

## Anion of Quinocyanomethylene: Simulation of Dimerization

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(Received 26<sup>th</sup> February 2007, revised 7<sup>th</sup> April 2007)

**Summary:** 3, 5-Bis (1,1-dimethylethyl)-4-oxo-2, 5-cyclohexadienyliideneacetonitrile, QM, is an electron acceptor. Simulation of cyclic voltammogram of QM, in acetonitrile at platinum electrode was carried out and a scheme was suggested to obtain the heterogeneous rate constants for electron transfer. The results of simulations based on two shareware programs are generally consistent with theoretical and experimental work.

### Introduction

Quinonemethides are important intermediates [1] in the redox chemistry of phenols and they are implicated as intermediates in both the biosynthesis and oxidative degradation of lignins. The rich redox chemistry of quinonemethides does, however include the interesting examples of cathodic dimerisation reactions including electrohydrodimerisation [1].

The electrochemistry of quinones received much early attention and provided some of the earliest examples of correlations between structure and redox potential, but little attention has been paid to the electrochemical behavior of quinocyanomethylenes. Among quinocyanomethylenes, relatively stable quinocyanomethylenes have been investigated electrochemically [2].

The electrochemical reduction of eight quinones, 9, 10-antraquinone, duroquinone, 2, 6-di-tert-butyl-1, 4-benzoquinone, 2, 6-dimethoxy-1, 4-benzoquinone, 9, 10-phenanthrenequinone, tetrachloro-1, 2-benzoquinone, tetrabromo-1, 2-benzoquinone and 3, 5-di-tert-butyl-1, 2-benzoquinone, have been studied in acetonitrile. In every case it was found that cyclic voltammograms differed in significant ways from those expected for simple stepwise reduction of the quinone to its radical anion and dianion. The various types of deviations for the eight quinones have been cataloged and some speculation is offered concerning their origins [3].

The anodic oxidation of 2, 6-di-t-butyl-4-methylphenolate, as well as the 4-ethyl and 4-n-butyl derivatives, has been studied by cyclic voltammetry in acetonitrile with a platinum disk

electrode. The initially formed phenoxyl radicals dimerize reversibly to form the *para*-quinol ethers and the reaction has been characterized quantitatively by cyclic voltammetry. The values of  $k_r^{1/2}K^{-3/4}$  are 0.20, 0.23 and 0.6 s<sup>-1/2</sup> (mol/l)<sup>1/4</sup>, where  $k_r$  is the dimerization rate constant and  $K$  is the dimerization equilibrium constant. Values of  $K$  have been estimated from peak potential measurements [4].

Examination of the cathodic hydrogenation of two examples of quinonemethides reveals an unusual pathway in which the anion radicals of the quinonemethides fuchson and its dimethyl analogue are protonated reversibly at oxygen by substituted phenols in DMSO to give relatively stable triarylmethyl radicals which are not reduced at the first reduction potential of the quinonemethides; this behaviour contrasts with that usually found, i.e. anion-radicals are usually formed at more cathodic potentials than reduction potentials of radicals derived from them by protonation [5].

The EE mechanism (two-electron transfer) for cyclic voltammetry was investigated in considerable detail along with the effect of disproportionation. The theory was developed for either the first or second electron transfer being slow while the other one was reversible. It was possible to develop generalized working curves for the height and shape of the wave regardless of the difference in  $E^0$ 's and the values of  $\alpha$  and  $k_s$ . This theory was applied to the analysis of the reduction of benzyl in the presence of alkaline earth ions in dimethylformamide [6].

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The electrochemical oxidation of 2, 4, 6-tri-*tert*-butylphenol as well as the phenoxide and phenoxy radical derived from it has been investigated in acetonitrile and ethanol+water. The ease of oxidation decreases in the order phenoxide, phenoxy radical, phenol with the separation between potentials for phenoxide oxidation and phenoxy radical oxidation being 1.2 V in acetonitrile. The phenoxide is oxidized to the stable phenoxy radical in a highly reversible reaction in acetonitrile and alkaline ethanol+water. Oxidation of the radical produces a phenoxonium ion which is attacked by water giving 2, 4, 6-tri-*tert*-butyl-4-hydroxy-2, 5-cyclohexadienone. This two electron product is also formed upon oxidation of the phenol in either solvent. However, in acidic media the hydroxydienone dealkylates give 2, 6-di-*tert*-butylhydroquinone which is oxidized to the final product 2, 6-di-*tert*-butyl-1, 4-benzoquinone. The dealkylation is quite rapid in anhydrous acetonitrile but the rate is depressed by the addition of water. A novel double potential step experiment was used to characterize the oxidation of the phenoxy radical. A step to a potential where the phenoxide is oxidized to the phenoxy radical is followed by a step to a potential where the phenoxy radical is oxidized. The current during the second step is unusually small because protons produced by the oxidation of the radical deactivate the phenoxide. The current-time curve was found to agree with that predicted by digital simulation [7].

Reduction half-wave potentials of several phenoxy radicals have been measured by photomodulated voltammetry in acetonitrile. Two of the investigated radicals exhibit a reversible behavior, but for the others a rather quasi-reversible nature of the heterogeneous electron transfer has to be considered. The measured reduction half-wave potentials are within 70 mV of reported values for formal one-electron potentials of the phenolate-phenoxyl couples. That is why one can assume that the values of half-wave reduction potentials are close to the standard potentials of the electrochemical reactions. Differences of the bond dissociation energy (BDE) (O-H), for the substituted phenols relative to the BDE (O-H) of the phenol were calculated and compared with corresponding data in the gas phase [8].

In this paper, the electrochemical simulation of cyclic voltammogram of quinocy-

anomethylene in acetonitrile at platinum electrode was studied using two shareware programs.

## Results and Discussion

Cyclic voltammetry of quinocyanomethylene (3, 5-bis (1, 1 - dimethylethyl) -4-oxo-2, 5-cyclohexadienylideneacetonitrile) also abbreviated as QM, was carried out at platinum electrode in dry acetonitrile containing 0.1 M sodium perchlorate at 0.2 V/ s scan rate, Fig. 1 [9]. One cathodic and one anodic peak were observed. No reversible peak corresponding to the cathodic peak was observed at the scan rate up to 200 V/s. The cathodic peak potential for the experimental voltammogram was -1402 mV and the anodic peak potential was 237 mV. At lower scan rates  $I_{p,c}$  scaled linearly with square root of scan rate,  $v^{1/2}$ .

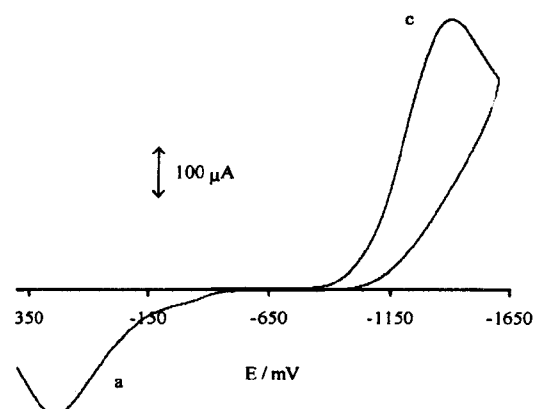


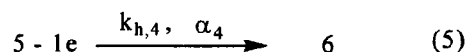
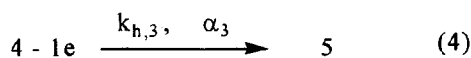
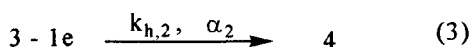
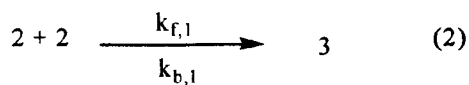
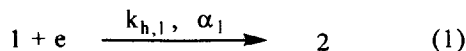
Fig. 1: Cyclic voltammogram of 3, 5-bis (1,1-dimethylethyl)-4-oxo-2, 5-cyclohexadienylideneacetonitrile, QM, at platinum electrode ( $0.07 \text{ cm}^2$ ). Electrolyte solution 0.1 M sodium perchlorate in acetonitrile. Potential sweep rate 0.200 V/ s. Potential vs.  $\text{Ag}/\text{Ag}^+ \sim 0.01 \text{ M}$ .

The initial heterogeneous electron addition to QM yields anion radical that dimerises to bibenzyl dianion. To elucidate the electro-reduction mechanism of QM, simulation according to Scheme 1 yielded a reasonable agreement with the experimental cyclic voltammogram of quinocyanomethylene, Fig. 1. The simulated cyclic voltammograms using CVSIM and ESP 2.4 are shown in Fig. 2 and Fig. 3, respectively.

Table-1: Parameters used for the simulation using Scheme 1.

Program	$k_{h,1}$ cm/s	$k_{h,2}$ cm/s	$k_{h,3}$ cm/s	$k_{h,4}$ cm/s	$k_{f,1}$ s <sup>-1</sup>	$k_{b,1}$ s <sup>-1</sup>	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$t^*$ s
CVSIM	0.001	0.0005	0.0014	0.0014	27200	0	0.23	0.70	0.60	0.52	123
ESP 2.4	0.001	0.0002	0.0012	0.002	27200	0	0.23	0.80	0.84	0.74	20

\* Time taken for simulation



Scheme-1: Sequence of electrochemical and chemical reactions for simulation.

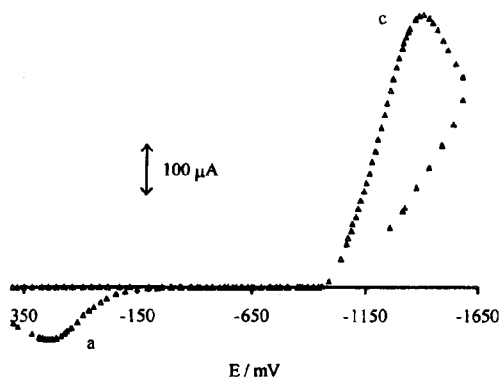


Fig. 2: Cyclic voltammogram of 3, 5-bis (1,1-dimethylethyl)-4-oxo-2, 5-cyclohexadieny-lideneacetonitrile, QM, simulated using CVSIM, parameters are given in Table-1.

The concentration of the species 1 which stands for QM, was taken equal to 2.44 mM. In Scheme-1, QM is represented by 1; 2 denotes QM<sup>-</sup> anion radical; 3 represents the corresponding dimer-di-anion (QM)<sub>2</sub><sup>2-</sup>; 4 the dimer-anion-radical (QM)<sub>2</sub><sup>-</sup> derived from oxidation of 3 (QM)<sub>2</sub><sup>2-</sup>. While 5 might possibly be dimer di-radical (QM)<sub>2</sub> and 6 takes into account the formation of cation radical [6-7] at higher anodic potential.

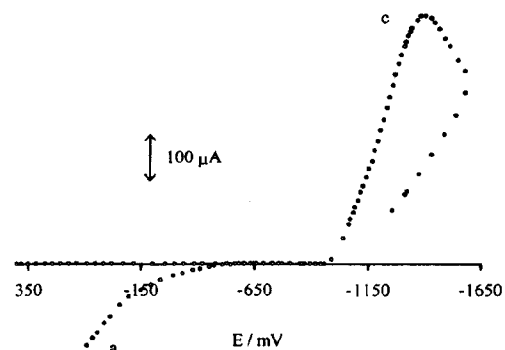


Fig. 3: Cyclic voltammogram of 3, 5-bis (1,1-dimethylethyl)-4-oxo-2, 5-cyclohexadieny-lideneacetonitrile, QM, simulated using ESP 2.4, parameters are given in Table-1.

Parameters given in Table-1 were used for simulations according to sequence of chemical and electrochemical reactions indicated in Scheme-1. The cathodic peak potential for simulated curves using both CVSIM and ESP 2.4 was, -1403 mV, while the anodic peak potential for CVSIM simulated voltammogram was 234 mV, while for ESP 2.4 it was 237 mV, as shown in Table-2. Potentials used for simulation using Scheme-1 are given in Table-3.

Table-2: Characteristics of simulated and experimental cyclic voltammograms, shown in Figs. 1, 2 and 3.

	$E_{p,c}$ mV	$E_{p,a}$ mV	$\Delta E_{p,c}$ mV	$\Delta E_{p,a}$ mV
Experimental Curve	-1402	237	-211	230
Simulated Curve using CVSIM	-1403	234	-208	158
Simulated Curve using ESP 2.4	-1403	237	-208	241

Table-3: Potentials for Scheme-1.

Reactions	Potentials, V	
	CVSIM	ESP 2.4
(1)	-1.156	-1.156
(3)	0.011	-0.379
(4)	0.190	0.000
(5)	0.270	0.072

The cathodic half-peak-widths,  $\Delta E_{p,c}$  ( $E_{p,c} - E_{p/2,c}$ ) for experimental and simulated voltammograms using CVSIM and ESP 2.4 were respectively  $-211$  mV and  $-208$  mV.

The anodic half-peak-width,  $\Delta E_{p,a}$  ( $E_{p,a} - E_{p/2,a}$ ) for experimental is  $230$  mV and for simulated cyclic voltammograms using ESP 2.4 was  $241$  mV. In case of CVSIM the anodic half-peak-width was  $158$  mV; and low anodic current was returned by simulation, Fig. 2. The variation of logarithm of the cathodic peak current and anodic peak current, as a function of logarithm of scan rate is shown as Figs. 4 and 5, respectively.

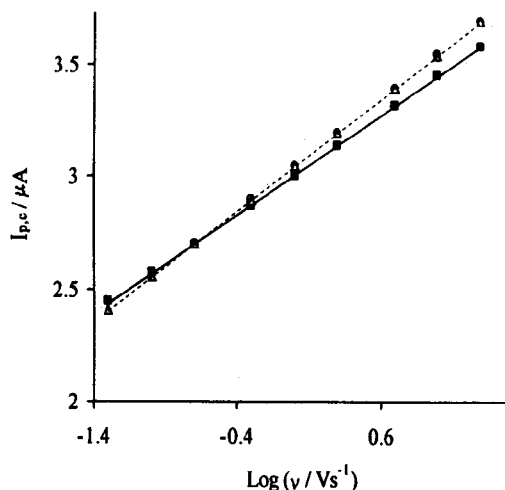


Fig. 4: Variation of the logarithm of the cathodic peak current,  $I_{p,c}$ , as a function of logarithm of scan rate. Solid line — for experimental  $y = 0.4387x + 3.0072$ ,  $R^2 = 0.9998$ , dotted line ----- for simulation  $y = 0.4934x + 3.0463$ ,  $R^2 = 1$

The slope,  $\log I_{p,c} / \log v$ , of the straight line was  $0.483$  for experimental and  $0.493$  for simulated, indicating acceptable agreement between experiment and simulation, while in case of  $\log I_{p,a} / \log v$ , the corresponding values are  $0.305$  for experimental curve and  $0.360$  for simulated curve using ESP 2.4.

The plot of  $E_{p,c}$  vs.  $\log v$  is shown in Fig. 6. Since the first heterogeneous electron transfer leads to several possible follow-up reactions, the agreement between the experimental and simulated slopes in Fig. 6, can be taken as fair. Tables- 4 and

Table-4: Characteristics of cathodic part of cyclic voltammometric curves of 3, 5-bis (1,1 dimethylethyl)-4-oxo-2, 5- cyclohexadienylidene-acetonitrile at different scan rates.

v V/s	Experimental			Simulation using CVSIM			Simulation using ESP		
	$E_{p,c}$ mV	$\Delta E_{p,c}$ mV	$I_{p,c}$ $\mu A$	$E_{p,c}$ mV	$\Delta E_{p,c}$ mV	$I_{p,c}$ $\mu A$	$E_{p,c}$ mV	$\Delta E_{p,c}$ mV	$I_{p,c}$ $\mu A$
0.050	-1295	-166	279	-	-	-	-1323	-204	256
0.100	-1340	-140	373	-	-	-	-1363	-208	357
0.200	-1389	-215	495	-1403	-207	504	-1403	-208	501
0.500	-1467	-242	739	-1455	-208	791	-1455	-208	787
1.000	-1517	-273	1000	-1495	-210	1110	-1494	-208	1110
2.000	-1574	-306	1370	-1533	-208	1570	-1532	-208	1556
5.000	-1664	-343	2070	-1584	-207	2480	-1583	-207	2460
10.00	-1751	-381	2830	-1622	-207	3500	-1622	-207	3470
20.00	-1869	-436	3800	-1662	-208	4950	-1661	-208	4910

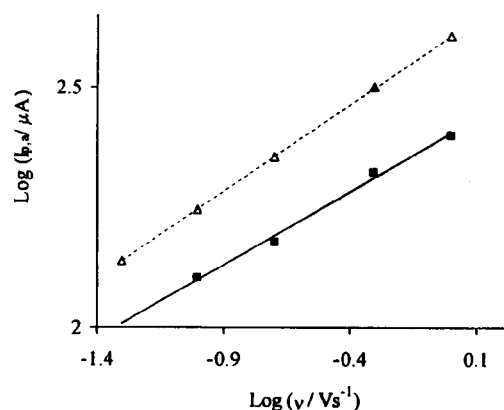


Fig. 5: Variation of the logarithm of the anodic peak current,  $I_{p,a}$ , as a function of logarithm of scan rate. Solid line — for experimental  $y = 0.3053x + 2.4044$ ,  $R^2 = 0.994$ , dotted line ----- for simulation  $y = 0.3608x + 2.6082$ ,  $R^2 = 0.999$ .

5 provide an overview of the comparison between experimental and simulated electrochemical characteristics of the cyclic voltammometric behavior of QM in acetonitrile at a platinum cathode.

### Experimental

Cyclic voltammogram of quinocyanomethylene (3, 5-bis (1, 1-dimethylethyl) -4-oxo-2, 5-cyclohexadienylideneacetonitrile) at platinum electrode in the electrolyte solution  $0.1$  M sodium perchlorate in acetonitrile were as published in literature [9]. The potential was measured vs. silver/silver ion  $\sim 0.01$  M reference electrode [10].

Table-5: Characteristics of anodic part of cyclic voltammetric curves of 3, 5-bis (1, 1 dimethylethyl)-4-oxo-2, 5- cyclohexadienylideneacetonitrile at different scan rates.

v V/s	Experimental			Simulation using CVSIM			Simulation using ESP		
	E <sub>p,a</sub> mV	ΔE <sub>p,a</sub> mV	I <sub>p,a</sub> μA	E <sub>p,a</sub> mV	ΔE <sub>p,a</sub> mV	I <sub>p,a</sub> μA	E <sub>p,a</sub> mV	ΔE <sub>p,a</sub> mV	I <sub>p,c</sub> μA
0.050	79	-146	129	-	-	-	153	184	-138
0.100	-123	-127	191	-	-	-	191	212	-176
0.200	-255	-151	121	234	158	-97.1	234	237	-227
0.500	-200	-211	114	273	157	-140	300	263	-317
1.000	226	-251	287	302	157	-182	348	270	-405

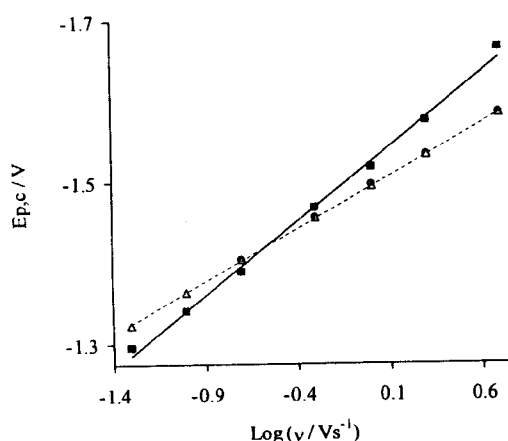


Fig. 6: Variation of the cathodic peak potential, E<sub>p,c</sub>, as a function of logarithm of scan rate. Solid line — for experimental  $y = -0.1834x - 1.524$ ,  $R^2 = 0.996$ , dotted line --- for simulation  $y = -0.13x - 1.4932$ ,  $R^2 = 0.999$ .

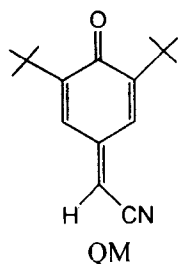


Fig. 7: Structural formula of quinocyanomethylene (QM)

3, 5-bis (1, 1- dimethylethyl ) - 4 - oxo - 2, 5 - cyclohexadienylideneacetonitrile, is the IUPAC

name of QM; also abbreviated as quinocyanomethylene, Fig. 7.

#### Electrochemical Simulation:

Two shareware programs were used: CVSIM [11] and ESP 2.4 [12]. CVSIM program written in Turbo Pascal was run using Turbo Pascal Free downloaded from web. The ESP 2.4 written in DOS was run using DOS. All the simulations were executed on a PC Pentium III 600 MHz processor with 64 MB RAM.

#### Conclusion

3, 5-Bis (1, 1-dimethylethyl)-4-oxo-2, 5-cyclohexadienylideneacetonitrile, QM, is an electron acceptor. Simulation of cyclic voltammogram of QM, in acetonitrile at platinum electrode was carried out. The out-come of simulation is generally consistent with theoretical [13] and experimental work [1,9].

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