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ELECTROCHEMICAL CHARACTERIZATION OF NEW (AZULEN-1-YL)ALLYLIDENE DERIVATIVES OF β–KETO COMPOUNDS

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Some β-keto compounds containing (azulen-1-yl)allylidene moiety were electrochemically characterized in view of their potential capacity to interact with trivalent cations of lanthanides.

Keywords: azulene; β-keto compounds; cyclic voltammetry, differential pulse voltammetry, rotating disk electrode, Samarium (III)

1. Introduction

Azulenes are organic compounds characterized by a five-membered cyclic moiety which is electron rich and a seven-membered cyclic moiety which is electron poor. This dual "push-pull" structure, where azulenyl is the electron donating group and the substituent is the accepting group, provides for some interesting properties to the molecule [1]. Due to this particular structure azulenes can be involved in both oxidation and reduction processes, and the nature of the substituent and its orientation greatly influences the electrochemical properties (number of redox waves and potentials) [2].

Azulene derivatives are also versatile starting materials and the formation of polymers has been widely reported [3-5]. Furthermore, there are many works now that describe the properties of azulene polymers formed by electrochemistry, which have very similar characteristics to the azulene polymers chemically synthesized. In the past years, a considerable number of studies have been made

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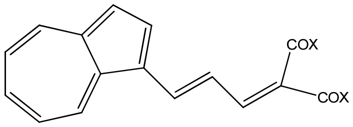
on the preparation of polyazulene films [4], or on metal complexes of azulene derivatives [5].

Similar compounds containing other electron donor moieties such as ferrocene [6], p-dimethylaminophenyl [7], fullerenyl [8] and electron rich groups, like crown ethers [9] or amides [10], have been already investigated as metal sensors [11, 12], and particularly as lanthanide sensors.

The versatility of some malonic acid derivatives towards the recognition of cations initiated the study of another large class of azulene compounds [13]. The current paper presents the electrochemical study of two 3-(azulen-1-yl)allyliden derivatives of β-keto compounds, (E)-diethyl 3-[3-(azulen-1-yl)allylidene]malonate (**1**) and (E)-3-[3-(azulen-1-yl)allylidene)pentane-2,4-dione] (**2**), in view of metal ions recognition.



1: X = OC_2H_5; **2**: X = CH_3

These compounds could interact with the metallic cations through the dicarbonyl moiety. The electrochemical properties were systematically studied for the new ester (**1**) and ketone (**2**) which are stabilized by electron withdrawing groups (ester and ketone, respectively) attached to the vinyl groups. The ability of the malonic moiety to complex metal ions was tested for Sm^{3+} ions in homogenous phase by electrochemical means.

2. Experimental Section

The azulene derivatives **1** and **2** were synthesized by condensation of 3-(azulen-1-yl)acrolein with acetylacetone and with malonic ester, respectively, in the presence of catalysts [13]. Acetonitrile and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for the solvent and supporting electrolyte.

The lanthanide electrochemical recognition was performed in acetonitrile (CH_3CN) solutions containing 0.1M TBAP. Sm^{3+} cations were used as triflate salts (from Alfa Aeser).

The electrochemical experiments were carried out by cyclic voltammetry (CV), differential pulse voltammetry (DPV), and rotating disk electrode voltammetry (RDE) using a PGSTAT12 AUTOLAB potentiostat coupled to a three-compartment cell. The CV curves were recorded at scanning rates between 0.1 - 1V/s. DPV curves were recorded at 0.01V/s with a pulse height of 0.025V and a step time of 0.2 s. RDE experiments were recorded at 0.01 V/s with rotation rates between 500 and 2000 rpm. The working electrode was a glassy carbon disk (3 mm in diameter). The active surface was polished before each determination with diamond paste (0.25 µm). Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN was used as the reference electrode. The potential was referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was +0.07 V. A platinum wire was used as the auxiliary electrode. The determinations were performed at 25ºC under argon atmosphere.

3. Results and discussion

The electrochemical behaviour of these new azulene derivatives was studied on glassy carbon electrode by electrochemical methods: cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode voltammetry. The redox processes evidenced by cyclic voltammetry and differential pulse voltammetry were established, analyzed and assessed to the particular functional groups at which they take place, according to the active structures in the molecules.

3.1. Study of 1

The electrochemical experiments for compound **1** were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Anodic and cathodic curves were recorded individually, starting from the stationary potential. CV and DPV curves (Fig. 1) were obtained for various concentrations (0 – 3 mM) of the studied compounds in solutions of 0.1M tetrabuthylammonium perchlorate (TBAP) in acetonitrile (CH_3CN). From the DPV curves (Fig. 1) three anodic (1a - 3a) and five catodic (1c - 5c) processes are observed, denoted in the order in which they appear in the voltammograms. The data from cyclic voltammetry (Fig. 2) experiments allow establishing the reversible (r), quasireversible (q) and irreversible (i) character of each peak (Table 1).

The influences of the scan domain and the scan rate upon the CV curves are presented in Fig. 2. The reversible character of each peak was determined from the voltammograms and it can be found listed in Table 1.

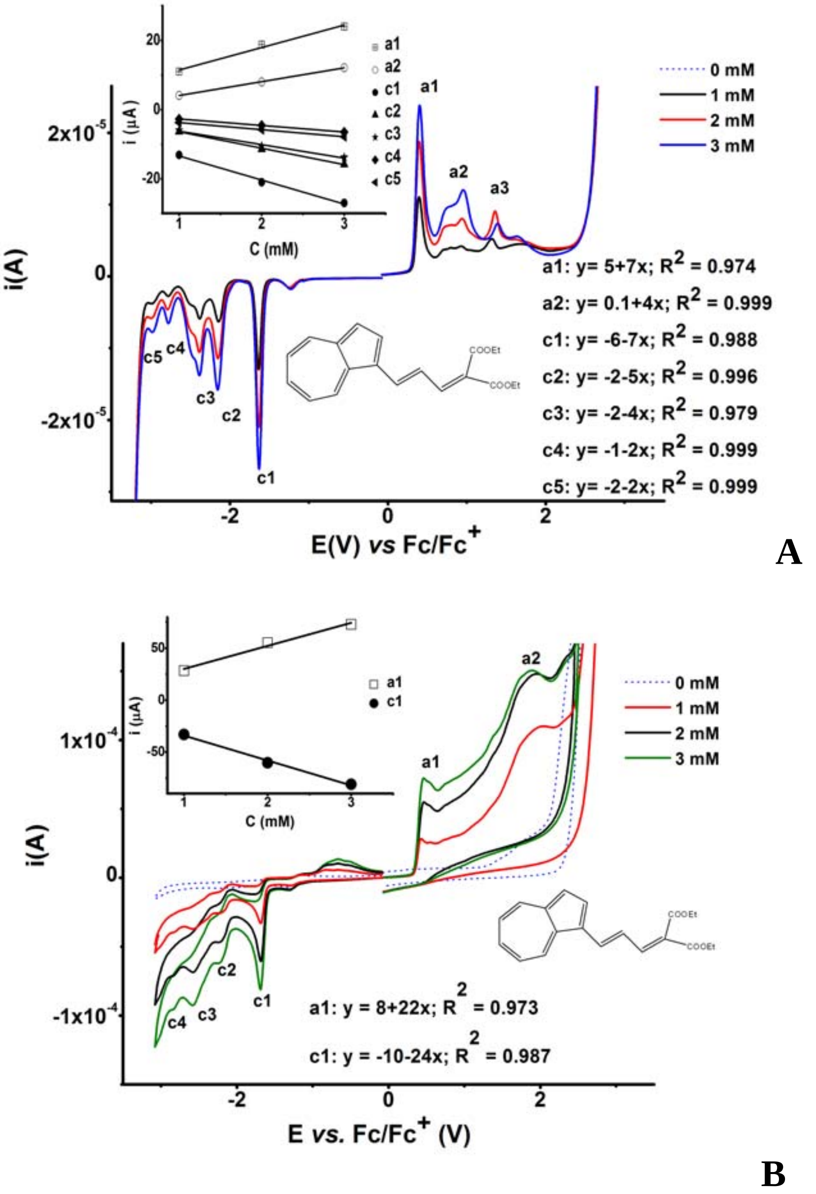


Fig. 1**.** DPV (A) and CV (B) curves for different concentrations of **1** in 0.1M TBAP, CH_3CN. Insets: peak current (in μA) dependencies on **1** concentration (mM) and their equations

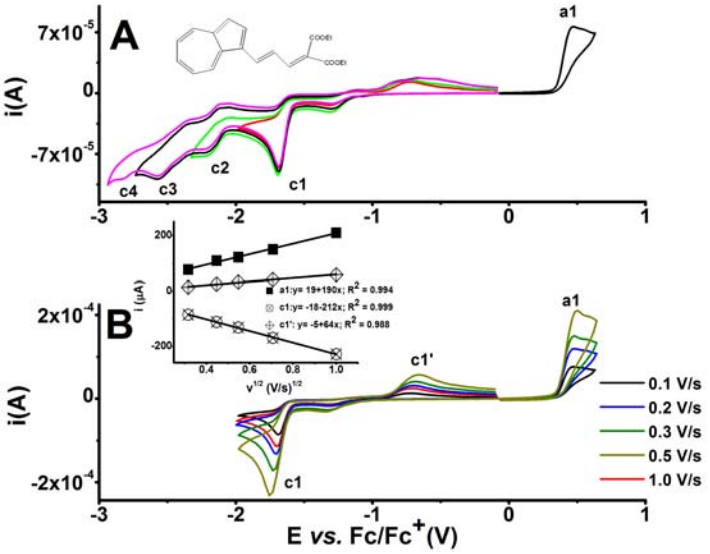


Fig. 2. CV curves for various scan domains at 0.1V/s (A) and at different scan rates in the domains of the peaks 1c and 1a (B), respectively, for **1** (3 mM) in 0.1M TBAP, CH_3CN. Inset Fig. 2B: peak current (in μA) dependency on the square root of scan rate (in (V/s)$^{1/2}$)

Table1

Potentials (V) of the peaks and their assessment for 1 (3mM) vs Fc/Fc$^+$

Peak\Method	DPV	CV	Assessed process
c1	-1.634	-1.702 (q) *	Radical anion formation followed by radical stabilization by polymerization
c2	-2.157	-2.212(r) *	Reduction of non-conjugated carboxylic groups
c3	-2.392 -2.500	-2.581 (r) *	Reduction of conjugated carboxylic groups
c4	-2.7828	-2.841 (i) *	Reduction of unsaturated C=C bonds (including partially polymerized azulene moiety)
c5	-2.977		Reduction of unsaturated C=C bonds (including partially polymerized azulene moiety)
a1	0.404	0.442 (i)	Radical cation formation with the radical stabilization by polymerization
a2	0.759 0.955	1.858 (i)	Oligomer oxidation
a3	1.391		Oligomer oxidation

*r - reversible process; q - quasi-reversible process; i - irreversible process

3.2. Study of 2

Compound **2** has a similar structure as **1** with the difference that it is a β-ketone (instead of diethyl ester). Therefore the electrochemical behavior is expected to be largely the same. The CV and DPV studies performed for various concentrations of **2** (0 – 1.5 mM) in 0.1M TBAP in CH_3CN are presented in Fig. 3. Six characteristic catodic peaks were put in evidence by CV (seven by DPV) and one anodic (three from DPV). Their reversible (r), quasireversible (q) or irreversible (i) character was established from voltammograms and is is given in Table 2.

In order to better estimate the characteristic oxido-reduction processes underwent by this compound a rotating disk electrode (RDE) method was also used (Fig. 4). The specific domains put in evidence by the CV curves are also found in RDE curves.

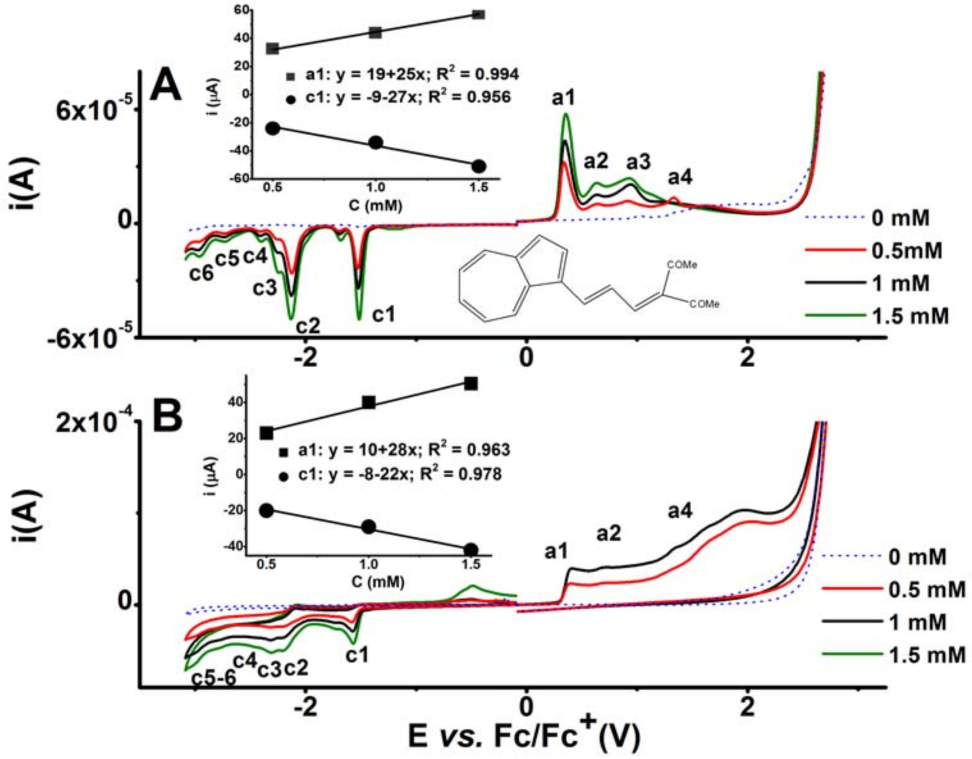


Fig. 3. DPV (A) and CV at 0.1 V/s (B) curves for different concentrations of **2** in 0.1M TBAP, CH_3CN. Insets: peak current (in μA) dependencies on **2** concentration (mM)

Table 2

Potentials (V) of the peaks and their assessment for 2 *vs*. Fc/Fc$^+$

Peak\Method	DPV	CV	Assessed process
c1	-1.53	-1.57 (i) *	Radical anion formation with the stabilization by polymerization
c2	-2.13	-2.19 (r) *	Reduction of nonconjugated C=O bonds
c3	-2.25	-2.32 (q) *	Reduction of conjugated C=O bonds
c4	-2.40	-	Unknown process
c5	-2.72	-2.80 (i)	Reduction of CH=CH bonds including the partially polymerized azulenes
c6	-2.95	-	Reduction of CH=CH bonds including the partially polymerized azulenes
a1	0.34	0.40 (i)	Radical cation formation with the radical stabilization by polymerization and proton eliminations
a2	0.62	0.71 (i)	Oligomer oxidation
a3	0.94	-	Oligomer oxidation
a4	1.33	1.36(i)	Oligomer oxidation

*r - reversible process; q - quasi-reversible process; i - irreversible process

A study was performed in the limits of the specific potential domain for each peak and, complementary, CV curves were recorded at increasing scanning rates in the potential domain of the first anodic and, respectively, cathodic, peaks (Fig. 5). The concentration chosen for this part of the electrochemical study was the highest allowed by solubility issues of **2**: 1.5 mM.

The CV and DPV curves for **1** and **2** are very similar, as expected. However, when examining the cathodic regions of CV curves on different domains (Fig. 3 and 5, respectively), there is a difference in reversibility of the peaks c2 and c3. It is induced by the higher stability to reduction of COOEt than that of COMe group. The ester groups are reduced selectively if they are conjugated or not, and they appear as separate peaks for **1**, while the keto groups are reduced at very close potentials, and they appear almost overlapped for **2**. In the case of carboxylic groups reduction certain reversibility is observed (Fig.3), when scanning in the specific domains. In the anodic region, the selectivity of the processes is lost after the first oxidation step for both compounds (Fig. 3 and 5).

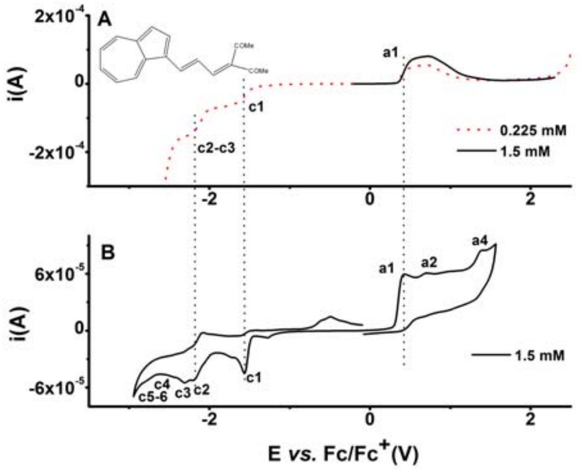


Fig. 4. Anodic and cathodic RDE curves (1000 rpm) at different concentrations (A) and CV curves at 0.1V/s (B) at 1.5 mM **2** in 0.1 M TBAP, CH_3CN

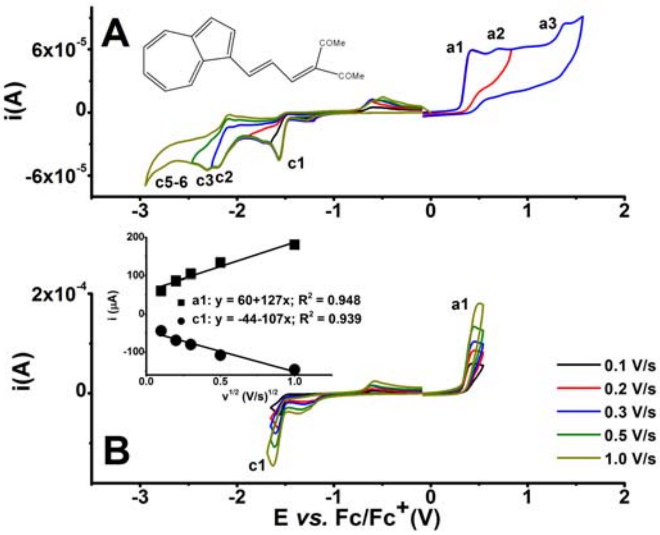


Fig. 5. CV curves for various scan domains at 0.1V/s (**A**) and at different scan rates in the domains of the peaks 1c and 1a, respectively, for **2** (1.5 mM) in 0.1M TBAP, CH_3CN (**B**). Inset Fig. 2B: peak current (in μA) dependency on the square root of scan rate (in $(V/s)^{1/2}$)

A study of the complexation of the azulenic ligand **2** with lanthanide cations of Sm^{3+} was performed by electrochemical methods. The characteristic redox properties for this β-keto compound, influenced by the addition of these lanthanide cations, are shown in Fig. 6. The electrochemical results show a linear decrease of the potential of the first cathodic peak of **2** till about 2 equivalents of Sm^{3+} added, then a slow variation of this potential till about 50 equivalents (Fig. 6). This stands for a slow stoichiometric complexation at 2 equivalents.

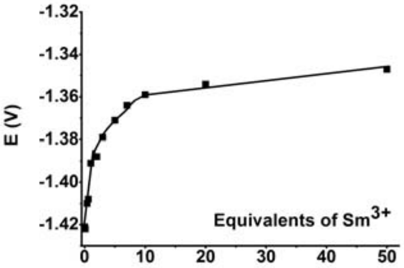


Fig. 6. Evolution of the potential for the first cathodic DPV peak (c1) with the amount of Sm^{3+} ions introduced in a 0.5 mM solution of **2** in 0.1M TBAP, CH_3CN

4. Conclusions

The electrochemical properties were systematically studied for two related (azulen-1-yl)allylidene β-keto compounds (bis-ester and bis-ketone). The main oxidation and reduction processes have been established. The DPV and CV curves are very similar. However, there are differences induced by the higher stability to reduction of COOEt than that of COMe group. The ester groups are reduced selectively if they are conjugated or not, and they appear as separate peaks, while the keto groups are reduced of very close potentials, and they appear almost overlapped. In the case of carboxylic groups reduction certain reversibility is observed, when scanning in the specific domains. In the anodic region, the selectivity of the processes is lost after the first oxidation step. The ability of their carboxylic moiety to complex metal ions was tested for Sm3+ ions in homogenous phase by electrochemical means. The result stands for a slow stoichiometric complexation at 2 equivalents.

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