ESR STUDY OF ANION RADICALS PRODUCED IN CATHODIC REDUCTION OF 2-FURFURAL DERIVATIVES*

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Furfural and its derivatives are reduced reversibly to the corresponding anion radicals during polarography in dimethylformamide. These radicals have been studied by ESR, and analysis of their spectra has been carried out. The calculated splitting constants and half-wave potentials (INDO method) agree well with the experiment. The maximum spin density of the unpaired electron has been found for the aldehydic proton of the furfural anion ($a_H = 1.01$ mT), the values for the remaining protons of furane ring being smaller ($a_H^3 = 0.115$ mT, $a_H^4 = 0.49$ mT, and $a_H^5 = 0.64$ mT). Introduction of nitro group in 5 position of furfural results in a marked shift of spin density to the nitrogen atom ($a_N = 0.533$ mT) and decrease of density at the aldehydic proton ($a_H = 0.334$ mT). Changes of half-wave potentials of the individual furfural derivatives correlate well with changes in the respective Hammett constants of the substituents.

So far polarographic reduction of furfural and its derivatives has been studied predominantly in protolytic systems[1-4] where the life of the radicals formed by one-electron reduction is very short due to possibility of their reactions with solvent. There are less communications dealing with nonprotolytic systems[5-7] where formation of anion radicals is presumed on the basis of analysis of polarographic data. However, identification of such radicals and analysis of their ESR spectra have been carried out only in the cases of some nitro derivatives of furane[7,8] which are characterized by relatively high stability.

At present furane derivatives are submitted to intensive investigation[9]. In this context their polarographic studies were carried out also in dimethylformamide[5,6]. Course of the reduction was followed by ESR and confirmed one-electron reduction step of formation of anion radicals. With respect to relatively complex structure of the compounds studied so far, the obtained spectra are very complicated, and their unambiguous analysis as well as determination of the unpaired electron distribution in the formed radicals were impossible. Therefore, the present study deals with ESR spectra of the following relatively simple furane derivatives:

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* The work is dedicated to our late friend Dr S. Tichý.
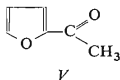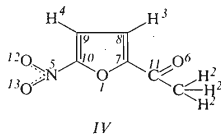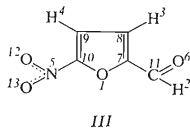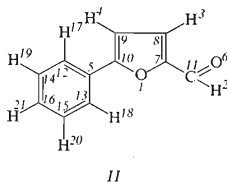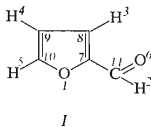
In spite of limited stability of the obtained radicals, especially in the case of the substrates *I* and *II*, we succeeded in obtaining their ESR spectra and carried out simulation of these spectra with the use of a computer. Assignement of the splitting constants and redistribution of spin densities of the unpaired electron are discussed on the basis of calculation by the INDO method.

EXPERIMENTAL

The measurements were carried out in absence of air and moisture under inert atmosphere of argon at 20°C. As the basic electrolyte we used 0.1 M-$[(n\text{-}C_4H_9)_4N]ClO_4$ in dimethylformamide. The solvent was purified according to ref.[10], tetrabutylamonium perchlorate was prepared from the respective hydroxide (BDA) by neutralization with $HClO_4$, whereafter it was dried in vacuum at 60°C at 10 Pa 5 h. The aldehyde *I* was commercial product (Merck) and was purified according to ref.[11], the compounds *II*, *III*, *IV* and *V* were prepared according to refs[12,11,13,14], respectively. The polarographic vessel and the electrolysis ESR cell were connected conductively with 4M-LiCl, Hg_2Cl_2/Hg reference electrode with the help of a bridge filled with the basic electrolyte separated by carbon closures. The polarograph OH 102 was used in three-electrode connexion, and the reversibility was tested by the Kalousek commutator with the pulse frequency within 1.5 to 25 Hz. Course of the cathodic reduction was followed by means of a Varian E-III ESR spectrometer equipped with a computer Varian Spectra System 100. The flat cell type Varian E-256 contained mercury or platinum cathode. During spectral measurements the cathode was polarized by means of a potentiostat OH 404/A by about 300 mV higher than the respective half-wave potential. Simulation of spectra was carried out with computer of the spectrometer, and the INDO calculations were carried out with a Computer Siemens 4004/150.

RESULTS AND DISCUSSION

Polarographic measurements. Survey of half-wave potentials of the investigated substrates, S values of their polarographic curves $(S = i_{comm}/i_d)$ and their logarithmic analyses are given in Table I. Starting from the non-substituted aldehyde I, change of half-wave potential accompanying its substitution corresponds to change of the Hammett substituent constants $(E_{1/2}$ is shifted to negative values (CH_3) or positive values $(Ph, NO_2))$. Experiments with the Kalousek commutator indicate a considerable degree of reversibility, and logarithmic analysis of the curves indicates the one--electron reduction step. Fig. 1 gives the typical course of *1*) depolarizer curve without application of the commutator, *2*) the depolarizer curve with applied commutator, *3*) curve of the basic electrolyte with applied commutator for the case of furfural.

TABLE I

Survey of Half-Wave Potentials, S-Values, and Logarithmic Analyses of Polarographic Curves of Substrates I to V

Substrate	$E_{1/2}$, V[a]	$S = i_{comm}/i_d$	$(E_{1/2} - E)/\log \dfrac{i}{i_d - i}$, mV
I	-1.81	1.19	80
II	-1.604	1.17	75
III	-0.59	1.37	67.5
	-1.315	1.64	88
IV	-0.665	2.05	64
	-1.375	1.58	77
V	-1.96	1.0	79

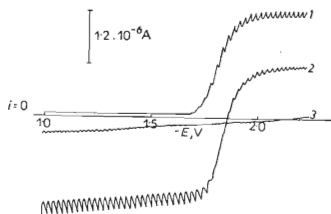[a] Against 4M-LiCl, Hg_2Cl_2/Hg reference electrode.

Fig. 1

Polarographic Curve of Furfural Obtained with Application of the Kalousek Commutator

1 The depolarizer curve without commutator; *2* the depolarizer curve with commutator; *3* the basic electrolyte curve with commutator.

The found reversibility of reactions (with the use of the Kalousek commutator) indicates adequate life-time of the formed radicals. This fact represents a good initial premise for study of the reduction products by ESR method.

ESR *Studies.* The experimental and the simulated spectra of the anion radicals *I* to *IV* are given in Figs 2 and 3, those of the formed secondary products are presented in Fig. 4. The spectra were obtained after 15 min potentiostatic polarization. Under the same initial conditions the highest concentration of the anion radical was obtained in the case of the derivative *III* ($>10^{-5}$M), gradually smaller concentrations were

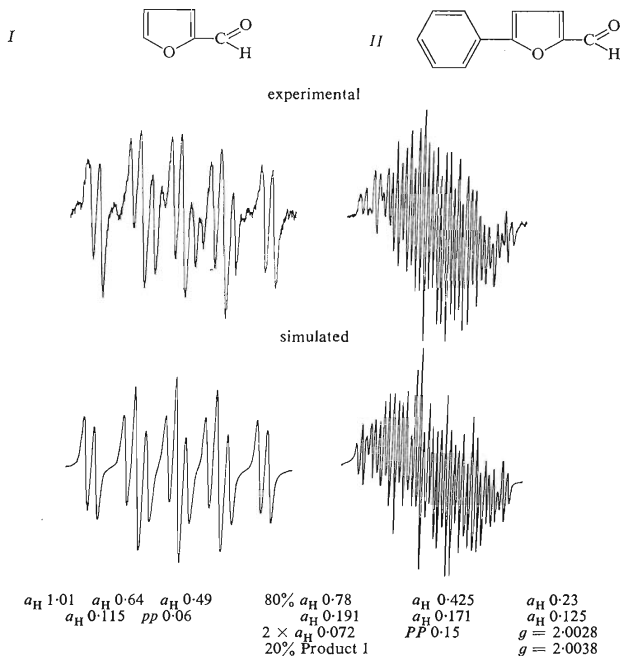| a_H 1·01 a_H 0·64 a_H 0·49 | 80% a_H 0·78 | a_H 0·425 | a_H 0·23 |
a_H 0·115 *pp* 0·06	a_H 0·191	a_H 0·171	a_H 0·125
	2 × a_H 0·072	*PP* 0·15	g = 2·0028
	20% Product 1		g = 2·0038

Fig. 2

Experimental and Simulated ESR Spectra Obtained in Cathodic Reduction of Furfural and 5-Phenylfurfural (a_H, pp and g mean the splitting constants, the peak-to-peak widths of the simulated spectra given in mT, and the g-factors, respectively)

obtained with the derivatives IV ($\sim 10^{-5}$M), II ($\sim 5 \cdot 10^{-6}$M), I ($\sim 10^{-6}$M) and V ($< 10^{-6}$M). If the magnitude of concentration is taken as a measure of stability of the generated radicals, then these values correlate suitably with the values of half-wave potential. The most stable radical has the most positive half-wave potential and the highest concentration ($E_{1/2} = -0.59$ V; $c_{III} > 10^{-5}$M), the reverse being true of the least stable one ($E_{1/2} = -1.96$ V and $c_{II} < 10^{-6}$M).

a_N 0.533 a_H 0.334 a_H 0.21
a_H 0.075 pp 0.03

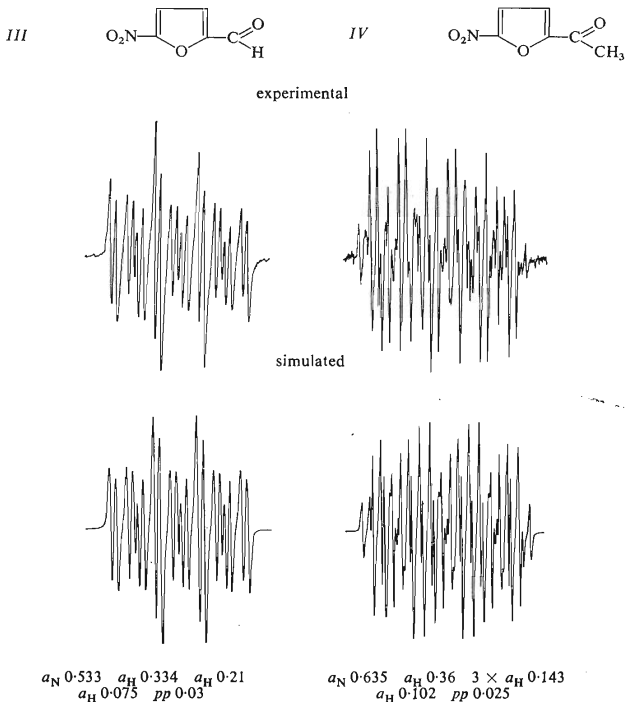a_N 0.635 a_H 0.36 $3 \times a_H$ 0.143
a_H 0.102 pp 0.025

FIG. 3

Experimental and Simulated Spectra Obtained in Cathodic Reduction of 5-Nitrofurfural and 2-Acetyl-5-nitrofurane (a_N and a_H are the splitting constants, pp are the peak-to-peak widths of the simulated spectra given in mT)

As a rule, in the first phases of the electrolysis (up to 15 min), especially with the derivatives *I* and *II*, we obtained pure ESR spectra of the anion radicals of the original substrates. In the further course of the electrolysis these spectra were overlapped by those of new radical products which were sometimes so marked that it was impossible to measure the individual spectrum of the original substrate. *E.g.* the differences between the experimental and the simulated spectra of the aldehyde *II* in Fig. 2 are due to that a new type of radical (product *1*) gradually appears. The given spectrum was, therefore, simulated as a sum of two spectra of radicals the parameters and relative population of which are given in the figure. The pure spectrum of the product *1* appeared in the later phases of the electrolysis (after about 30 min) and is given in Fig. 4. The product formed could not be identified unambiguously. With respect to the number of nuclei interacting with the unpaired electron it is obvious that the product 1 could consist of at least two molecules of the original aldehyde. Equivalence of the pairs of the splitting constants indicates symmetrical structure of the radical.

Fig. 4 gives the spectrum of the radical observed in reduction of acetylfurane. Analysis and assignement of this spectrum are un ambiguous and are discussed below. We

Product 1
experimental

simulated

Product 2
experimental

2 mT

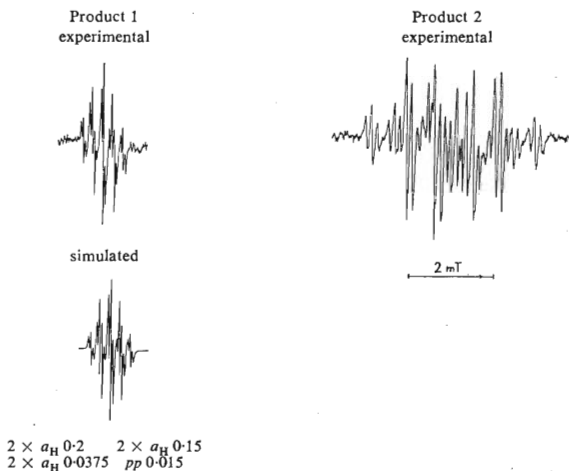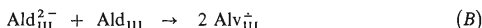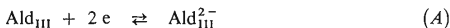$2 \times a_H$ 0·2 $2 \times a_H$ 0·15
$2 \times a_H$ 0·0375 pp 0·015

Fig. 4

Experimental and Simulated Spectra (product **1**) Obtained in Cathodic Reduction of 5-Phenyl-furfural and Experimental Spectrum (product **2**) Observed in Cathodic Reduction of 2-Acetylfura-ne

submitted to ESR studies also 5-bromo-2-furfural and 5-methyl-2-furfural. In spite of variation of experimental conditions (use of platinum and mercury electrodes at various concentrations, various polarization potentials and solvents) we failed in obtaining ESR spectra with good resolution.

In case of 5-nitrofurfural the ESR technique was used for study of the reduction product of the second polarographic wave, too. Increasing of the polarization voltage from the plateau of the first to the second polarographic wave led to no observable new radical type in the ESR spectrum, only a marked increase of concentration of the anion radical from the one-electron reduction of the first wave was observed. Formation of a dianion by two-electron reduction could theoretically make itself felt by a new type of spectrum in the case of triplet state or by disappearance of spectrum in the case of the singlet state of the dianion. None of these possibilities was observed, only concentration increase of the product of one-electron reduction was noticed. This phenomenon can be explained as it follows: The two-electron reduction results in formation of the dianion of the aldehyde III (Ald_{III}) at the surface of the electrode according to Eq. (A).

$$Ald_{III} + 2 e \rightleftarrows Ald_{III}^{2-} \qquad (A)$$

$$Ald_{III}^{2-} + Ald_{III} \rightarrow 2 Alv_{III}^{\cdot -} \qquad (B)$$

However, this dianion represents a very strong reduction agent and, therefore, reduces neutral molecules of the aldehyde Ald_{III} in solution to the respective anion $Ald_{III}^{\cdot -}$. This subsequent reaction (B) has the result that in the two-electron reduction the concentration of the anion radical (which is the usual product of one-electron reduction) increases.

Simulation of spectra. Before we start with assignement of the splitting constants using the INDO calculations, let us mention the information obtained from simulation of spectra which elucidates some problems of identification of radicals and their structural arrangement.

Besides the abovementioned difficulties due to formation of secondary products, there appeared another problem of complication of spectra, especially with the substrate IV, which is (according to our considerations) due to isomers of the radical. Detailed analysis of assymetry of the fine structure of the experimental spectrum in Fig. 3 indicates that the spectrum represents a sum of spectra of two radicals with very related splitting constants and slight difference in their g-factors. The two radical isomers could correspond to the basic structure of the substrate IV with two orientations of acetyl group in the plane of the furane ring (rotation by 180°C). The simulation presents satisfactory average values of the splitting constants. Attempts at simulation of sum of the two spectra were very difficult and gave no satisfactory result, as none of the pure isomer spectrum is known.

So far no suitable interpretation was found for the spectrum obtained in reduction of acetylfurane (Fig. 4). Similar values of splitting constants would be expected for acetylfurane as those found for furfural $\left(1xa_{\mathrm{H}} = 0{\cdot}115 \text{ mT}, 1xa_{\mathrm{H}} = 0{\cdot}49 \text{ mT}, 1xa_{\mathrm{H}} = 0{\cdot}64 \text{ mT and } 3xa_{\mathrm{H}} = 1{\cdot}01 \text{ mT}\right)$. From analysis of the outside part of the spectrum it is obvious that its basic component is a triplet formed by interaction of two approximately equivalent protons with unpaired electron $\left(2xa_{\mathrm{H}} = 0{\cdot}138 \text{ mT}\right)$. This triplet is split to doublet with $a_{\mathrm{H}} = 0{\cdot}538 \text{ mT}$. These constants could be assigned to the positions 3, 4, 5 $\left(a_{\mathrm{H}}^3 = 0{\cdot}138 \text{ mT}, a_{\mathrm{H}}^4 = 0{\cdot}138 \text{ mT and } a_{\mathrm{H}}^5 = 0{\cdot}538 \text{ mT}\right)$. The constants a_{H}^3 and a_{H}^5 seem to have the approximately expected values, however, the value found for the constant a_{H}^4 $(0{\cdot}138 \text{ mT})$ is very small, if it is compared with the corresponding constant of the substrate I $\left(a_{\mathrm{H}}^4 = 0{\cdot}49 \text{ mT}\right)$. The simulation could not describe centre of the spectrum within $3{\cdot}1 \text{ mT}$ where it remains to assign the interaction of the methyl group. High intensity of the central part of the spectrum could correspond to the

TABLE II

Spin Densities of Unpaired Electron at Individual Atoms of Anion Radicals of Structures I to IV (calculated by INDO method)

Atom	Structure			
	I	II	III	IV
1	0·0090	0·0086	0·0072	0·0085
2	0·0196	0·0150	0·0064	0·0031
3	0·0027	0·0026	0·0018	0·0021
4	0·0088	0·0084	0·0050	0·0076
5	0·0115	0·0472	0·0221	0·0238
6	0·0875	0·0823	0·0596	0·0482
7	0·0402	0·0384	0·0399	0·0357
8	0·0397	0·0395	0·0306	0·0389
9	0·0425	0·0421	0·0398	0·0411
10	0·0355	0·0352	0·0328	0·0305
11	0·0405	0·0827	0·0398	0·0483
12	0·0410	0·0410	0·0912	0·0976
13		0·0402	0·0912	0·0976
14		0·0259		
15		0·0257		
16		0·0521		
17		0·0037		
18		0·0033		
19		0·0017		
20		0·0015		
21		0·0046		

character of quartet which would be expected for interaction of the methyl protons with the unpaired electron, but complexity of this central part of spectrum is far greater as compared with that which would correspond to combination of the splitting constants of the structure *V*. An alternative explanation of this complexity could be in the existence of isomers of acetylfurane (different orientation of methyl group in the plane of the furane ring) or formation of anion radicals of secondary reduction products.

Assignement of splitting constants and INDO *calculations.* The anion radical of furfural has not yet been described by ESR spectroscopy, therefore we assigned the obtained splitting constants on the basis of INDO calculations. All the systems were considered planar with CHO (or $COCH_3$) group oriented in the way enabling interaction between the carbonyl oxygen and 3-hydrogen by which the system is stabilized. The calculated spin densities for individual atoms of the structures *I* to *IV* are given in Table II, the respective splitting constants being presented in Table III.

Results of the calculations of splitting constants correlate very well with experimental values, the trend of changes of the splitting constants of the individual structures being correctly reproduced. The calculated splitting constant also agree with the present knowledge about anion radicals which usually predicts the maximum spin density in the vicinity of aldehydic group or nitro group. In accordance therewith the greatest splitting constants were calculated for the aldehydic proton and for nitrogen nucleus of nitro group. When going from the structure *I* to *II*, 5-hydrogen is substituted by phenyl group. This substitution resulted in decrease of the splitting constants of the proton of furane ring due to pull-effect of phenyl group, and no splitting constant of 5-position is found in the spectrum, which supports the assignement of this constant to the given position. Splitting constants of the phenyl protons are also assigned in accordance with the currently known redistribution of the unpaired electron in aromatic compounds; the greatest splitting constant (0·23 mT) is assigned to *para* position, the two smaller ones are assigned to *ortho* positions (0·171 mT and 0·191 mT), and the smallest one (0·072 mT) is assigned to *meta* positions. The non equivalence of the *ortho* protons indicates hindered rotation of phenyl group with respect to the plane of furane nucleus.

Redistribution of spin densities of the unpaired electron on the furfural nucleus is noteworthy. In some aspects this aldehyde resembles the aromatic ones *e.g.* benzaldehyde the anion radical of which has the highest spin densities of the unpaired electron on the protons at *para* and *ortho* positions, the smallest density being at *meta* protons. In this context it is interesting to mention that analogous values of spin densities corresponding to *para* and *ortho* positions of benzaldehyde were found at 5 and 4 positions of furfural, and that analogy with *meta* position of benzaldehyde is exhibited by 3-position of furfural.

Table III gives the values of Koopman ionization potentials I_p calculated by INDO

method. For the sake of clearer comparison of the calculated I_p values (in eV) with the experimental values of half wave potentials $E_{1/2}$ (in V), the former are correlated with the latter by equation: $I_p = a + bE^c_{1/2}$, where $a = 0.10110$, $b = 0.03562$, $E^c_{1/2}$ are the correlated values of half-wave potentials, the correlation coefficient being 0.99874. Agreement between the calculation and experiment is relatively very good. The deviations could be due to solvent effects, too, which were not considered in the calculations.

TABLE III
Experimental and Calculated Values of Splitting Constants a_H and a_N of Anion Radicals of the Investigated Substrates, Their Experimental Half-Wave Potentials $E_{1/2}$, and the Koopmans Ionization Potentials I_p Calculated by INDO Method ($E^c_{1/2}$ are the correlated values using the equation $I_p = a + b\,E^c_{1/2}$, where $a = 0.10110$, $b = 0.03562$)
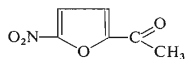
Structure	$E_{1/2}$, V $E^c_{1/2}$, V I, eV	Splitting constants, mT							
		a_N	a_H^2	a_H^3	a_H^4	a_H^5	$a_H^{0,0'}$	$a_H^{m,m'}$	a_H^p
I	exp. −1.81	—	1.01	0.115	0.49	0.64			
	calc. −1.75	—	1.06	0.145	0.475	0.621			
	0.0388								
II	exp. −1.64	—	0.78	0.125	0.425	—	0.171	0.072	0.23
							0.191	0.072	
	calc. −1.68	—	0.812	0.138	0.456	—	0.185	0.085	0.249
							0.194	0.087	
	0.0412								
III	exp. −0.59	0.533	0.334	0.075	0.21				
	calc. −0.61	0.838	0.348	0.098	0.271				
	0.0786								
IV	exp. −0.665	0.635	0.143	0.102	0.36				
	calc. −0.63	0.904	0.165	0.115	0.411				
	0.0795								
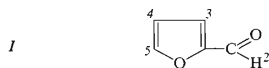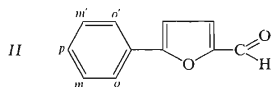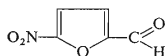
I

II

III

IV

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