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Electrochemical reduction of 3,3´-bi(2-R-5,5-dimethyl-4-oxopyrrolinylidene)-1,1´-dioxides in water and its binary mixtures with acetonitrile*

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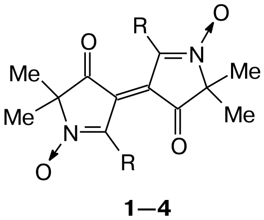
It has been shown by cyclic voltammetry for the first time for nitrons that the first step of electrochemical reduction of 3,3´-bi(2-R-5,5-dimethyl-4-oxopyrrolinylidene)-1,1´-dioxides in water and its binary mixtures with acetonitrile is a reversible one-electron process. The potentials of the first one-electron reduction peaks shift toward less negative values with an increase in the water content in the binary mixture, being in water equal to –0.14, –0.09, –0.08, and +0.19 V *vs.* saturated calomel electrode for dinitrons with R = Me, Ph, Bu^t, and CF_3, respectively. Such very low reduction potentials allow one to use derivatives of these dinitrons as redox-active labels in applied bioorganic electrochemistry.

Key words: 3,3´-bi(2-R-5,5-dimethyl-4-oxopyrrolinylidene)-1,1´-dioxides, cyclic nitrons, electrochemical reduction, cyclic voltammetry, binary mixtures, redox-active labels.

We have earlier[1,2] described for the first time the electrochemical behavior of a new class of heterocyclic nitrons, *viz.*, 3,3´-bi(2-R-5,5-dimethyl-4-oxopyrrolinylidene)-1,1´-dioxides **1—4**, with a very high electron-withdrawing ability prone to the formation of stable molecular ions in aprotic media. The electrochemical reduction of dinitrons **1—4** is an EE-process with two reversible electron-transfer steps. The potentials of the first one-electron peaks of electrochemical reduction of dinitrons **1—4** ($E_\mathrm{p}^{\mathrm{C}1}$) in MeCN are rather low in absolute value and comparable with the corresponding potentials of the strongest organic electron-acceptors.[1] The nature of the R substituent (except for CF_3) exerts no substantial effect on the potentials of electrochemical reduction: their values for dinitrons with R = Me, Ph, and Bu^t almost coincide.[1,2] In this work, we studied the first steps of electrochemical reduction of compounds **1—4** in water and its binary mixtures with MeCN.



1—4

R = Me (**1**), Ph (**2**), Bu^t (**3**), CF_3 (**4**)

Experimental

Dinitrons **1—4** were synthesized by the oxidative dimerization of the starting pyrrolinones according to a described procedure.[3] Their structures were confirmed by ^{1}H NMR, IR, and UV spectroscopy data. The spectral characteristics coincide with the earlier published values.[3]

Dinitrons **1—4** were studied by cyclic voltammetry using an CVA-1BM electrochemical system (Bulgaria) equipped with a LAB-MASTER polyfunctional interface (Novosibirsk Institute of Nuclear Physics), which allows the complete digital control of the system to be performed. Measurements were carried out in the triangular pulse mode of the potential sweep at the rate $\upsilon = 0.1$ V s^{-1}. A standard electrochemical cell with a working volume of 5 mL connected to the system *via* the three-electrode scheme was used. The working electrode was a stationary platinum spherical electrode with a surface area of 8 mm^2. The auxiliary electrode was a Pt helix, and the reference electrode was an aqueous saturated calomel electrode (SCE). The supporting electrolyte was $LiClO_4$ (0.1 mol L^{-1}). The CV curves were recorded in MeCN—H_2O binary mixtures of variable composition, and oxygen was removed by purging argon through the working solution. The concentration of depolarizers was $1 \cdot 10^{-3}$ mol L^{-1} for mixtures with a high content of MeCN, whereas saturated solutions of depolarizers with equilibrium (for the corresponding composition of the mixture) concentrations were used in mixtures with the volume fraction of MeCN lower than 0.5.

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Results and Discussion

Among dinitrons **1—4**, methyl-substituted compound **1** is most water-soluble. In a saturated aqueous solution containing the supporting electrolyte $LiClO_4$ (0.1 mol L^{-1}) at 25 °C, its concentration (~$6 \cdot 10^{-4}$ mol L^{-1}) is sufficient for the direct CV study of electrochemical reduction. Due to a lower solubility, the electrochemical reduction potentials of dinitrons **2—4** in water were determined by the extrapolation method, starting from the dependences of the reduction potentials on the water content in MeCN—H_2O binary mixtures. The same dependence was obtained for comparison for dinitron **1**.

The transition from the Et_4NClO_4 supporting electrolyte (see Ref. 2) to $LiClO_4$ shifts the potentials of the first cathodic peaks ($E_p^{C_1}$) measured[2] in MeCN by 0.1 V, on the average, toward less negative potentials.* The diffusion nature and reversible one-electron character of the first reduction peak are retained upon this transition. The region of reduction potentials accessible for measurement in MeCN—H_2O binary mixtures is $0.5 \text{ V} > E > -1.1$ V and restricted by the potential of water discharge on Pt under these conditions. When the water content in the binary mixture increases, the potentials of the first reduction peaks of compounds **1—4** shift toward less negative values (Fig. 1), reaching in water very low values (Table 1). In all cases, the first peaks are one-electron and reversible in the whole range of compositions of MeCN—H_2O mixtures. The plots of the potentials of the first reduction peaks *vs.* MeCN content in the mixture are linear and described by the regressions in the form

$$E_p^{C_1} = E_p^{C_1}(H_2O) + A \cdot V_{MeCN}, \qquad (1)$$

where $E_p^{C_1}(H_2O)$ is the potential of the first cathodic peak in the CV curve in water, V_{MeCN} is the volume fraction of MeCN, and r is the correlation coefficient. The regression parameters A and r are given in Table 1. Unlike dinitrons **1—3**, on going from MeCN to H_2O the potential of the first reduction peak of trifluoromethyl derivative **4** lies in the region of positive values *vs.* SCE.

Note that the second reversible reduction peak distinctly seen in MeCN for dinitrons **1—4** (C_2) and related to the formation of the corresponding dianions (see Fig. 1, *a*) becomes quasi-reversible (see Fig. 1, *b*) upon the addition of even small amounts of H_2O (~2%), $E_p^{C_2}$ shifts to the region of less negative values, and the limiting current of the second peak decreases appreciably compared to a similar value for the first peak with an increase in the water content. For $0 < V_{MeCN} < 0.5$, the second peak disappears (see Fig. 1, *c*). Elucidation of a reason for the sharp decrease in the limiting current of the second peak ($i_p^{C_2}$) with an increase in the water content is beyond the present report and will be considered elsewhere.

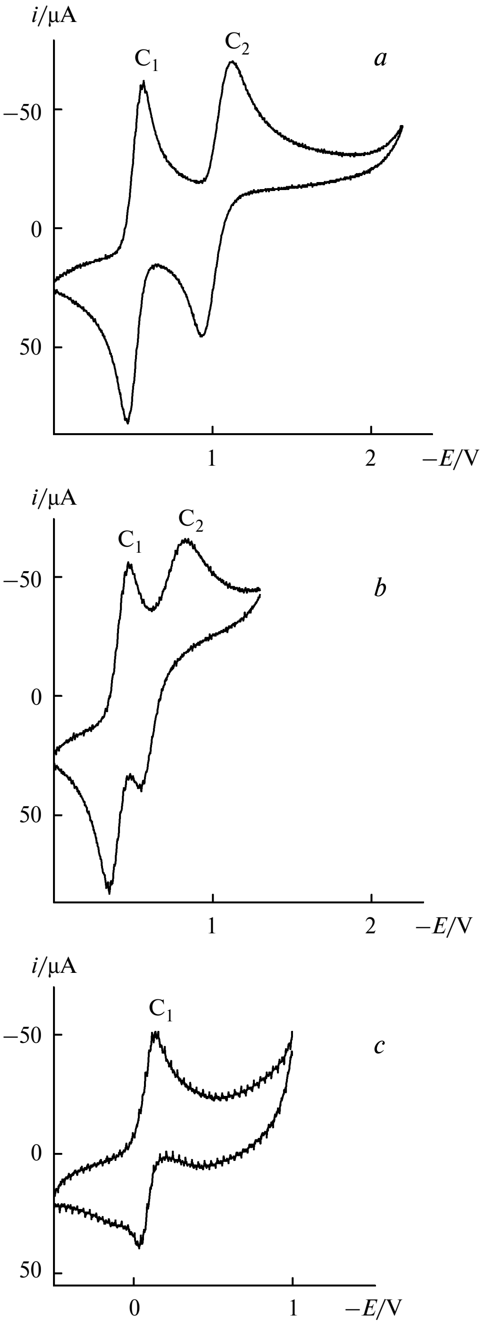

Fig. 1. Cyclic voltammograms of dinitron **1** in MeCN (*a*), MeCN—H_2O binary mixture (V_{MeCN} = 0.98) (*b*), and H_2O (*c*) ($\upsilon = 0.1 \text{ V s}^{-1}$, supporting electrolyte 0.1 *M* solution of $LiClO_4$).

The result is unexpected: for the first time for compounds of the dinitron series we succeeded to observe the reversible one-electron process in the first step of their electrochemical reduction in aqueous solutions and binary mixtures of the aprotic solvent—water type.

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* For dinitrons **1—4** the $E_p^{C_1}$ values in MeCN are −0.58, −0.55, −0.52, and −0.18 V, respectively (*vs.* SCE at the Pt electrode in a 0.1 *M* solution of Et_4NClO_4, $\upsilon = 0.1 \text{ V s}^{-1}$).

Table 1. Parameters of the linear dependences of the potentials of the first reduction peaks of dinitrons **1—4** ($E_p^{C_1}$) on the volume fraction of acetonitrile in MeCN—H_2O binary mixtures[a] (see Eq. (1))

Compound	$E_p^{C_1}(H_2O)$	$-A$	r
	V		
1	−0.13[b]	0.35	0.998
2	−0.09	0.33	0.998
3	−0.08	0.32	0.998
4	0.19	0.52	0.989

[a] Potentials *vs.* SCE at the Pt electrode in a 0.1 *M* solution of $LiClO_4$; $\upsilon = 0.1$ V s^{-1}.

[b] The potential of the first reversible one-electron reduction peak measured directly in H_2O at the Pt electrode is −0.14 V *vs.* SCE in a 0.1 *M* solution of $LiClO_4$ at $\upsilon = 0.1$ V s^{-1}.

The corresponding values of the potentials of the first peaks of electrochemical reduction of dinitrons **1—4** in water are rather low and close to the redox potentials of the ferrocene derivatives, which are widely used in the recent time as redox-active labels in electrochemical detection of nucleic acid hybridization,[4,5] particularly, for the development of DNA-microarrays with electrochemical detection of hybridization.[6] We believe that the dinitron derivatives, which possess low potentials of electrochemical reduction and contain appropriate active groups (substituents) capable of binding with DNA, can be rather efficient redox-active labels for the electrochemical detection of DNA hybridization when the double DNA chain undergoes no irreversible destruction. Our further studies will be focused on the development of this direction.

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References

1. L. A. Shundrin, V. A. Reznikov, I. G. Irtegova, and V. F. Starichenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 892 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 939].
2. L. A. Shundrin, I. G. Irtegova, A. D. Rogachev, and V. A. Reznikov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1148 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1178].
3. V. A. Reznikov, V. V. Martin, and L. B. Volodarskii, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1990, 1398 [*Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 1990, **39**, 1261 (Engl. Transl.)].
4. T. S. Zatsepin, S. Yu. Andreev, T. Gianik, and T. S. Oretskaya, *Usp. Khim.*, 2003, **72**, 602 [*Russ. Chem. Rev.*, 2003, **72**, 537 (Engl. Transl.)].
5. A. Anne, A. Bouchardon, and J. Moiroux, *J. Am. Chem. Soc.*, 2003, **125**, 1112.
6. S. Abramowitz, *J. Biomed. Dev.*, 1999, **1**, 107.

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