PULSED VOLTAMMETRY OF 2-[3,5-BIS(1,1-DIMETHYLETHYL)-4-OXO-2,5-CYCLOHEXADIEN-1-YLIDENE]ACETONITRILE

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ABSTRACT: Simulation of differential pulse voltammogram of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile was attempted using diagnostic criteria for dimerization following its electrochemical reduction at platinum cathode in acetonitrile.

INTRODUCTION

Redox processes surrounding quinone methides continue to be of contemporary interest [1-2]. Previous reports based on cyclic voltammetry [3-4] suggested that 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile dimerized upon electroreduction. Pulsed voltammetric study of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile was undertaken at platinum electrode in acetonitrile containing sodium perchlorate.

EXPERIMENTAL

Electrochemical behaviour of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile was investigated by carrying out following sets of experiments.

Differential pulse voltammetry at platinum

Differential pulse voltammetry of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene] acetonitrile was carried out at platinum (0.07 cm^2) electrode. Potential reported is in volts with respect to silver/silver chloride, chloride electrode. Parameters utilized were scan rate, ν = 20 Vs^{-1}; pulse width, t_p = 50 ms; step time, τ = 100 ms; pulse height, ΔE = 25 mV.

Normal pulse voltammetry at platinum

Normal pulse voltammetry of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile was carried out at platinum (0.07 cm^2) electrode. Potential reported is in volts with respect to silver/silver chloride, chloride electrode. Parameters utilized were scan rate, ν = 20 Vs^{-1}; pulse width, t_p = 50 ms; step time, τ = 100 ms; pulse height, ΔE = 25 mV.

Chemicals and Materials

2-[3,5-Bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]-acetonitrile was synthesized using di-tertiarybutyl substituted p-cresol [1]. Sodium perchlorate and acetonitrile were from E. Merck.

RESULTS AND DISCUSSION

Differential pulse voltammetry of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile

Fig. 1 shows cathodic peak centered about -1.1 V for differential pulsed voltammetric reduction of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile. Characteristics of the pulsed voltammograms are summarized in Tables 1 and 2. Since diagnostic criteria for various nuances of dimerization of anion radicals arising upon electroreduction of substrates are available in literature [5], pulsed voltammetric study of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile was undertaken at platinum electrode in acetonitrile containing sodium perchlorate. The main peak in Fig. 1 was simulated as per criteria in literature [5]. However, the full width at half peak height of the experimental voltammogram (200 mV, Fig. 1) compared unfavorably with full width at half peak height of the corresponding simulated voltammogram (100 mV, Fig. 2).

Table 1: Characteristics of repeat cathodic differential pulsed voltammograms of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile

is, µA	Es, V	EPW, V
149.0	-1.072	-0.200
153.0	-1.060	-0.192
133.0	-1.088	-0.208

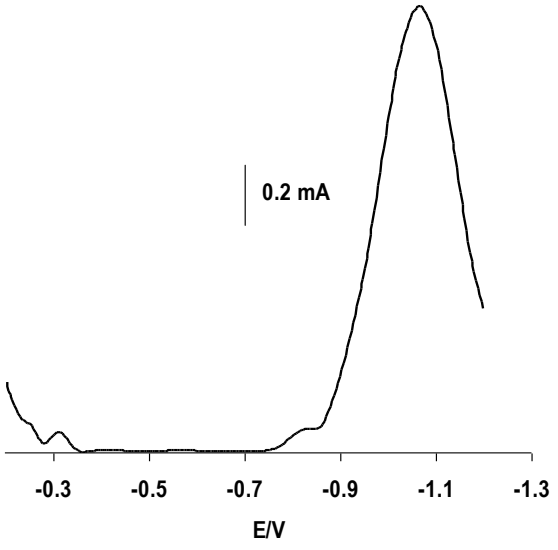

Fig. 1: Cathodic differential pulse voltammogram of 0.7 mM 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile at platinum in 0.1 M sodium in acetonitrile solution

Table 2: Characteristics of repeat cathodic normal pulsed voltammograms of 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile

ip, mA	Ep, V	E1/2, V	EHPW, V
0.555	-1.328	-1.124	-0.204
0.632	-1.264	-1.100	-0.164
0.576	-1.304	-1.124	-0.180

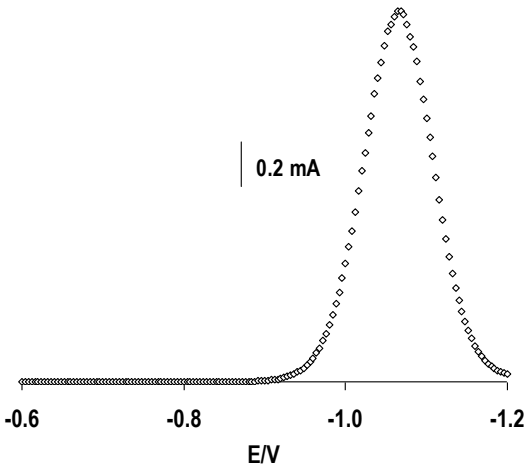

Fig. 2: Simulated differential pulse voltammogram for the cathodic scan of 0.7 mM 2-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]acetonitrile; parameters as per established schemes [5] based on approximate explicit equations in differential pulse voltammetry

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