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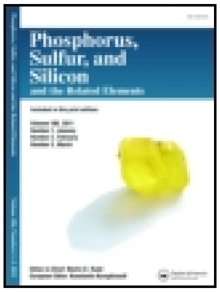

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Electrochemical Oxidation of Catechols in the Presence of Triethylphosphite

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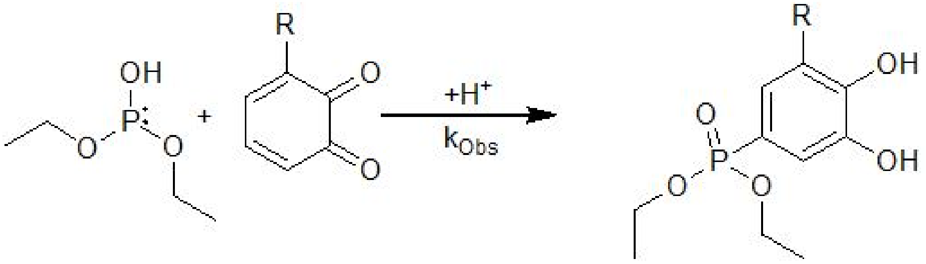
The mechanism of electrochemical oxidation of catechol and some of its derivatives have been studied in the presence of triethyl phosphite as a nucleophile in aqueous solution. Voltammetric studies indicate that the quinones derived from catechol, and its derivatives, participate in Michael addition reaction with triethyl phosphite. The reaction mechanism consists of electron transfer followed by a chemical reaction which is named as an EC mechanism. The homogeneous rate constants (k_{obs}) were estimated by comparing the experimental cyclic voltammograms with the digitally simulated voltammograms based on EC mechanism. Also the effects of nucleophile concentration and substituted group of catechols on voltammetric behavior and the rate constants of chemical reactions were examined.



Keywords: cyclic voltammetry; catechol; triethyl phosphite; digital simulation

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INTRODUCTION

Among electrochemical methods, cyclic voltammetry is one of the most convenient and most frequently used techniques for kinetic and thermodynamic study of the coupled electrochemical reactions. It consists of simple, low-cost and rapid potentiodynamic measurement. [1] 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 the chemical reaction to the scan rate. The effect of the scan rate is shown in the shape of the cyclic voltammograms which may be useful in the obtaining information about the mechanism of reactions. [2] Furthermore, among organic compounds, catechols are known as electrochemically active species with a relatively simple and quasi-reversible electron transfer. [3] The oxidation potential of catechol is low and the product of oxidation is *o*-quinone and it is a reactive species that is produced only in-situ. [4] Electrochemical generation of *o*-quinone followed by a desired chemical reaction is a convenient tool for electrochemical synthesis of new catechol derivatives. [5] Voltammetric study of catechol derivatives in the presence of variety of organic compounds that undergo chemical reactions with *o*-quinones and their potential application in organic synthesis has been published in a recently published review. [6] In addition, catechol derivatives play an important role in the biologically important phenomena such as antioxidant activity. Finally interest in the preparation of organophosphorus compounds has continued to expand in recent years. This is a direct result of developing applications for phosphorus compounds in numerous synthetic procedures as well as an understanding of the role of the element in biological systems [7] synthetic intermediates [8] coordination chemistry as ligands [9] and agricultural chemicals. [10-12] There are few reports on the electrochemical oxidation of catechols in the presence of phosphorus containing nucleophile such as triphenyl phosphine. [13,14] The aim of this study is the kinetic study of C-P bond formation based on the electrooxidation of catechol derivatives in the presence of triethyl phosphite. Also there are reports that the reaction of trialkylphosphites with o-quinones leads to the formation of pentaoxyphosphorane compounds.[15]

RESULTS AND DISCUSSION

Voltammetric Study

The electrochemical study of a 1.0 mM solution of catechol at a glassy carbon electrode in aqueous solution containing phosphate buffer (pH 7.0) as supporting electrolyte was performed using cyclic voltammetry. The voltammogram shows one anodic (A_1) and corresponding cathodic peak (C_1), at 0.35 and -0.01 V *vs.* Ag/AgCl (Fig. 1, curve a). Fig. 1 curve b shows also the cyclic voltammogram of catechol in the presence of triethyl phosphite; the most important differences between the voltammograms are decreasing the magnitude of cathodic peak (C_1) currents and appearing new anodic peak (A_2) at more positive potentials. This reaction causes to removing *o*-quinone from the electrode surface and decreasing the related currents. Also the product of chemical reaction is electroactive and undergoes electron transfer at more positive potentials (A_2 Anodic peak).

Figure 1

An important parameter in the study of coupled chemical reaction with electron transfer is the ratio of rate constant of chemical reaction to the scan rate of voltammetric experiments, the time scale of a voltammetric experiment is inversely related to scan rate. [16] Therefore the electrochemical studies were extended at various scan rates (time scale).

Figure 2

Figure 2 shows the voltammograms of catechol in the presence of triethylphosphite at pH 7.0 with various scan rates. At low scan rate the cyclic voltammograms don't show any cathodic peak (C_1); the cathodic currents reach to zero at very low scan rates. By increasing scan rate the height of C_1 peak increases and reach to its maximum value; same as absence of triethyl phosphite. Inset of Figure 2 shows variation of cathodic to anodic peak currents ratio versus scan rate for a mixture of catechol and triethyl phosphite. This is a good criterion for the reactivity of electrochemically produced *o*-quinone toward triethyl phosphite. Normalized cyclic voltammograms are obtained by dividing the current of cyclic voltammograms by the square root of the scan rate. [17] Multiple files at different scan rates can be normalized and overlaid for obtaining more information.

Figure 3

Figure 3 shows the normalized current voltammograms and variation of normalized peak currents at various scan rates. As shown in this figure the normalized currents of A_1 peak don't change considerably. It confirms that addition of triethyl phosphite doesn't affect the oxidation of catechol. Significant increase in the height of C_1 peak currents parallel to increasing scan rates approve that the electron transfer of catechol followed by a chemical reaction in the presence of triethyl phosphite [18]. The voltammetric results are in good agreement with an EC mechanism where ‘E’ represents an electron transfer at the electrode surface, and ‘C’ represents a homogeneous chemical reaction [18]. Based on the above results the following mechanism is proposed for the electrochemical oxidation of catechol in the presence of triethyl phosphite.

Scheme 1

Based on proposed mechanism and the reactivity of triethyl phosphite toward water and formation of diethyl phosphite [19] the addition of diethyl phosphite to the *o*-quinone is another competitive reaction but its reactivity is less than triethyl phosphite [20].

The results for the investigation of the electrochemical behavior of 3-methylcatechol and 3-methoxycatechol in the presence of triethyl phosphite were the same as those obtained for catechol. Figure 4 shows the voltammograms of catechol and 3-methoxycatechol in the presence of triethyl phosphite. It is shown that in this figure the height of cathodic peaks for 3-methoxycatechol is more than catechol under same conditions. Then the reactivity of produced *o*-quinone from oxidation of 3-methylcatechol is less than catechol toward the Michael addition reaction.

Figure 4

In basic solutions, the height of catechol reduction peak decreases considering some side reactions such as the coupling of anionic or hydroxide ion with electrochemically produced *o*-quinones. But the peak current ratio near unity at neutral and acidic solutions can be considered as relative stability of the *o*-quinone.[2] Therefore the effect of pH has been studied at pHs lower than 7.0. Voltammetric studies at various pHs show that the cathodic to anodic peak currents ratio decrease with increasing pH. The effect of pH and substituent will be discussed in more details and quantitatively based on simulation results in the next section.

Kinetic Studies

A proposed scheme for the electrochemical oxidation of catechols in the presence of triethyl phosphite was tested by digital simulation. On the basis of an *EC* mechanism, the observed homogeneous rate constants (k_{obs}) for the reaction of *o*-quinones with triethyl phosphite have been estimated by comparison of the simulation results (Fig. 5 curves b) with experimental cyclic voltammograms (Fig. 5 curves a). The transfer coefficient (α) was assumed to be 0.5, and the formal potentials were obtained experimentally as the average of the two peak potentials (Ep_{A1} and Ep_{C1}) observed in cyclic voltammetry. The heterogeneous rate constants were estimated by the use of an experimental working curve.[21]All these parameters were kept constant throughout the fitting of the digitally simulated voltammograms to the experimental data. The parameters k_{obs} were allowed to change through the fitting processes. There are good agreements between the simulated voltammograms with those obtained experimentally (Figure 5).

Figure 5

The obtained homogeneous rate constants are given in Table 1. As shown in Table 1, the magnitudes of homogeneous rate constants are dependent on the nature of the substituted group on the catechol ring. Same as the previously reported result on this Michael addition reactions.[14] the presence of electron-donating groups such as methyl or methoxy on catechol ring causes a decrease in the rate constant of reactions. The observed rate constants (k_{obs}) increase linearly as a function of triethyl phosphite concentrations. These results are consistent with the attack of triethyl phosphite as a nucleophile. [13] The observed rate constants of coupling reaction of oxidized catechol with triethyl phosphite at various pHs and based on these results the rate of reaction enhances at high pH values.

Table 1

CONCLUSION

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 triethyl phosphite to form alkyl phosphonate derivatives. The overall reaction mechanism is presented based on the voltammetric results and its diagnostic criteria and believed to be an EC mechanism. This is a good example of electrochemical activation that leads to formation of a carbon-phosphorous bond. C-P bond formation may be interesting from the synthetic aspect of view due to the importance of phosphorous containing aromatic compounds[7]. The cyclic voltammograms were digitally simulated under EC mechanism and the effect of some experimental conditions and substituents has been discussed. The simulated cyclic voltammograms show good agreement with those obtained experimentally. The results of the homogeneous second order rate constants (k_{obs}) are presented in Table I that confirms the decrease of rate constants in the presence of electron-donating groups. Furthermore the synthetic application of this reaction and the effect of nucleophile substituents are under investigation in our research group.

Experimental

Apparatus

Cyclic voltammetric studies were performed using a Behpajoh model BHP-2062 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8mm diameter), and platinum wire was used as counter electrode. The working electrode potentials were measured versus Ag/AgCl (all electrodes from AZAR Electrodes). The homogeneous rate constants were estimated by analyzing the cyclic voltammetric responses, using the CVSIM simulation software. [22]

Reagents and solutions

Catechols, and triethyl phosphite were reagent-grade materials; sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium phosphate, and phosphoric acid were reagent-grade materials, from E. Merck, respectively. These chemicals were used without further purification. The stock solutions of the catechols were prepared fresh daily by dissolving the compounds in distilled water. Also the stock solution of triethyl phosphite was prepared by dissolution in water/acetonitrile (50/50 v/v) mixture. Samples were prepared by taking the appropriate aliquots from the stock solutions followed by dilution with buffer solutions. All voltammetric experiments were performed in water/acetonitrile (20/80 v/v) solution.

Compound characteristics

Controlled-potential coulometry was performed in water/acetonitrile (20/80 v/v) solution containing 1 mmol of catechol and 1 mmol of triethyl phosphite at 0.48 V versus Ag/AgCl. Voltammetric analysis carried out during the electrolysis shows the progressive decreasing and disappearance of A_1 peak . All anodic and cathodic peaks disappear when the charge consumption becomes about $2e^-$ per molecule of catechol.

diethyl 3,4-dihydroxyphenylphosphonate (5a) ($C_5H_{15}O_5P$). ^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 1.31 (t, 6H), 3.64 (m, 4H), 6.59 (m, 1H), 6.91 (s, 1H),6.98 (d, 1H), 8.9 (br, 2OH); MS (70 eV, EI): m/z (%): 247 (2), 236 (4), 185 (3), 165 (4) ,158 (5), 152 (11), 148 (3), 139 (10), 111 (55), 97 (100); IR (KBr): ν(cm^{-1}) = 3449, 2919, 1652, 1462, 1432, 1268, 1170, 1057.

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Figures Caption

Figure 1 Cyclic Voltammograms of 1.0 mM catechol: (a) in the absence and (b) in the presence of 5.0 mM triethylphosphite in phosphate buffer solution (pH=7, c=0.2 M) at glassy carbon electrode, scan rate: 20 mV s^{-1}.

Figure 2 Cyclic Voltammograms of 1.0 mM catechol in the Presence of 5.0 mM triethyl phosphite at various scan rates; scan rate from (a) to (d) are: 10, 20, 40, 80 mV s^{-1}.

Figure 3 Normalized cyclic Voltammograms of 1.0 mM catechol in the Presence of 5.0 mM triethyl phosphite at various scan rates; scan rate from (a) to (d) are: 10, 20, 40 and 80 mV s^{-1}.

Figure 4 Cyclic Voltammograms of (a) catechol and (b) 3-methoxycatechol in the presence of 5.0 mM triethyl phosphite in phosphate buffer solution (pH=7), scan rate: 40 mV s^{-1}.

Figure 5 Experimental (curves a blue) and simulated (curves b red) cyclic voltammograms of 1.0 mM catechol in the presence of 5.0 mM triethyl phosphite. Scan rate: 80 mV s^{-1}.

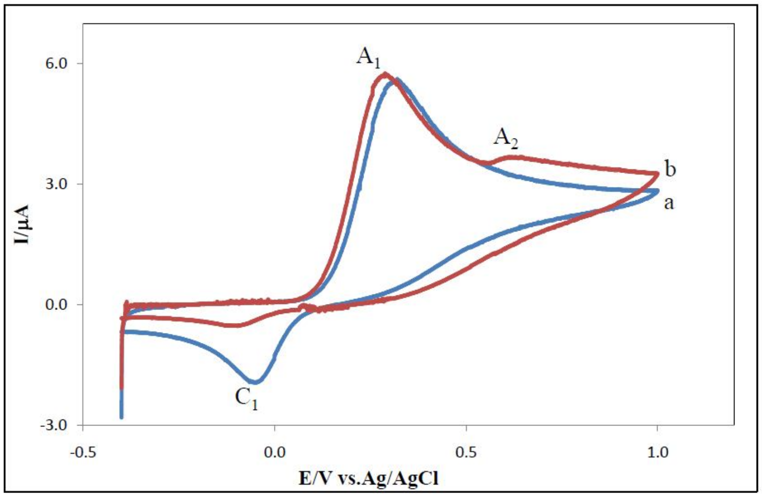


Figure 1.

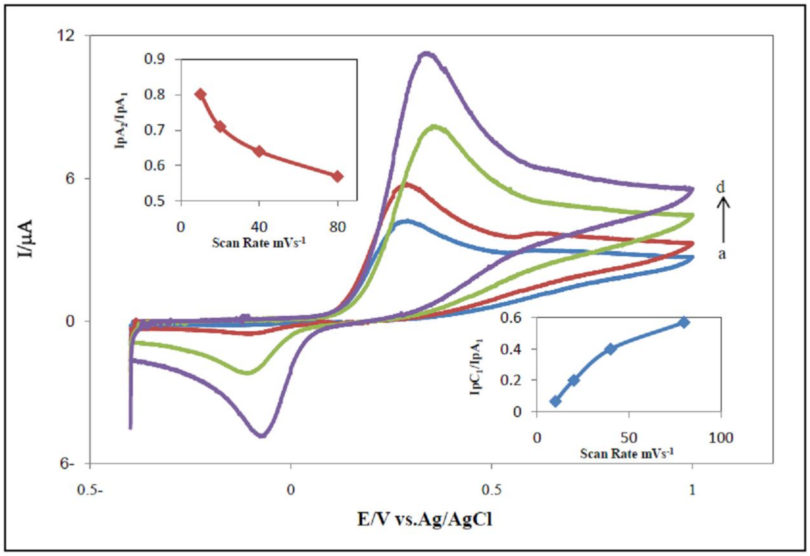


Figure 2

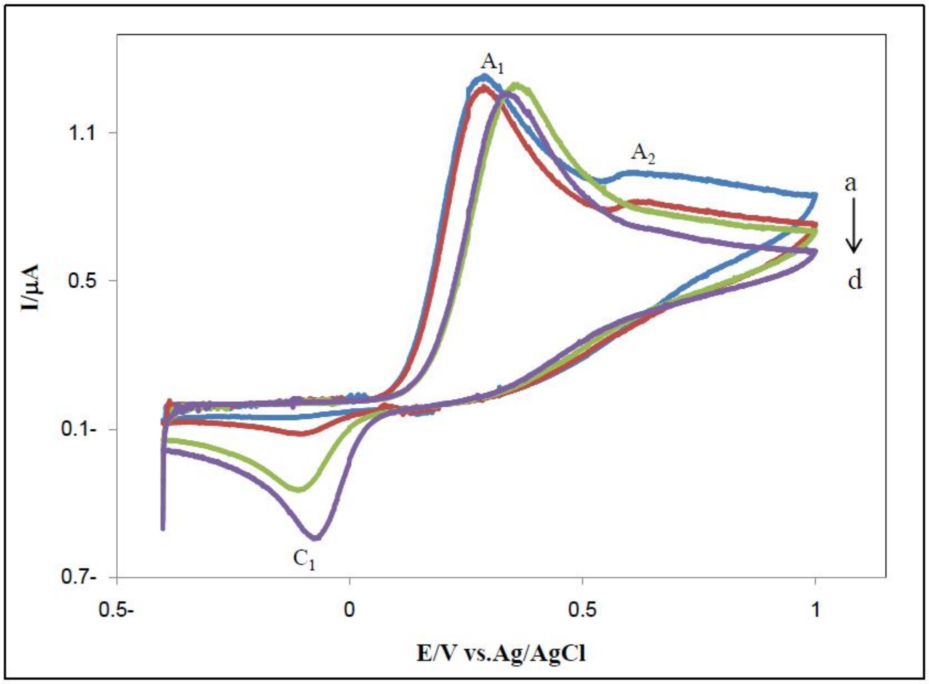


Figure 3

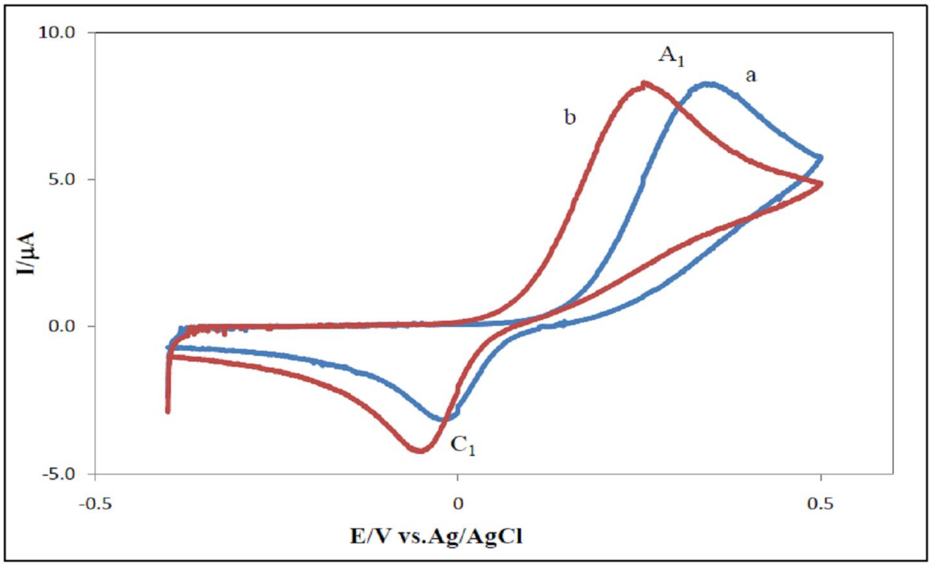


Figure 4

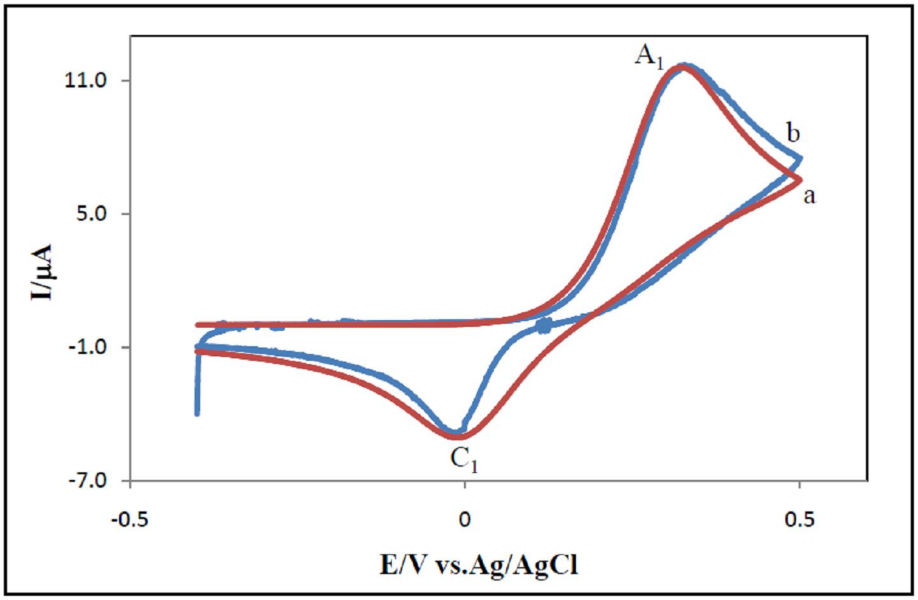
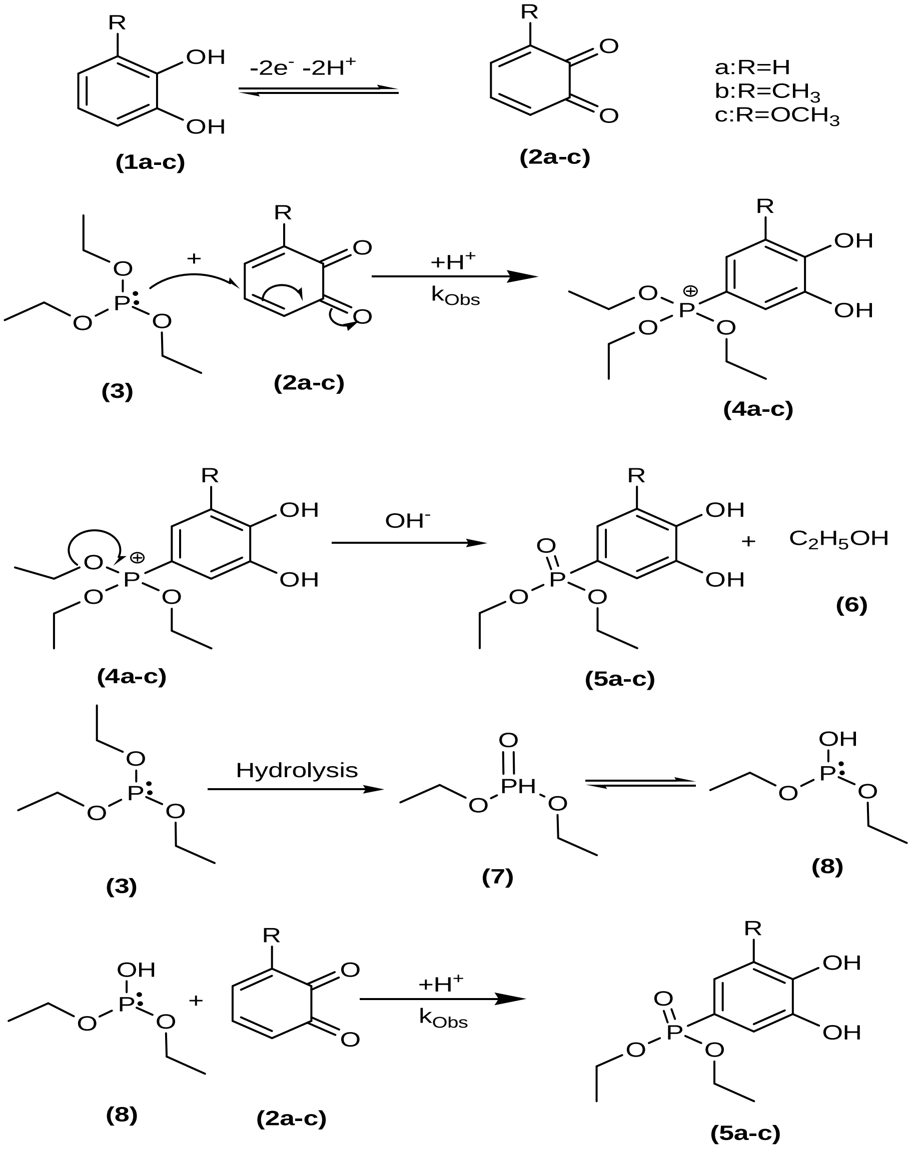


Figure 5

Table 1 The observed homogeneous rate constants (k_{obs}) of the reaction of electrochemically generated o-quinones with triethyl phosphite

Catechol derivatives	k_1 /$M^{-1}s^{-1*}$
Catechol	0.057±0.004
3-Methyl catechol	0.040±0.003
3-Methoxy catechol	0.030±0.003

* Each value is the average of four independent measurements.



Scheme 1. Proposed mechanism for electrochemical oxidation of catechols in the presence of triethyl phosphite.