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ORIGINAL PAPER

# Electrochemical pyridination of hydroquinone in aqueous solution

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**Abstract** Electrochemical oxidation of hydroquinone was studied in the presence of pyridine and 4-methylpyridine as nucleophiles in aqueous solution. The results indicate the participation of electrochemically generated *p*-benzoquinone in Michael addition reaction with pyridine and 4-methylpyridine, converting it to pyridinated compounds.

**Keywords** Electrochemical pyridination · Cyclic voltammetry · Hydroquinone · Michael addition

## Introduction

Pyridinium-substituted hydroquinones have attracted interest as a partial structure of modified rifamycins with antibacterial activities [1–3]. Also, *N*-pyridinium phenolates (betaines of *N*-pyridinium) are interesting compounds because of their clear solvatochromism, thermochromism, and halochromism [4]. The importance of these compounds has prompted many workers to synthesize [4–11] or study a number of them [4, 12–16]. To the best of our knowledge, no reports exist on the electrochemical synthesis or mechanistic studies of pyridinated hydroquinone. With due attention to our experiences on mechanistic studies of organic processes by electrochemical techniques [17, 18] and electrosynthesis of organic compounds [19–24], we thought that mechanistic studies and synthesis of new *N*-pyridinium phenolates would be useful from the point of view of pharmaceutical or industrial properties. This idea motivated us to investigate the electrochemical oxidation of hydroquinone in the presence of pyridine and 4-methylpyridine as nucleophiles.

## Results and discussion

The cyclic voltammogram of 1 mM hydroquinone (**1**) in aqueous solution containing phosphate buffer ($pH = 7.0$, $c = 0.2$ M) shows one anodic ($A_1$) and the corresponding cathodic peak ($C_1$), which corresponds to the transformation of hydroquinone (**1**) to *p*-benzoquinone (**2**) and vice versa within a reversible two-electron process (Fig. 1, curve a). The peak current ratio ($I_{pC1}/I_{pA1}$) is nearly unity, which can be considered as a criterion for the stability of *p*-benzoquinone produced at the surface of the electrode under the experimental conditions [17, 22]. The oxidation of **1** in the presence of pyridine (**3a**) as a nucleophile was studied in some detail. Figure 1, curve b shows the cyclic voltammogram obtained for a 1 mM solution of **1** in the presence of pyridine (20 mM). In this condition, the height of the cathodic counterpart ($C_1$) decreased, and a new anodic and cathodic peak couple ($A_2$ and $C_2$) appeared in more positive potentials. In this figure, curve c is the cyclic voltammogram of pyridine (**3a**). This voltammogram shows that pyridine (**3a**) is not electroactive in the studied potential range (Fig. 1, curve c).

The existence of a subsequent chemical reaction between *p*-benzoquinone (**2**) and pyridine (**3a**) is supported by the following evidences: (a) Decreasing of $I_{pC1}$ during the reverse scan, this could be indicative of the fact that electrochemically generated *p*-benzoquinone (**2**) is

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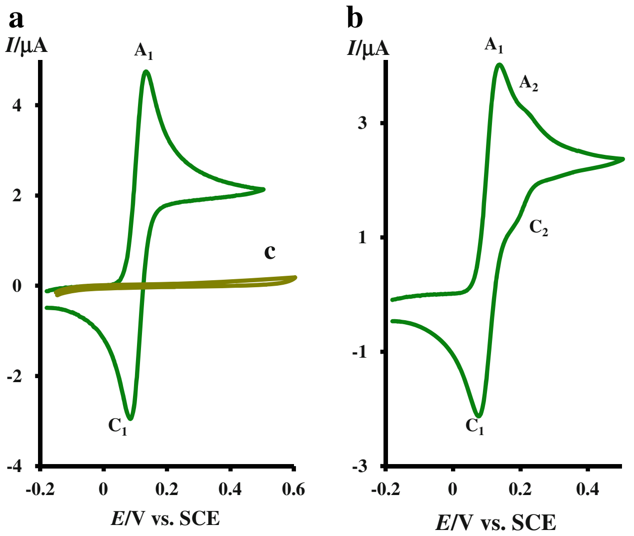


**Fig. 1** Cyclic voltammograms of (**a**) 1 mM hydroquinone, (**b**) 1 mM hydroquinone in the presence of 20 mM pyridine at a scan rate of 5 mV $s^{-1}$ in phosphate buffer solution (pH = 7.0, $c = 0.2$ M) at glassy carbon electrode, $T = 25 \pm 1$ °C

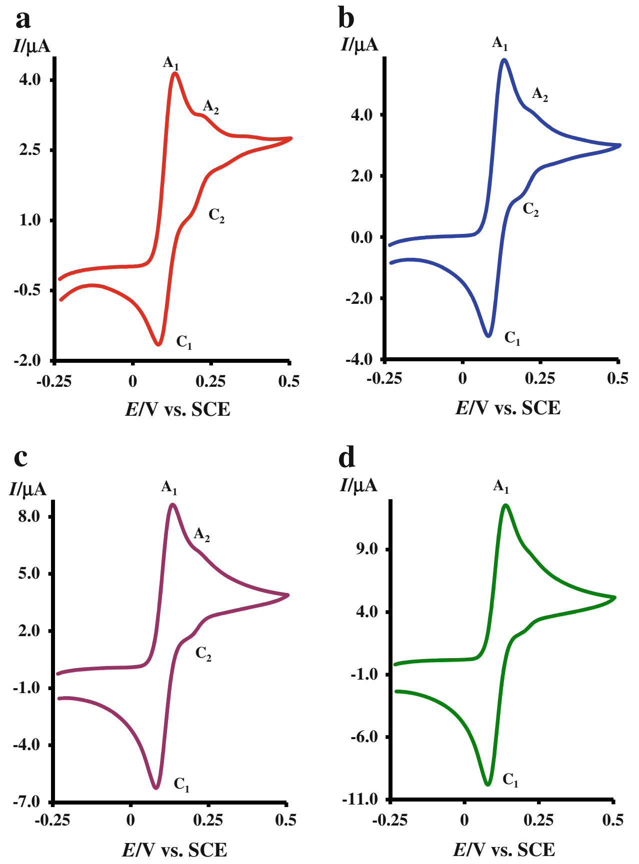


**Fig. 2** Cyclic voltammograms of 1 mM hydroquinone in the presence of 20 mM pyridine at various scan rates. Scan rates from **a** to **d**: 5, 10, 25, and 50 mV $s^{-1}$ in phosphate buffer solution (pH = 7.0, $c = 0.2$ M) at glassy carbon electrode, $T = 25 \pm 1$ °C

removed partially by chemical reaction with pyridine (**3a**). (b) Dependency of the peak current ratio ($I_{pC1}/I_{pA1}$) on the potential sweep rate (Fig. 2). In this case, for the highest sweep rate employed a well-defined cathodic peak $C_1$ is observed. For lower sweep rates, the peak current ratio ($I_{pC1}/I_{pA1}$) is less than one and increases with increasing sweep rate (Fig. 2). This is indicative of departure from the intermediate and arrival to the diffusion reign [25] with an increasing sweep rate. (c) Appearance of an anodic peak $A_2$ and its cathodic counterpart ($C_2$) in more positive potentials that shows the product of the following chemical reaction is electroactive [25]. (d) Dependency of the peak current ratio ($I_{pA2}/I_{pA1}$) on the potential sweep rate (Fig. 2). This is related to the decrease of the effect of the following chemical reaction with increasing sweep rate. (e) Dependency of peak current ratios ($I_{pC1}/I_{pA1}$) and ($I_{pA2}/I_{pA1}$) on the concentration of pyridine (Fig. 3). This is related to the increase of the homogeneous reaction rate of the following chemical reaction.

Controlled-potential coulometry was performed in aqueous solution (phosphate buffer, $c = 0.2$ M, pH = 7.0) containing 0.1 mmol of hydroquinone (**1**) and 0.1 mmol of pyridine (**3a**) at potential of peak $A_1$ ($E_{pA1}$). Cyclic voltammetric analysis carried out during the electrolysis shows the progressive formation of a new anodic peak $A_2$, parallel to the disappearance of peak $A_1$. The anodic peak $A_1$ and cathodic peak $C_1$ disappear when the charge consumption becomes about $3e^-$ per molecule of **1** (Fig. 4).

These coulometry and voltammetry results accompanied by the spectroscopic data of final products obtained from exhaustive oxidation of a solution containing 1 mmol of hydroquinone (**1**) in the presence of **3a** (1 mmol) or 4-methylpyridine (**3b**, 1 mmol) by applying 0.15 V versus SCE allow us to propose the mechanism for the electro-oxidation of **1** in the presence of **3a** and **3b** (Scheme 1).

Accordingly, the 1,4-addition (Michael) reaction of **3a**, **3b** to *p*-benzoquinone (**2**) leads to intermediates **4a**, **4b**. In the next step, Michael reaction of **4a**, **4b** to **2** converts **4a**, **4b** to intermediates **5a**, **5b**. Oxidation of **5a**, **5b** and the next Michael addition leads to the formation of final products **7a**, **7b**. The oxidation of **7a**, **7b** is more difficult than the oxidation of the starting molecule **1** by virtue of the presence of the electron-withdrawing pyridine group on **7a**, **7b**. Therefore, over-oxidation of **7a**, **7b** was circumvented during the reaction because of the presence of the electron-withdrawing group. As a result, the anodic peak $A_1$ pertains to the oxidation of hydroquinone **1** to *p*-benzoquinone **2**. Obviously, the cathodic peak $C_1$ corresponds to the reduction of *p*-benzoquinone **2**. The anodic peak $A_2$ can be related to electrochemical oxidation of

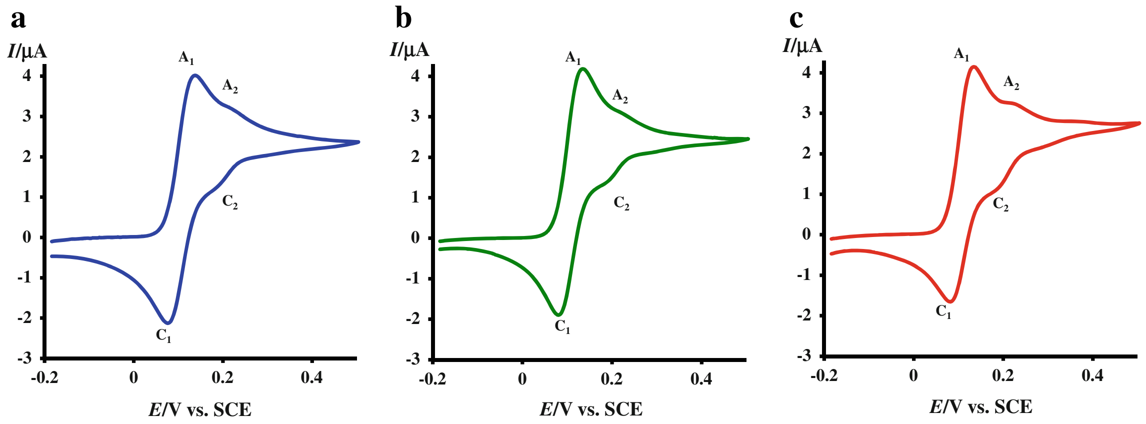


**Fig. 3** Cyclic voltammograms of 1 mM hydroquinone in the presence of (**a**) 20, (**b**) 30, and (**c**) 40 mM pyridine in phosphate buffer (pH = 7.0, $c = 0.2$ M) at glassy carbon electrode, scan rate 5 mV $s^{-1}$, $T = 25 \pm 1$ °C

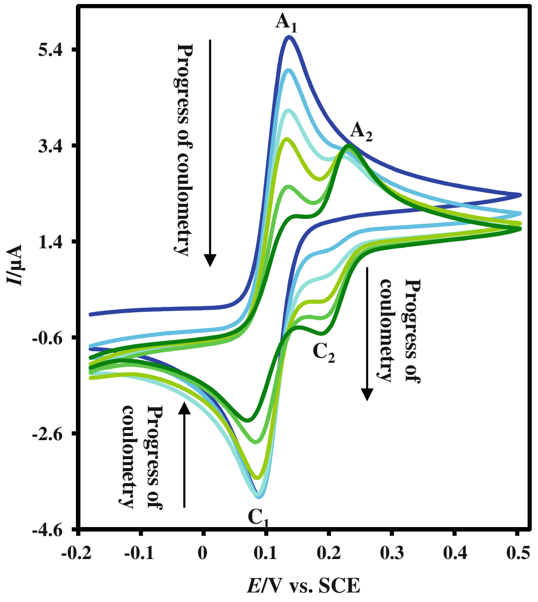
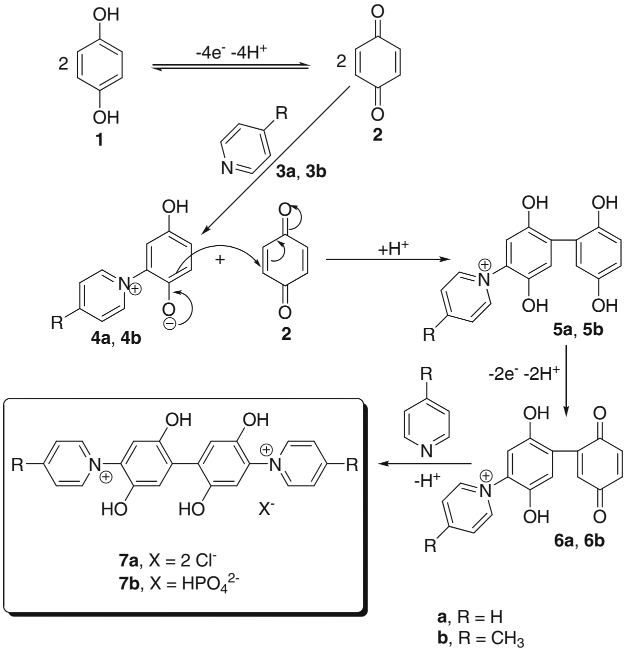


**Fig. 4** Cyclic voltammograms of 0.1 mmol hydroquinone in the presence of 0.1 mmol pyridine in phosphate buffer (pH = 7.0, $c = 0.2$ M) at glassy carbon electrode during controlled-potential coulometry at 0.15 V versus SCE. After consumption of 0, 5, 10, 15, 20, and 25 °C. Scan rate 5 mV $s^{-1}$, $T = 25 \pm 1$ °C



**Scheme 1**

pyridinated hydroquinone **4a** to its related pyridinated *p*-benzoquinone. Clearly, the cathodic peak $C_2$ corresponds to the reduction of the pyridinated *p*-benzoquinone to pyridinated hydroquinone **4a**.

The same voltammetric behaviors are observed in electrochemical oxidation of **1** in the presence of 4-methylpyridine (**3b**). The only difference in electrochemical behavior of **1** in the presence of **3b** is related to higher nucleophilicity of **3b** in comparison with **3a**. This property of **3b** has two effects in the cyclic voltammograms of **1** in the presence of **3b** (Fig. 5): (a) the peak current ratio ($I_{pC1}/I_{pA1}$) decreases, and (b) new anodic and cathodic peaks ($A_3$ and $C_3$) appear in more positive potentials. These peaks ($A_3$ and $C_3$) are related to the oxidation and reduction of dipyridinated hydroquinone/dipyridinated *p*-benzoquinone redox couple. These effects are enhanced by increasing the concentration of **3b** (Fig. 5).

## Conclusions

For the first time in this report, the electrochemical pyridination of hydroquinone was studied. The results of this work show that hydroquinone is oxidized to *p*-benzoquinone, which is then attacked by pyridine. A novel pyridinated dimer of hydroquinone is obtained after

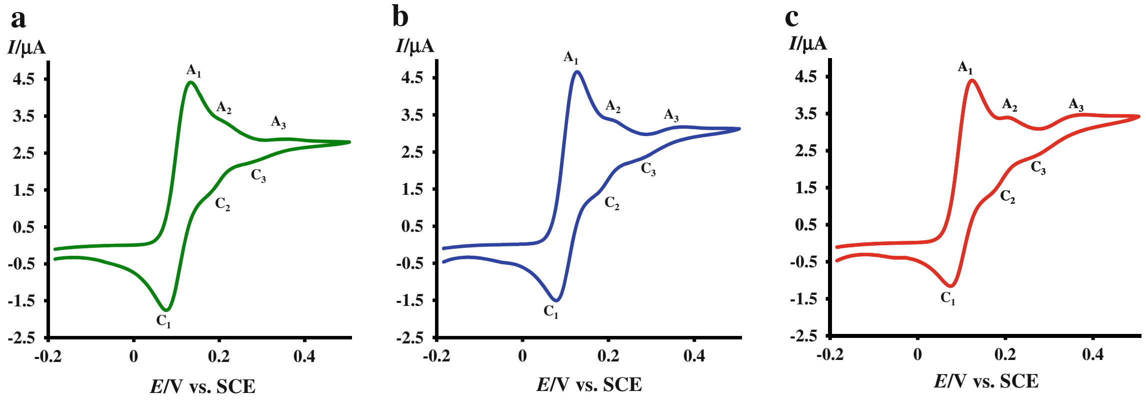


**Fig. 5** Cyclic voltammograms of 1.0 mM hydroquinone in the presence of (**a**) 20, (**b**) 30, and (**c**) 40 mM 4-methylpyridine in phosphate buffer (pH = 7.0, $c = 0.2$ M) at glassy carbon electrode, scan rate 5 mV $s^{-1}$, $T = 25 \pm 1$ °C

consumption of $3e^{-}$ per molecule of hydroquinone as final product. The reaction mechanism for anodic oxidation of hydroquinone in the presence of pyridine is presented in Scheme 1. From the point of view of green chemistry, use of the electrosynthesis method has some important advantages. Clean synthesis, the use of electricity instead of chemical reagents, and the achievement of high atom economy via a one-step process conducted under ambient conditions are of preeminent green advantages.

## Experimental

Cyclic voltammetry, controlled-potential coulometry, and preparative electrolysis were performed using an Autolab model PGSTAT 30 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 $mm^2$ area), and a platinum wire was used as a counter electrode. The working electrode used in controlled-potential coulometry and macroscale electrolysis was an assembly of four carbon rods (31 $cm^2$) and a large steel sheet constituting the counter electrode. The working electrode potentials were measured vs. SCE and Ag/AgCl (from AZAR electrode and Metrohm). All chemicals (hydroquinone, pyridine, and 4-methylpyridine) were reagent-grade materials, and phosphate salts were of pro-analysis grade. These chemicals were used without further purification.

### *Synthesis of compounds 7a, 7b*

Aqueous phosphate buffer solution (80 $cm^3$, $c = 0.2$ M, pH = 7.0) containing 1 mmol of hydroquinone (**1**) and 1 mmol of pyridine (**3a**) or 4-methylpyridine (**3b**) was electrolyzed at potential of peak $A_1$ (0.15 V vs. SCE) in an undivided cell equipped with a carbon anode and a large stainless steely gauze as cathode at 25 °C. The electrolysis was terminated when the current decayed to 5% of its original value. The process was interrupted during the electrolysis, and the carbon anode was washed in acetone in order to reactivate it. At the end of electrolysis, the precipitated solid was collected by filtration and washed with water. In the case of compound **7a**, the resulting product was diluted with 4 $cm^3$ water, heated, and treated with 0.26 $cm^3$ of 18% hydrochloric acid. On cooling, solids precipitated that were filtered off, washed with water, and dried in vacuum. After drying, products were characterized by IR, $^1H$ NMR, $^{13}C$ NMR, and MS.

*1,1′-(2,2′,5,5′-Tetrahydroxy-1,1′-biphenyl-4,4′-diyl)bispyridinium dichloride* (**7a**, $C_{22}H_{18}Cl_2N_2O_4$)
Yield 54.4%; m.p.: >260 °C (dec.); IR (KBr): $\bar{\nu}$ = 3,436, 3,073, 1,667, 1,602, 1,495, 1,398, 1,267, 1,187, 862, 837, 779, 682 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta = 5.91$ (t, 2H), 6.76 (d, 4H), 7.02 (t, 4H), 7.36 (s, 4H), 8.24 (s, 2H), 9.22 (s, 2H) ppm; $^{13}C$ NMR (75 MHz, DMSO-$d_6$): $\delta = 117.0$, 122.1, 123.2, 127.8, 144.7, 146.3, 146.6, 156.2, 159.9 ppm; MS (70 eV): *m/z* (relative intensity) = 41 (49), 57 (43), 69 (100), 81 (49), 95 (22), 109 (12), 121 (24), 137 (16), 149 (92), 167 (31), 185 (6), 203 (6), 217 (2), 236 (6), 252 (6), 264 (2), 279 (15), 299 (1), 321 (1), 341 (3), 353 (1), 368 (3), 410 ($M^+$ + HCl, 1).

*1,1′-(2,2′,5,5′-Tetrahydroxy-1,1′-biphenyl-4,4′-diyl)bis(4-methylpyridinium) hydrogenphosphate*
(**7b**, $C_{24}H_{23}N_2PO_8$)
Yield 60.2%; m.p.:>260 °C (dec.); IR (KBr): $\bar{\nu}$ = 3,392, 3,205, 3,120, 1,637, 1,505, 1,446, 1,351, 1,274, 1,202, 827, 614, 502 $cm^{-1}$; $^1H$ NMR (300 MHz, DMSO-$d_6$): $\delta = 2.70$ (s, 6H), 7.03 (m, 4H), 8.07 (d, 4H), 9.00 (d, 4H), 9.28 (br, about 2H), 10.27 (br, about 2H) ppm; MS (70 eV): *m/z* (relative intensity) = 41 (46), 238 (94), 267 (27), 295 (50), 322 (100), 397 (49), 425 (45), 498 ($M^+$ + $HPO_4$, 42).

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