcatechol was as same as 4-*tert*-butylcatechol. For catechol, 3,4-dihydroxybenzoic acid and 3,4-dihydroxybenzonitril uncolored solution and also positive current for starting point of cyclic voltammograms after consumption of $6e^-$, $4e^-$ and $4e^-$ per molecule (respectively), are criteria for ECECEC (Scheme 2)and ECEC (Scheme 3) mechanism.

According to our results, it seems that the 1,4-(Michael) addition reaction of **3** to *o*-quinones (**1a-e**) (Eq. (2)) is faster than other secondary reactions, leading to the intermediate **3a-e**. The oxidation of these compounds (**3a-e**) is harder than the oxidation of parent starting molecules (**1a-e**) by virtue of the presence of electron-withdrawing group.

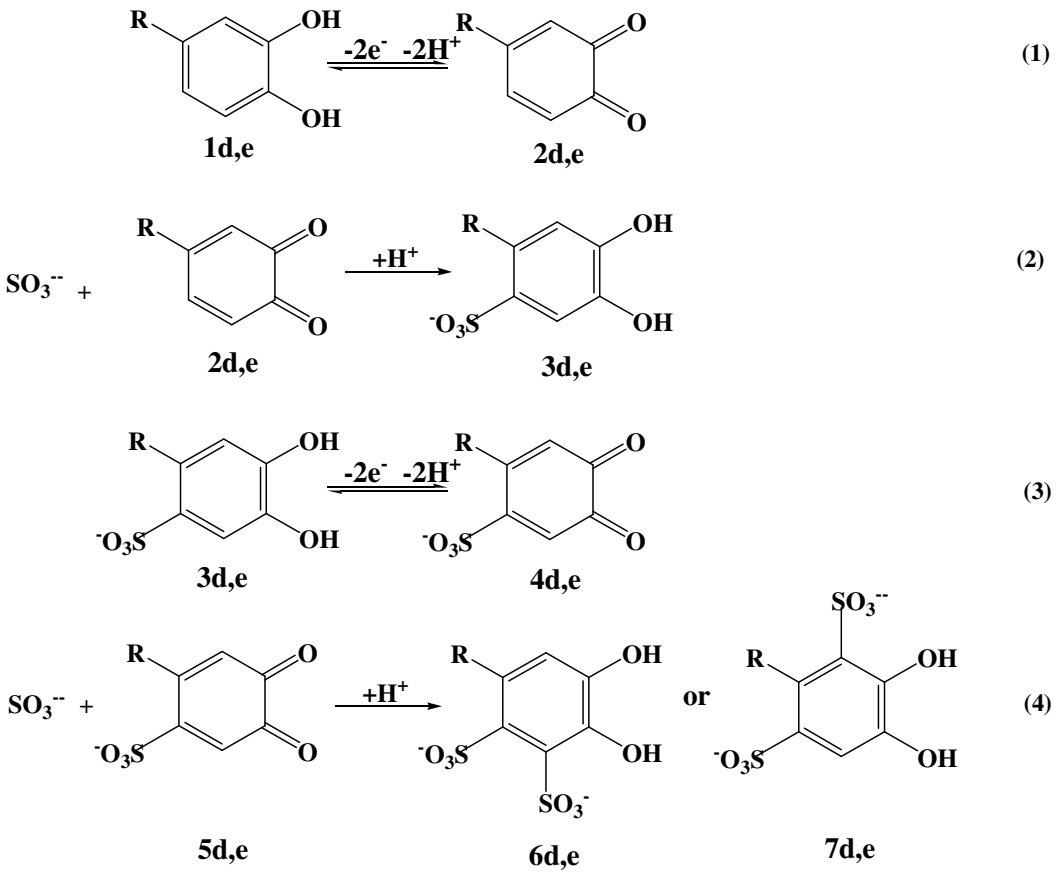


Scheme 2

Cyclic voltammograms of 1.0 mM solution of 4-*tert*-butylcatechol (**1a**) in the presence of sulfite in aqueous solutions at various pHs are shown in figure 5. In acidic medium (pH 3.0) (Figure 5, curve a) cyclic voltammogram doesn't show reactivity between *o*-quinone and sulfite. Clearly it is because of protonation of sulfite ion in acidic medium. Figure 5, b-d show the cyclic voltammograms of 4-*tert*-butylcatechol (**1a**) in the presence of sulfite in aqueous solutions at 4.0, 5.0 and 6.0 pHs. A peak current ratio (I_{C1p} /I_{A1p}) of nearly unity for 4-*tert*-butylcatechol, in investigated pH range can be considered as criteria for the stability of *o*-quinone (**2a**) produced at the surface of electrode under the experimental conditions (Figure 5, e). On the other hand decreasing of (I_{C1p} /I_{A1p}) for oxidation of 4-*tert*-butylcatechol in the presence of sulfite ion indicates the rate of the reaction increases by increasing pH [13]. The investigation of pH effect for catechol, 4-methylcatechol, 3,4-dihydroxybenzoic acid and 3,4-dihydroxybenzonitrile show same rule.

The scheme for the electrochemical oxidation of catechols in the presence of sulfite ion were proposed and tested by digital simulation [14]. The simulation was carried out assuming semi-infinite one-dimensional diffusion and planar electrode geometry. The experimental parameters entered for digital simulation consisted of the following: analytical concentration of catechols 1.0 mM, the transfer

coefficients (α) were assumed to be 0.5 and the formal potentials were obtained experimentally as the midpoint potential between the anodic and cathodic peaks (E_{mid}) and the heterogeneous rate constants (0.002 cm s^{-1}) for oxidation of catechols were estimated by use of an experimental working curves [15]. All these parameters were kept constant through out the fitting of the digitally simulated voltammogram to the experimental data. The parameter k was allowed to change through the fitting processes. Further refinement was accomplished by holding the best-fit parameters and varying (slightly) of D ($1.0 \pm 0.2 \times 10^{-5}$ cm^2 s^{-1}) throughout the fitting process. The simulation was performed base on ECE electrochemical mechanism for 4-*tert*-butylcatechol and 4-methylcatechol, ECECEC for catechol and ECEC for 3,4-dihydroxybenzoic acid and 3,4-dihydroxybenzonitrile. The calculated values of rate constants for first reaction of *o*-benzoquinones (**2a–e**) with sulfite ion (**3**) have shown in Table 1. As shown in Table 1, the magnitude of homogeneous rate constant (k) is dependent on the nature and position of the substituted group on the catechol ring. The presence of electron-donating groups such as methyl or *tert*-butyl on catechol ring causes a decrease in k. In contrast, in the case of **1d** and **1e** the presence of carboxylic or nitrile group with electron-withdrawing character causes an increase in k.



R= COOH 1d, 2d, 3d, 4d, 5d, 6d, 7d
R= CN 1e, 2e, 3e, 4e, 5e, 6e, 7e

Scheme 3

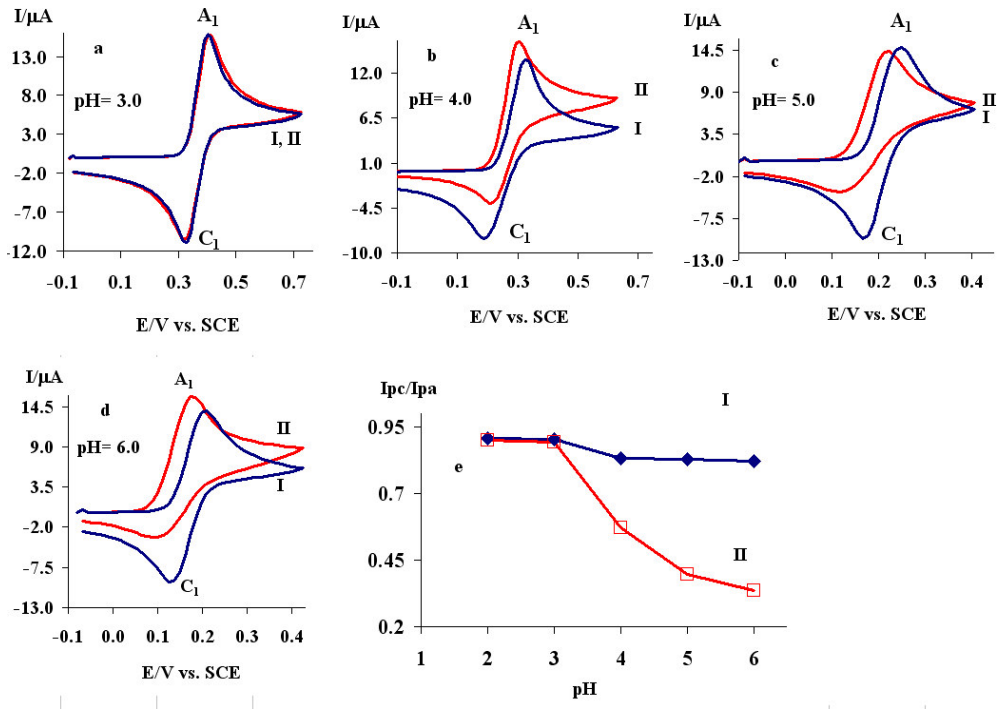


Figure 5. Cyclic voltammograms of 1.0 mM 4-*tert*-butylcatechol: (I) in the absence, (II) in the presence of 1.0 mM sodium sulfite at a glassy carbon electrode in solution containing 0.2 M phosphate or acetate buffers. (a) pH= 3.0, (b) pH= 4.0, (c) pH= 5.0, (d) pH= 6.0 and (e) analysis of variation of I_{pc}/I_{pa} vs. pH. Scan rate: 100 mVs^{-1}.

Table 1. The calculated values of rate constants for first reaction of *o*-benzoquinones (**2a–e**) with sulfite ion

Entry	K/ L mol^{-1} s^{-1}	Relative rate constant
4-*tert*-butylcatechol	703± 2.67	1
4-metylcatechol	1050± 4.71	1.5
catechol	1995± 1.49	2.8
3,4-dihydroxybenzoic acid	5500± 13.6	7.8
3,4-dihydroxybenzonitrile	10066± 27.2	14.3

The rate constants (k) can be related with the Hammett ρ–σ parameters, where the Hammett equation is

$$\log k_i = \log k_0 + \rho\sigma$$

where k_i is the rate constant for substituted catechol, k_0 is the rate constant for catechol, σ is a constant characteristic of a given substituent group [16], and ρ is the slope of the $\log k_i$ - σ graph. The Hammett plot is shown in figure 6. The ρ value is 1.39. This positive ρ value means that the transition

state has a substantial negative charge because the reaction rate is increased significantly for electron-withdrawing substituents. This result is consistent with the attack of sulfite ion to the *o*-benzoquinone.

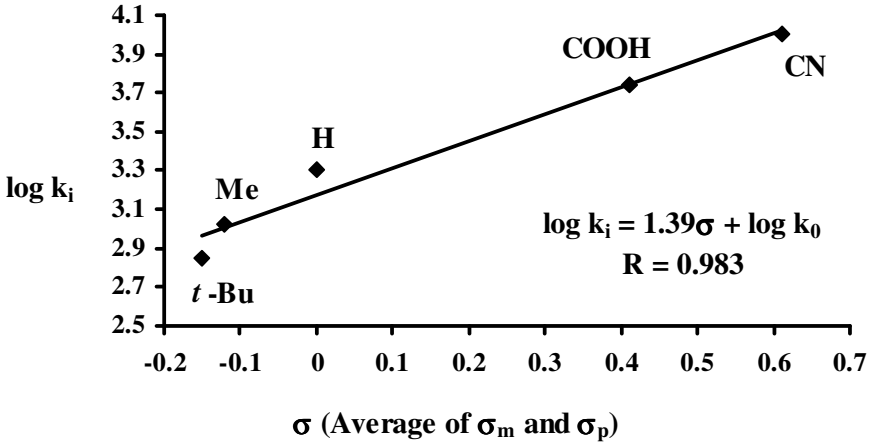


Figure 6. Hammet plot for studied catechols

4. CONCLUSIONS

The results of this work show that catechols are oxidized in aqueous solutions to their respective *o*-benzoquinones. The generated quinones are then attacked by sulfite ion to form sulfocatechols. The overall reaction mechanism for anodic oxidation of catechols in the presence of sulfite ion as nucleophile is presented in Schemes 1-3. In addition, we examined the kinetics of the reactions of the electrogenerated quinones with sulfite ion by cyclic voltammetry technique. The cyclic voltammograms were digitally simulated under various electrochemical mechanisms. The simulated cyclic voltammograms show good agreement with those obtained experimentally. The results of the homogeneous rate constants (k) are presented in Table 1. Furthermore, the sulphonation of aromatic compounds mostly performed based on their nucleophilicity, however, in this work; we investigate sulphonation of catechols based on electrophilicity of electrochemically generated *o*-benzoquinone. This is a good example of conversion of a nucleophile to electrophile via an electrochemical process. The presented sulfonation method is an advancement from green chemistry point of view.

ACKNOWLEDGMENTS

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