π-ELECTRON STRUCTURE OF THE NITROFURAN SYSTEM

III.* EFFECT OF THE MEDIUM ON THE CHARACTER OF THE ESR SPECTRA OF 5-NITROFURAN ANION RADICALS

R. A. Gavar, L. Kh. Baumane,
Ya. P. Stradyn', and S. A. Giller

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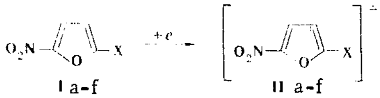
The effect of the ionic composition and the concentration of the components of a mixed water–dimethylformamide medium on the π-electron structure of anion radicals of the nitrofuran series was studied. The formation of ion pairs with the cations and hydration of the anion radicals somewhat increase the hyperfine structure constants in their ESR spectra, especially those caused by the nitrogen atom of the nitro group, and this should be taken into account in high-accuracy quantum-chemical calculations. A mathematical description of the change in the hyperfine structure constants in mixed water–dimethylformamide media is given, and a number of empirical regularities that link the magnitudes of the constants with the electronic effects of substituents and media factors are presented.

Anion radicals II, which have sufficient stability for their detection by ESR even in aqueous media [2,3], are formed in the one-electron electrochemical reduction of 5-nitrofuran and its derivatives (I). Our previously determined hyperfine structure (HFS) constants of the ESR spectra of II, which characterize the distribution of the density of the unpaired electron in the investigated anion radicals (II), the electrophilicities of the individual positions of the starting I molecules [4,5], and the polarographic potentials for the addition of the first electron have served as an experimental basis for the calculation of the molecular orbitals of the π-electron system of 5-nitrofurans by the Hückel method [1, 6]. Our subsequent investigations have demonstrated that when 5-nitrofurans undergo one-electron electrochemical reduction in dimethylformamide (DMF), their half-wave potentials and the HFS constants of II differ markedly from the corresponding values for the same anion radicals in aqueous media [7]. In this connection, a question arose as to how adequately the quantum-chemical calculations made on the basis of starting parameters selected from the experimental data in aqueous media reflect the true π-electron structure of the 5-nitrofuran system and whether effects of solvation, formation of ion pairs, etc., are introduced in this case. The effect of the medium (ion composition, fraction of the organic component in the aqueous organic mixture) on the HFS constants of the ESR spectra of anion radicals II and, consequently, on the π-electron structure of this system was therefore studied in detail in the present paper.

The effect of the ionic composition of the medium on the ESR spectra of anion radicals II was followed by means of the one-electron electrochemical reduction of 5-nitrofurans I in DMF according to the reaction



I a-f II a-f (1)

a $X = CH_3$; b $X = H$; c $X = COOH$; d $X = CN$; e $X = COCH_3$; f $X = CHO$

When the nature of the indifferent salt (tetraethylammonium halide) changes, an insignificant (<0.3 Oe) decrease in the $a_{N,5}$ value is observed in the case of anion radicals IIa as the anion (Cl^-, Br^-, I^-) radius

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*See [1] for communication II.

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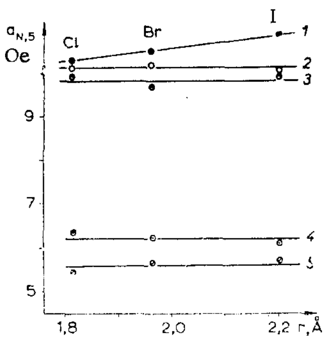

Fig. 1

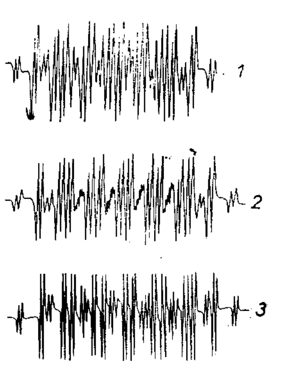

Fig. 2

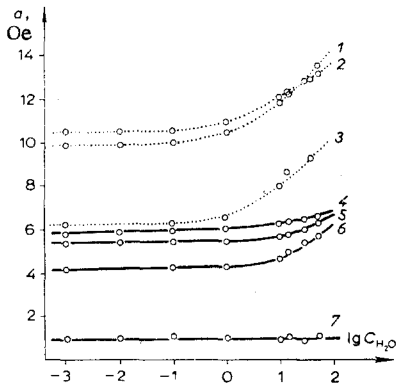

Fig. 3

Fig. 1. Changes in the HFS constants ($a_{N,5}$) of the ESR spectra of anion radicals II as a function of the cation radius: 1) IIa; 2) IIb; 3) IIc; 4) IIe; 5) IIf.

Fig. 2. ESR spectra of anion radical IIa at various concentrations of water in a water–DMF medium: 1) 0 M H_2O; 2) 10 M H_2O; 3) 56 M H_2O.

Fig. 3. Changes in the HFS constants of the ESR spectra of anion radicals II as a function of the molar concentration of water in a water–DMF medium: 1) IIb, $a_{N,5}$; 2) IIa, $a_{N,5}$; 3) IIe, $a_{N,5}$; 4) IIa, $a_{H,4}$; 5) IIb, $a_{H,4}$; 6) IId, $a_{H,4}$; 7) IIb, $a_{H,3}$ [the points are the experimental values, while the dotted lines are the curves calculated from Eq. (3)].

TABLE 1. HFS Constants of the ESR Spectra of Anion Radicals IIb in DMF Containing Various Cations

Cation	HFS constants, Oe			
	$a_{N,5}$	$a_{H,4}$	$a_{H,3}$	$a_{H,2}$
Na^+	11,5	5,8	1,1	4,3
K^+	10,8	5,7	1,0	4,1
$(C_2H_5)_4N^+$	10,1	5,5	1,0	4,0
$(C_4H_9)_4N^+$	10,1	5,5	0,9	3,9

TABLE 2. HFS Constants of the ESR Spectra of Anion Radicals II

X	Spectrum, length, Oe		HFS constants, Oe							
			$a_{N,5}$		$a_{H,4}$		$a_{H,3}$		$a_{H(N),2}$	
	DMF	H_2O	DMF	H_2O	DMF	H_2O	DMF	H_2O	DMF	H_2O
CH_3	38,1	48,3	10,2	13,2	5,8	6,5	0,9	0,8	3,9	4,8
H	30,1	38,5	9,9	13,2	5,6	6,1	1,0	0,9	4,0	4,7
COOH	25,8	31,1	9,8	12,1	5,1	5,6	1,0	1,2	—	—
CN	21,1	31,6	6,9	11,6	4,4	5,6	1,0	1,5	0,8	0,8
$COCH_3$	21,1	—	6,2	—	3,7	—	1,2	—	1,3	—
CHO	17,0	25,6	5,3	9,2	3,4	4,4	2,0	1,5	0,8	1,3

decreases [8] (Fig. 1). However, this sort of effect was not observed for the other anion radicals studied. The HFS constants, which correspond to the distribution of the density of the unpaired spins on the ring carbon atoms, proved in all cases to be absolutely insensitive (within the limits of the resolving power of the spectrometer) to a change in the nature of the anions in the order Cl^-, Br^-, I^-. This sort of weakly expressed effect of the anions on the π-electron system of II is explained by mutual repulsion because of like charges.

The effect of various cations on the HFS constants of II in DMF is illustrated in the case of the anion radical of 5-nitrofuran (IIb): the $a_{N,5}$ constant increases in the order Na^+, K^+, $(C_2H_5)_4N^+$, $(C_4H_9)_4N^+$ as the volume of the singly charged cation decreases (Table 1). This sort of effect is explained by the fact that a decrease in the cation volume facilitates its approach and also promotes a stronger interaction with the anion radical, which has the opposite charge. Proceeding from this sort of concept, it is preferable to use indifferent salts that contain cations with a large radius or have a substituent-shielded cation charge (tetraalkylammonium salts, for example) to decrease the perturbation of the π-electron system of anion radicals by the medium during their electrochemical generation (ECG).

The most pronounced changes in the ESR spectra occur on passing from protogenic (H_2O, CH_3OH, C_2H_5OH) to aprotic media (acetonitrile, DMF) [9-11]. In view of this, we decided to follow the manner in which these changes are realized and the factors responsible for them on passing from a protogenic to an aprotic solvent, i.e., in mixed media containing different concentrations of water in DMF. In the case of the ESR spectra of the anion radicals of 5-nitro-2-methylfuran (IIa) (Fig. 2), it is seen that the ESR spectra are gradually elongated, and the resolution of the components improves as the concentration of water in DMF increases. The same thing is also observed for other anion radicals II. A gradual change in the composition of the medium makes it possible to follow the change in the components of the ESR spectra and thereby facilitates the interpretation of the HFS of the ESR spectra.

The character of the change with the composition of the water–DMF medium for various HFS constants of the ESR spectra of anion radicals IIb is presented in Fig. 3. The same type of change is also peculiar to the remaining anion radicals (II) studied: a characteristic sharp increase in the $a_{N,5}$ and $a_{H,4}$ HFS constants is observed as the concentration of water in the mixed medium increases. An increase in the HFS constant, which is due to splitting in the nitrogen atom of the nitro group ($a_{N,5}$), is observed at water concentrations above 10^{-2} M in DMF. A change in this HFS constant possibly also occurs at lower water concentrations, but we did not observe this because of the inadequate resolving power of the ESR spectrometer and because the water content during ECG of free radicals may reach a concentration of the order of 10^{-3} M as a result of manipulations with anhydrous DMF [12].

Changes in the a_H HFS constants caused by splitting in the protons of the furan ring are observed only when the water concentration in a sample is about 10 M. By comparing the HFS constants for the same form of ion radicals II with one another and the change in these values on gradual transition from DMF to an aqueous medium, one can observe approximate symbatic character between these values (Fig. 3), i.e., the larger the HFS values, the greater the changes that they undergo on passing from one medium to another.

A comparison of the HFS constants of anion radicals in DMF and in water is presented in Table 2. By comparing the HFS constants due to the protons, we see that the $a_{H,4}$ constant and thereby the density of the unpaired electron [13] in the 4 position can change by up to 30% of the initial density in this position, measured in DMF, for anion radicals II on passing from DMF to water. In the II series, the changes in the HFS constants as a function of the medium for the same ion radical are interrelated (Fig. 4). This is evidence that the effect of the medium on the anion radicals is not restricted only by the "reaction center" (i.e., the solvation center) but is distributed over the entire π-electron system. By comparing the magnitudes of the HFS constants due to the protons of the benzene [10] and furan rings, respectively, for the anion radicals of nitrobenzene and nitrofuran, one may note that the changes in these values on passing from DMF to water are greater in the case of nitrofuran. This confirms our previous conclusion, drawn on the basis of the character of the PMR spectra [14], that the π-electron system of the furan ring is more mobile than the π-electron system of benzene. The changes in the HFS constants (redistribution of the density of the unpaired electron) for various anion radicals II on passing from DMF to water are inversely proportional to the HFS values measured in DMF (Fig. 3); i.e., the mobility of the unpaired electron in the π system increases as the electrophilicity of substituent X increases. Interaction of anion radicals II with water molecules fixes the π-electron system and makes it less susceptible to the effect of substituent X than is the case with DMF The slope of the curves that represent the changes in the HFS constants with the nature of the substituent in DMF and water (Fig. 5) attests to this. The changes in the HFS constants as a function of the nature of substituent X in DMF proved to be greater by a factor of 1.2 than in water.

The decrease in the effect of substituent X on the π-electron system of anion radicals II on passing from DMF to water and the character of the change in the HFS constants during this transition (which is similar to the character of the changes in these values as the cation radii decrease) are evidence that anion radicals II are more strongly solvated by water molecules than by DMF molecules.

The mechanism of the interaction of the medium with anion radicals II, which determines the redistribution of the unpaired electrons in these particles, does not change basically on passing from DMF to water (Fig. 4). The dynamics of the interaction of the anion radicals with the solvent molecules can be represented mathematically by an equation of the change in the $a_{N,5}$ constants, which are quite accurately

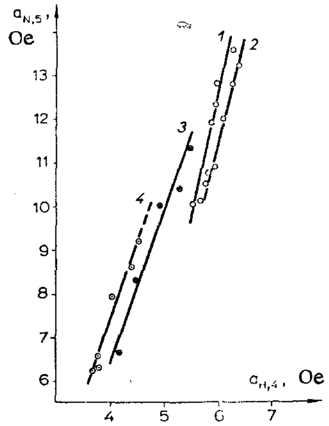

Fig. 4. Interrelationship between the $a_{N,5}$ and $a_{N,4}$ HFS constants during a gradual change in the water concentration in a DMF–water medium: 1) IIb; 2) IIa; 3) IId; 4) IIe.

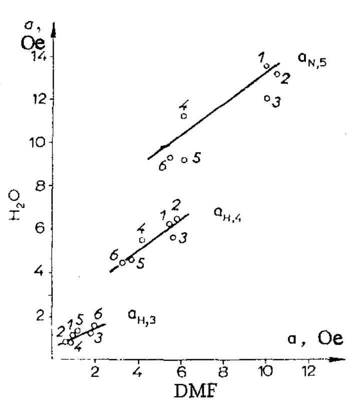

Fig. 5. Interrelationship between the HFS constants of anion radicals in DMF and water: 1) IIb; 2) IIa; 3) IIc; 4) IId; 5) IIe; 6) IIf.

measured experimentally. In conformity with the concepts in [15], we assume that free anion radical II in DMF and H_2O forms the relatively stable solvates $(II)_{DMF}$ and $(II)_{H_2O}$ with molecules of each of the solvents and that the solvated complexes are in equilibrium in the mixed media:

$$(II)_{DMF} + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} (II)_{H_2O} + DMF \tag{2}$$

If resolvation in a mixed medium were accomplished slowly, overlapping of the ESR spectra of two forms – one corresponding to anion radicals II solvated by water molecules and the second corresponding to II solvated by DMF molecules – should be observed [16]. However, this sort of additional splitting of the ESR spectra is not observed for anion radicals II. This is evidence that the lifetime (τ) of the individual solvates is much less than the difference $a_{H_2O} - a_{DMF}$ expressed in reciprocal frequency units, i.e., $\tau \ll 10^{-7}$ sec. In this case, in conformity with [14], the observed $a_{N,5}$ constant in a mixed medium can be expressed by Eq. (3):

$$a = 1/2(a_{DMF} + a_{H_2O}) + 1/2[(K\alpha - 1)(K\alpha + 1)^{-1}](a_{H_2O} - a_{DMF}), \tag{3}$$

where a_{DMF} and a_{H_2O} are the $a_{N,5}$ constants in pure DMF and in pure water, respectively, $\alpha = C_{H_2O}/C_{DMF}$ is the ratio of the molar concentrations of the solution components, and $K = k_1/k_2$ is the solvation equilibrium constant.

The experimentally found $a_{N,5}$ values (Fig. 3) lie satisfactorily on the calculated [from Eq. (3)] curves that reflect the dependence of the $a_{N,5}$ HFS constants on the molar concentration of water in the mixed medium. Side phenomena such as the instability of the anion radicals and the admixture of water in the starting DMF samples introduce a certain inaccuracy into the HFS constants. The K values for anion radicals IIa, IIb, and IIe prove to be 1.86, 1.80, and 1.5, respectively, from which it follows that the stability of the hydrates increases somewhat as the electron-donor properties of substituent X increase.

It follows from the present investigation that the previously [1,6] calculated π-electron structure of the 5-nitrofuran system to a first approximation qualitatively reflects the true distribution of the π electrons, since the solvation effects change symbatically with the effect of substituent X on the distribution of the π-electron density in various media (pure water, pure DMF, and mixed water–DMF media). However, as a consequence of specific solvation and the formation of ion pairs of anion radicals with cations, there is a certain redistribution of the π-electron density, and this should be taken into account in high-accuracy quantum-chemical calculations of the systems.

EXPERIMENTAL

The anion radicals of the investigated compounds were obtained by ECG on the surface of a mercury drop in a microcell installed in the H_{011} cylindrical resonator of an ESR spectrometer [17]. For this, solutions of the indicated substances were prepared in a solvent (DMF, water, water–DMF) in a concentration of 10^{-3} M containing 10^{-1} M of an indifferent salt [NaI, Ki, $(C_2H_5)_4NI$, $(C_2H_5)_4NBr$, $(C_2H_5)_4NCl$]. The electrochemical generation of the anion radicals was accomplished at the plateau potentials of the limiting currents of the first polarographic wave. The ESR spectra of the anion radicals were recorded with an RÉ-1301 spectrometer with a resolving power of about 0.4 Oe. The magnetic-field scanning was calibrated from the ESR spectrum of nitrobenzene anion radicals [18].

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