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Abstract

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Electrochemical Generation of Free-Radical Anions in the 5-Nitrofuran Series

Electrochemical generation of free-radical ions directly in the resonator of an EPR spectrometer was first carried out by Geske and Maki in aprotic media (1-3), and was later also developed for aqueous solutions (4, 5). Thus a new method was created for the stationary production of short-lived particles, making it possible, moreover, to follow unstable intermediate products of an electrode reaction.

On the basis of the character of the polarographic curves, we had previously postulated the formation of the radical anion of 5-nitrofuran as the primary product of the polarographic reduction of 5-nitrofuran and its derivatives (6). For experimental proof of this proposition, in the present work microelectrolysis of solutions of 5-nitrofuran and its derivatives was carried out according to modified versions of the methods of Geske and Maki (1, 2, 5). During electrolysis the EPR spectra of the free radicals formed were recorded. In this way it proved possible for the first time to obtain free-radical anions in the 5-nitrofuran series, i.e., the primary products of electron addition to the 5-nitrofuran molecule:

$$O_2N-\boxed{O}-R + e \longrightarrow \left[O_2N-\boxed{O}-R\right]^-$$

and to study the distribution of electron density in the anion radicals from the hyperfine structure (h.f.s.) of the EPR spectrum. Analogous data in the literature are available only for the anion radicals of nitrobenzene and of certain aliphatic nitro compounds (1-5). In the nitrofuran series, the preparation of free-radical anions by reduction of nitro compounds with metallic potassium proved impossible, and electrochemical generation represents the most accessible method for obtaining them. We studied: 5-nitrofuran (I), 5-nitropyromucic acid (II), ethyl ester of 5-nitropyromucic acid (III), 5-nitrofurfuryl alcohol (IV), 2-oxymethyl-5-nitrofuran (V), and β-(5-nitrofuryl)acrylic acid (VI).

Aqueous solutions of the nitro compounds were prepared at concentrations of 10^{-2}-10^{-3} mole/liter, to which, in order to create the necessary electrical conductivity, KCl was added at a concentration of $4 \cdot 10^{-1}$-$1 \cdot 10^{-1}$ N. Electrolysis was carried out on a stationary mercury drop in a specially designed microelectrolyzer placed in the resonator of the EPR spectrometer. The voltage was supplied to the electrolyzer from an accumulator through a rheostat and was

Fig. 1. E.P.R. spectra of anion-radicals of 2-R-substituted 5-nitrofurans: I –R = H; II –R = COOH, (III –R = $COOC_2H_5$); IV –R = CHO; V –R = CH_2OH

Figure 1: Fig. 1. E.P.R. spectra of anion-radicals of 2-R-substituted 5-nitrofurans: I –R = H; II –R = COOH, (III –R = $COOC_2H_5$); IV –R = CHO; V –R = CH_2OH

kept constant throughout the entire electrolysis. Simultaneously with electrolysis, the EPR spectrum was recorded on the recorder of an RE-1301 instrument (resolving power ~ 0.4 oersted). The spectrum was calibrated with 1,1-diphenyl-2-picrylhydrazyl, the N-oxide of 2,2,5,5-tetramethylpyrrolidine-3-carboxamide, and refined against the spectrum of the nitrobenzene radical anion in aqueous medium ([4]). EPR signals during electrolysis of 5-nitrofuran derivatives can be obtained in a neutral or slightly alkaline medium, where the nitrofuran molecules are not subject to decomposition and the concentration of proton donors is low. In the presence of a sufficient concentration of proton donors in the solution, the primary product of one-electrode reduction (radi-

(calanion) is immediately protonated and then further reduced to the corresponding hydroxylamine derivative, making it impossible to isolate the stage of radical-anion formation.

Before beginning the experiments, we first obtained polarograms of the indicated 5-nitrofuran derivatives and refined the corresponding half-wave potentials ([7]). Initially, electrogeneration of the radicals was carried out at potentials corresponding to the steep part of the polarographic wave, with strict maintenance of the potential (~0.6 V relative to the S.C.E.). However, this proved unnecessary, since the signal intensity even increased with increasing potential. Details of the experiment will be described separately.

The E.P.R. spectra of compounds (I–V) are shown in Fig. 1. From the hyperfine structure, the splitting constants were calculated (Table 1). The splitting constant ΔH_N corresponds to the interaction of the unpaired electron with the nitrogen atom of the nitro group; the subsequent constants correspond to interaction with the nonequivalent protons of the furan ring and the protons of the substituent R. Since the magnitude of splitting on a proton is proportional to the spin density of the unpaired electron on the π-orbital of the neighboring carbon atom, the distribution of the unpaired π-electron density in aromatic radicals can be determined from this:

$$\rho_{C^i} = \frac{\Delta H_{C^iH}}{Q},$$

where $Q = 22.7$ Oe ([8]-[10]).

Fig. 1. E.P.R. spectra of anion-radicals of 2-R-substituted 5-nitrofurans: **I** –R = H; **II** –R = COOH, (**III** –R = $COOC_2H_5$); **IV** –R = CHO; **V** –R =

Fig. 2. Dependence of the splitting constant of the spectrum of the anion radical of 2-R-substituted 5-nitrofuran on the Hammett constant σ_p of substituent R

Figure 2: Fig. 2. Dependence of the splitting constant of the spectrum of the anion radical of 2-R-substituted 5-nitrofuran on the Hammett constant σ_p of substituent R

CH_2OH.

The spin density of the unpaired electron on the carbon atom in the 4-position of the furan ring, adjacent to the nitro group, proves to be considerably higher than the density in the 3-position. With increasing electron-donor properties of the substituent R, the spin density in the 3-position increases, whereas in the 4-position it decreases; moreover, the change in both cases approximately follows the Hammett equation (Fig. 2).

Table 1

Values of the splitting constants (in oersteds) and spin density for the radical anions of various nitrofuran derivatives

Nos.	Substituent R	ΔH_N	ΔH_{C^4H}	ΔH_{C^2H}	ΔH_{C^2H}	ΔH^R_{CH}	ρ_{C^4}	ρ_{C^3}	ρ_{C^2}
I	H	13.2	6.1	0.9	4.7	–	0.27	0.04	0.21
II	COO–	12.1	5.6	1.2	–	–	0.25	0.05	–
(III)									
IV	CHO	9.2	4.4	1.5	–	1.3	0.20	0.07	–
V	CH_2OH	12.9	6.2	0.9	–	2.2	0.27	0.04	–

The sum of the two corresponding splitting constants for all the compounds studied is constant (with the exception of IV). Consequently, the total density of the unpaired electron on the π-orbitals in positions 3 and 4 does not depend on the nature of the substituent R, but the latter causes a redistribution of the density between these positions. The splitting constants on the N atoms of the nitro group vary depending on the nature of the substituent, following approximately the Hammett equation.

Fig. 2. Dependence of the splitting constant of the spectrum of the anion radical of 2-R-substituted 5-nitrofuran on the Hammett constant σ_p of substituent R

In comparison with the anion radicals of nitrobenzene and its derivatives (^{4}), in the anion radicals of nitrofuran and its derivatives the density of the unpaired electron spin on the nitro group is somewhat smaller, while the spin densities in the 2- and 4-positions of the furan nucleus are substantially greater; in position 3 of the furan ring the spin density of the corresponding derivatives of both series is approximately the same. The special features of the furan ring are due to the interaction of the oxygen heteroatom with the corresponding atoms of the ring.

The established course of the change in the splitting constants as a function of the nature of the substituent fully corresponds to the course of the change in the polarographic half-wave potentials in the same series ([6],[7] ,[11]).

On the basis of the data obtained one may draw the preliminary conclusion that radical anions in the 5-nitrofuran series are less stable than anions in the nitrobenzene series, and their preparation is associated with considerably greater experimental difficulties; the lifetimes of the radical anions of 5-nitrofuran derivatives are of the order of 0.1–1 sec.

The investigations are continuing.

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Note: Figure translations are in progress. See original paper for figures.