ELECTROCHEMICAL INVESTIGATION OF RADICAL-ANION REACTIONS OF 5-NITRO-2-FURFURYL DERIVATIVES

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In the studies on nucleophilic substitution of 5-nitro-2-furfuryl derivatives the function of nucleophilic agent was substituted by electrolysis. The electrochemical reduction of these substances and the follow-up reactions of the intermediates were studied by cyclic voltammetry, dc-polarography and ESR spectroscopy. The primary reduction step is the uptake of a single electron giving rise to the radical anion $R{-}CH_2{-}X^{\overset{\cdot}{-}}$ which spontaneously splits off the anion X^- and forms the neutral 5-nitro-2-furfuryl radical $R{-}CH_2^{\cdot}$. This radical may either dimerize to 1,2-bis(5-nitro-2-furyl)ethane or yield 5-nitro-2-methylfuran (*VI*) through abstraction of hydrogen from the solvent or from the supporting electrolyte or through the uptake of an electron and the following protonation. The mechanism found here confirms the validity of the formerly suggested radical-anion mechanism in the nucleophilic substitution of some 5-nitro-2-furfuryl derivatives.

The first step of many chemical reactions is the interaction of two molecular species associated with an electron transfer. An electrophilic substrate is initiated to further reactions by the capture of an electron from a nucleophile. This reaction type also includes the electron-transfer chain reaction in which the initiated substrate further reacts by a radical-anion mechanism[1-5]. For S_{RN} substitution the following general scheme holds:

$$R{-}X + Y^{(-)} \rightarrow R{-}X^{(\overset{\cdot}{-})} + Y^{\cdot}, \tag{1}$$

$$R{-}X^{(\overset{\cdot}{-})} \rightarrow R^{\cdot} + X^{(-)}, \tag{2}$$

$$R^{\cdot} + Y^{(-)} \rightarrow R{-}Y^{(\overset{\cdot}{-})}, \tag{3}$$

$$R{-}Y^{(\overset{\cdot}{-})} + R{-}X \rightarrow R{-}Y + R{-}X^{(\overset{\cdot}{-})}, \tag{4}$$

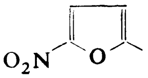
where R is aryl, heteraryl, or, alkyl.

The radical anion resulting from the electron transfer to the substrate (step (*1*)) is spontaneously split with the formation of the neutral radical R$^\bullet$ and the anion X$^-$, *e.g.* of a halogen (step (*2*)). In the third step the $S_{RN}1$ substitution takes place – the neutral radical is attacked by the nucleophile Y$^-$ under formation of a radical anion (step (*3*)) which passes over the electron to a further substrate molecule (step (*4*)). The reaction continues by the step (*2*). We assumed this mechanism to be operative also with reactions of 5-nitro-2-furfuryl bromide (*III*) and 5-nitro-2-furfuryl nitrate (*VIII*) with various nucleophiles[6–8]. In these processes, however, parallel reactions[6] also take place which lead to the formation of further products, the quantity of which is dependent on the nature of the nucleophilic reagent and on the reaction conditions[7].

The transfer of the electron onto the substrate may be also achieved by an electrochemical process. Moreover, such a procedure exhibits two more advantages: on the one hand it does not introduce a further substance into the reaction mixture, on the other hand one may arbitrarily and continuously choose a suitable working potential. Moreover, the existence of intermediates, or of final products may be often proved during the reaction, by an electrochemical method or in combination with ESR spectroscopy.

The aim of the present communication was an electrochemical verification of the formerly suggested radical-anion mechanism making use of the electrode as an electron donor instead of a nucleophilic reagent. In addition to electrochemical methods ESR spectroscopy was used for proving the existence of some intermediates and products of their follow-up reactions. Except for substances *I* and *V* which we applied as starting materials in the preceding papers[6,7], further 5-nitro-2-furfuryl derivatives *II*, *III*, *IV* were chosen for comparison the formerly studied compounds[9] *VI* and *VII* and the possible final products *VIII* and *IX* were subjected to investigation.

Ar =



I, Ar—CH$_2$—Br
II, Ar—CH$_2$—SO$_2$—C$_6$H$_5$
III, Ar—CH$_2$—SO$_2$—C$_6$H$_4$—CH$_3$-*p*
IV, Ar—CH$_2$—SO$_2$—CHCl$_2$
V, Ar—CH$_2$—ONO$_2$

VI, Ar—CH$_3$
VII, Ar—CHO
VIII, Ar—CH$_2$—CH$_2$—Ar
IX, Ar—CH=CH—Ar

EXPERIMENTAL

The above derivatives were prepared by the following methods. By nitrating furfuryl alcohol with acetyl nitrate 5-nitro-2-furfuryl nitrate (*V*) was obtained which yielded 5-nitro-2-furfuryl bromide[10] (*I*) by refluxing it with sodium bromide in acetone. The reaction of the bromide *V* with the corresponding sulphinates led to 5-nitro-2-furfuryl phenyl sulfone[11] (*II*), 5-nitro-2-furfuryl tolyl sulfone[12] (*III*), and 5-nitro-2-furfuryl dichloromethyl sulfone[13] (*IV*). 1,2-Bis(5-nitro-5-furyl)ethane (*VIII*) and 1,2-bis(5-nitro-2-furyl)ethylene (*IX*) were prepared according to[6].

Dimethylformamide was purified by azeotropic distillation with benzene and water at atmospheric pressure. Before use it was rectified under reduced pressure. 0·1M tetrabutylammonium hexafluorophosphate served as supporting electrolyte. The oxygen was removed from the solution by a stream of argon.

Polarographic and voltammetric measurements were carried out with a GWP 673 polarograph (Zentrum für wissenschaftlichen Gerätebau, Akademie der Wissenschaften der DDR, Berlin). An electronic memory, Scan Recorder 4101, produced by PAR was used for recording cyclic voltammograms at higher scan rates. The hanging mercury drop was a product of Metrohm.

The wave height was determined by comparing it with the height of the first reduction wave of 2-methyl-5-nitrofurane (*VI*) which is, according to[9], one-electronic.

The ESR spectra were measured with the Varian E-4 spectrometer. The electrolysis was performed within the spectrometer cavity, making use of the electrolytic cell of our construction[14,15].

RESULTS AND DISCUSSION

The potential of the first electron transfer of the studied compounds was determined by dc-polarography. The experimental half-wave potentials of these first cathodic waves are shown in Table I. The wave-height roughly corresponds to the transfer of a single electron, except for substances *V*, *VIII* and *IX*, which yield 2-electron waves.

Within the region of the above potentials radical-anions are evidently formed with all compounds studied here. Their formation is evidenced by the appearance of a cathodic-anodic couple of peaks in the cyclic voltammogram, corresponding to a reversible one-electron process at the potential of the first wave with *I*, *II* and *III*. The ratio of the height of the anodic to the cathodic peak increases significantly with increasing scan rate (rate of polarization): This points to a fast follow-up chemical reaction in which the primarily generated radical anion decays[16]. This follow-up reaction decreases the life-time of these radicals to such a degree that their

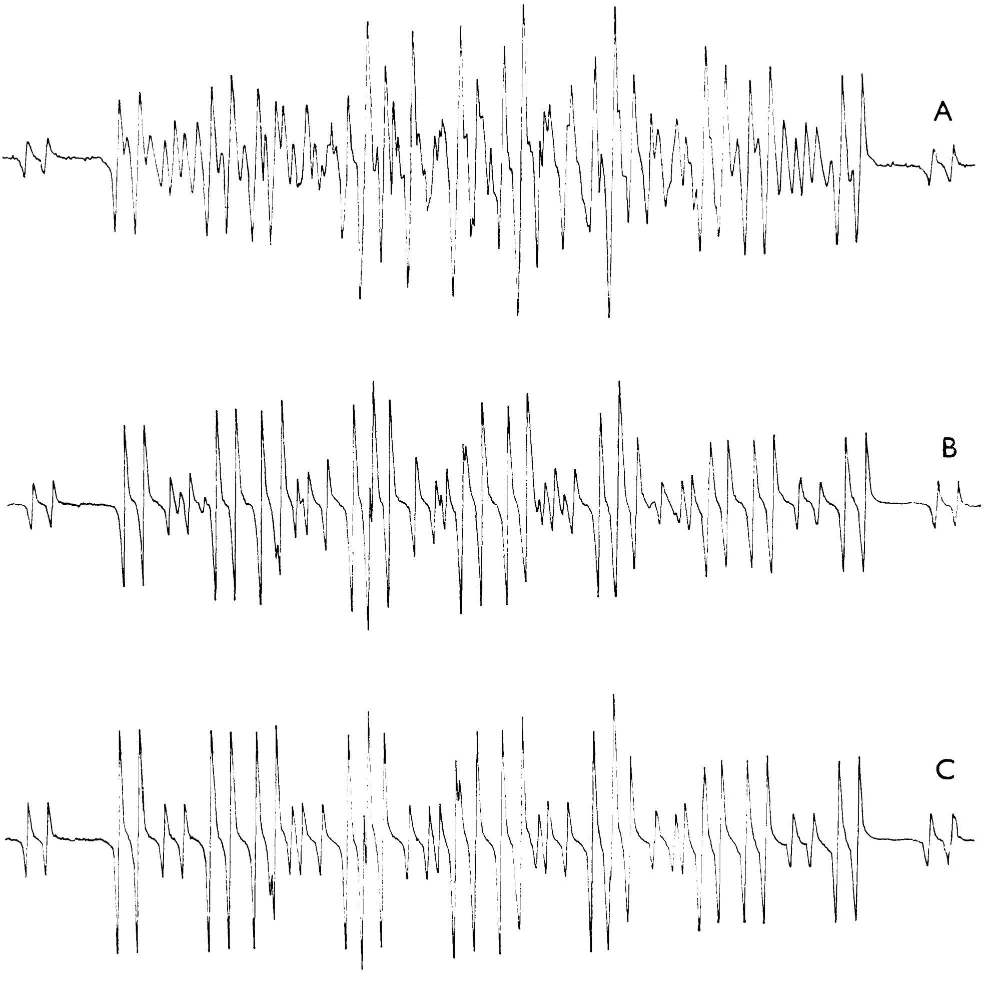
TABLE I

Half-wave potentials of substituted 2-methyl-5-nitrofurans

Substance $E_{1/2}$	(V *versus* S.C.E.)	Substance $E_{1/2}$	(V *versus* S.C.E.)
I	$-0{\cdot}22_5$	*VI*	$-1{\cdot}08_5$
II	$-0{\cdot}97_5$	*VII*	$-0{\cdot}74_0$
III	$-0{\cdot}96_5$	*VIII*	$-0{\cdot}65_5$
IV	$-0{\cdot}83_0$	*IX*	$-1{\cdot}10_5$
V	$-0{\cdot}70_0$		

existence could not be proved during the electrolysis by ESR spectroscopy and in case of *IV* and *V* even with cyclic voltammetry.

The first ESR signal appears only after increasing the generating potential to above $-1{\cdot}1$ V. With all substances investigated a spectrum of the same stable radical results at this potential (Fig. 1). The analysis of the spectrum revealed a splitting by a single nitrogen nucleus (splitting constant $a_{\mathrm{N}} = 1{\cdot}03$ mT), by three equivalent protons ($a_{\mathrm{H}}^{3} = 0{\cdot}39$ mT) and by two non-equivalent protons ($a_{\mathrm{H}}^{3} = 0{\cdot}084$ mT, $a_{\mathrm{H}}^{4} = 0{\cdot}58$ mT). These values are unambiguously characteristical for a 5-nitro-2-furfuryl radical anion since the splitting constants agree with the values published for this radical in the literature[9] and during electrolysis of the comparative substance *VI* an identical



spectrum was obtained (Fig. 2). The formation of this secondary radical can be explained by the following mechanism:

$$\text{Ar—CH}_2\text{—X} \xrightarrow{+e} (\text{Ar—CH}_2\text{—X})^{(\overset{\cdot}{-})}\,, \tag{5}$$

$$(\text{Ar—CH}_2\text{—X})^{(\overset{\cdot}{-})} \longrightarrow (\text{Ar—CH}_2)^{\cdot} + \text{X}^{(-)}\,, \tag{6}$$

$$(\text{Ar—CH}_2)^{\cdot} + \text{H Solv} \longrightarrow \text{Ar—CH}_3 + (\text{Solv})^{\cdot}\,, \tag{7}$$

$$(\text{Ar—CH}_2)^{\cdot} \xrightarrow{+e} (\text{Ar—CH}_2)^{(-)}\,, \tag{8}$$

$$(\text{Ar—CH}_2)^{-} \xrightarrow{+H^+} \text{Ar—CH}_3\,, \tag{9}$$

$$\text{Ar—CH}_3 \xrightarrow{+e} (\text{Ar—CH}_3)^{\dot{-}}\,. \tag{10}$$

The radical anion of the substituted 5-nitro-2-furfuryl derivative (substances *I*–*V*) primarily formed at the electrode (*cf.* Eq. (*5*)) spontaneously splits off the anion X^- under formation of a neutral radical (Eq. (*6*)) which either acquires a hydrogen atom by extracting it from the solvent molecule (Eq. (*7*)) or takes up a further electron and is then protonated (Eq. (*8*) and (*9*)). In the reaction path (*5*)–(*6*)–(*7*) one electron

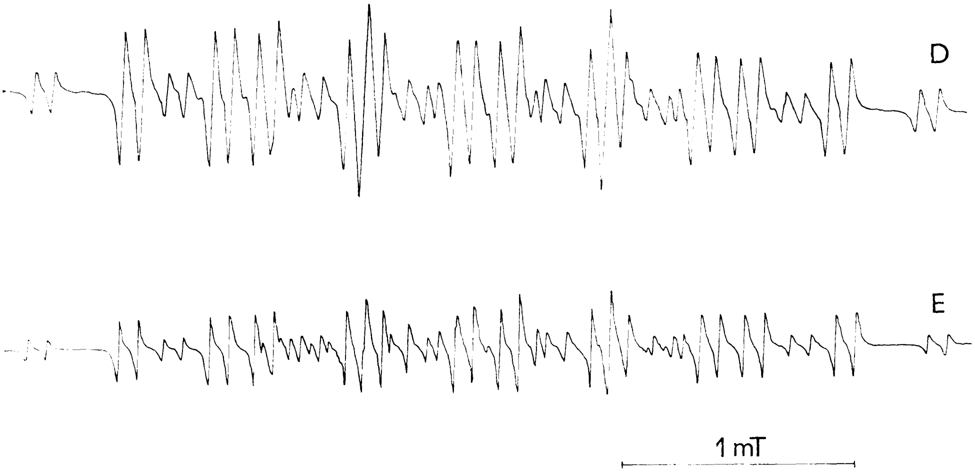


FIG. 1

ESR Spectra obtained by electrolysis of studied substances at potential above −1·1 V, A substance *I*, B *II*, C *III*, D *IV*, E *V* is consumed whereas the path (5)–(6)–(8)–(9) leads to consumption of two electrons; depending on the rate of reaction (6) this may result in an increase of the dc-polarographic wave up to a 2-electron consumption (substance *V*). 2-Methyl-

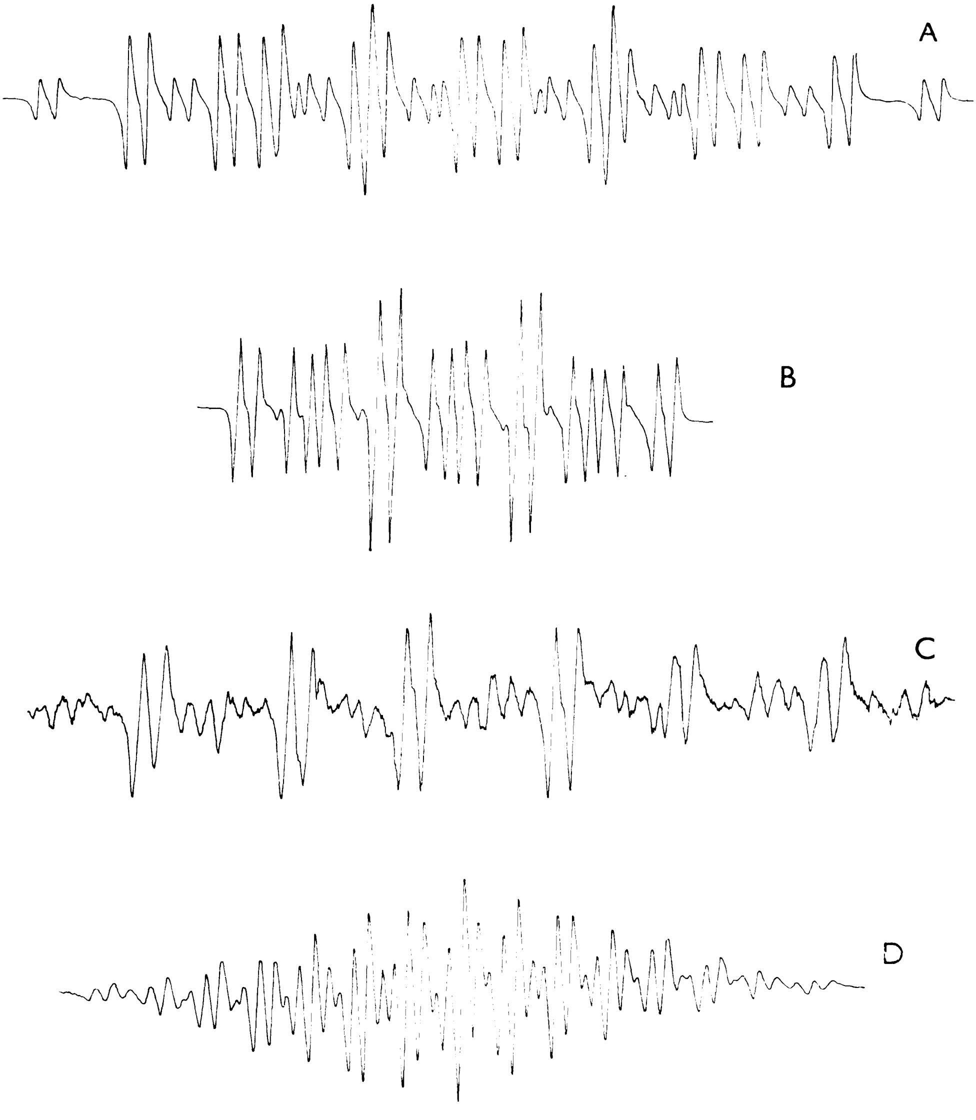


FIG. 2

ESR Spectra obtained by electrolysis of comparative substances, A substance *VI*, B *VII*, C *VIII*, D *IX*

-5-nitrofuran (*VI*) is further reduced by a single electron at potentials above $-1{\cdot}1$ V to a stable radical anion (Eq. (*10*)).

In cyclic voltammetry the formation of 2-methyl-5-nitrofuran (*VI*) by reduction of all studied compounds is evidenced by a couple of peaks corresponding to a reversible process at potentials about $-1{\cdot}1$ V. With substances *I*–*IV* where reaction (*6*) is slower, a longer period of time is required for the formation of 2-methyl-5-nitrofuran, and this is why the redox couple only appears after a longer electrolysis at a potential more negative than $E_{1/2}$ of the first wave. To achieve this longer period of time, a sufficiently slow polarization rate and/or, a time delay at E above $-1{\cdot}1$ V or a repeated cycling are used. The same couple has been also obtained with the compound *VI*.

From a detailed comparison of ESR spectra obtained during the electrolysis of substances *I*, *II* and *III* with the spectra of the radical anion of the unsubstituted 2-methyl-5-nitrofuran it follows that in addition to the radical anion of *III* a further radical is present in the solution at a considerably lower concentration. We have not succeeded in analyzing its spectra; by comparing it with the spectra of the radical anion of *VIII* (Fig. 2) one may conclude with highest probability that it is the same radical anion. The formation of *VIII* during electroreduction of the studied compounds can be only explained by dimer formation of the radical formed in reaction (*6*):

$$2(\mathrm{R{-}CH_2})^{\bullet} \rightarrow \mathrm{R{-}CH_2{-}CH_2{-}R}\,. \qquad (11)$$

Because of a small difference between the half-wave potentials corresponding to the reduction of *VIII* and *VI* to radical anions these two processes cannot be distinguished in an electrochemical way: consequently, even by a suitable choice of the potential one cannot reach the generation of a higher concentration of the radical anion of the product *VII* as compared to *VI* and obtain thus a spectra which would unambiguously enable a proof of its existence.

On comparing the scheme describing the electrochemical behaviour of the studied compounds (Eqs (*5*)–(*11*)) with the above general scheme (Eqs (*1*)–(*4*)), an obvious analogy may be seen. The equations (*5*) and (*6*) correspond to the equations (*1*) and (*2*). Regarding the fact that the nucleophilic reagent $\mathrm{Y^-}$ has been superseded by electrochemical generation, the radical $\mathrm{R^{\bullet}}$ cannot further react according to the reaction path (*3*)–(*4*) but according to (*8*)–(*9*) or (*7*) to $\mathrm{R{-}CH_3}$ as the main product of the electrochemical process, the formation of which has been in all cases unambiguously proved. The radical $\mathrm{R^{\bullet}}$ may possibly dimerize (Eq. (*11*)) with the formation of *VIII*. The substances *VI* and *VIII*, however, resulted as side products even in the chemical reaction of *I* and *V* with a nucleophile[6]. If the nucleophile is substituted by the electrode and the reaction (*3*) is made thus impossible, the processes and products which had to be considered minor reactions and minor resulting substances, become in this way main ones.

The analogy between both mechanisms leads to the verification of the radical-anion mechanism of the nucleophilic substitutions of 5-nitro-2-furfuryl derivatives suggested earlier[6,7], basing only on the product analysis of such a reaction.

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