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FREE-RADICAL INTERMEDIATES IN THE ELECTROCHEMICAL REDUCTION OF α,β DERIVATIVES OF β-(5-NITRO-2-FURYL)-α-CYANOETHYLENE

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It was found by cyclic voltammetry and ESR that the excitation of the molecules of α,β derivatives of β-(5-nitro-2-furyl)-α-cyanoethylene in the radical-anion state by one-electron electrochemical reduction promotes chemical transformation of the other reaction centers, while preserving the nitrofuran group.

Earlier it was established that the products from one-electron reduction, i.e., radical-anions, were obtained during the electrochemical reduction of the 2-vinylene derivatives of 5-nitrofuran [1]. The formation of such radical-anions is due to the priority for the reduction of the nitro group. However, it is known [2] that the C=C bond of the vinylene group, conjugated with electron-withdrawing substituents and particularly with the cyano group, can also undergo electrochemical reduction, or the substituent may be removed electrochemically (with cleavage of the C—CN, C—Cl, or C—N$^+$ bond) [3]. These effects can hinder the formation of radical-anions of the initial compounds sufficiently stable for study by ESR. Such features must also be expected in our investigated α,β derivatives of β-(5-nitro-2-furyl)-α-cyanoethylenes (I-VIII), the free radicals of which we attempted to generate in the present work.
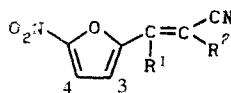
I - VIII

I R^1=NMePh; II R^1=NH$_2$; III, VII R^1=NHPh; IV, VIII R^1=morpholino; V R^1= =NH(CH$_2$)$_2$OH; VI R^1=Cl; I—V R^2=CO$_2$Et; VI—VIII R^2=CN

TABLE 1. Potentials of the Cathodic (E_c, V) and Anodic (E_a, V) Peaks on the Cyclic Voltammetric Curves for the Electrochemical Reduction of Compounds (I-VIII) and also the Potentials of the Additional Peaks during Repeated Cycles after the Attainment of the Identified Cathodic Potentials of the First Cycle

Compound	E_c/E_a	E_c/E_a of repeated cycles
I	−0,71*/−0,65; −0,80/−0,74	*−/−0,16
II	−0,74*/−0,66; −1,15/−0,99; ∼−2,0/−	*−/0,40
III	−0,72*/−; −0,96/−; −1,13/−0,99; −1,70**/−	*−0,38/−0,17; **−0,90/−0,82; −/−1,29
IV	−0,75*/−0,67; −0,99/−0,91	*−0,40/−0,20
V	−0,80*/−; −1,00/−0,92; −1,14/−1,01; ∼−2,0**/−	*−/−0,40; **−1,01/−0,95; −/−1,28
VI	−0,34/−; −0,48/−; −0,60/−; −1,00/−0,84; ∼−1,6*/−	*−0,73/−0,67
VII	−0,59*/−; −0,92/−; −1,03/−0,96; ∼−1,7**/−	*−/0,0; **?/−0,75
VIII	−0,70*/−0,61; −0,97/−0,88	*−/−0,18

*In DMFA, glassy graphite electrode.

TABLE 2. Electrochemical Generation Potentials (E) of Compounds (I-VIII) in DMFA and the HFS Constants (a, G) in the ESR Spectra of the Radical-Anions

Compound	E, V*	$a_N^{NO_2}$	a_H^4	a_H^3	$a_N^{R^1}$	Radical†	Remarks
I	−0,8 −1,0	8,07	4,56	1,17		B	HFS not established
II	−0,85 −1,3	6,32 10,71	3,74 4,68	0,94 —	0,94 1,17	A C	$a_N = 0,64$
III	−1,25	8,19	4,68	1,40	1,40	B	Average of two conformers
IV	−0,55 −1,1	∼5,6 9,01	∼5,6 4,75	∼1,6 1,17	∼1,6	A B	Low concentration of radicals An unidentified radical is also formed
V	−1,2 −1,9	8,4	3,56	1,17	1,38	B	$a_H = 2,16$; 1,93 HFS not established
VI	−0,5 −1,0 −1,3	8,61 10,06	4,68 5,15	1,17 1,05		B C	HFS not established
VII	−1,25 −1,25	8,02 8,31	4,72 4,72	1,17 1,08	1,17 0,67	B B	One of the conformers One of the conformers
VIII	−0,7 −1,0	∼4,2	∼4,2	∼1,7	∼1,7	A	Broad signals Low concentration of radicals $(3_N \times 2_H \times 2_H) + (3_N \times 2_H \times 2_H)$

*E (V) with reference to a silver electrode. †A is the primary radical-anion, B is the radical having a vinylene group in the substituent, and C is the radical not having a vinylene group in the substituent.

The electrochemical reduction of compounds (I-VIII) in DMFA at a glassy graphite electrode, which takes place as a complex many-stage process, was studied in the range of 0- to −2.0 V (Table 1). Substitution of the ethoxycarbonyl substituent R^2 at the α-carbon atom of the vinylene group by a cyano group reduces the first reduction potential. It was found by polarography that the initial electrochemical reduction process has one-electron character. On the basis of general ideas about the electrochemical reduction of compounds of the nitrofuran series in nonaqueous media [4,5] and of data obtained from the cyclic voltammetric curves of compounds (I-VIII) (Table 1) it can be supposed that the nitro group is affected first in the reduction process. It is true on account of the above-mentioned electrochemical behavior of the vinylene group that this cannot

be confirmed unambiguously on the basis of cyclic voltammetric data alone particularly in the case of the dicyano-substituted compounds (VI-VIII).

The initial electrochemical reduction of compounds (I, II, IV, VIII) has partial reversible character, which indicates the possible formation of radical-anions of the initial compounds in this process, but the presence of the mobile proton in the substituent $R^1 = NH_2$ of compound (II) may give rise to low stability of these radicals insufficient for recording by the ESR method. In the case of the other compounds, for which the electrochemical process is irreversible, it is necessary to expect the formation of radical-anions sufficiently stable for recording by the ESR method.

In the course of the electrochemical reduction of compounds (I-VIII) free radicals (the intermediate products of the electrochemical and associated chemical processes) were obtained in all cases by the electrochemical generation method. All the radicals whose concentration was sufficient for investigation by the ESR method have the structure of the radical of 2-substituted 5-nitrofuran (Table 2). It is noteworthy that several different free radicals of nitrofuran type were obtained for each of compounds (II, IV, VI, VII), depending on the generation potential. Thus, for example, in the case of compound (VI) three free-radical intermediates of various structures are formed. For two of them we determined the hyperfine structure (HFS) in the ESR spectra, on the basis of which it was established that all the generated radicals (even those obtained at E = -1.3 V) contain a nitro group. Having a nitrofuran group, all the generated radicals differ in the substituents at position 2 of the 5-nitrofuran ring. During comparison of the a_N^{NO2} values for the primary and secondary or secondary and tertiary free radicals of a specific compound it was found that the electrophilic characteristics of this substituent decrease during electrochemical reduction. In the HFS of the ESR spectra, however, the interaction of the unpaired electron with the nuclei of the atoms in the substituent at position 2 shows up weakly, and this limits the possibility of determining its structure. Some indirect data on the structure of the substituent can be obtained by comparing the electrochemical generation potential of the free radical (Table 2) with the data from cyclic voltammetry of specific derivatives of the series (Table 1) and also the HFS constants due to the nucleus of the nitrogen atom in the nitro group (a_N^{NO2}) of the investigated radical and the same constant for the radical-anions of 2-alkyl- and 2-vinyl-substituted 5-nitrofurans [5].

Thus, it was established for compounds (II, IV, VIII) at the electrochemical generation potentials E = -0.85, -0.55, and -0.7 V respectively that the radical-anions of the initial compounds are formed. This is indicated by the values of the a_N^{NO2} constant, the correspondence of the electrochemical generation potential to the potential of the first cathodic peak of the cyclic voltammograms, and the partial reversibility of the reduction process, which is typical of the formation of the radical-anions of the 5-nitrofuran series.

The remaining free radicals of compounds (I-VIII) have a substituent at position 2 of the 5-nitrofuran, which is transformed during the electrochemical reduction of these compounds, and the process [with the exception of compounds (II, VI)] did not affect the vinylene group of this substituent. This is indicated by the a_N^{NO2} values characteristic of such free radicals.

The free radicals of compounds (II, VI), obtained at -1.3 V, do not correspond to the last condition. The a_N^{NO2} value of their ESR spectra is typical of 5-nitro-2-alkyl-substituted free radicals [5]. Such a structure for these radicals probably results from reduction of the vinylene group and subsequent dimerization (oligomerization) of the obtained radicals at the carbon atoms of this group, which is typical of an activated vinylene group [2].

As shown by quantum-chemical calculations [6-8], the highest density of the unpaired electron in free radicals of the nitrofuran type is largely localized at the nitro group. On this basis and also on the basis of the relatively high electrophilicity of the nitro group it can be concluded that the reaction center of one-electron reduction in the investigated compounds and in the formation of their radical-anions is the nitro group. However, both at the formation potential of the radical-anion of the initial compound and at more negative potentials (up to a certain limit) further transformation occurs not in the nitro group but in the other chemically or electrochemically active groups at position 2 of the 5-nitrofuran, which are usually electrochemically inactive in the molecule at these potentials. It can be supposed that, while not being transformed chemically, the nitro group (the nitrofuran group) in the molecule provides the means for latent chemical transformations of the fragments of the molecule through its excitation in the radical-anion state.

EXPERIMENTAL

The free radicals were generated in the standard regime at a platinum cathode in a cell placed in the rectagonal resonance cavity (of the H_{102} type) of the Carl Zeiss ER-9 (Jena) ESR spectrometer by the method in [9]. The electrochemical generation potentials were measured by a three-electrode scheme with reference to a silver electrode. The ESR spectra were

recorded with a magnetic field sweep rate of 0.004 mT/sec with high-frequency (100 kHz) magnetic field modulation of 0.005-0.08 mT and a constant recording time of 0.45 sec. The magnetic field sweep was calibrated against the ESR spectrum of the nitrobenzene radical-anion [10].

For electrochemical generation of the free radicals we used $5\cdot10^{-4}$-$5\cdot10^{-3}$ M solutions of compounds (I-VIII) in DMFA; the solutions contained 0.1 M of tetrabutylammonium perchlorate. The cyclic voltammetric curves at the glassy graphite electrode were recorded by means of the PAR-170 electrochemical system with a potential sweep rate of 0.1 V/sec by the method in [11]. The procedure for the synthesis of the investigated compounds and references to it were given in [12].

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