U.P.B. Sci. Bull., Series B, Vol. 76, Iss. 1, 2014 ISSN 1454 – 2331

ELECTROCHEMICAL CHARACTERIZATION OF SOME AZULENE SELENIUM COMPOUNDS

Georgiana Anca INEL[1], Maria-Laura SOARE[2], Magdalena-Rodica BUJDUVEANU[3], Ştefan VARGA[4], Eleonora-Mihaela UNGUREANU[5], Liviu BIRZAN[6]

This work is devoted to the electrochemical characterization of two related azulene selenium compounds. The investigations were performed by cyclic voltammetry and differential pulse voltammetry. The redox processes for each compound are established, analyzed and assessed to the particular functional groups at which they take place. This assessment was based on the comparison between the electrochemical behaviour of the compounds and the similarities and differences in their structures, connected to their substituent effects.

Keywords: azuleneselenium compounds, cyclic voltammetry, differential pulse voltammetry

1. Introduction

Organoselenium compounds are well known for their antimicrobial [1–4], anti-inflammatory [5, 6], and biocidal activities [7]. Organoselenium compounds have found applications as oxygen transfer reagents in organic [1], and organometallic [2] synthesis, and as oxygen donor ligands in main and transition metal complexes.

The electrochemical behaviour of some organoselenium compounds [8–11], as well as of some organotellurium compounds (diphenyl and bis(p-anisyl) tellurium dichloride, bis(p-anisyl) telluride [4], diphenyl ditelluride [5], and aromatic diselenidesditellurides and diphenyl selenide) have been reported on

---

[1] PhD. student, Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania, e-mail: georgianainel@gmail.com

[2] PhD. Eng., SC METAV SA, Bucharest, Romania

[3] PhD. Eng., Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania

[4] Eng., Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania

[5] Prof., Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania em_ungureanu2000@yahoo.com,

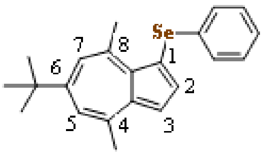
[6] Scientific Researcher, Institute of Organic Chemistry "C.D. Nenitzescu" of Romanian Academy, Bucharest, Romania, lbirzan@yahoo.com

rotating glassy carbon electrode in aprotic solvents (CH_3CN) [6, 7]. Aromatic selenides are relatively stable toward electrochemical reduction [12].

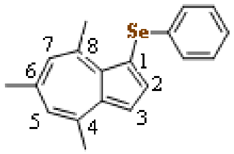
In this paper the electrochemical behaviour of two azulene selenium compounds 4,8-dimethyl-6-tert-butyl-1-phenylselanylazulene (compound denoted as **1**), and 1-phenylselanyl-4,6,8-trimethylazulene (compound **2**), was studied on a stationary electrode in acetonitrile (AN) containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. In order to elucidate the electrode reactions cyclic voltammetry and differential pulse voltammetry were employed using a glassy carbon electrode.

The present paper is focused on the electrochemical behaviour of these new azuleneselenium compounds (**1** and **2**) with similar structure (Fig. 1), having t-butyl or methyl substituents graphted in the position 6 of the azulene skeleton. The differential pulse and cyclic voltammetry data were examined in the light of the influence of the chemical nature of the substituents (trimethyl and methyl).

The characterization and assessment of the redox processes that are made in each case was reported.



1



2

Fig. 1. Structures of the investigated compounds

2. Experimental

All compounds used for synthesis were purchased from Aldrich and used without further purification. Acetonitrile and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received as solvent and supporting electrolyte, respectively. Azulene selenium derivatives **1** and **2** have been prepared by phenylselanylation starting from azulene alkylated derivatives and phenylselanyl chloride (compound **3**) according to [1].

The electrochemical experiments were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a PGSTAT 12 AUTOLAB potentiostat at which a three-compartment cell was coupled. The CV curves were generally recorded at 0.1 Vs^{-1} scan rate or at various scan rates (0.1 - 1 Vs^{-1}) - when studying the influence of the scan rate. DPV curves were recorded at 0.01 Vs^{-1} with a pulse height of 0.025 V and a step time of 0.2 s. The working electrode was a glassy carbon disk (having diameter of 3 mm). The active surface was polished before each determination with diamond paste (200 μm) and cleaned with bidistilled water. The Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN was used as 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 auxiliary electrode. The determinations were performed at room temperature (25ºC) under argon atmosphere.

3. Results and Discussion

Anodic and cathodic curves in cyclic voltammetry and differential pulse voltammetry experiments were recorded individually, starting from the stationary potential. CV and DPV curves were recorded for various concentrations (0 – 1.5 mM) of the studied compounds in 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile (CH_3CN). The data from cyclic voltammetry experiments allow establishing the reversible (r), quasireversible (q) and irreversible (i) character of each peak.

Study of **1**

The DPV curves obtained for different concentrations of **1** are presented in Figure 2. Four anodic (1a - 4a) and two cathodic (1c - 2c) processes are observed, denoted in the order in which they appear in the voltammograms. The CV curves for increasing concentrations of **1** are also shown in Fig. 2.

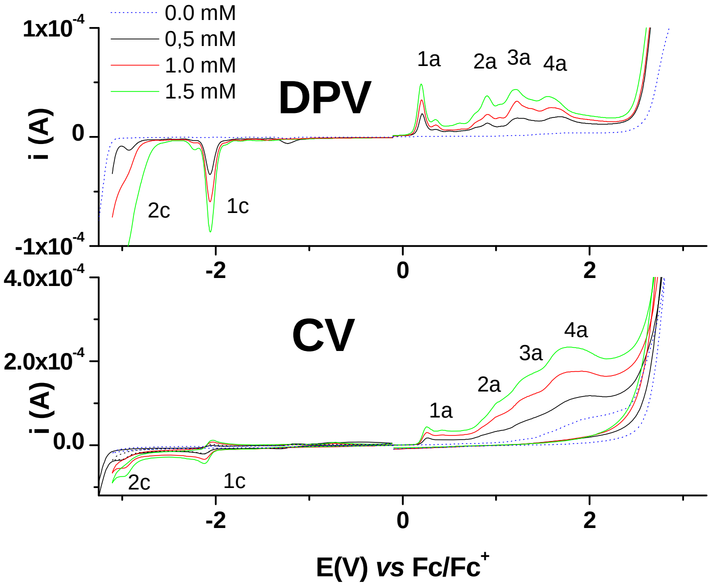


Fig. 2. DPV and CV curves (0.1 Vs^{-1}) for different concentrations of **1** in 0.1M TBAP, CH_3CN

The influences of the potential range scanned and scan rate on the CV curves are presented in Fig. 3. The data from Figs. 2 and 3 allow establishing the character of each peak (Table 1).

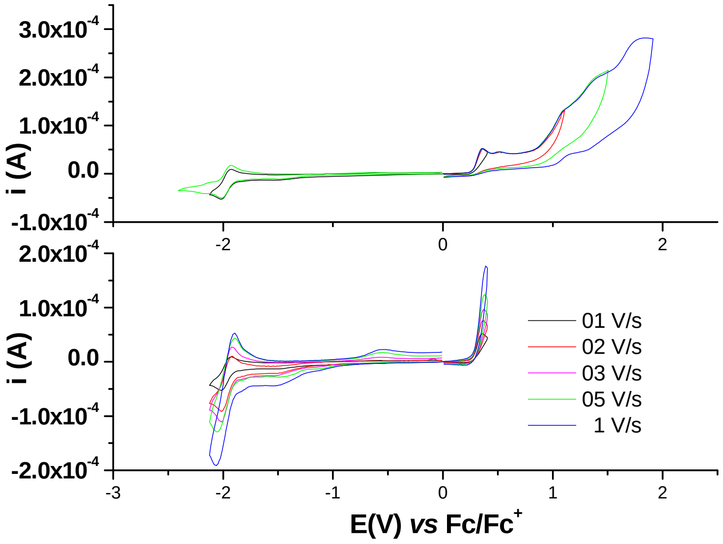


Fig. 3. CV curves for various scan domains at 0.1 Vs^{-1} (a) and at different scan rates in the domains of the peaks 1c and 1a, respectively, for **1** (1.5 mM) in 0.1M TBAP, CH_3CN

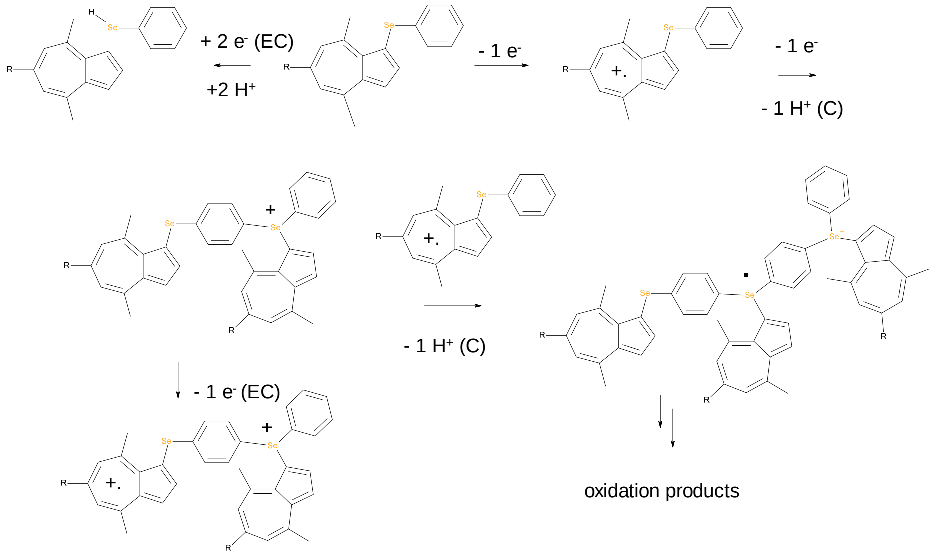
The obtained peaks for **1** were assessed as summarized in Table 1, according to Scheme 1, where the main oxidation and reduction processes are included.

Table 1.

Potentials (V) of the peaks and their assessment for **1**

Symbol of the peak	**Technique**		**Assessed process**
	DPV	**CV**	
1c	-2.060	-2.133 **(r/q) ***	Benzeneselenol formation
2c	-2.935	-2.984 **(i) ***	Azulene reduction
1a	0.196	0.266 **(i)**	Radical cation formation
2a	0.899	0.997 **(i)**	Oligomer oxidation
3a	1.205	1.291 **(i)**	Oligomer oxidation
4a	1.565	1.725 **(i)**	Oligomer oxidation

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



Scheme 1

Study of **2**

The DPV curves obtained for different concentrations of **2** are presented in Figure 4. Four anodic (1a - 4a) and two cathodic (1c - 2c) processes are observed, denoted in the order in which they appear in the voltammograms. The CV curves for increasing concentrations of **2** are also shown in Fig. 4.

The influences of the scan domain and scan rate on the CV curves are presented in Fig. 5. The data from Figs. 2 and 4 allow establishing the character of each peak (Table 2).

From Tables 1 and 2 it can be seen that there is no too much differences in the behaviour of these compounds. However, in a detailed analysis, there are some different values that could be explained by examining the electronic and steric effects of methyl and trimethyl groups connected to the azulene moiety. The potentials of the reduction peaks 1c for **1** and **2** are of -2.060 and -2.037 V, while those for the oxidation peaks 1a are 0.196 and 0.193V, respectively. These values for the reduction process are in agreement with the electron-donating effect of the t-butyl and methyl groups, which is stronger for **1** than for **2**, and therefore **1** is easier to be reduced. On the contrary, in the electrochemical oxidation process, the experimental peak potential values are opposite to the theoretical expectations (**1** should be reduced easier than **2**). It is probable that the steric effect overpasses the electronic effect, and consequently **1** is more difficultly oxidized than **2** (trimethyl group is bulkier than methyl) and, therefore **1** is more hindered than **2** to reach the electrode. The oxidation process is represented by a one-electron wave (to radical cation), while the reduction process corresponds to two-electron wave, according to Scheme 1.

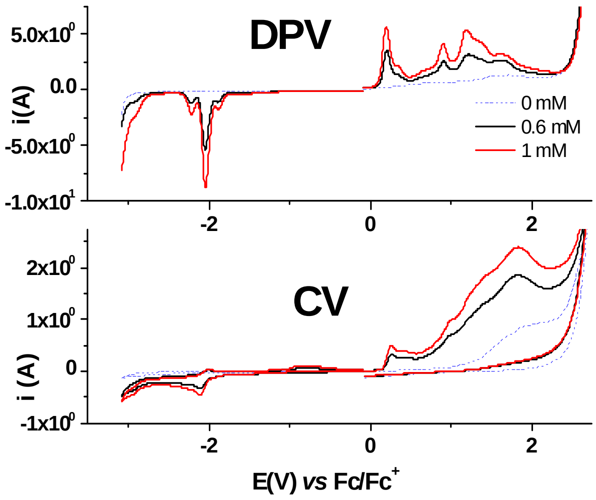


Fig. 4. DPV and CV curves for different concentrations of **2** in 0.1M TBAP, CH_3CN

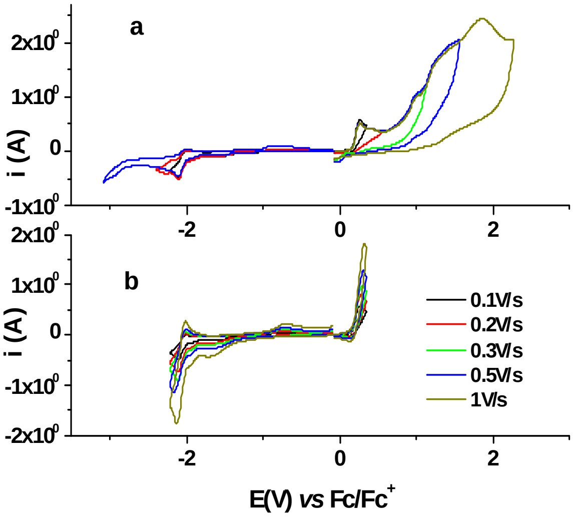


Fig. 5. CV curves for various scan domains at 0.1 Vs^{-1} (a) and at different scan rates (b): 0.1; 0.2; 0.3; 0.5; 1 Vs^{-1} in the domains of the peaks 1c and 1a, respectively, for **2** (1 mM) in 0.1M TBAP, CH_3CN

Table 3.

Potential values (V) of the peaks and their assessment for **2**

Symbol of the peak	**Technique**		**Functional group involved/process**
	DPV	**CV**	
1c	-2.037	-2.107 **(r)**	Benzeneselenol formation
2c	-2.931	-2.960 **(i)**	Azulene reduction
1a	0.193	0.264 **(i)**	Radical cation formation
2a	0.910	0.975 **(i)**	Oligomer oxidation
3a	1.194	1.438 **(i)**	Oligomer oxidation
4a	1.672	1.840 (i)	Oligomer oxidation

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

4. Conclusions

The electrochemical behaviour of the organoselenium compounds studied in this report is deeply influenced by the chemical nature of their substituents. That is why a detailed analysis of the peaks shapes and heights could bring information about the redox behaviour of these compounds. The peak potential values and, therefore, the order in reduction or oxidation processes of compounds 1 and 2 were explained by examining both the electronic and steric effects of the groups connected to the azulene moiety. At the same time, azulene moiety is a peculiar aromatic system that has high chemical reactivity that allows the evidence of more subtle interactions (involving compounds with very similar structure). These possible interactions were evidenced by the redox schemes elaborated for the investigated azulene selenium compounds.

Acknowledgements

The authors are grateful for the financial support from European Social Fund through UEFISCDI project ID 15/2011.

REFERENCES

1. *A.C. Razus, L. Birzan, M. Cristea, E.A. Dragu, A. Hanganu*, Monatsh. Chem., vol. 142, pp. 1271-82, 2011.
2. *H.M. Priestly*, “Dialkyl Selenoxide Hydronitrates”, US patent 3642909, 1972.
3. *S.J. Kuhn, and J. C.Mcintyre,* “3-(beta-aryl-beta-(arylthio) (orarylseleno)-propionyl)pyrone products”, US patent 3493586, 1970.
4. *A. Schwarcz, and G.D. Brindell*, “Preparation of diisocyanate dimers in aqueous medium”, US patent 3489744, 1970.
5. *T.N. Srivastava, R.C. Srivastava, M. Srivastava*, Indian J. Chem. Section A, vol. 21, pp. 539, 1982.
6. *B.M. Phillips, L.F. Sancilio, and E. Kurchacova*, “In vitro assessment of anti-inflammatory activity,” Journal of Pharmacy and Pharmacology, vol. 19, no. 10, pp. 696–697, 1967.

7. *W.E. Rutzinski, T.M. Amiabhavi, N.S. Birdarar, and C.S. Patil,* “Biologically active sulfonamide schiff base complexes of selenium(IV) and tellurium(IV),” Inorg. Chim. Acta, vol. 67, pp. 177–182, 1982.
8. *I.D. Sadekov, I.A. Barchan, A.A. Maksimenko, et al*., Khim.-Farmats. Zh., vol. 9, pp. 1073, 1982.
9. *P. Silks and A. Louis*, “Hot topic: advances in asymmetric synthesis using organoselenium chemistry,” Current Organic Chemistry, vol. 10, no. 15, pp. 1891, 2006.
10. *V.A. Potapov and S.V. Amosova*, “New methods for preparation of organoselenium and organotellurium compounds from elemental chalcogens,” Russ. J. Org. Chem.,vol. 39, no. 10, pp. 1373–1380, 2003.
11. *M.R. Detty and M.E. Logan*, “One- and two-electron oxidations and reductions of organoselenium and organotellurium compounds,” Adv. Phys. Org. Chem., vol. 39, pp. 79–145, 2004.
12. *J. Mochowski, et al*., Eur. J. Inorg. Chem., vol. 2003, no. 22, pp. 4328, 2003.
13. *J.P. Marino and A. Schwartz*, “Selective catechol oxidations with diphenyl selenoxide. Applications to phenolic coupling,” Tetrahedron Lett., vol. 20, no. 35, pp. 3253–3256, 1979.
14. *Y. Liftman and M. Albeck*, “The electrochemistry of organotellurium compounds-IV. The electrochemistry of diphenyl ditelluride and difuryl ditelluride in methylene chloride,” Electrochim. Acta, vol. 29, no. 1, pp. 95–98, 1984