

Reduction of 1-nitro-1-(5-nitro-2-furyl)-2-(substituted phenyl)-ethylenes on mercury electrode

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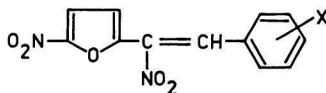
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1-Nitro-1-(5-nitro-2-furyl)-2-(substituted phenyl)ethylenes in dichloromethane solutions are reduced on the dropping mercury electrode in two or three one-electron steps ($E_{1/2}^1 \doteq -0.6$ V, $E_{1/2}^2 \doteq -1.25$ V, and $E_{1/2}^3 \doteq -1.4$ V against 1 M-LiCl, Hg₂Cl₂/Hg electrode). In the reduction, instable radicals with lifetime of a few seconds and with centre of the unpaired electron on the nitro group (e.s.r. investigation) are formed. $E_{1/2}$ and splitting constants of the nitrogen nucleus a_N correlate satisfactorily with the Hammett constants σ_x of substituents on the benzene ring ($E_{1/2}^1 = -0.704 + 0.347 \sigma_{o,p}$ and $a_N^1 = 0.678 - 0.0339 \sigma_{o,p}$).

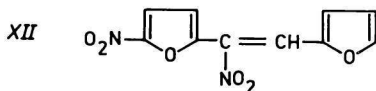
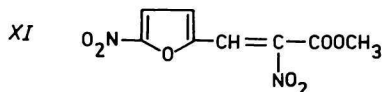
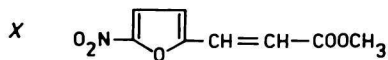
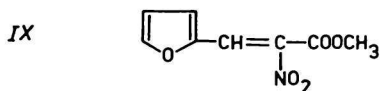
1-нитро-1-(5-нитро-2-фурил)-2-(замещенные-фенил)этилены восстанавливаются на капельном ртутном электроде в дихлорметане в двух или трех одноэлектронных волнах ($E_{1/2}^1 \doteq -0,6$ в, $E_{1/2}^2 \doteq -1,25$ в, $E_{1/2}^3 \doteq -1,4$ в по сравнению с 1 M-LiCl на каломельном электроде). При этом возникают нестабильные радикалы с периодом жизни несколько секунд и с центром неспаренного электрона на нитрогруппе (ЭПР). $E_{1/2}$ и константы расщепления азотного ядра a_N хорошо коррелируют с константами Гамметта σ_x заместителей в бензольном кольце ($E_{1/2}^1 = -0,704 + 0,347 \sigma_{o,n}$ и $a_N^1 = 0,678 - 0,0339 \sigma_{o,n}$).

The subsequent substances are the object of interest in microbiology and pharmacology and for this reason, the polarographic reduction was comprised in the scope of their complex study. The following derivatives were investigated



where X stands for: *I* —H; *II* —4-CH₃; *III* —4-Cl; *IV* —2-F; *V* —4-HNCOOCH₃; *VI* —4-N(CH₃)₂; *VII* —2-NO₂; *VIII* —4-NO₂.

Further investigated structures are



Experimental

A polarograph OH 102 Radelkis in three-electrode connection and with compensation of potential drop iR was used. The potentiostatic reductions in the cavity of EPR spectrometer Varian E-3 were accomplished by means of a potentiostat UNIT OH 404/A Radelkis. The obtained spectra were simulated with a computer Varian Spectro System 100. Dichloromethane was purified as described in paper [1]. Tetrabutylammonium perchlorate (TBAP) was prepared by neutralizing tetrabutylammonium hydroxide (BDH-Chemicals Ltd.) with perchloric acid (Merck). The above ethylene derivatives were prepared by condensation of 5-nitrofuryl nitromethane with the corresponding aldehydes in the medium of concentrated acetic acid [2].

Results and discussion

The investigated trisubstituted ethylenes are very reactive with respect to solvents, such as dimethylformamide, pyridine, and dimethyl sulfoxide with which they form intensely coloured products. For instance, substance *III* immediately forms with dimethylformamide a purple-red product with $\lambda_{\max} = 570$ nm. Anhydrous dichloromethane is an inert solvent convenient for electrochemical investigations. It was used for preparing 0.1 M-solution of TBAP. Substances *I*—*VIII* dissolved in this solution were reduced on the dropping mercury electrode (DME)

Table 1

Half-wave potentials of the first ($E_{1/2}^1$), second ($E_{1/2}^2$), and third ($E_{1/2}^3$) polarographic wave of substances I—XII measured against 1 M-LiCl, Hg₂Cl₂/Hg electrode and the corresponding values of the Hammett constants of substituents $\sigma_{o,p}$

Substrate	$E_{1/2}^1/V$	$E_{1/2}^2/V$	$E_{1/2}^3/V$	$\sigma_{o,p}$
I	-0.70	-1.32		0.0
II	-0.76	-1.34		-0.17
III	-0.61	-1.23		+0.23
IV	-0.63	-1.22		+0.24
V	-0.72	-1.32		-0.01
VI	-0.88	-1.37		-1.05
VII	-0.44	-1.30	-1.45	+0.80
VIII	-0.42	-1.20	-1.41	+0.78
IX	-0.79	-1.55		
X	-0.78	-1.18		
XI	-0.34	-1.14		
XII	-0.65	-1.20		

in two or three one-electron waves. Their half-wave potentials and Hammett constants of substituents are in Table 1. Substrates I—VIII (except VI) were subjected in the first reduction step to analysis with the Kalousek commutator at the frequency of 6.25 Hz. We obtained the switched-over curves which were typical of irreversible systems [3]. A small anodic current of switched-over curve was in most cases observed at higher switching frequencies. This phenomenon is due to a short lifetime of the primary product. On the other hand, the behaviour of substance VI in this analysis was reversible and the switched-over curve manifested a relatively high value of anodic current ($i_{\text{comm}}/i_d = 1.0$). Substances IX and X gave at the switching frequency of 6.25 Hz in the first reduction stage one-electron reversible waves, the ratio i_{comm}/i_d being 1.0 for substance IX and 1.2 for substance X. A smaller anodic current was observed in the reduction of substances XI and XII.

We also performed the cathodic reduction in the resonator cavity of EPR spectrometer. At potentials of the first as well as higher reduction steps, we observed a radical product corresponding to one-electron process similarly as described in preceding papers [4—6]. The experimental and simulated spectrum of the anion radical of substrate III which is also typical of substrates II, VI, and VII is represented in Fig. 1. A survey and assignment of the splitting constants found by simulation is given in Table 2. The assignment of constants ensued from preceding study of simpler furan derivatives [5, 6]. The centre of the unpaired electron is the nitro group of the furan ring in position 5 and the spin densities in the aromatic ring are negligibly small.

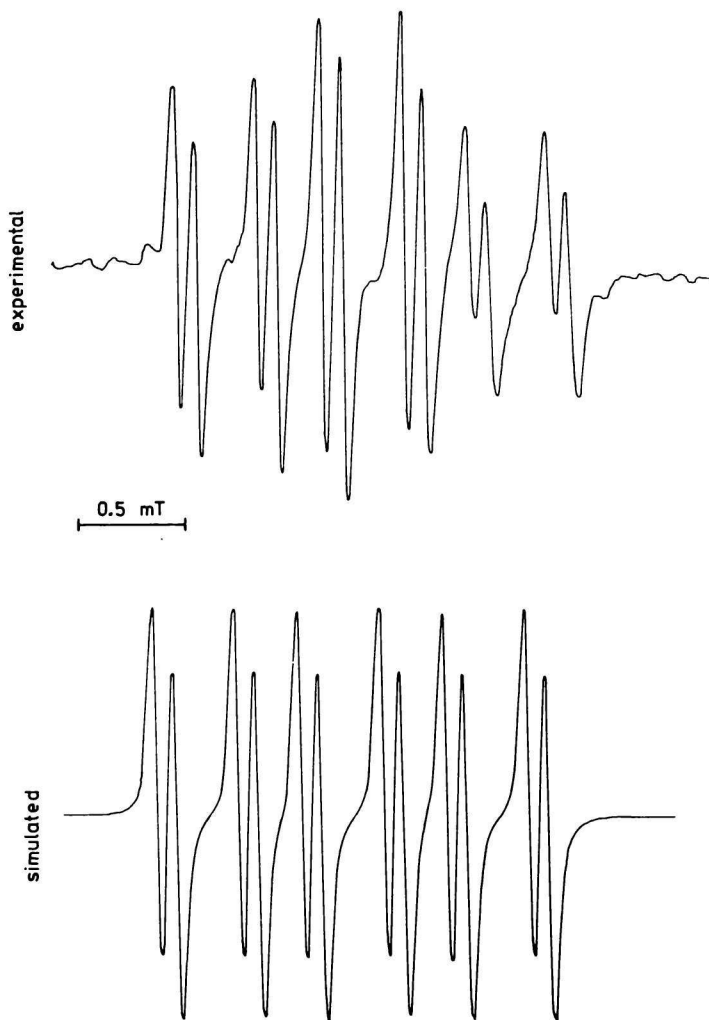


Fig. 1. Experimental and simulated e.s.r. spectrum of the anion radical formed in reduction of substance III.

The e.p.r. study is completed by the analysis of the anion radical of substrate X the experimental as well as simulated spectrum of which is in Fig. 2. In this case, the centre of the unpaired electron is also the nitro group in position 5 of the furan ring.

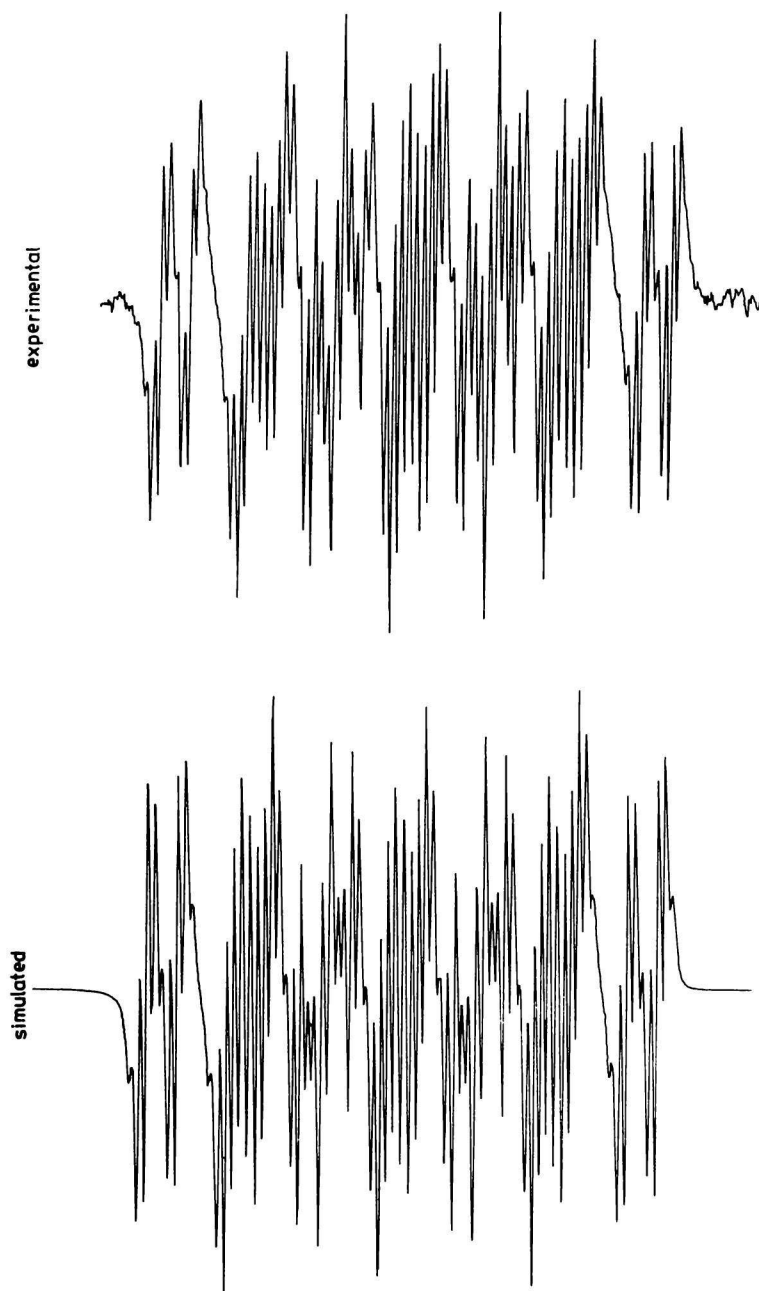
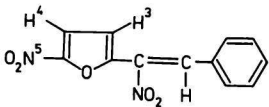
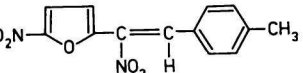
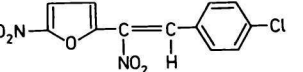
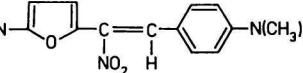
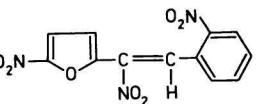
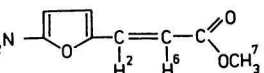
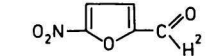
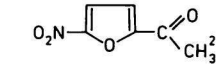


Fig.2. Experimental and simulated e.s.r. spectrum of the anion radical formed in reduction of substance X.

Table 2

Splitting constants of anion radicals of some investigated substances

Substrate	Splitting constants, mT					
	a_N^5	a_H^2	a_H^3	a_H^4	a_H^6	a_H^7
I 						
II 	0.694		0.10	0.388		
III 	0.665		0.09	0.375		
VI 	0.71		0.10	0.391		
VII 	0.65		0.10	0.369		
X 	0.706	0.43 (0.37)	0.14	0.37 (0.43)	0.034	0.034
XIII 	0.533	0.334	0.075	0.24		
XIV 	0.635	0.143	0.102	0.36		

On the basis of these electrochemical and spectroscopic measurements, the dependence of $E_{1/2}^1$ and a_N on the Hammett constants of substituents σ_x was evaluated. Linear correlations (Figs. 3 and 4) which may be expressed by the equations $E_{1/2}^1 = -0.704 + 0.347 \sigma_{o,p}$ and $a_N^5 = 0.678 - 0.0339 \sigma_{o,p}$ were established. Substance VI with the group 4-(CH₃)₂N— distinctly disobeys the correla-

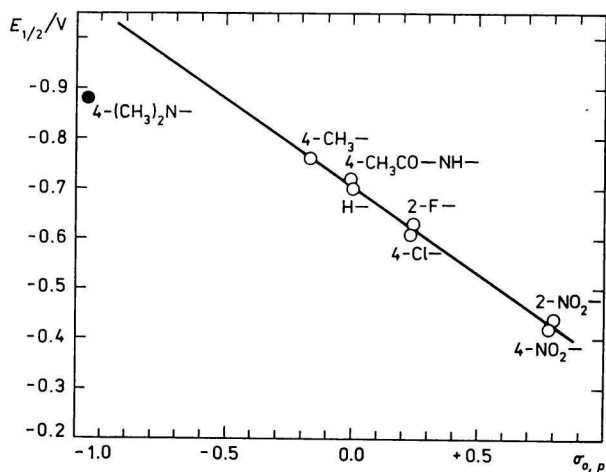


Fig. 3. Dependence of half-wave potentials of the first polarographic wave $E_{1/2}$ of substances I—VIII on values of the Hammett constants of substituents.

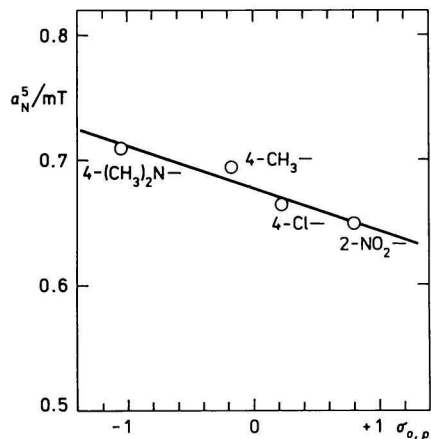


Fig. 4. Dependence of splitting constants a_N^s of nitrogen nucleus of the anion radicals of substances II, III, VI, and VII on values of the Hammett constants of substituents.

tion between $E_{1/2}$ and $\sigma_{o,p}$. Similarly, substance VI behaved differently in the analysis by means of the Kalousek commutator because a relatively great anodic current of the switched-over curve was observed. This fact may be explained by mesomery [7] which involves the formation of a quinone structure owing to interaction between an electron-donating ($-\text{N}(\text{CH}_3)_2$) and electron-withdrawing substituent ($-\text{NO}_2$).

For substances II, III, VI, and VII quoted in Table 2, the course of their cathodic reduction was investigated by the e.p.r. technique as described in

introductory part. After 5 min potentiostatic reduction, the spectra of radicals appeared. Their concentration was stationary for about 20 min and afterwards it started to decrease simultaneously with the limiting current, which was caused by a decrease in substrate. However, if the electrolysis was interrupted, the radicals disappeared almost instantaneously. This fact reveals their rather low stability in the investigated system.

The experimental as well as simulated spectra of substance *III* are represented in Fig. 1. Besides higher medium bands of the experimental spectrum which could be due *e.g.* to different line half-width, there are other bands in the experimental spectra which may correspond to impurities or consecutive products. The assignment of splitting constants was performed on the basis of preceding work [6] where some less complicated structures of this type (*XIII*, *XIV*) listed in Table 2 were investigated similarly as described above and to which splitting constants were assigned. The splitting constants of structure *XIV* are very near to the splitting constants corresponding to structures *II*, *III*, *VI*, and *VII*. It may be deduced from this fact that the major part of spin density of the unpaired electron is, in all cases, localized in an analogous skeleton, *i.e.* in the furan ring and its nitro group in position 5. In conformity with this fact, the fairly high splitting constant a_N^5 is to be assigned to the nitrogen nucleus in the furan ring in position 5. The second possible alternative involving the idea that the nitrogen on carbon in position 2 of the furan ring could be the centre of the unpaired electron is less presumable because an interaction with three protons at least (one of the vicinal carbon and two of the furan ring) should be expected in this case which, of course, was not observed in the spectrum.

The influence of substitution in the benzene ring on the character of spectra is also consistent with the above-mentioned assumption employed for assignment of splitting constants. If different substituents were used, no change in constitution of the spectra, *i.e.* in the number of interacting nuclei with unpaired electron was observed. This fact indicates that the investigated substituents are rather distant from the centre of the unpaired electron. This postulate is very well fulfilled by the assumption that the nitrogen atom in position 5 of the furan ring is the centre of the unpaired electron.

While the substituents did not exhibit influence on constitution and hyperfine structure of spectra, a relatively small but significant influence on splitting constants could be, however, observed. The splitting constant of the nitrogen nucleus a_N^5 and proton a_H^4 increases with electronegativity of the substituents in the benzene ring. The trend of this change is in good correlation with the Hammett constants of the substituents (Fig. 4).

Structure *VII* (Table 2) contains basic skeleton with three nitro groups, *i.e.* one nitro group is also in the benzene ring. The obtained data suggest that not even this group functions as a centre of the unpaired electron, because the number and

values of splitting constants remain analogous to the values found for structures *II*, *III*, and *VI*. The greatest decrease of splitting constants in the series of the investigated substituents indicates a rather high electron-withdrawing effect of the nitro group.

In order to complete the data concerning the distribution of spin density of the unpaired electron in this type of substances, an anion radical of substance *X* was generated (Table 2). Its experimental and simulated spectrum is represented in Fig. 2. The found values of splitting constants were similar to those attributed to structures *II*, *III*, *VI*, *VII*, and *XIV*. Their assignment was performed on the basis of the following reasoning. As structure *X* has only one nitrogen nucleus, the assignment of the splitting constant a_N is unambiguous. Then the interaction of three equivalent protons with the unpaired electron in the given structure can correspond only to the methyl group. A small value of this splitting constant ($a_H^7 = 0.034$ mT) indicates a considerable distance of the methyl group from the centre of the unpaired electron which is represented (according to the value $a_N^{\dot{z}} = 0.706$ mT) by the nitrogen atom. The splitting constants of four protons with the values 0.43, 0.37, 0.14, and 0.034 mT are to be assigned. On the basis of analogy with foregoing considerations, we assigned the first three ones to the protons in the furan ring, i.e. the lowest one (0.14 mT) to position 3 and the remaining two (0.43 and 0.37 mT) to positions 2 and 4.

Because of comparable values of the constants a_H^2 and a_H^4 , both alternatives of assignment as suggested in Table 2 must be taken into consideration. The last splitting constant (0.034 mT) was assigned to the proton denoted by index 6 in Table 2. The small value of this splitting constant is in good agreement with a relatively great distance of the corresponding proton from the centre of the unpaired electron on nitrogen.

Structure *I* escapes by its behaviour from the series of investigated structures *II*, *III*, *VI*, and *VII* because no radical product was observed after its reduction. The speciality of substance *I* consists in the fact that it has not any substituent on the benzene ring. The peculiarity of this structure could be explained by the reactivity of the nonsubstituted *para* position which renders possible consecutive reactions.

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