Electrochemical oxidation of catechol in the presence of cyclopentadiene. Investigation of electrochemically induced Diels–Alder reactions†

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We describe the synthesis and kinetic evaluation of compounds from [4 + 2] alone and [4 + 2] followed by [2 + 2] cycloaddition reactions of electrochemically generated *o*-benzoquinone with 1,3-cyclopentadiene.

We report the first successful electrochemical study, electrochemical synthesis and kinetic evaluation of oxidation of catechol in the presence of 1,3-cyclopentadiene. Previously we have shown that catechols can be oxidized electrochemically to *o*-benzoquinones and the formed quinones can be attacked as Michael acceptors by a variety of nucleophiles.[1] In contrast to our previous works, in this work the electro-generated *o*-benzoquinone is used as a dienophile. The purpose of this communication is to describe an electrochemical method for synthesis of compounds from [4 + 2] alone and [4 + 2] followed by [2 + 2] cycloaddition reactions of *o*-benzoquinone with 1,3-cyclopentadiene and also an investigation of the solvent effect on reaction kinetics, as well as an estimation of the homogeneous rate constant of this reaction in various percentages of ethanol–water mixtures using a cyclic voltammogram simulation method.

Cyclic voltammograms of a 1 mM solution of catechol (**1**) in various mixtures of ethanol–water solution containing 0.3 M lithium perchlorate as supporting electrolyte and 0.1 M acetic acid are shown in Fig. 1, curves a. The cyclic voltammograms shows one anodic (A_1) and a corresponding cathodic peak (C_1), which correspond to the transformation of catechol (**1**) to *o*-benzoquinone (**1a**) and *vice versa* within a quasi-reversible two-electron process. The oxidation of catechol (**1**) in the presence of cyclopentadiene (**2**) was studied in some detail. Fig. 1 (curves b) shows the cyclic voltammogram obtained for a 1 mM solution of **1** in the presence of 3 mM of cyclopentadiene (**2**) in various mixtures of ethanol–water. Comparison of the voltammograms shows that peak current ratio (I_{pC1}/I_{pA1}) decreases with increasing percentage of water in the mixture. This can be related to the acceleration of the Diels–Alder reaction of cyclopentadiene (**2**) as diene with electro-generated *o*-benzoquinone (**1a**) as dienophile in aqueous solutions.[2] In this study, because of the low solubility of cyclopentadiene (**2**) in aqueous solutions, a mixture of ethanol–water (80 : 20 v/v) was selected as a suitable medium for controlled-potential coulometry and electrochemical synthesis. Also, it is seen that the height of the C_1 peak increases proportionally to the augmentation of the potential sweep rate (Fig. 2). A similar situation is observed when the 1,3-cyclopentadiene (**2**) to **1** concentration ratio is decreased. A plot of peak current ratio (I_{pA1}/I_{pC1}) *versus* logarithm of scan rate for a mixture of catechol (**1**) and 1,3-cyclopentadiene (**2**), appearing as an increase in the height of the cathodic peak C_1 at higher scan rates, confirms the reactivity of **1** towards **2** which is in agreement with the simulated result (Fig. 2, curve i). On the other hand, the current function for the A_1 peak, ($I_{pA1}/v^{1/2}$), slightly changes on increasing the scan rate and such behavior is viewed to be an EC (electrochemical followed by a chemical reaction) mechanism.[3]

Controlled-potential coulometry was performed in ethanol–water (80 : 20 v/v) solution containing 4.0 mmol of **1** and 16.0 mmol of **2** at 0.80 V *versus* SCE. The electrolysis was monitored by cyclic voltammetry. It was observed that anodic

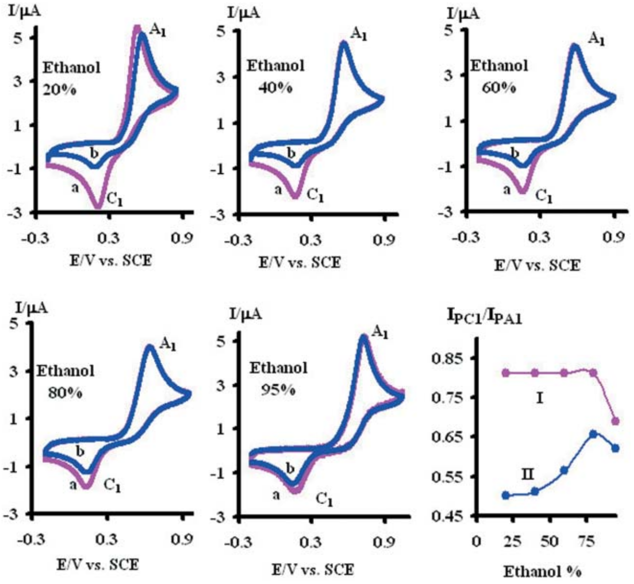

Fig. 1 Cyclic voltammograms of 1 mM catechol (**1**): (a) in the absence, (b) in the presence of 3 mM 1,3-cyclopentadiene (**2**), in various percentages of ethanol in mixture of ethanol–water (20, 40, 60, 80 and 95%) containing 0.30 M lithium perchlorate as supporting electrolyte and 0.1 M acetic acid, at a glassy carbon electrode (1.8 mm diameter), $v = 15$ mV s^{-1}. Analysis results: curve I, variation of peak current ratio (I_{pC1}/I_{pA1}) in the absence of cyclopentadiene (**2**); curve II, variation of peak current ratio (I_{pC1}/I_{pA1}) in the presence of cyclopentadiene (**2**). $t = 25 \pm 1$ °C.

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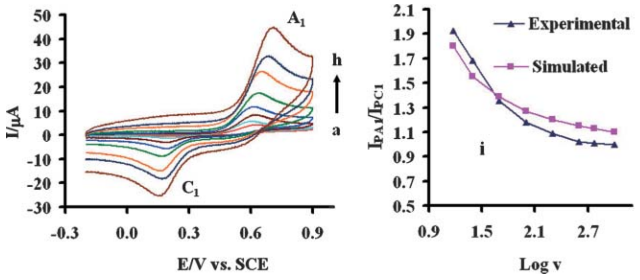


Fig. 2 Typical voltammograms of 1 mM catechol in the presence of 9 mM 1,3-cyclopentadiene in an ethanol–water (80 : 20) mixture at various scan rates. Scan rates from (a) to (h) are 15, 25, 50, 100, 200, 400, 600 and 1000 mV $s^{-1,}$ respectively. Curve i: variation of experimental peak current ratio (I_{pA1}/I_{pC1}) *vs.* scan rate and its related simulated curve. Other conditions are the same as reported in Fig. 1.

peak A_1 decreases proportionally to the advancement of coulometry. All anodic and cathodic peaks disappear when the charge consumption becomes about $2e^-$ per molecule of **1** (Fig. 3). These observations allow us to propose the pathway in Scheme 1 for the electro-oxidation of **1** in the presence of **2**.

According to our results, it seems that the [4 + 2] cycloaddition reaction of 1,3-cyclopentadiene (**2**) to *o*-benzoquinones (**1a**) (Scheme 1, eqn (2)) is faster than other secondary reactions, leading to the intermediate **3**.‡ During electrolysis and in the presence of room light, **3** is unstable and in the [2 + 2] cycloaddition reaction (Scheme 1, eqn (4)) converts to novel symmetric dimer **4** in good yield (64% isolated yield).§ The reaction (Scheme 1, eqn (4)) stopped in the absence of light. Therefore, when electrolysis is performed in a dark cell, the final products are **3** and **3a** (isolated yields 41% and 43% respectively).‡ The relationship between **3** and **3a** was stated by Ansell and others.[4] These are potentially thermally interconvertible by a reversible Cope rearrangement (Scheme 1, eqn (3)).

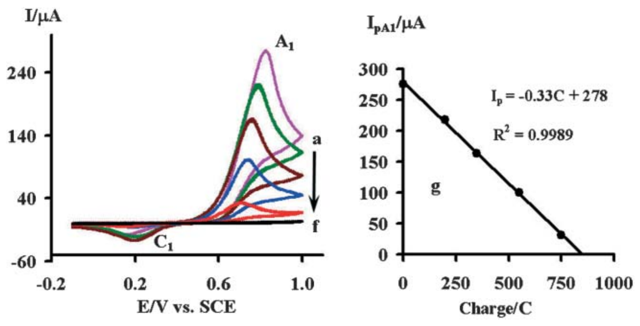
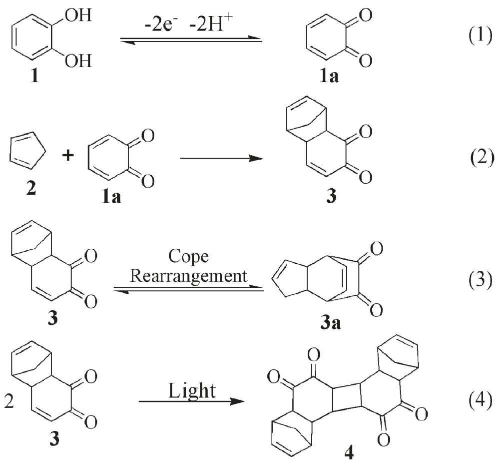


Fig. 3 Cyclic voltammograms of 4.0 mmol catechol (**1**) in the presence of 16.0 mmol 1,3-cyclopentadiene (**2**), in an ethanol–water (80 : 20) mixture during controlled-potential coulometry at 0.80 V *vs.* SCE after the consumption of (a) 0, (b) 200, (c) 350, (d) 550, (e) 750 and (f) 850 C. (g) Variation of peak current (I_{pA1}) *vs.* charge consumed. Scan rate: 20 mV s^{-1}. Other conditions are the same as reported in Fig. 1.



Scheme 1

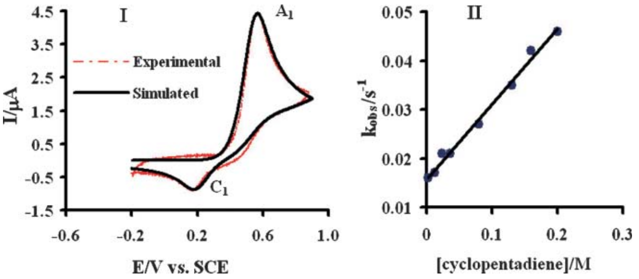


Fig. 4 (I) Agreement of the simulated and experimental cyclic voltammograms of 1.0 mM catechol (**1**) in the presence of 3 mM 1,3-cyclopentadiene (**2**) in an ethanol–water (40 : 60) mixture. Scan rate: 15 mV s^{-1}. (II) Linear relation between k_{obs} (s^{-1}) and concentration of cyclopentadiene. A least-squares fit of these linear data gave the second-order rate constants k_{DA} (M^{-1} s^{-1}).

The scheme for the electrochemical oxidation of catechols in the presence of 1,3-cyclopentadiene (**2**) was proposed and tested by digital simulation. The transfer coefficients (α) were assumed to be 0.5, the formal potentials were obtained experimentally as the midpoint potential between the anodic and cathodic peaks (E_{mid}), and the heterogeneous rate constants (0.008 cm s^{-1}) for oxidation of catechol were estimated by use of an experimental working curve.[5] The observed homogeneous rate constants (k_{obs}/s^{-1}) of the reaction of *o*-benzoquinone (**1a**) with 1,3-cyclopentadiene (**2**) were estimated by comparison of the simulation results with experimental cyclic voltammograms in various concentrations of cyclopentadiene (**2**) for each of the percentages of studied ethanol–water mixtures (Fig. 4, I). The simulation was performed base on an EC electrochemical mechanism under pseudo-first-order conditions (Fig. 4). Fig. 4, II shows that the pseudo first-order rate constants increase linearly with the increasing of concentration of cyclopentadiene (**2**). The second-order rate constants (k_{DA}/M^{-1} s^{-1}) were determined from the slope of the best fit line on this curve.[6] The estimated values (Table 1) correspond with those reported by Mrksich and co-workers.[6]

As it is shown, the magnitude of the homogeneous Diels–Alder rate constant (k_{DA}) is dependent on the percentage of water in the mixture and increases proportionally to the increase of water percentage. This corroborates previous reports that rate constants

Table 1 Estimated k_{DA} for Diels–Alder reaction in various mixtures of ethanol–water

Ethanol (%)	20	40	60	80	95
k_{DA}/M^{-1} s^{-1}	0.38	0.31	0.20	0.15	0.11

for Diels–Alder reactions in water are larger than those in organic solvents.[2]

Notes and references

‡ Synthesis of **3** and **3a**: A solution (*ca.* 100 mL) of lithium perchlorate solution (0.3 M) in ethanol–water (80 : 20 v/v) containing 5 mmol of catechol (**1**), 20 mmol of cyclopentadiene (**2**) and 1 ml acetic acid was electrolyzed in an undivided cell equipped with a glassy carbon anode (an assembly of two rods) and a large platinum gauze as cathode, at 25 °C at 0.8 V *vs.* SCE, in a dark cell. The electrolysis was terminated when the current decayed to 5% of its original value. The resulting yellow solution was concentrated under reduced pressure and the residue was extracted with benzene. The extracted portion was washed with water, dried over $MgSO_4$ and concentrated. The residue (0.8 g) was maintained below −5 °C for several days in diethyl ether. The resulting yellow–orange crystals (**3**) (mp 87–89 °C (lit. 89–91 °C[4a,b,7])) and orange crystals (**3a**) (mp 137–139 °C (lit. 139–141 °C[4a,b])) were obtained and characterized by comparison of their spectra and physical data with those obtained by the literature method.[4,7]

§ Synthesis of **4**: Electrolysis was performed in a normal glass cell. The general procedure was the same as was described for **3** and **3a**. The resulting yellow solution was concentrated under reduced pressure and the residue was extracted with benzene. The extracted portion was washed with water, dried over $MgSO_4$ and concentrated. The residue was washed with acetone several times. The resulting yellow powder (0.56 g) (mp 223–225 °C) was characterized by IR (KBr) (cm^{-1}): 2901, 2855, 1733, 1709, 1446, 1352, 1311, 1297, 1256, 1176, 1094; ^{1}H NMR: δ ppm (400 MHz, $CDCl_3$): 2.10 (m, 1H), 2.15 (m, 1H), 2.28 (m, 2H), 2.40 (m, 2H), 2.89 (m, 2H), 3.20 (m, 4H), 3.46 (m, 2H), 3.64 (m, 2H), 5.40 (m, 2H), 5.56 (m, 2H); ^{13}C NMR, δ ppm (400 MHz, $CDCl_3$): 31.9, 37.6, 43.0, 47.4, 52.9, 54.1, 60.6, 129.1, 133.5, 196.6, 197.4; MS (*m*/*z*) (relative intensity): 348.3 (95), 320.3 (76), 292.3 (51), 264.3 (29), 213.2 (22), 198.2 (22), 169.2 (27), 155.2 (42), 115.1 (58), 91.1 (76), 66.1 (27).

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