

Electrooxidation of the calix[4]arenedihydroquinone mechanistic investigation and electrodeposition of the oxidised form on platinum grid

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Abstract The electrochemical behaviour of 5,17-di-tert-butyl-11,23,25,27-di-dihydroxy-26,28-diméthoxy calix[4]-arene has been investigated at a platinum electrode in aprotic solvent by cyclic, square wave and rotating-disk voltammetry as well as by controlled potential coulometry. By comparing to the ferrocene, the height of the first irreversible transfer process involves only one-electron transfer, which corresponds to the formation of the radical cation. However, the last substance undergoes a fast chemical reaction and follows an $EC_H E$ sequence. But, the large scale electrolysis at the first anodic peak required a consumption of 2.25 Faradays per molecule. When we interrupt the electrolysis after consumption of 1 Faraday per molecule, an intermediate compound was formed, which is the calix[4]arenequinhydrone ($X_4Me_2(H_2Q)Q$) through a partial reduction of the start product. Furthermore, the reaction may evolves in solution following an $EC_H EC_H$ redox process for generating the calix[4]arenedi-quinone ($X_4Me_2Q_2$). On the other hand, the voltammetric follow-up shows the electrogeneration to the departure product during the macroscale electrolysis according an $EC_H E$ -disproportionation mechanism. When the electrolysis was performed after the third oxidation peak, ($X_4Me_2Q_2$) was electrogenerated in solution and was deposit, afterward, on the platinum grid.

Keywords Calix[4]arenedihydroquinone · Calix[4]arenequinhydrone · Anodic oxidation · Cyclic voltammetry · Square wave voltammetry · Electrodeposition

Introduction

The electrochemical oxidation of different calixarenes has been widely investigated in aprotic media and at several working-electrodes. Their application in the field of electrochemistry has been reviewed [1, 2]. Cyclic voltammetry (CV) of the unsubstituted calix[4]hydroquinone was studied by Suga et al. [3] in *N,N*-dimethylformamide at glassy carbon electrode. Two electron transfers have been attributed to the first anodic wave like the classic hydroquinone [4].

Morita et al. [5, 6] and Gutsche and co-workers. [7, 8] showed that the chemical oxidation of the unsubstituted phenol rings containing calix[*n*]arenes studied results in the formation of calix[4]arene-mono-, -di-, -tri- and tetra-quinones, depending on the number of free phenolic rings in the starting calixarenes. Recent works by Vataj et al. [9] interested to the electrochemical oxidation of calixarene diamides and confirmed that the electrooxidation of the calixhydroquinones studied generate the corresponding diquinone. However, in voltammetric studies, they showed that the apparent electron transfer [10] of the studied calixarenes could not be confirmed by coulometric measurements in macroscale electrolysis. Nevertheless, electrodeposition of phenolic derivatives was performed at a glassy carbon electrode in aprotic solvent by repetitive CVs [11].

A very simple and interesting example is the well-known quinhydrone that is a molecular complex between *p*-benzoquinone (BQ) and hydroquinone (H_2Q). Its crystal

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structure reveals the formation of regular alternate donor/acceptor stacks [12, 13]. The quinhydrone role was evidenced in biological systems: the quinone reductase activity of the inner-membrane protein DsbB, which is present in *Escherichia coli*, involves a quinhydrone type charge-transfer complex [14]. The family of calixarenes occupies an important place in host–guest chemistry, [15, 16] but only a few examples of calixarènes are known to accommodate neutral entities [17, 18]. The chemical reduction of the Di(methoxy-*p*-*tert*-butyl)calix[4]arene-diquinone led to its calix[4]arene-dihydroquinone and its partial reduction led to the calix[4]arene-quinhydrone charge transfer complex [19].

In the present work, the electrochemical study of the 5,17-di-*tert*-butyl-11,23,25,27-di-dihydroxy-26,28-dimethoxy calix[4]arene $X_4Me_2(H_2Q)_2$ in acetonitrile at Pt electrodes by CV square wave (SWV) and rotating-disk voltammetries are used to elucidate the mechanism of formation of the above products and to determine the standard potential E^0 of the couple cation/radical.

The preparative electrolyses demonstrate that heterogeneous oxidation of that substrate allows the synthesis of 5,17-di-*tert*-butyl-23,25-di-dihydroxy-26,28-dimethoxy calix[4]quinhydrone ($X_4Me_2(H_2Q)Q$) as an intermediate product and the 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]arene-diquinone ($X_4Me_2Q_2$) as a final product in aprotic media. The formed products were analysed by 1H NMR and IR spectroscopic techniques. Mass spectroscopy analysis was used to characterize the products isolated from the electrochemical reaction. Our target molecules [19] are 5,17-di-*tert*-butyl-11,23,25,27-di-dihydroxy-26,28-dimethoxy calix[4]arene ($X_4Me_2(H_2Q)_2$) (**1**), 5,17-di-*tert*-butyl-23,25-di-dihydroxy-26,28-dimethoxy calix[4]quinhydrone ($X_4Me_2(H_2Q)Q$) (**2**) and 5,17-di-*tert*-butyl-26,28-dimethoxycalix[4]diquinone ($X_4Me_2Q_2$) (**3**).

The oxidation mechanism of the calix[4]dihydroquinone is of primary interest in view of the existence of an intermediate product such as calix[4]quinhydrone (diquinone-dihydroquinone pair). Taking into account that the oxidation mechanism of calix[4]dihydroquinone are under the control of acid/base reaction [20]. In some way, it could be considered that intermolecular protonation/deprotonation influence deeply the mechanism [9, 10].

Experimental

Tetrabutylammonium perchlorate TBAP (Fluka) was used as supporting electrolyte. The acetonitrile 99% was purchased from Acros organics and was used as received.

The synthesis of 5,17-di-*tert*-butyl-11,23,25,27-di-dihydroxy-26,28-dimethoxy calix[4]arene $X_4Me_2(H_2Q)_2$ (**1**) were carried out under argon using Schlenk tube techniques and dichloromethane were distilled before use from over CaH_2 under argon. Trifluoroacetic acid and thallium (III) trifluoroacetate were purchase from Strem Chemicals Alfa-Aesar, respectively, and used as received. $NaBH_4$ (Acros) and NaH were used as received. Using the methodology developed by McKillop et al. [21] we synthesized from dimethoxycalix[4]arene $X_4Me_2H_2$ [22], the dimethoxycalix[4]arene-diquinone $X_4Me_2Q_2$ as described by Beer et al. [23]. On reduction of dimethoxycalix[4]arene-diquinone by $NaBH_4$ we synthesized the corresponding dimethoxycalix[4]arene-dihydroquinone **1** [24] as white powder (Scheme 1). **1** was considered as the starting product for the present electrochemical studies.

The electrochemical set-up consisted of a Tacussel (PGP 201) potentiostat. A three-electrode cell with compartments separated by a porous glass was used. The working electrode was a platinum disc electrode ($\phi = 2$ mm) (EDI type Radiometer) and a platinum wire as counter electrode. The reference electrode (saturated calomel electrode, SCE) was separated from the bulk solution by a sintered-glass bridge filled with the solvent and the supporting electrolyte.

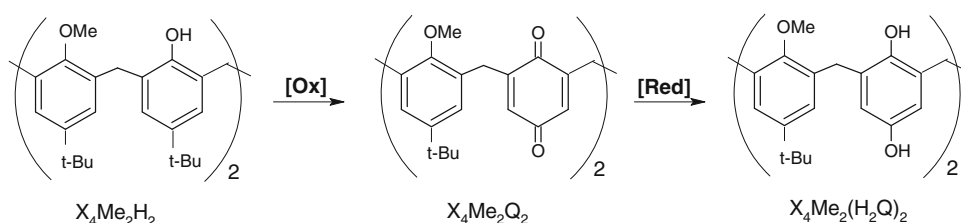
Prior to each measurement, the working electrode was polished with a set of fine alumina powders. All the experiments were carried out at laboratory temperature.

Solutions containing TBAP 0.1 M as supporting electrolyte were protected from atmosphere with argon prior to each cyclic voltammetry measurement and the gas flow maintained during the CV experiments.

An Autolab potentiostat/galvanostat PGSTAT 30 assisted by GPES electrochemical software was used for macroelectrolysis and square wave voltammetry (SWV) measurements.

Macroelectrolysis of **1** was carried out under argon atmosphere in a separated cell. The separation was realized with a sintered glass (porosity number 4). An 8 cm^2

Scheme 1 Schematic pathway of dimethoxycalix[4]arene-dihydroquinone $X_4Me_2(H_2Q)_2$ **1** electrooxidation



platinum grid was used as working electrode and a 2.5 cm² platinum grid was used as counter electrode. SWV were realized in the potential range 0.5–2.4 V, with frequency (f) of 10 s⁻¹, pulse amplitude (ΔE_p) of 25 mV, step potential (ΔE_s) of 20 mV and equilibration time of 5 s.

¹H NMR analyses were recorded with a Bruker 300 MHz. ATR diamond was used as characterization technique of spectroscopy IR and was performed with a BRUKER TENSOR 27 spectrometer. The MALDI-TOF mass spectrum was achieved by a UPMC-LCSOB apparatus in a HCCA (α CYANO-4-HYDROXY) as a matrix.

Electrochemical synthesis of 5,17-di-tert-butyl-23,25-dihydroxy-26,28-dimethoxy calix[4]quinhydrone ($X_4Me_2(H_2Q)Q$) (2) and 5,17-di-tert-butyl-26,28-dimethoxycalix[4]diquinone ($X_4Me_2Q_2$) (3). A 0.1 M TBAP solution of **1** (46.5 mg; 0.078 mmol) was electrolysed at a potential of 1.3 V versus SCE. Electrolysis was stopped after a consumption of 1 electron per molecule. After evaporation of the solvent, the crude material was extracted with diethyl ether and purified on column chromatography (silica gel 60, CH₂Cl₂-(CH₃)₂CO, 95/5, v/v). The obtained products were separated by chromatography on preparative patches of silica gel (eluent: CH₂Cl₂-(CH₃)₂CO, 95/10, v/v) to give **2** (10 mg; yield: 21.5%) and **3** (12 mg; yield: 25.8%), additionally to starting material **1** (11 mg; yield: 23.6%). The yield was calculated as the ratio $m_{product}/m_{initial\ substrate}$.

Compound 2: TLC (SiO₂, eluent CH₂Cl₂-(CH₃)₂CO, 90/10, v/v) $R_f = 0.59$; MALDI-TOF MS: m/z 594 (M⁺); 616 (M + Na⁺); 633 (M + K⁺). IR (KBr) 1655, 1604, 1490, 1300, 1207, 1013 cm⁻¹. ¹H NMR (300 Hz, CD₃CN): δ (ppm) 1.17 [s, 9H, C(CH₃)₃]; 3.31 (d, $J = 13$ Hz, 1H, ArCH₂Ar), 3.93 (s, 6H, OCH₃), 4.22 (d, $J = 13$ Hz, 1H, ArCH₂Ar), 6.20 (s, 2H, OH), 6.60 (s, 4H, ArH), 7.15 (s, 4H, ArH), 7.74 (s, 2H, OH).

Compound 3: TLC (SiO₂, eluent CH₂Cl₂-(CH₃)₂CO, 90/10, v/v) $R_f = 0.85$; MALDI-TOF MS: m/z 594.39 (M + 2H⁺); 615.37 (M + Na⁺) and 631.35 (M + K⁺). IR (KBr): 1650(s) (C = O), 1610, 1485, 1295, 1201, 1114, 1007, 923, 884 cm⁻¹. ¹H NMR (300 Hz, CDCl₃): δ (ppm) 1.31 [s, 18H, C(CH₃)₃]; 2.16 [s, 6H, OCH₃]; 3.75 [br s, 8H, ArCH₂Ar]; 6.29 [s, 4H, QuH]; 7.19 [s, 4H, ArH].

Results and discussion

Voltammetric studies

The electrochemical behaviour of **1** was investigated by cyclic voltammetry, square wave voltammetry and rotating-disk voltammetry at platinum electrode in CH₃CN–0.1 M TBAP.

Figure 1 shows the cyclic voltammogram of **1** at 100 mVs⁻¹. Four main oxidation peaks were detected. The first

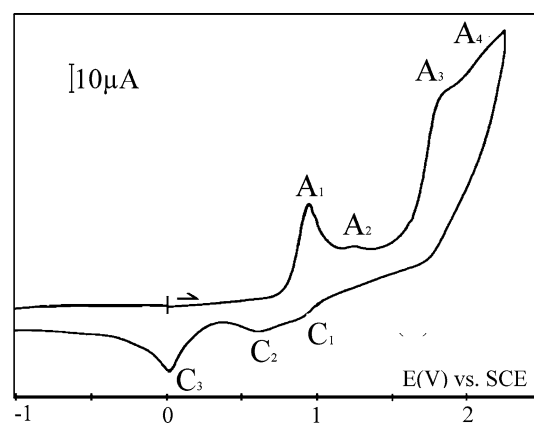


Fig. 1 Cyclic voltammogram at Pt disk electrode ($\Phi = 2$ mm) of 1.44 mM **1** in CH₃CN + 0.1 M TBAP. Sweep rate: 100 mV s⁻¹

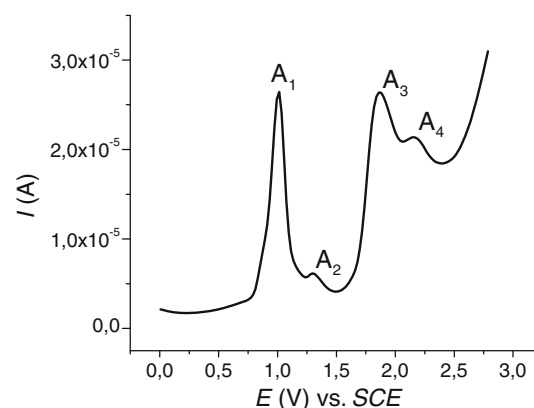


Fig. 2 SWV response of the Pt electrode in 1.95 mM **1** (CH₃CN + 0.1 M TBAP). $a = 25$ mV; $\Delta E_s = 20$ mV; $f = 10$ s⁻¹. Curve corresponding to the anodic scan

anodic peak (A₁) was observed at 0.94 V. A small oxidation peak (A₂) appears at 1.23 V. In the potential range between 1.8 and 2.2 V, two overlapped waves (A₃ and A₄) were noticed. In reverse direction, two small and irreversible cathodic waves (C₁ and C₂) were observed at 0.89 and 0.62 V, respectively. At 0.00 V, a well-defined and irreversible peak C₃ appears.

SWV (Fig. 2) confirmed the electroactivity of **1** obtained in the potential range 0.3–2.4 V. In fact, four redox processes were observed at 1.01, 1.31, 1.86 and 2.18 V, respectively. The height of the first and the third (A₁ and A₃) peak was similar. However, they shows that the number of electrons displayed are similar too.

Figure 3 reported the cyclic voltammograms of **1** evolution with scan rates. It was evident that for $\nu \geq 50$ mV s⁻¹ a cathodic peak (C₃) (Fig. 3, curves c, d and e) centered at ca. 0.00 V with a current maximum of $I_{max} = 86$ μ A (scan rate: 500 mVs⁻¹) was detected.

The repetitive CV in the aprotic media was examined and does not show passivation of the electrode. However,

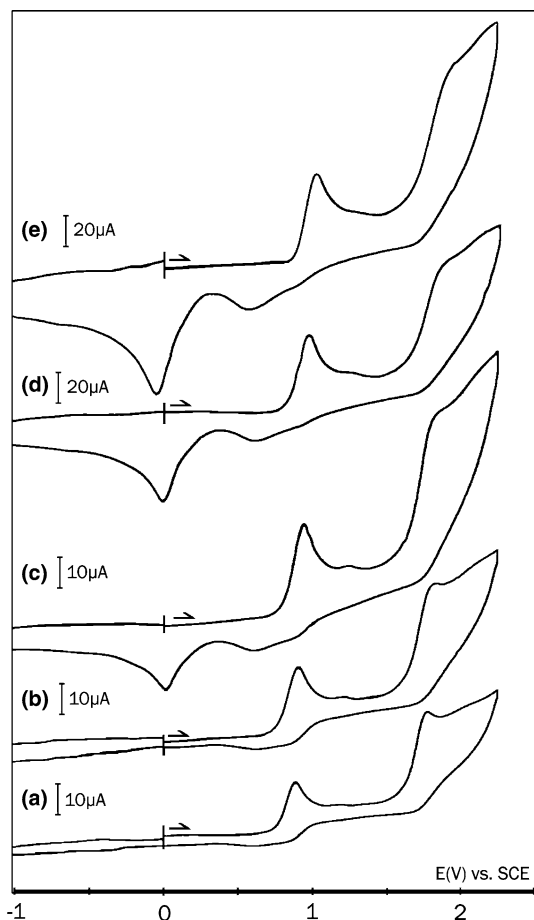


Fig. 3 Cyclic voltammogram at Pt disk electrode ($\Phi = 2$ mm) at various scan rates of 1.44 mM **1** in $\text{CH}_3\text{CN} + 0.1$ M TBAP. Sweep rates from (a) to (e) were: 25, 50, 100, 250, 500 mVs^{-1}

this result was in good agreement with that reported in the literature for different phenolic derivatives and is usually associated with various chemical reactions leading to different oxidation products (dimerization products, quinones derivatives) that do not necessarily passivate the electrode surface [25, 26].

Based on the two-electron character of the oxidation wave, it was proposed that the electrochemical oxidation of hydroquinone in acetonitrile consists in a sequence of two electrons and one proton transfer reactions [3]. By comparing the intensity of the first peak with the reversible system of the ferrocene (Fc^+/Fc) in the same conditions, one electron transfer have been determined for A_1 . However, A_1 could be assigned to the formation of a radical monocation of **1** through an irreversible system.

The maximum currents for process A_1 were measured and plotted as a function of the concentration of **1**. A linear relationship was obtained in the range 0.356–8 mM, in agreement with the Randles-Sevcik equation [27].

The plots of the first peak currents versus $\nu^{1/2}$ and the logarithm of the current versus the logarithm of the

substrate concentration were linear (slope: 0.967 $\mu\text{A}/\text{decade}$) in the sweep rate range 25–500 mVs^{-1} , showing diffusion control process at the electrode [28] and follow the theoretical previsions established by Nicholson and Shain [29].

No evidence for reversibility was seen for the first peak in the range of sweep rates 25–500 mVs^{-1} . It follows from linear plot of the logarithm of the peak current as a function of the logarithm of the sweep rate, that the mass transfer is controlled by diffusion process and the chemical reaction because the slope value of the straight line $\log I_p = f(\log \nu)$ is equal to 0.426 (≈ 0.5) (Fig. 4).

On the other hand, the increase of the scan rate leads to a shift of the peak potential to anodic value. The slope value of about 30 mV of the linear representation of $E_p = f(\log \nu)$ illustrated in Fig. 5 [30] and the irreversibility of the first oxidation peak in the range of scan rate allowed in this experiment are in agreement with a fast electron transfer followed by a first-order chemical reaction [31]. In addition, the peak potential shifts positively by about 30 mV per decade of the substrate concentration (Fig. 6). In our point of view and according to the literature, this chemical reaction is probably the deprotonation reaction of the cationic radical emerging from the first electron transfer.

Figure 7 depicts the voltammogram of **1** which was obtained at a rotating platinum-disk electrode in the supporting electrolyte in the potential range 0–2.5 V; compound **1** exhibits two oxidation process. The first wave shows a clear potential-independent plateau. The plots of E versus $\omega^{1/2}$ (ω : rotating-disk rate) in a first time and E versus $\log(I/I_L - I)$ in a second time resulted in a straight line with a slope of 63 mV per decade. The slope was in agreement with the value of 58 mV for a reversible one-electron transfer [32]. From the slopes, the value of the diffusion coefficient of **1** in acetonitrile was obtained: $D = 3.07 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$. Moreover, the standard potential was calculated: $E = 1.06$ V.

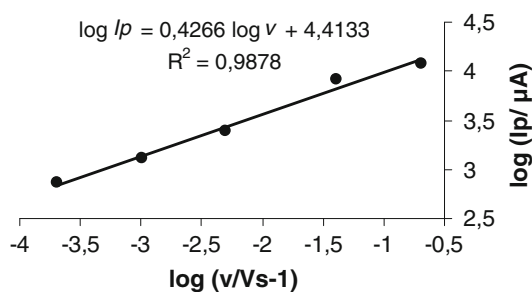


Fig. 4 Variation of the logarithm of the first peak current of **1** in $\text{CH}_3\text{CN} + 0.1$ M TBAP as a function of the logarithm of the sweep rate. Platinum electrode ($\Phi = 2$ mm), reference SCE. Concentration 144 mM

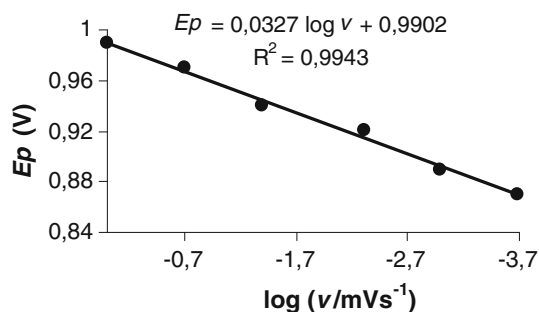


Fig. 5 Variation of the oxidation peak potential of **1** in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ as a function of the logarithm of the sweep rate. Platinum electrode ($\Phi = 2 \text{ mm}$), reference SCE. Concentration 144 mM

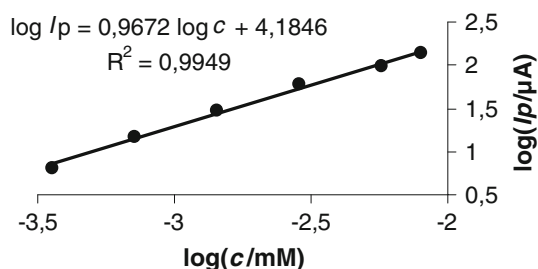


Fig. 6 Variation of the logarithm of the first peak current of **1** in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ as a function of the logarithm of substrate concentration. Platinum electrode ($\Phi = 2 \text{ mm}$), reference SCE. Sweep rate $\nu = 100 \text{ mV s}^{-1}$

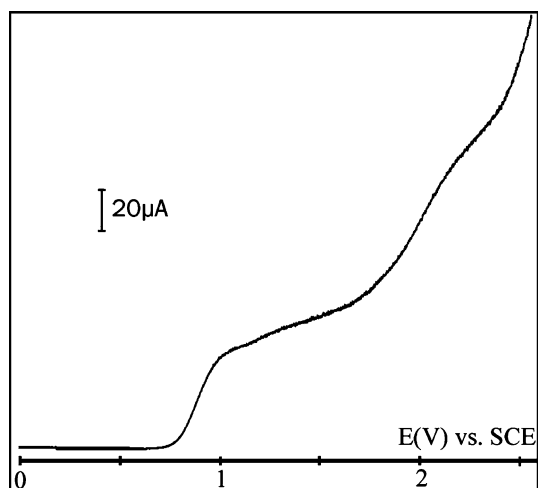


Fig. 7 Rotating disk voltammogram of **1** in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. Platinum electrode ($\Phi = 2 \text{ mm}$), reference SCE. Concentration $1,44 \text{ mM}$ (rotation rate 800 rev min^{-1})

Cyclic voltammograms obtained by changing the potential range were illustrated in Fig. 8. When the first anodic wave A_1 is observed separately over a short potential range (-0.2 to 1.12 V), (Fig. 8, curve a) the classic CV of the hydroquinone in acetonitrile solution were obtained [20]. It shows that to the anodic wave A_1

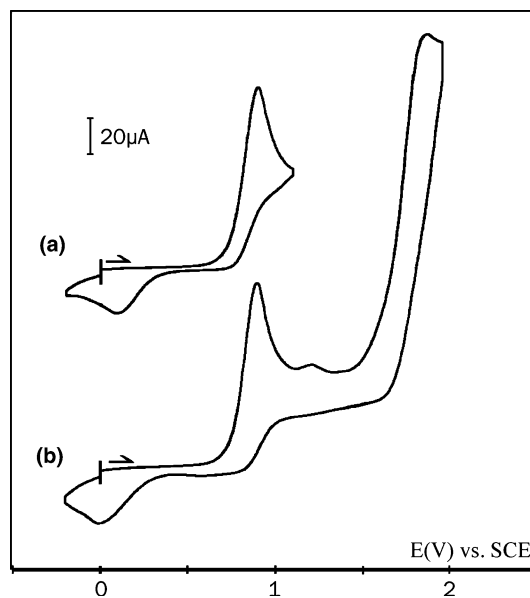


Fig. 8 Cyclic voltammogram at Pt disk electrode ($\Phi = 2 \text{ mm}$) at several potential range of $8 \cdot 10^{-3} \text{ M 1}$ in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. $\nu = 100 \text{ mV s}^{-1}$. Potential range: a -0.2 to 1.12 V ; b -0.2 to 1.99

corresponds a cathodic peak C_3 through an irreversible system ($\Delta E_p(A_1/C_3) = 0.94 \text{ V}$). It could be assigned to the monoprotonated quinone [4]. The first anodic peak A_1 shifts slightly towards the highest potential value when the potential range decreases, the cathodic peak C_3 as well. When the potential range was switched at 1.99 V (Fig. 8 curve b), the cathodic peaks C_1 and C_2 disappear.

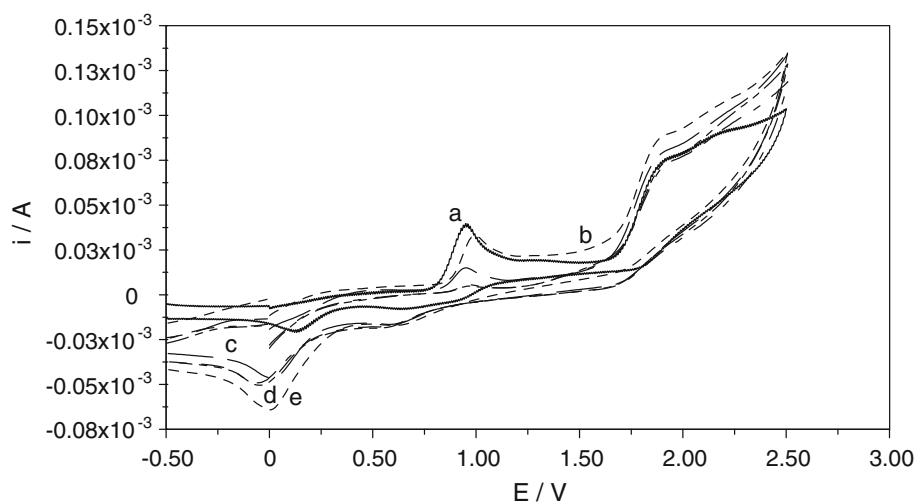
Chronoamperometry

Bulk electrolysis of **1** (46.5 mg ; 0.078 mmol) was accomplished at a potential slightly more anodic than the first anodic wave (1.3 V). Homogenization of the electrolytic solution was ensured by a mechanical stirring.

The cyclic voltammetry applied for the substrate explain that the first anodic peak involves only one electron (paragraph 3.1), when we interrupt the electrolysis after consumption of 1 electron per molecule, the corresponding CV (Fig. 9, curve b, time scale of electrolysis: 2 h ; $Q_{th} = 7.52 \text{ C}$: Theoretical quantity of coulomb) shows that the first peak intensity value slightly decrease. Two compounds, **2** (10 mg ; yield: 21.5%) and **3** (12 mg ; yield: 25.8%) were isolated as a pure compounds additionally to the starting material **1** (11 mg ; yield: $23, 6\%$), which were characterized by Maldi-Tof, $^1\text{H NMR}$ and ATR IR spectrometric analyses (structure defined in the “Experimental” section). Product **2** was slightly yellowish and presents an intermediate product which forms during the electrolysis, **3** is an intense yellow powder and could be the majority product.

The total electrolysis was stopped when the level of intensity became sufficiently low, required a consumption

Fig. 9 Cyclic voltammograms at Pt disk electrode in 1.95 mM **1** in CH₃CN + 0.1 M TBAP. Scan each time scale of 2 h of electrolysis at 1.3 V vs. SCE. Scan rate $\nu = 100 \text{ mVs}^{-1}$



of 2.25 Faradays per molecule. The solution becomes yellowish. The solvent was removed under vacuum and the oxidation residue mixture was extracted with diethyl ether. The products were separated by chromatography on preparative patches of silica gel with a mixture of dichloromethane-acetone (95/5, v/v). Two products were obtained, the starting substrate **1** and a yellowish product, which corresponds to the calix[4]diquinone **3**, was characterized by ATR IR, ¹H RMN and Maldi-Tof (see link “[Experimental](#)” section). To form the **3** product it is necessary the consumption of 4 electrons per molecule. We observe that, just the amount of 2.25 electrons transfer producing at the electrode surface and the rest of electrons transfer producing in the electrolytic solution to form the resulting product (**3**).

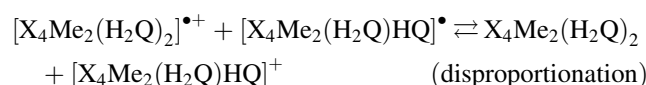
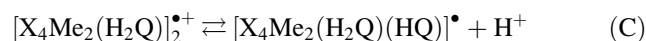
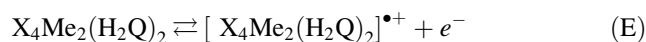
On the other hand, an electrolysis was achieved at 2.1 V (42 mg; 0.07 mmol) subsequent to the third oxidation peak potential (the height wave is approximately equal to one electron) required a consumption of 4.15 Faradays per molecule. This result was in agreement with the number of electron transfer necessary to electrogenerate the final product. The solvent was removed and the residue obtained was extracted with diethyl ether and purified by column chromatography (Silica gel 60, CH₂Cl₂-(CH₃)₂CO, 95/5, v/v). The formed products was purified by chromatography on silica gel with a mixture of dichloromethane-acetone (95/5, v/v) as eluent. Two resulting products were separated, the initial substrate **1** and the product **3**.

Under the experimental conditions, a yellowish product was deposit on the platinum grid. The deposited product on the platinum grill was analysed and it appears that the electrodeposited yellow substance was the calix[4]diquinone **3**.

The macroelectrolysis was controlled by cyclic voltammetry. The voltammograms (Fig. 9) shows that the exhaustive electrooxidation makes the first peak height

very low, but he does not entirely disappear. The bulk electrolysis was controlled by SWV too. Different anodic scans were performed before, during and after electrolysis at 1.3 V. The height of the first peak was decrease as well as the time scale of chronoamperometry increase and becomes almost constant after a time scale of 6 h. This behaviour was similar to that previously observed from CV.

These results indicate that the initial substrate was generating into the oxidation reaction. The situation is of the same type as for a classical ECE-disproportionation mechanism [33]:



The follow-up by cyclic voltammetry and SWV of the chronoamperometry applied at a controlled potential of 2.1 V shows that the first peak height decrease on the first time, later the third peak begin to attenuate.

Nevertheless, after purification, the product **3** was examined by cyclic voltammetry. Figure 10A shows the electroactivity domain of the product. In the potential range of -1.2 to 0 V (Fig. 10B) two reversible reduction processes were obtained (First system: $E_p^{1/2} = -0.675 \text{ V}$; $\Delta E_p = 0.07 \text{ V}$; second system $E_p^{1/2} = -0.815 \text{ V}$; $\Delta E_p = 0.065 \text{ V}$). This result was in agreement with literature [2] and will be present the double reduction of the calix[4]diquinone in acetonitrile media. The product **2** was not examined by CV because the quantity of the isolated product is very small.

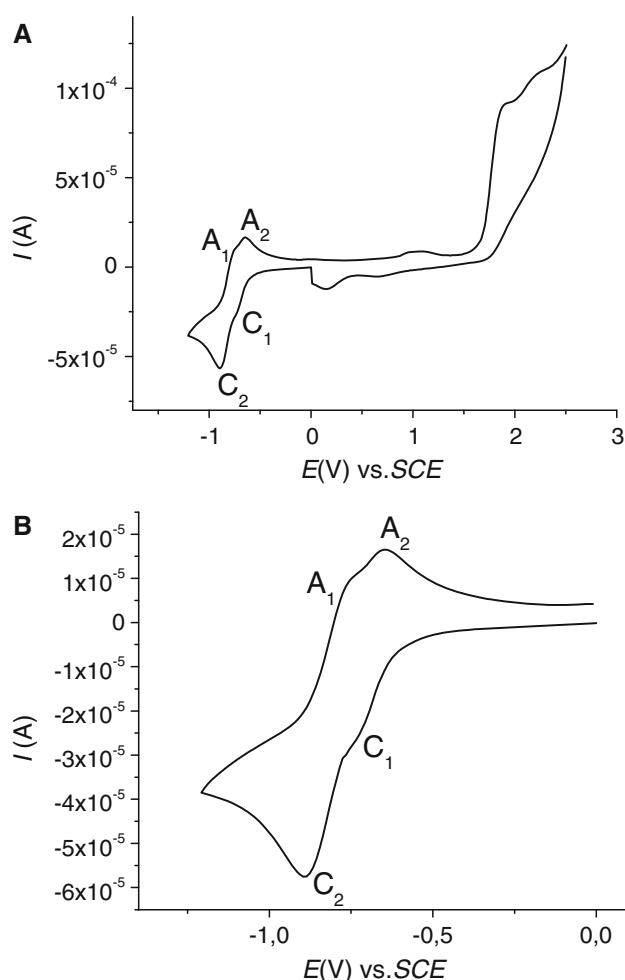


Fig. 10 Cyclic voltammogram at Pt disk electrode of 3.22 mM **3** in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. **A** Potential range: 0 to -1.2 to 2.5 V ; **B** Zoom of (A), potential range: 0 to -1.2 to 0 V . Platinum electrode ($\Phi = 2 \text{ mm}$), reference SCE. Sweep rate $\nu = 100 \text{ V s}^{-1}$

Voltammetric measurements shows that the first electrochemical process A_1 involves an apparent one-electron (n_{app}) [27] transfer mainly produced at the electrode surface. However, this could not be confirmed by coulometric measurements in macroscale electrolysis [9]. On the other hand, cyclic voltammogram obtained at a potential range from -0.2 to 1.31 V , show a new positive/negative peak system at a slightly more positive potential than that of the first oxidation peak. These results clearly indicate the presence of a further electron transfer reaction and also of its coupling with a chemical reaction.

The third anodic step A_3 involves one-electron transfer; it could be assigned to the oxidation of the intermediate product formed in route to generate essentially the final product. Therefore, the first and the second anodic peaks in the cyclic voltammogram may correspond to the oxidation of the first hydroquinone moiety to the monoprotonated quinone moiety. The third and the fourth peaks, may

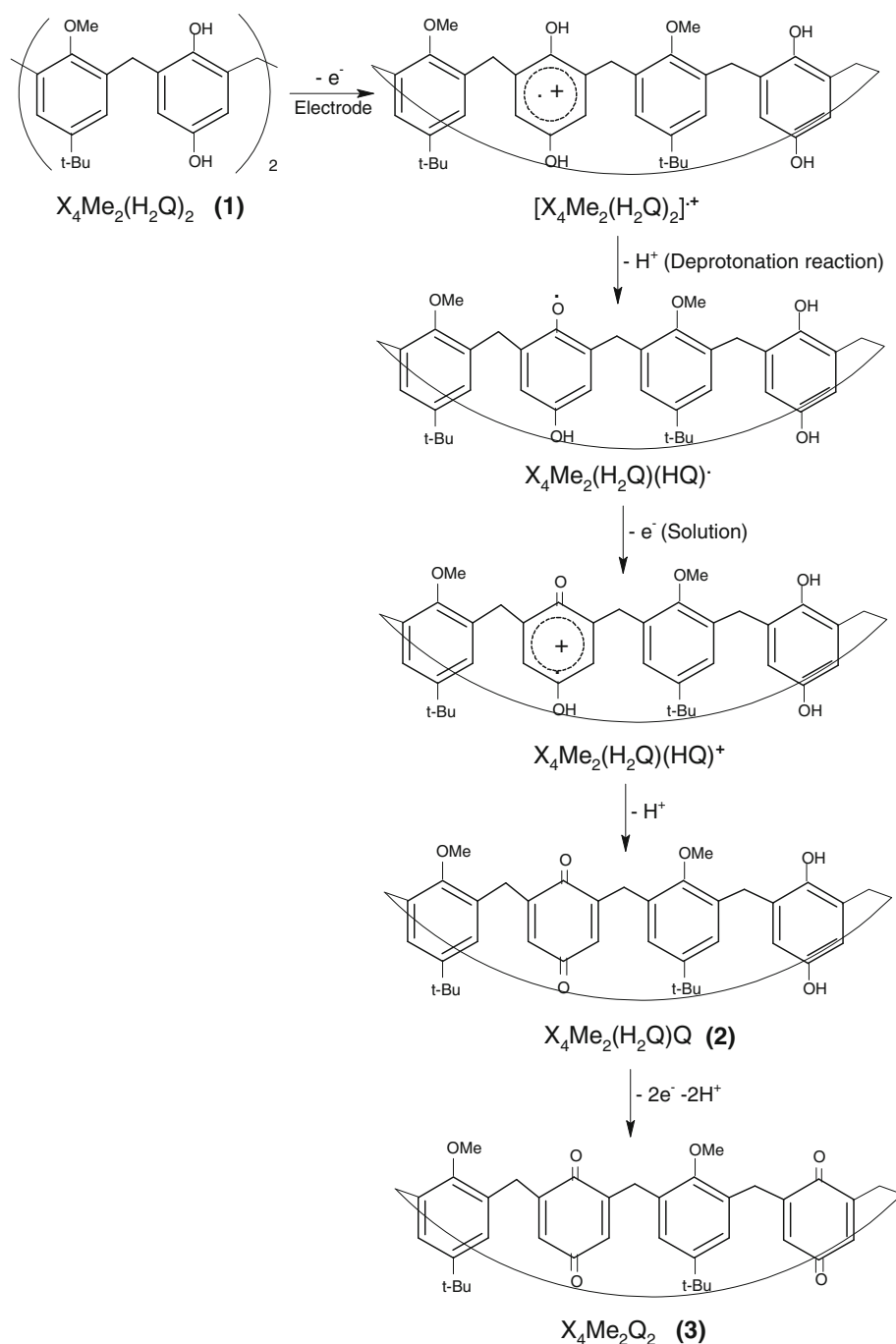
correspond to the oxidation of the next hydroquinone moiety to give the calix[4]arenequinone. The evolving in solution may follow an ECE sequence [34, 35]. It is generally accepted that the two-electron reduction of $\text{X}_4\text{Me}_2\text{Q}(\text{QH}^+)$ occurs at the level of wave C_3 [36]. The low current intensity of wave C_3 with respect to wave A_1 can be explained by a slow reduction kinetics of $\text{X}_4\text{Me}_2\text{Q}(\text{QH}^+)$, as it is shown by a significant peak potential variation with the scan rate (75 mV/dec).

Taking into account the voltammetric patterns of **1** and **3** and electrolysis results, the detailed mechanism of anodic oxidation of the 5, 17-di-*tert*-butyl-11, 23, 25, 27-di-dihydroxy-26, 28-dimethoxy calix[4]arene is projected in Scheme 2. The mechanism could involve in the first step one-electron transfer (E) which allows the formation to the radical cation $\mathbf{1}^{\bullet+}$. The latter undergoes a deprotonation (C_H) to give $\mathbf{1}^\bullet$. The radical undergoes a further electron-transfer reaction in solution. Then, a disproportionation occurs, and generates the departure substrate **1** (see the mechanism of EC_HE -disproportionation). The cationic intermediate $\text{X}_4\text{Me}_2(\text{H}_2\text{Q})(\text{HQ})^+$ undergoes deprotonation to generate a product, which is the calix[4]quinhydrone **2**. The rest of the electrochemical and chemical processes occur in the solution. In fact, the literature [37] confirms that the role of electron transfer reactions in solution should be considered as well as electron transfers at the electrode. The calix[4]quinhydrone **2** undergoes an EC_HEC_H mechanism, with the loss of two electrons and two protons to generate the foremost product **3**.

Conclusion

In this communication we have shown the oxidative electroactivity using cyclic, square wave and rotating-disk voltammetry. The obtained results show the 5, 17-di-*tert*-butyl-11, 23, 25, 27-di-dihydroxy-26, 28-dimethoxy calix[4]arene exhibit that the first irreversible wave with a mass transfer controlled both by diffusion process and a deprotonation reaction of the cation radical emerging from the charge transfer. The macroscales electrolysis investigated at the first and the third peak potential lead to show that the departure substrate is entirely electrolysed but it was regenerating involving a classical ECE-disproportionation mechanism. The electrochemical generation of the intermediate compound which is the calix[4]quinhydrone is followed by the electrosynthesis in solution of the calix[4]diquinone. Thus, we confirm that under conditions of macroelectrolysis requiring long duration experiments, phenolic sites are readily converted into the corresponding quinones. We show too, that when the electrolysis was performed after the third oxidation peak, ($\text{X}_4\text{Me}_2\text{Q}_2$) was

Scheme 2 Schematic pathway from dimethoxycalix[4]arene $X_4Me_2H_2$ to the dimethoxycalix[4]arene-quinone $X_4Me_2Q_2$ and dimethoxycalix[4]arene-dihydroquinone $X_4Me_2(H_2Q)_2$



electrogenerated in solution and was deposited, afterward, on the platinum grid.

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