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Electrochemical synthesis of *p*-tolylsulfonylbenzenediols

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Abstract—The electrochemical synthesis of *p*-tolylsulfonylbenzenediols (**4a–c**) by anodic oxidation of catechols (**1a–c**) in the presence of 4-toluene sulfinic acid (**3**) is described. Products were obtained in an undivided cell in good yields and purity. The mechanism of oxidation has been studied in aqueous solution using cyclic voltammetry and controlled-potential coulometry.

1. Introduction

Previously we have shown that catechols can be oxidized electrochemically to *o*-quinones. The quinones formed are quite reactive and can be attacked by a variety of nucleophiles such as methanol,[1–3] ethanol,[4] 4-hydroxycoumarin,[5–7] β-diketones[8] and 2-thiobarbituric acid;[9] they have been converted to the corresponding alkoxyquinone, coumestan, benzofuran and dispirothiopyrimidine derivatives, respectively. The importance of sulfones such as arylsulfonylbenzenediols that are known as thermally sensitive materials[10,11] has prompted many workers to synthesize a number of these compounds by chemical routes.[12] However, no report has been published until now about the electrochemical synthesis of arylsulfonylbenzenediol derivatives. Therefore, we have investigated the electrooxidation of catechol and 3-substituted catechols in the presence of 4-toluenesulfinic acid as the nucleophile and describe a facile electrochemical method for the synthesis of some new sulfone derivatives in good yield and purity.

Cyclic voltammetry of 1 mM catechol (**1a**) shows one anodic (A_1) and the corresponding cathodic peak (C_1), which correspond to the transformation of catechol (**1a**) to *o*-benzoquinone (**2a**) and vice versa within a quasi-reversible two-electron process (Fig. 1, curve a). A peak current ratio (I_P^{C1}/I_P^{A1}) of nearly unity, particularly during the repetitive recycling of the potential, can be considered as a criterion for the stability of the *o*-quinone produced at the surface of the electrode under the experimental conditions. In other words, any hydroxylation[13–16] or dimerization[17,18] reactions are occurring too slowly to be observed in the time scale of cyclic voltammetry. The oxidation of catechol (**1a**) in the presence of 4-toluenesulfinic acid (**3**) as a nucleophile was studied in some detail (Fig. 1 (curve b)). Under these conditions, the cathodic counterpart of the anodic peak A_1 disappears. The positive shift of the A_1 peak in the presence of 4-toluenesulfinic acid (Fig. 1, curve b) that was enhanced during the repetitive recy-

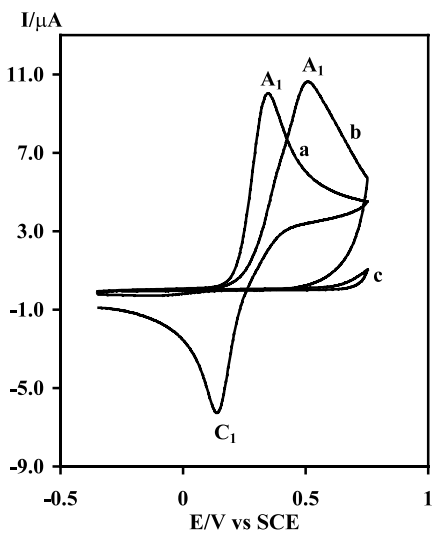

Figure 1. Cyclic voltammograms of 1 mM catechol: (a) in the absence; (b) in the presence of 1 mM 4-toluenesulfinic acid, and (c) 1 mM 4-toluenesulfinic acid in the absence of catechol, at a glassy carbon electrode, in acetate buffer solution ($c=0.2$ M, pH 4.5); scan rate: 50 mV s^{-1}; $T=25\pm1$°C.

Keywords: electro-organic synthesis; catechol; 4-toluenesulfinic acid; sulfone derivatives.

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cling of potential is probably due to the formation of a thin film of product at the surface of the electrode, inhibiting, to a certain extent, the performance of the electrode process.[5–9]

Furthermore, it is seen that proportional to the augmentation of the potential sweep rate, the height of the C_1 peak of **1a** increases (Fig. 2). A similar situation is observed when the 4-toluenesulfinic acid (**3**) to **1a** concentration ratio is decreased. On the other hand, the current function for the A_1 peak, ($I_P^{A1}/v^{1/2}$), changes only slightly with increasing scan rate (Fig. 2, curve h) and such behaviour has been adopted as being indicative of the EC mechanism.[5–9]

Controlled-potential coulometry was performed in aqueous solution containing 0.33 mmol of **1a** and 0.33 mmol of 4-toluenesulfinic acid (**3**) at 0.45 V versus SCE. Monitoring of the electrolysis progress was carried out by cyclic voltammetry. It is shown that, proportional to the advancement of coulometry, anodic peak A_1 decreases and disappears when the charge consumption becomes about $2e^-$ per molecule of **1a**.

These observations allow us to propose the pathway in Scheme 1 for the electrooxidation of **1a** in the presence of 4-toluenesulfinic acid (**3**).

According to our results, it seems that the Michael addition reaction of anion **3** to *o*-quinone (**2a**) (Eq. (2)) is faster than other secondary reactions, leading to the product **4a**. The oxidation of this compound (**4a**) is more difficult than the oxidation of the parent starting molecule (**1a**) by virtue of the presence of the electron-withdrawing phenylsulfonyl group on the catechol ring. The overoxidation of **4a** was circumvented during the

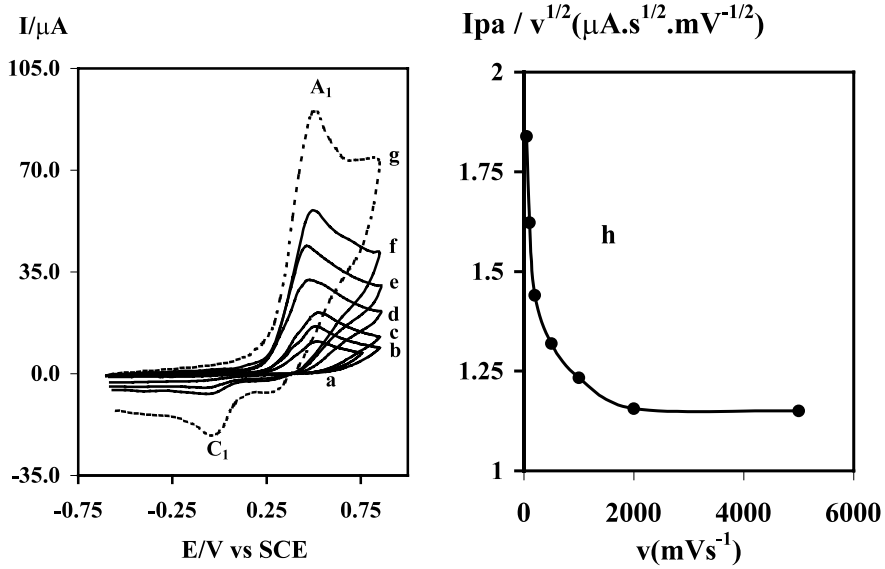
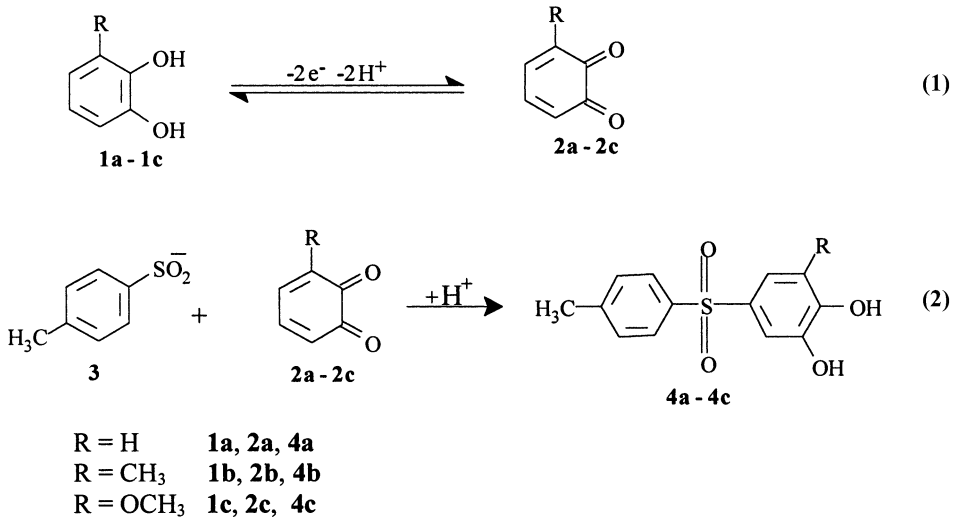


Figure 2. Typical voltammograms of 1 mM catechol in water in the presence of 1 mM 4-toluenesulfinic acid at a glassy carbon electrode, in acetate buffer solution ($c=0.2$ M, pH 4.5), at various scan rates. Scan rates from (a) to (g) are: 50, 100, 200, 500, 1000, 2000 and 5000 mV s^{-1}, respectively; (h) variation of peak current function ($I_P^{A1}/v^{1/2}$) versus scan rate. $T=25\pm1$°C.



Scheme 1.

Table 1. Electroanalytical and preparative data

Conversion	Applied potential V (SCE)	Product yield (%)	Melting point (°C)	Sulfur content	
				Calcd	Found
1a→4a[a]	0.45	93	100–101 (dec.)	12.12	12.01
1b→4b[b]	0.40	84	140–142 (dec.)	11.51	11.39
1c→4c[c]	0.40	80	185–187 (dec.)	10.88	10.65

[a] (**4a**): *4(4-Methylphenylsulfonyl)-1,2-benzenediol* ($C_{13}H_{12}O_4S$), $IR_{(KBr)}$: 3320, 1593, 1508, 1443, 1371, 1292, 1145, 1089, 915, 810, 685, 564 cm^{-1}. ^1H NMR, δ (90 MHz, DMSO-d_6): 2.38 (s, 3H methyl) [7.33 (d, $J=6.1$ Hz); 7.83 (d, $J=7.1$ Hz) 7H, aromatic]; 10.0 (broad, 2H hydroxy). MS: m/e (relative intensity); 264(100), 157(37), 140(63), 108(78), 92(86), 65(69), 39(80).

[b] (**4b**): *3-Methyl-5-(4-methylphenylsulfonyl)-1,2-benzenediol* ($C_{14}H_{14}O_4S$), $IR_{(KBr)}$: 3400, 2900, 1620, 1589, 1512, 1419, 1299, 1138, 1093, 1029, 904, 807, 670, 590 cm^{-1}. ^1H NMR, δ (DMSO-d_6): 2.24 (s, 3H methyl); 2.38 (s, 3H methyl); [7.28 (d, $J=3$ Hz); 7.38 (s); 7.78 (d, $J=7.7$ Hz) 6H, aromatic]; 9.4 (broad, 1H hydroxy), 10.1 (broad, 1H hydroxy). MS: m/e (relative intensity); 278(100), 171(25), 139(68), 121(40), 92(60), 65(64), 39(59).

[c] (**4c**): *3-Methoxy-5-(4-methylphenylsulfonyl)-1,2-benzenediol* ($C_{14}H_{14}O_5S$), $IR_{(KBr)}$: 3520, 3240, 2920, 1605, 1500, 1456, 1295, 1202, 1141, 1081, 952, 807, 670, 581 cm^{-1}. ^1H NMR, δ (DMSO-d_6): 2.39 (s, 3H methyl); 3.89 (s, 3H methoxy); [7.10 (s); 7.42 (d, $J=8$ Hz); 7.77 (d, $J=7.9$ Hz) 6H, aromatic] 9.5 (broad, 1H hydroxy), 9.8 (broad, 1H hydroxy). MS: m/e (relative intensity); 294(100), 187(31), 155(46), 139(74), 108(23), 91(47), 65(47), 39(52).

preparative reaction because of the presence of the electron-withdrawing group as well as the insolubility of the product in the acetate buffer solution media.

The electrooxidation of **1b** and **1c** in the presence of 4-toluenesulfinic acid (**3**) as a nucleophile in acetate buffer solution proceeded in a manner similar to that of **1a**.

The existence of a methyl or a methoxy group at the C-3 position of **1b** and **1c** probably causes these Michael acceptors (**2b** and **2c**) to be attacked by the anion (**3**) from the C-4 and/or the C-5 positions to yield two types of products in each case. However, according to thin layer chromatography (TLC) and ^1H NMR results, we suggest that *o*-quinones **2b** and **2c** are attacked in all probability only at the C-5 position by anion (**3**) leading to the formation of the products **4b** and **4c**, respectively.[19]

2. Experimental

2.1. Apparatus and reagents

Reaction equipment is described in an earlier paper.[9] All chemicals (catechols and 4-toluenesulfinic acid sodium salt) were reagent-grade materials from Aldrich and sodium acetate was of pro-analysis grade from E. Merck. These chemicals were used without further purification.

2.2. Electroorganic synthesis of 4a–c

In a typical procedure, 80 ml of acetate buffer solution ($c=0.2$ M, pH 4.5) was pre-electrolyzed at the chosen potential (see Table 1) in an undivided cell, then 2 mmol of catechol (**1a–c**) and 4-toluenesulfinic acid (2 mmol) were added to the cell. The electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted several times during the electrolysis and the graphite anode was washed in acetone in order to reactivate it. At the end of electrolysis, about 0.5 ml of acetic acid was added to the solution and the cell was placed in a refrigerator overnight. The precipitated solid was collected by filtration and recrystallized from a mixture of water/acetone. After recrystallization, the products were characterized by IR, ^1H NMR, MS and sulfur content.

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