

Electrochemical study on azulene-1-yl-methylene-2,2-dimethyl-[1,3]dioxane-4,6-diones

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Abstract An electrochemical study of several azulene-1-yl-methylene-2,2-dimethyl-[1,3]dioxane-4,6-diones compounds was performed by cyclic and differential pulse voltammetry in order to characterize them and establish the influence of donor and acceptor substituents on their electrochemical properties. It was established the number and characteristics of the redox processes for each compound. The comparison of the electrochemical parameters was connected with the difference between the functional groups grafted on the azulene moiety.

Keywords: methyl-3-benzoyl indolizine carboxylates, cyclic voltammetry, differential pulse voltammetry.

1. Introduction

This study is a part of a large investigation of azulene derivatives, compounds with potential NLO properties and electrochromic behavior [1-3]. The paper is devoted to three new azulene-methylene-malonates with structural similarities which were synthesized by our group [4]. These new vinyl azulenes have special properties due to the weak reactivity of the double bond, leading to compounds that could be selectively halogenated, reduced or hydrolyzed.

2. Experimental

Reagents, instrumentation and methods

Acetonitrile (Rathburn, HPLC grade), tetra-*n*-butylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolytes. The investigated compounds were obtained by specific chemical reaction [4]. Structure and physical characteristics were confirmed by elemental and spectral (¹H NMR, ¹³C NMR, GC-MS) analyses. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) electrochemical experiments were conducted in a conventional three-electrode cell under argon

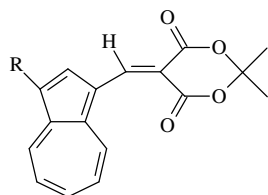
atmosphere at 20 °C using a PGSTAT 12 AUTOLAB potentiostat. The working electrode was a glassy carbon disk (3-mm diameter from CH Instruments) polished with 200 μm diamond paste. An Ag/10mM AgNO₃ in CH₃CN + 0.1M TBAP system was used as reference electrode. All potentials were referred to the potential of ferrocene/ferricinium (Fc/Fc⁺), which was 0.07V with our experimental conditions. CV experiments were usually performed at 0.1 V/s, and with different scan rates (0.1–1V/s), for investigation of scan rate influence. DPV curves were recorded at 10mV/s with a pulse height of 25mV and a step time of 0.2 s.

3. Results and Discussions

CV and DPV studies

The electrochemical behaviour of azulene-1-yl-methylene-2,2-dimethyl-[1,3]dioxane-4,6-diones derivatives was studied in acetonitrile with 0.1MTBAP as a supporting electrolyte. Investigated compounds have the general formula shown in Fig. 1. They are all derivatives of 5-azulene-1-yl-methylene-2,2-dimethyl-[1,3]dioxane-4,6-dione (**1**). The substituents have different electronic effects, carboxyl in **2** being an electron withdrawing group

and bromine in **3** an electron donor group. The DPV study for each compound (Fig. 1) at different concentrations (0.4 – 2mM) enabled the measurement of anodic and cathodic peak potentials and currents. The CV study, which was performed at different concentrations, scan rates and potential ranges, enabled the establishment of reversible and irreversible processes.



R: H (**1**); -COOH (**2**); -Br (**3**)

Fig. 1 Formula of the investigated compounds

The results obtained by CV and DPV were concordant, with respect to peak potentials, and were complementary, yielding specific features for each process. Fig. 2 shows characteristic DPV, and CV curves obtained for azulene derivative **1**. Anodic and cathodic curves are shown in each graph. Comparative analysis of the data from DPV and CV curves shows that DPV curves give the best peak position and the actual number of processes occurring. These methods yield complementary information about the electrochemical behavior of derivative **1**. For instance, in the DPV curve obtained at a 2mM concentration of **1**, two distinct anodic peaks can be observed at 0.87V (1a) and 1.10V (2a). 1a and 2a can be attributed to substrate oxidation. In the cathodic region, two reduction processes of derivative **1** were found at -1.37 V (1c), and -2.25V (2c). From the cyclic voltammograms at different scan ranges (Fig. 2C), the reversibility of each oxidation and reduction process was investigated. For anodic scans, CV curve revealed one anodic process, 1a, which present an irreversible peak. In a cathodic scan including only the first process, an irreversible process can be seen. Upon extension of the cathodic limit scan to include the other cathodic process (2c), in reverse scans, a corresponding anodic peak (2c') appeared at -2.18V indicating a reversible process.

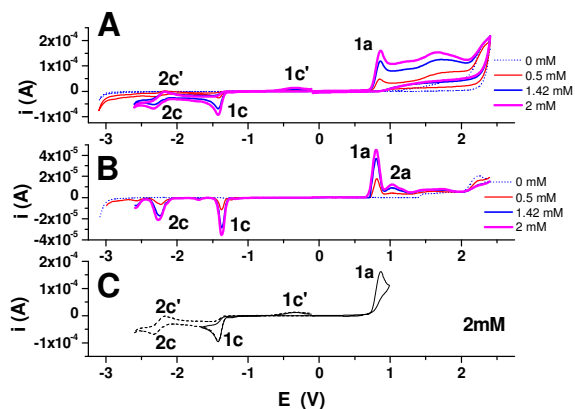


Fig. 2 CV (A, C) at 0.1 V/s and DPV (B) for **1** at different concentrations (mM) on glassy carbon (3mm in diameter) in 0.1M TBAP, CH₃CN

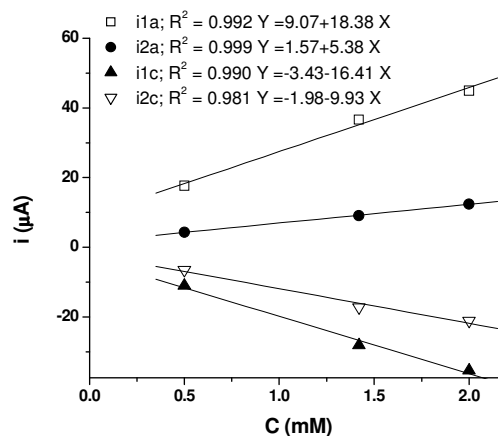


Fig. 3 Influence of concentration (C) on the DPV currents (i) for azulene derivative **1** on glassy carbon (3mm in diameter) in 0.1M TBAP, CH₃CN

Figure 3 presents peak current dependence on concentration, as obtained from DPV experiments for the compound **1**. Peaks currents increased linearly with substrate concentration. Owing to these linear dependences, the current peaks could be used in analytical determinations of the substrate by this electrochemical method. Dependences obtained from cyclic voltammograms at different concentrations of

the derivative **1** showed constant peak potentials for processes 1a and 1c. Peak currents were linear with concentration, as shown in Fig. 4. For the others compounds (**2** and **3**) the current dependences are given in Table 1 and 2, showing a linear variation with substrate concentration.

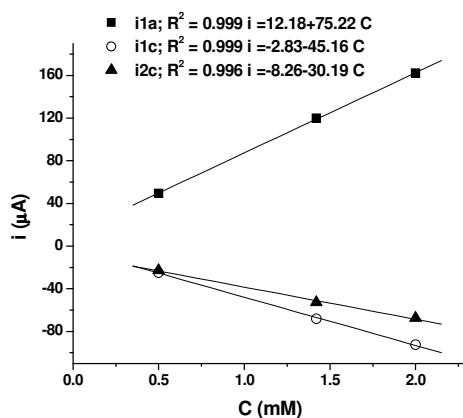


Fig. 4 Influence of concentration (C) on peak currents (i) in CV for **1** (0.1 V/s) on glassy carbon (3mm in diameter) in 0.1M TBAP, CH_3CN (total currents are represented)

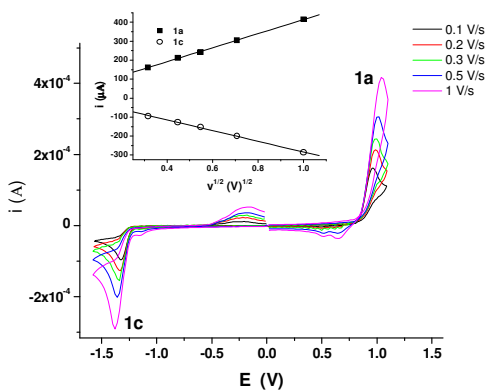


Fig. 5 Influence of the scan rate (ν) on the CV currents on glassy carbon (3mm in diameter) for **1** (2mM) in 0.1M TBAP, CH_3CN . Inset: Dependence of the first anodic and cathodic current peak on the square root of the scan rate.

Influence of the scan rate on CV curves for the compound **1** is shown in Fig. 5 for the first anodic and cathodic processes. These peaks correspond to the formation of the radical cation (1a) and radical anion (1c). Similar studies have been performed for each substrate from Fig. 1 and the results are given in Table 3.

Table 1. Dependence equations of the peak currents in DPV and CV on the substrate concentration for anodic process 1a

Comp.	Method	i_{1a} (μA)
1	DPV	$R^2 = 0.992$; $i = 9.07 + 18.38 C$
	CV	$R^2 = 0.999$; $i = 12.18 + 75.22 C$
2	DPV	$R^2 = 0.987$; $i = 3.15 + 12.89 C$
	CV	$R^2 = 0.981$; $Y = 5.16 + 52.5 X$
3	DPV	$R^2 = 0.995$; $i = 1.04 + 15.68 C$
	CV	$R^2 = 0.999$; $i = -0.48 + 39.98 C$

Table 2. Dependence equations of the peak currents in DPV and CV on the substrate concentration for cathodic processes 1c and 2c

Comp.	Method	i_{1c} (μA)	i_{2c} (μA)
1	DPV	$R^2 = 0.990$; $i = -3.43 - 16.41 C$	$R^2 = 0.981$; $i = -1.98 - 9.93 C$
	CV	$R^2 = 0.999$; $i = -2.83 - 45.16 C$	$R^2 = 0.996$; $i = -8.26 - 30.19 C$
2	DPV	$R^2 = 0.978$; $i = 0.42 - 5.16 C$	$R^2 = 0.959$; $i = 1.59 - 7.90 C$
	CV	$R^2 = 0.964$; $Y = -0.87 - 9.41 C$	$R^2 = 0.970$; $Y = 1.53 - 17.95 C$
3	DPV	$R^2 = 0.995$; $i = 0.78 - 14.1 C$	$R^2 = 0.999$; $i = -0.05 - 2.86 C$
	CV	$R^2 = 0.986$; $i = -0.66 - 29.11 C$	$R^2 = 0.985$; $i = -1.53 - 14.51 C$

Table 3. Equations for the dependence of the CV peak currents on the square root of the scan rate (V/s) for the investigated compounds

Comp.	i_{1a} (μA)	i_{1c} (μA)
1	$Y = 43.75 + 369.89 X$ $R^2 = 0.999$	$Y = -1.91 - 282.40 X$ $R^2 = 0.998$
2	$Y = 12.09 + 163.32 X$ $R^2 = 0.998$	$Y = -3.10 - 29.19 X$ $R^2 = 0.961$
3	$Y = 9.33 + 128.72 X$ $R^2 = 0.992$	$Y = -6.22 - 101.52 X$ $R^2 = 0.989$

Comparison between substrates

Azulene is an easily oxidizable aromatic hydrocarbon, having an anodic peak at 0.54V [5]. Owing to its peculiar polarization, azulene is stabilized during oxidation by its substitution, in position 1, with electron-withdrawing groups and it becomes unstable with electron-donating groups, especially those possessing a heteroatom with a pair of free electrons linked to azulene.

The studied compounds have all a double bond (in position 1) connected to the 2, 2-dimethyl-[1,3]dioxane-4,6-dione and H, COOH or Br in position 3. In their DPV and CV curves, the oxidation and reduction potentials varied according to the substituent (Table 4).

Table 4. Peak potentials in CV and DPV

Comp.	Technique	E_{1a} (V)	E_{1c} (V)
1	CV	0.863	-1.42
	DPV	0.873	-1.37
2	CV	1.2	-1.28
	DPV	1.146	-1.245
3	CV	0.938	-1.26
	DPV	0.88	-1.22; -1.43*

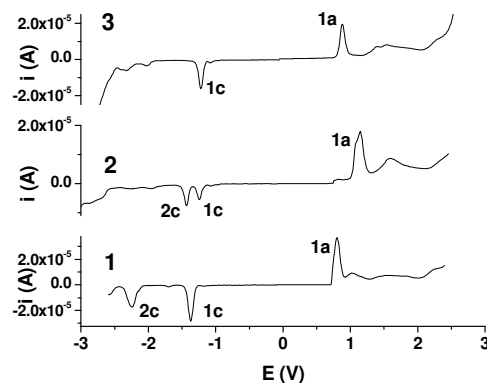
* $E_{1c3} = -1.22\text{V}$; $E_{2c3} = -1.43\text{V}$; $E_{1c3} = -1.32\text{V}$

From Table 1 it can be seen that the variation with concentration of the DPV curves has for the anodic peak 1a positive slopes of about $15\mu\text{A}/\text{mmol}$ while the CV curves have slopes of about $50\mu\text{A}/\text{mmol}$. From analytical point of view it seems that the CV method gives a more sensitive response having a bigger slope. However, in general the DPV method allows the recording of much lower concentrations than CV. From Table 2 it can be seen that the variation with concentration of the DPV

curves has for the cathodic peaks 1c and 2c. They have negative slopes with absolute values similar to those for the anodic peak 1a.

Comparison of the equations showing the influence of the scan rate on CV curves for all the compounds is done in Table 3 for the first anodic and cathodic processes. Positive and negative slopes of about 145 and $-110\mu\text{A}(\text{V/s})^{-1/2}(\text{mM})^{-1}$ are obtained for 1a and 1c, respectively.

The peak potentials are invariant with concentration for CV (at the same scan rate) and DPV curves. Their values are given in Table 4 for all the compounds. A detailed comparison between their DPV curves is given in Fig. 6.

**Fig. 6** DPV curves for the investigated compounds ($\sim 1\text{mM}$ in 0.1M TBAP, CH_3CN) on glassy carbon (3mm in diameter).

They show almost the same types of peaks. At a closer look to the compound 2, it seems that the two peaks 1c and 2c correspond to a cathodic process split in two (having the same area as the anodic process 1a). The potential values from Table 4 for the first oxidation peak (1a) vary ($E_{1a1} < E_{1a3} < E_{1a2}$) according to the electron-withdrawing effect of the substituent R ($\text{H} < \text{Br} < \text{COOH}$). The potential values for the first reduction process follow the same variation ($E_{1c1} < E_{1c3} < E_{1c2}$) if we assume the potential of the compound 3 has a mean value between the first two reduction peaks (-1.32V), as mentioned before.

The study by CV shows that these compounds are irreversibly reduced in the first step (Fig. 7-9). The second reduction potential is reversible for 1 and

quasi reversible for **2** and **3**. In the case of compound **3**, supplementary cathodic peaks, **3c** and **4c**, appeared (due to the breaking of the C-Br bond).

Successive scans in the domain of the first anodic (**1a**) and cathodic (**1c**) processes did not lead to the formation of polymeric films in CH₃CN + 0.1 M TBAP (Fig. 10). In successive anodic scans the oxidation peak is shifted progressively to positive values while the successive curves in cathodic sense are practically unchanged.

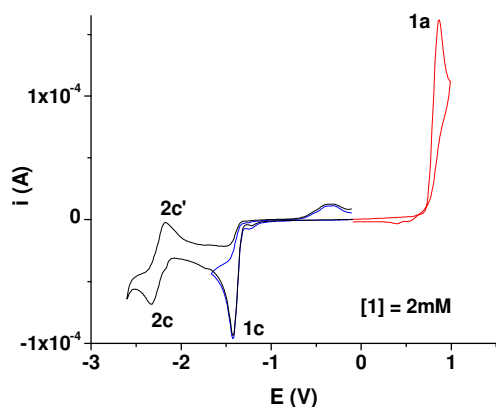


Fig. 7. Cyclic voltammograms for **1**, on glassy carbon in 0.1M TBAP, CH₃CN at 0.1 V/s.

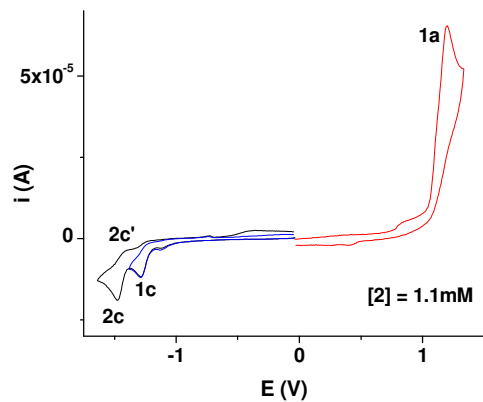


Fig. 8. Cyclic voltammograms for **2**, on glassy carbon in 0.1M TBAP, CH₃CN at 0.1 V/s.

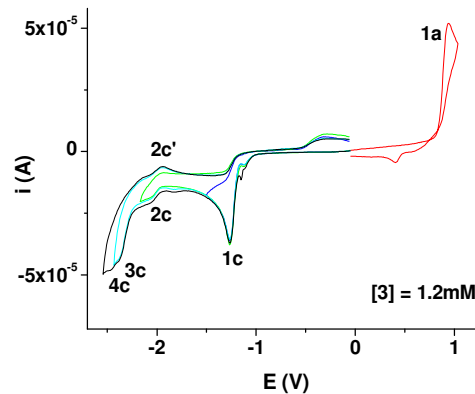


Fig. 9. Cyclic voltammograms for **3**, on glassy carbon in 0.1M TBAP, CH₃CN at 0.1 V/s.

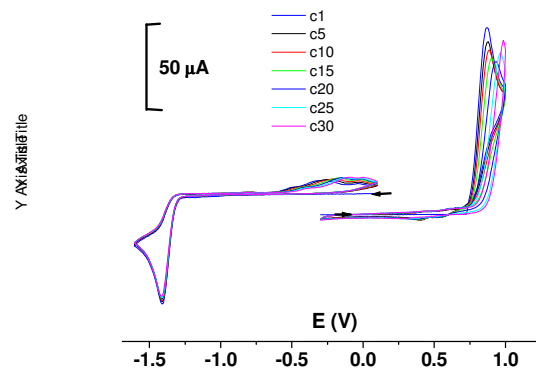


Fig.10 Successive anodic and cathodic cyclic voltammograms for **1** on glassy carbon in 0.1M TBAP, CH₃CN at 0.1 V/s.

4. Conclusions

This work explored the electrochemical properties of some azulene-1-yl-methylene 2,2 - dimethyl-[1,3] dioxane -4,6-diones and established the effect of two substituents (Br and COOH) upon the electrochemical behaviour of azulene derivatives. Two methods were used for this purpose. Differential pulsed voltammetry enabled

the precise determination of oxidation and reduction potentials, which were found to be constant when compounds concentrations were varied. Unique compound fingerprints were produced with this method. The DPV peak current values were proportional to substrate concentrations, representing a preliminary test of the analytic value of this method. CV enabled the establishment of reversible character in electrode processes. Although the azulene moiety was by far the most sensitive to oxidation, an important peak potential variation was observed with respect to the nature of the other substituents of azulene. The oxidations were completely irreversible for all compounds, while the reductions occur either irreversibly or reversibly.

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6. References

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