

Simulation of Voltammogram of a Hindered Quinomethylene

Inam-ul-Haque* and Asim Khan

Department of Chemistry, University of Engineering and Technology, Lahore-54890, Pakistan

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Abstract. Electrochemical simulation of the cyclic voltammogram of a sterically hindered quinomethylene in dimethyl formamide (DMF) tetra-*n*-butylammonium perchlorate at mercury bead electrode was studied using two shareware simulation programs, namely, cyclic voltammetry simulation (CVSIM) and Electrochemical simulation package 2.4 (ESP 2.4). Two cathodic and two anodic peaks were analysed. ESP 2.4 took lesser time for simulations.

Keywords: electrochemical simulation, hindered quinomethylene, cyclic voltammetry

Introduction

The cathodic reactions of a number of relatively stable quinomethides have been examined by cyclic voltammetry, controlled potential coulometry, and rigorous product analysis by following preparative-scale electrolysis. The results of cyclic voltammetric experiments differ in some respects from those of earlier polarographic work. The life times of the electrogenerated radical-anions and dianions, in the absence of an added electrophile, were governed by steric hindrance. Though hindered intermediates are relatively long-lived, yet they hydrogenate in the presence of proton donors and alkylate in the presence of methyl iodide. The less hindered analogs efficiently and rapidly dimerize, at carbon, with concomitant protonation or O-methylation depending on the added electrophile. The ambient cathodically generated nucleophiles alkylate at both carbon and oxygen and the competition is crucially dependent on the cation (tetra-butylammonium ion or lithium ion). An efficient reaction between oxygen and triarylmethyl radicals has been shown (Goulart and Utley, 1988).

Six extended *para*-quinones, with sterically hindered keto groups, have been characterized by UV-vis, ¹H NMR and ¹³C NMR spectroscopy. Their electrochemical properties have been investigated in pyridine solution using cyclic voltammetry, differential pulse voltammetry, chronoamperometry and controlled potential electrolysis. All species exhibit two successive one electron reductions leading to the dianions via monoanions. The dianions can be reoxidized to the quinones. An EE-type mechanism for the studied quinones was verified by computer simulation; the standard rate constants (k_{s1} and k_{s2}) of the heterogeneous charge-transfer were in the region of $6.5\text{--}12.5 \times 10^{-3} \text{ cm.s}^{-1}$. The first reduction peak potentials showed a good linear relationship with the calculated lower unoccu-

pied molecular orbital (LUMO) energy levels. The radical anions, prepared electrochemically in the first reduction step, were persistent for several hours in the absence of air. They were also characterized by ultra violet-visible (UV-vis), electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopy revealing that the odd electron was delocalized over the whole π -system (Zhou and Rieker, 1997).

The electrochemical reductions of eight quinones, namely, 9, 10-anthraquinone; 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 has been offered concerning their origins (Lehmann and Evans, 2001).

Cyclic voltammetry of QM [= 3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylideneacetonitrile] has been investigated at the platinum cathode in dry acetonitrile containing sodium perchlorate. Two peaks, one cathodic and one anodic, were observed. The peak currents in both the cases scaled linearly with square root of the scan rate. The initial heterogeneous electron addition to QM yielded an anion radical that dimerises to bibenzyl dianion. The dianion is a mixture of meso, and (\pm) isomers. The anodic peak corresponding to the oxidation of these isomers was broad, which resulted from overlap of individual peaks from various bibenzyl isomers (Haque *et al.*, 2005).

The cyclic voltammetry experiments have demonstrated that 2-methoxy-4-[2-(2-methoxyphenoxy)propylidene]-2,5-cyclohexadien-1-one, as the model for lignin, accept electrons

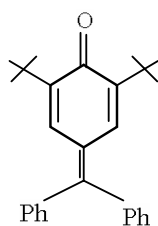
*Author for correspondence; E-mail: inamul.haque@gmail.com; namihaque@yahoo.com

from reduced anthraquinone and then rapidly fragment at methoxyphenoxy linkage to the corresponding phenolic products, namely, guaiacol and isoeugenol. When the two reactants have similar reduction potentials, the electron transfer step between anthrahydroquinone radical anions with quinonemethides (I) is fast and efficient, and the reduction potentials vary with the structure of quinonemethides and the solvent used. In the time-scale of the voltammetric experiments, the electron transfer occurs in preference to the adduct formation reactions (Dimmel *et al.*, 1985). Redox and related reactions of quinomethylenes have been reviewed recently (Haque and Razvi, 2005).

Materials and Methods

Cyclic voltammograms. The cyclic voltammograms of hindered quinomethylene (**DQM**) at mercury bead electrode, in 0.1 M DMF/tetra-*n*-butylammonium perchlorate versus Ag/AgCl as the reference were, as published in literature (Goulart and Utley, 1988).

Electrochemical simulation. Two shareware programmes were used: Cyclic voltammetry simulation (CVSIM) (Gosser, 1993), and Electrochemical simulation package 2.4 (ESP 2.4) (Nervi, 1998). CVSIM programme, written in Turbo Pascal, was run using Turbo Pascal Free downloaded from the 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. The **DQM** used was 2,6-di-tert-butyl-4-(diphenylmethylene)-2,5-cyclohexadiene-1-one as shown below:



Results and Discussion

The cyclic voltammogram of the hindered quinomethylene **DQM**, [2,6-di-tert-butyl-4-(diphenylmethylene)-2,5-cyclohexadiene-1-one] at a mercury bead electrode in DMF containing 0.1 M tetra-*n*-butylammonium perchlorate at a scan rate of 0.05 V/s is shown in Fig. 1 (Goulart and Utley, 1988).

Cathodic **peak I** corresponds to the formation of **DQM** monoanion radical, which accepts the second electron (**peak II**) to yield the dianion of **DQM**. This second cathodic peak does not become partially or fully reversible at higher scan rates. **Peak III** is the anodic counterpart of the cathodic **peak I**.

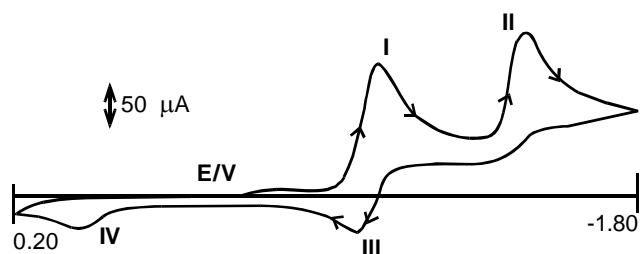
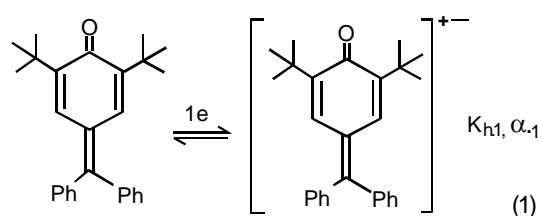
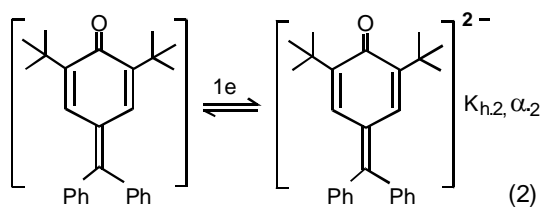


Fig. 1. Experimental cyclic voltammogram of the sterically hindered quinomethylene (**DQM**) after, Goulart and Utley (1988).



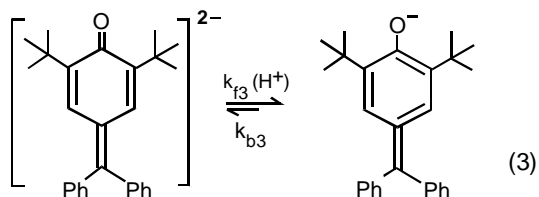
DQM

DQM^{•-}



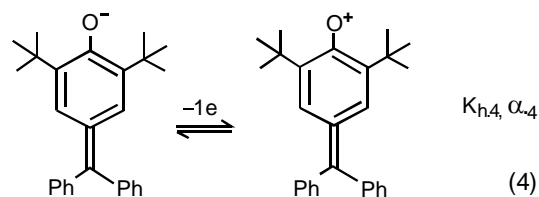
DQM^{•-}

DQM²⁻



DQM²⁻

DQM^{H2-}



DQM^{H2-}

DQM^{H+}

Scheme 1

Table 1. Parameters used for the simulation using **scheme 1**

| Share-ware | $k_{h,1}$ (cm/s) | $k_{h,2}$ (cm/s) | $k_{h,4}$ (cm/s) | $k_{f,3}$ (s ⁻¹) | $k_{b,3}$ (s ⁻¹) | α_1 | α_2 | α_4 | t^* (s) |
|------------|---------------------|---------------------|---------------------|---------------------------------|---------------------------------|------------|------------|------------|--------------|
| CVSIM | 0.010 | 0.00009 | 0.0002 | 2000 | 0 | 0.5 | 0.54 | 0.74 | 13 |
| ESP.2.4 | 0.011 | 0.00007 | 0.0002 | 2000 | 0 | 0.5 | 0.56 | 0.74 | 4 |

* = time taken for simulation; $k_{h,1}, k_{h,2}, k_{h,4}$ = heterogeneous rate constants for reaction 1, 2 and 4 respectively; $k_{f,3}$ = forward rate constant for reaction 3; $k_{b,3}$ = backward rate constant for reaction 3; $\alpha_1, \alpha_2, \alpha_4$ = transfer coefficients for reaction 1, 2 and 4 respectively.

Table 2. Potentials used for **scheme 1**

| Reaction* | Potentials (V) | |
|-----------|----------------|---------|
| | CVSIM | ESP.2.4 |
| (1) | -0.924 | -0.924 |
| (2) | -1.216 | -1.215 |
| (4) | -0.330 | -0.330 |

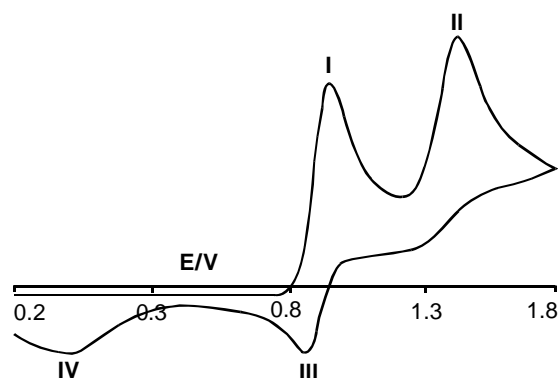
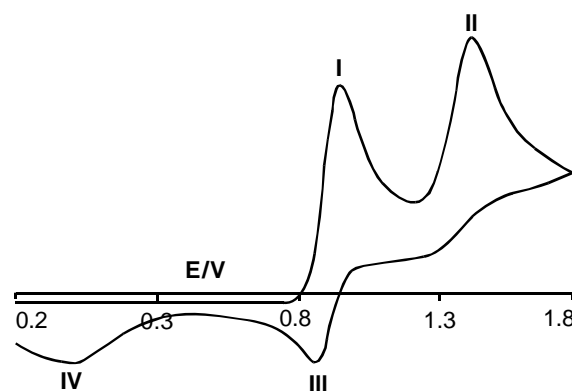
* = refer **scheme 1**

The irreversibility of **peak II** arises from the diprotonation of the dianion of **DQM**, leading to the formation of corresponding 2,4,6-trialkyl phenol as revealed by product analysis. Since **DQM**-dianion is a very strong base, anodic **peak IV** results from the phenolate of the product formed subsequent to second cathodic peak. It shows higher currents in the presence of the added base (Goulart and Utley, 1988).

The electrode process, as represented in Fig. 1, was simulated with **scheme 1**, where 1, 2 and 3 stand for **DQM**, **DQM**-monoanion radical and **DQM**-dianion, respectively. Best fits were realized with the parameters contained in Table 1, and the potentials were selected as given in Table 2. Characteristics of the experimental and simulated voltammograms are summarized in Table 3, indicating a reasonable agreement, as visually apparent from Fig. 2 and Fig. 3.

Conclusion

The simulation reported in this paper is consistent with an electrochemical-electrochemical (EECE-type) mechanism


Fig. 2. Simulated cyclic voltammogram of **DQM**, obtained using CVSIM, as per parameters given in Table 1.

Fig. 3. Simulated cyclic voltammogram of **DQM**, obtained using ESP 2.4 as per parameters given in Table 1.

(Utley *et al.*, 1998). As summarized in **scheme 1** and Table 1, the first electron transfer is fast, the second electron transfer being slow, which is followed by a very fast chemical step. That the chemical step is not of higher order is consistent with the fact that subsequent scans do not show any noticeable decrease in peak currents. The product arising from the chemical step shows a slow electron transfer. It may be noted that the ESP affords economy in time over CVSIM.

Table 3. Characteristics of simulated and experimental cyclic voltammograms as shown in Figs. 1-3.

| | E_I (V) | E_{II} (V) | E_{III} (V) | E_{IV} (V) |
|--|-----------|--------------|---------------|--------------|
| Experimental curve (Fig. 1) | -0.98 | -1.500 | 0.91 | -2 |
| Simulated curve using CVSIM (Fig. 2) | -0.97 | -1.442 | 0.88 | 6 |
| Simulated curve using ESP 2.4 (Fig. 3) | -0.96 | -1.442 | 0.88 | 6 |

E_I = first cathodic peak potential; E_{II} = second peak potential; E_{III} = first anodic peak potential; E_{IV} = second anodic peak potential; V = potential in volts

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