COLLOID CHEMISTRY
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Cyclic Voltammetry Study of (5-Ethoxycarbonylmethylidene-4-oxothiazolidin-2-ylidene)-N-phenylethanamide*

I. Cekić-Lasković[a, b], D. M. Minić [a, b], M. Baranac-Stojanović[b, c],
R. Marković[b, c], and E. Volanschi[d]

[a] *Faciulty of Physical Chemistry, University of Belgrade, Studentski trg 12, Belgrade, Serbia,*

[b] *Center for Chemistry ICTM, P.O. Box 473, 11001 Belgrade, Serbia*

[c] *Faculty of Chemistry, University of Belgrade, Studentski trg 16, 11001 Belgrade, Serbia*

[d] *Department of Physical Chemistry, University of Bucharest, Blvd Elisabeta 4-12, RO-030018, Bucharest, Romania*

e-mail: isidora@ffh.bg.ac.rs

Abstract—As a continuation of our ongoing project on electrochemical properties of *push-pull* 5-substituted 2-alkylidene-4-oxothiazolidines (**1a**) differing in substituent R at C5-position and electron withdrawing group (EWG), we nave investigated the electrochemical behaviour of (5-etoxycarbonylmethylidene-4-oxothiazolidin-2-ylidene)-N-phenylethanamide **1a** (R: =CHCO$_2$Et; EWG: CONHPh), consisting as a (2E,5Z)/(2Z,5Z) mixture, by cyclic voltammetry in polar as well as non-polar solvent (0.1 M TBAHFP in DMSO and CHCl$_3$, respectively). Cyclic voltammetry at stationary electrode was employed to characterize the electron transfer steps. Based on electrochemical criteria and correlation with the DigiSim simulations, an ECE mechanism, involving two electrochemical steps and one isomerisation step, was suggested.

INTRODUCTION

Push-pull alkenes are defined as substituted olefins containing one or two electron-donating substituents (D) on one end of a C=C double bond and one or two electron-accepting substituents (A) at the other end. Electronic D–A interactions *via* the C=C bond result in a polarization of the "*push-pull*" system [1]. Consequently, an increase of the *push-pull* character is associated with a decrease of the π-bond character of the polarized C=C bond. In turn, the corresponding π-bond orders of the C–D and C–A bonds are increased. The *push-pull* effect has major impact on both, the dynamic behavior and the chemical reactivity of these compounds:

(1)
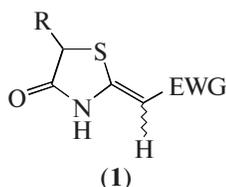
EWG = COPh, CONHPh, CN
R = Me, CH$_2$CO$_2$Et, H,
=CHCO$_2$Et

Stereodefined 2-alkylidene-4-oxothiazolidines (**1**), which have been previously characterized by ^{1}H NMR, ^{13}C NMR, IR, UV, MS spectroscopy and

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X-ray structural analysis [2], exemplify typical *push-pull* compounds. They exist in different configurational and conformational forms. One of the characteristic processes of *push-pull* alkenes **1**, based on a lowering of the rotational barrier of the C=C bond at the C2 position, is configurational isomerization which can be followed, under proper experimental conditions, by dynamic ^{1}H NMR spectroscopy [3].

Herein, we report an extension of our study on electrochemical behavior of *push-pull* alkenes, that is the functionalized 4-oxothiazolidine **1a** (R: =CHCO$_2$Et; EWG: CONHPh), having two exocyclic C=C bonds at C2 and C5 positions. In addition, the configurational isomerization at the C2 double bond, occurring during the electrochemical reduction in wet DMSO, has been examined.

EXPERIMENTAL

Cyclic voltammetry (CV) experiments were performed on a VOLTALAB-40 electrochemical device using thermostated one-compartment electrolytic cell with stationary Pt-EDI 101 of 2 mm diameter as working electrode, Pt counter electrode and Ag-quasi reference electrode. Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) 0.1 M was employed as supporting electrolyte. The solution in the electrochemical cell was deaerated with high-purity Ar before starting the CV experiments and an atmosphere of Ar was maintained over the solution in the cell during measure-
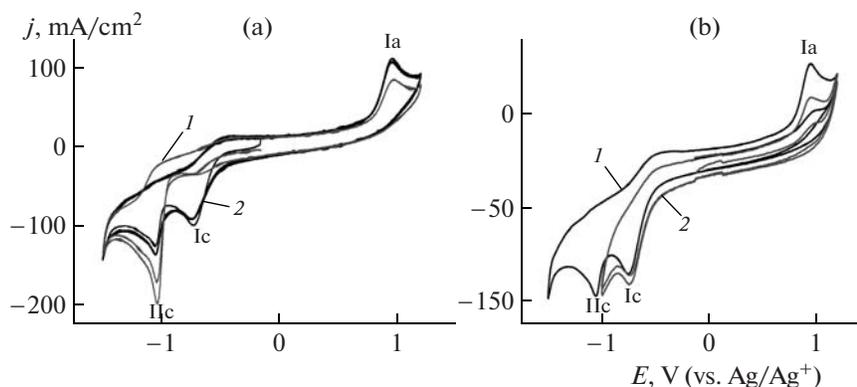
Fig. 1. Cyclic voltammograms of mixture of the 2E, 5Z-**1a** and 2Z, 5Z-**1a** isomers in 0.1 M TBAHPF/DMSO; c = 4 mM; v = 0.1 V/s, room temperature; (a) starting with reduction (potential range −1.5 to 1.2 V); (b) starting with oxidation (potential range 1.2 to −0.95 V); (1) freshly dissolved isomer mixture, (2) after a few polarization cycles; Ic is first cathodic peak, IIc is second cathodic peak, Ia is first anodic peak.

ments. Experimental results were correlated with results obtained by simulation, accomplished by the software DIGISIM 3.03. Bioanalytical Systems Inc.

RESULTS AND DISSCUSION

CV measurements were performed in solution of the mixture of configurational isomers (2E, 5Z)-**1a**, and (2Z, 5Z)-**1a**, in molar ratio 63 : 37 (total concentrations 2, 4, 6, and 8 mM) in 0.1 M TBAHFP/DMSO and 0.1 M TBAHFP/CHCl$_3$, used without further purification, by variation of temperature and scan rate.

The voltammetric reduction of freshly dissolved mixture of the 2E, 5Z-**1a** and 2Z, 5Z-**1a** isomers, in the potential range −1.5 to +1.2 V starting from the open circuit potential (−0.16 V), is characterised by an appearance of two irreversible cathodic peaks located at −0.73 V (Ic) and −1.04 V (IIc), and one anodic peak at +0.95 V respectively (Fig. 1a).
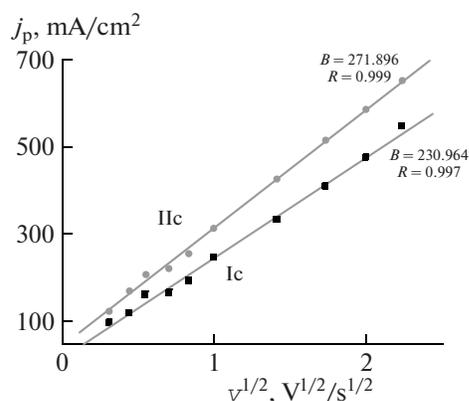
Starting with oxidation, 4 mM compound **1a**, in the potential range 1.2 V to −1.5 V, at the first scan, practically no peak is observed on the first cycle, showing that this substance is not electrochemically active in the investigated oxidation range up to 1.2 V. An appearance of one oxidation peak after sweeping the potential in reduction till −1 V, suggests that the oxidation peak is the result of the prior reduction, after the first, as well as after the second peak. On subsequent scans, the peak Ia increases (Fig. 1b).

Analysis of the cathodic peaks according to usual electrochemical criteria allows characterization of the electron transfer steps involved [4]. The peak current density increases with square root of the scan rate for both redaction peaks of the isomer mixture **1a**.

The plot of the peak current density versus the square root of the scan rate ($j_{pc} = f(v^{1/2})$, Fig. 2) is fairly linear, which is characteristic for diffusion controlled processes, $R = 0.997$ for the first peak and $R = 0.999$ for the second peak [5].

The $E_p = f(\log v)$ dependence (Fig. 3) for both reduction peaks has linear character with the slope values correspondingjto $B = 77$ and 37 mV, respectively, indicating either, a slow electron transfer, or an ET followed by a chemical step (EC sequence).

The current function ($j_p/v^{1/2}$ vs. v) dependence on the scan rate for both electron transfer steps Ic and IIc, presented in Fig. 4, corroborated with all electrochemical criteria discussed above, is an indication that both reduction peaks steps can be assigned to quasireversible ET steps, followed by a chemical reaction, (i.e. ECE sequence), as demonstrated for numerous organic compounds [4, 6, 7].

Fig. 2. Cathodic peak current density (j_p)-square root of the scan rate ($v^{1/2}$) relationship of the 2E, 5Z-**1a**/2Z, 5Z-**1a** mixture in 0.1 M TBAHPF/DMSO.

Influence of Concentration

The effect of the concentration was followed at $T = 20°C$, in the range from 2 mM to 4, 6, and 8 mM by considering the dependences of E_p vs. log c, and j_p
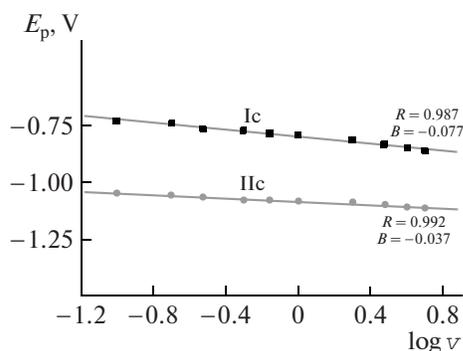
Fig. 3. E_p–$\log v$ relationship of (2E, 5Z)-**1a**/(2Z, 5Z)-**1a** (mixture of isomers) in 0.1 M TBAHPF/DMSO.
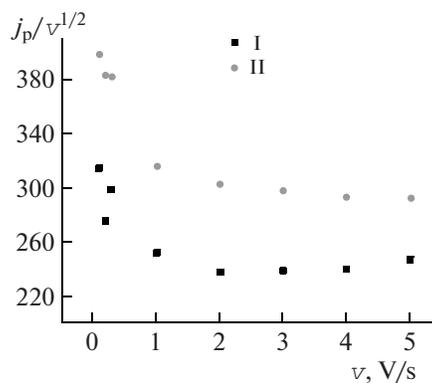

Fig. 4. Current density function ($j_p v^{-1/2}$)–v relationship.
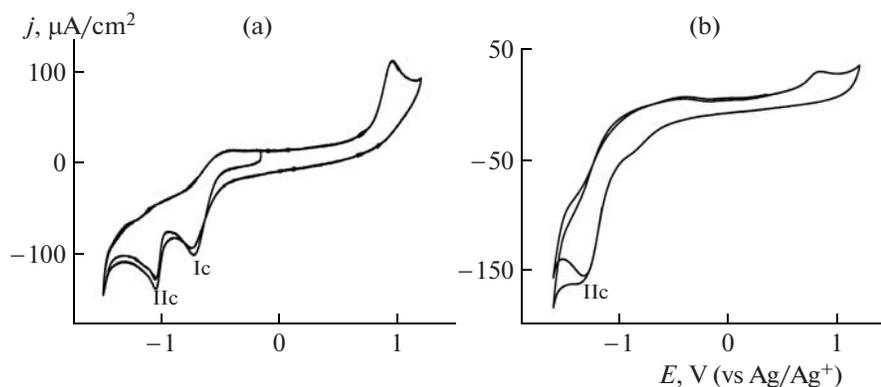

Fig. 5. Cyclovoltamgramms of 2 mM compound **1a** in (a) DMSO and (b) CHCl$_3$, at 20°C, potential range from −1.6 to 1.2 V, v = 0.1 V/s.

vs. c for both reduction peaks. These dependences show only the decrease of the current density for second reduction peak with dilution starting from 8 mM solution. The current density for the first reduction potential, as well as the potential values for both peaks, stay unchanged, thus, indicating a pseudo-first order chemical step in the electrode process. This chemical step can be assigned to the (2E, 5Z)/(2Z, 5Z)-isomerization process already mentioned above. The fact that the height of the first peak remains unchanged in spite of the dilution is a consequence of the isomerization in polar solvent, such as DMSO.

In order to assign these processes and to elucidate the nature of the chemical steps involved, the influence of the solvent polarity and temperature on the electrochemical behavior was also investigated.

Influence of Solvent

The influence of solvent polarity on reduction processes was studied in the polar DMSO and non-polar CHCl$_3$ solvent for scan rate 0.1 V/s at 20°C, in potential range from −1.6 to 0.1 V (Fig. 5). The appearance of only one reduction peak on the CV of compound **1a**

in non-polar solvent (CHCl$_3$) is in accordance with our previous results which indicated the presence of only (2E, 5Z)-isomer, being the dominant one in non-polar solvents [3, 8, 9]. On the contrary the appearance of two reduction peaks on the CV of compound **1a** (involving a mixture of both isomers) in a polar solvent may be assigned to the reduction of both isomers at different potential values.

This is in agreement with the ratio of the peak currents Ic/IIc of about 0.6 in the fresh solution after a few reduction cycles, corresponding to the 2Z, 5Z/2E, 5Z molar ratio of 37 : 63 in the starting compound. Variation of the intensity ratio in time and/or by increasing temperature is the result of the isomerization occurring in the polar solvent [3, 10] attenuated by the electrochemical reduction. According to this, the first reduction peak (Ic) at potential −0.73 V can be assigned to (2Z, 5Z)-isomer, whereas the second reduction peak (IIc) at potential −1.04 V can be assigned to (2E, 5Z)-isomer. This assignment is justified because the (2E, 5Z)-isomer is expected to be less prone to reduction and consequently appears at the more negative potential, due to the intramolecular H-bond stabilization. The appearance of the oxida-
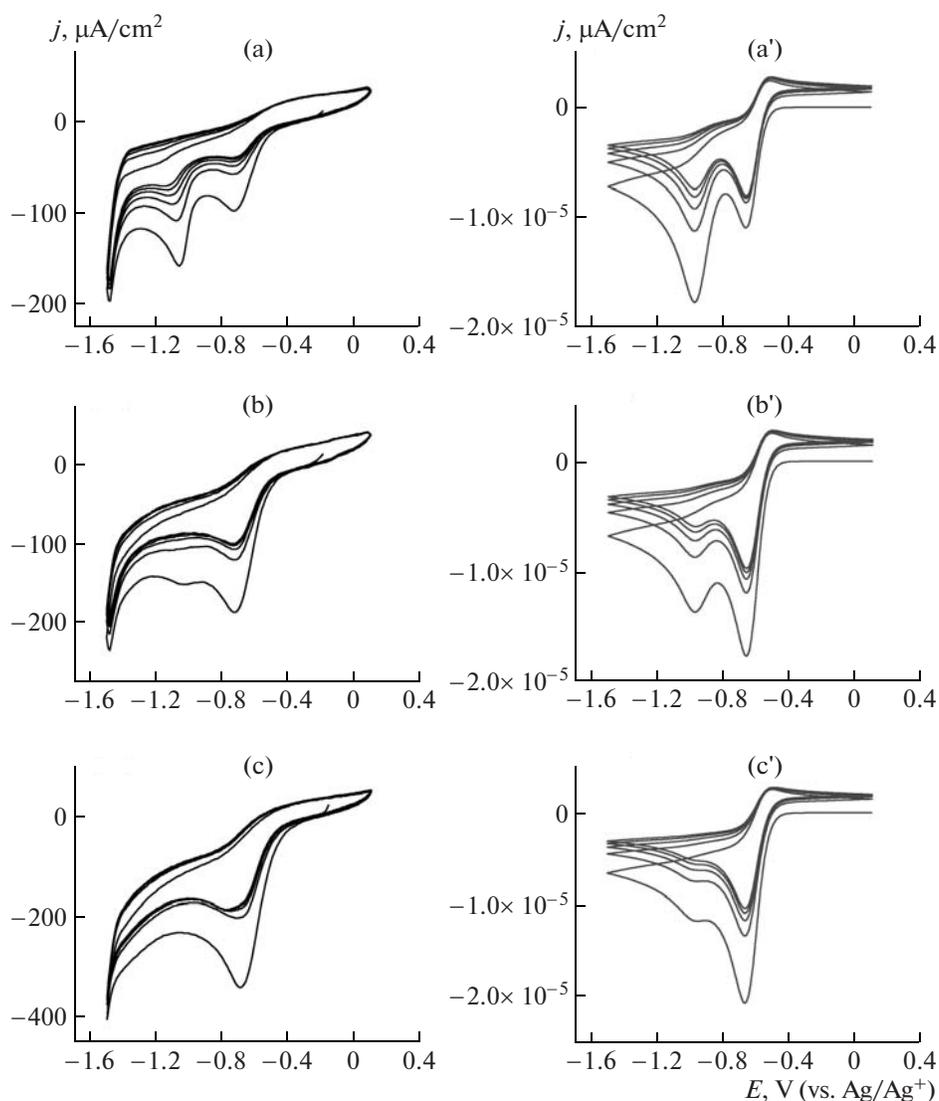
Fig. 6. (a–c) Experimental and (a'–c') simulated cyclic voltammetry curves of compound **1a** at (a, a') 20, (b, b'), 40 and (c, c') 65°C; $c = 2$ mM (mechanism and parameters in the text).

tion peak after sweeping the potential in reduction, suggests that the oxidation peak is the result of the prior reduction of both isomers.

Influence of Temperature

The influence of temperature on reduction processes was investigated at scan rate 0.1 V/s, in DMSO in temperature range 20–65°C (Fig. 6).

The increase of the temperature in the polar solvent (DMSO) causes a change of intensities of both cathodic peaks, leading to a reverse ratio of the current density of the first reduction peak (Ic) (assigned to the 2*Z*, 5*Z*-isomer) as against that of the second reduction process (IIc) (assigned to the reduction of the 2*E*, 5*Z*-isomer). This is most likely the consequence of the 2*E*, 5*Z*/2*Z*, 5*Z*-isomerization process, induced by the

electrochemical reduction in the presence of a polar solvent. The *cis–trans* isomerization under cathodic electron transfer is a frequent reaction for the organic compounds containing sulphur and nitrogen [11, 12].

This process is well accounted for by Digisim simulations with an ECE-Disp sequence (Fig. 6), together with the experimental curves in the potential range from −1.5 to 0 V, and parameters given below.

Proposed Mechanism of the Reduction

Taking into account electrochemical criteria, the following reduction mechanism of compound **1a**, based on an ECE-Disp sequence and experimental results regarding the influence of solvent, concentration and temperature on CV curves, can be suggested
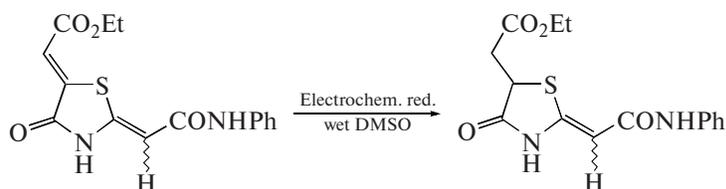
The thermodynamic and kinetic data used to perform the simulation of the experimental voltammograms are presented below:

$$(2E, 5Z)\text{-}\mathbf{1a} + e^- \longrightarrow (2E, 5Z)^{-\cdot}\text{-}\mathbf{1a} \qquad E_0 = -0.8 \text{ V}, \quad k_s = 0.0005 \text{ cm/s},$$

$$(2E, 5Z)\text{-}\mathbf{1a} \rightleftharpoons (2Z, 5Z)\text{-}\mathbf{1a} \qquad K_{eq} = 2000, \quad k_f = 10 \text{ s}^{-1},$$

$$(2Z, 5Z)\text{-}\mathbf{1a} + e^- \longrightarrow (2Z, 5Z)^{-\cdot}\text{-}\mathbf{1a} \qquad E_0 = -0.6 \text{ V}, \quad k_s = 0.000625 \text{ cm/s},$$

$$(2E, 5Z)^{-\cdot}\text{-}\mathbf{1a} + (2E, 5Z)^{-\cdot}\text{-}\mathbf{1a} \rightleftharpoons (2E, 5Z)\text{-}\mathbf{1a} + (2Z, 5Z)^{2-}\text{-}\mathbf{2a}$$

$$(2Z, 5Z)^{2-}\text{-}\mathbf{2a} + (2E, 5Z)\text{-}\mathbf{1a} \rightleftharpoons (2Z, 5Z)^{-}\text{-}\mathbf{1a} + (2E, 5Z)^{-}\text{-}\mathbf{1a}$$

$$(2E, 5Z)^{-\cdot} + (2E, 5Z)^{-\cdot} \rightleftharpoons (2Z, 5Z)^{-} + (2E, 5Z)^{-} \qquad K_{eq} = 10, k_f = 10 \text{ s}^{-1},$$

$$(2Z, 5Z)^{-}\text{-}\mathbf{1a}, (2E, 5Z)^{-}\text{-}\mathbf{1a} \longrightarrow P_{ox} + e^- \qquad E_0 = 1 \text{ V}, \quad k_s = 0.001 \text{ cm/s}.$$
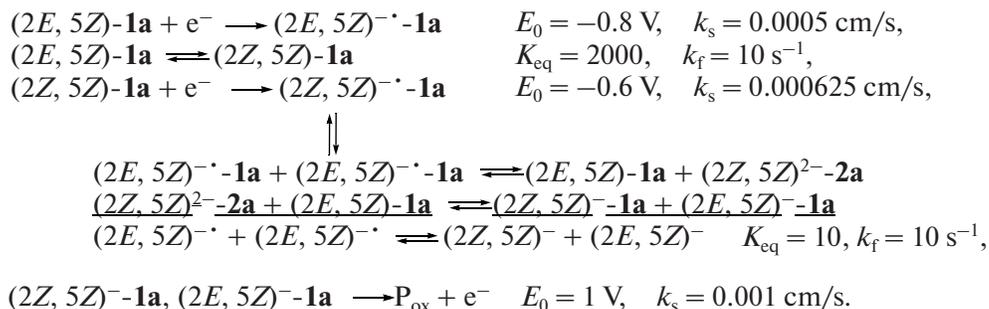
On the first scan the major 2E, 5Z-isomer is reduced in a monoelectronic step to its anion radical at the potential corresponding to the IIc couple. As electrochemical reduction implies diminished double bond character of the C(2) double bond, the isomerization is possible and is favored thermodinamically, the 2Z, 5Z-**1a**-isomer being reduced at a less negative potential of peak Ic [10, 13]. The second electron transfer step corresponds to the monoelectronic reduction of the 2Z, 5E-**1a**-isomer. This is followed by a chemical step, that is, an intermolecular disproportionation consisting of successive electron and proton transfers leading to the anions of both isomers [14], which can be subsequently oxidized (P_ox) in the reverse anodic scan.

The simulated CV as well as the experimental CV are presented in Fig. 6. The temperature dependence was simulated by varying the equilibrium constant in a range from 2000 at 20°C to 4000 at 40°C and 5800 at 65°C.

Reasonably good agreement between the experimental and simulated CV was obtained at all three selected temperatures, indicating that the proposed mechanism accounts correctly for the main features of the investigated process. However, we found that there is no exact correlation between the experimental and simulated behavior because of the great number of variables involved in the simulation, and due to the limitations of the program, allowing only three electron transfer steps [15].

CONCLUSION

Electrochemical properties of (5-ethoxycarbonyl-methylidene-4-oxothiazolidin-2-ylidene)-N-phenyl-ethanamide (**1a**) as the 2E, 5Z/2Z, 5Z-isomer mix-ture, were studied by cyclic voltammetry in polar solvent (DMSO), as well as in non-polar solvent (CHCl₃), at various temperatures and for different concentrations. By correlation of the experimental results and simulation of experimental CV, using the electrochemical package (DigiSim 3.03 Bioanalytical Systems Inc.) the most probable mechanism of the reduction of compound **1a** in DMSO, involving electrochemical reduction and that of the 2E, 5Z/2Z, 5Z-**1a**-isomerization, was proposed.

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