ELECTROCHEMICAL REDUCTION OF *para*-SUBSTITUTED 2-ACYL-5-PHENYLFURANES IN DIMETHYLFORMAMIDE

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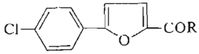
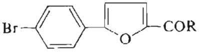
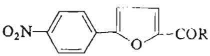
para Substituted chloro, bromo, and nitro derivatives of 2-acyl-5-phenylfurane are reduced polarographically in a one-electron wave to the corresponding anion radicals, which were studied by the EPR method. The reduction of nitro derivatives, studied by the Kalousek switch, is reversible and leads to a stable anion radical with an unpaired electron center on the nitrogen nucleus; the reduction of the halogen derivatives is only partly reversible and leads to unstable ketyl radicals. The bromo derivatives give polarographic maxima typical for concurrent reactions.

The study of furane derivatives has gained importance in recent years mainly in connection with their effect on bio systems. Many authors studied their electrochemical reduction mechanism in various media. The present work deals with the reduction of some *para* substituted 2-acyl-5-fenylfuranes on a mercury electrode in the medium of anhydrous dimethylformamide. The radical products of this reduction were analysed by the methods of the Kalousek switch and EPR spectroscopy. The following compounds were studied:

Group	Structure	Substituent R	Number
1.		CH_3	*I*
		C_2H_5	*II*
		$n\text{-}C_3H_7$	*III*
2.		CH_3	*IV*
		C_2H_5	*V*
		$n\text{-}C_3H_7$	*VI*
3.		CH_3	*VII*

EXPERIMENTAL

Apparatus. Polarographic curves were recorded on an OH 102 type apparatus of the firm Radelkis (Hungary) with a three-electrode system and compensation of the ohmic potential drop, and on an LP 60 polarograph (Laboratorní přístroje, Prague). A Unit OH 404/A potentiostat (Radelkis) was used for potentiostatic reductions in a cuvette of a Varian E-3 EPR spectrometer. Mass spectra of the studied compounds were obtained on an apparatus of the type MS 902-S. The dropping mercury electrode had a drop time 3·43 s and rate of flow 1·24 mg/s at a height of mercury column 55 cm. A calomel electrode filled with 4M-LiCl with a salt bridge filled with the base electrolyte served as reference. A quartz glass cuvette used in measuring the EPR spectra enabled to generate radicals directly in the resonator cavity.

Solvents and chemicals. Dimethylformamide (Soyuzkhimexport, USSR) was purified according to Thomas and Rochov[1]. The base electrolyte was tetrabutylammonium perchlorate (TBAP), prepared by neutralization of the hydroxide (BDH Chemicals) with $HClO_4$ (Jenapharm, GDR) The structure and purity of the studied compounds was checked by mass spectrometry and by determining the melting point.

RESULTS AND DISCUSSION

According to their polarographic behaviour, the studied compounds can be divided into three groups: The first group comprises compounds *I*, *II*, and *III*, which differ by the alkyl group (CH_3, C_2H_5, n-C_3H_7). Their reduction proceeded on the dropping electrode in anhydrous dimethyl formamide in the presence of TBAP in two waves, the first of which was actually an ill-developed double wave with $E_{1/2}$ in the region from 1·75 to 1·77 V; its limiting current plotted against the height of mercury column gave a straight line. When studying the first reduction step with the aid of the Kalousek switch, we obtained a curve with a relatively less developed anodic portion when the auxiliary potential was in the region of the limiting current of the double wave and the frequency was 12·5 Hz. The anodic limiting current, which is only about as large as the cathodic one (Fig. 1), suggests a small stability of the primary reduction product, which undergoes a subsequent chemical reaction[2,3] as evidenced by EPR measurements: the EPR signal decayed rapidly after stopping the generation of the primary reduction product.

The second group comprises bromo substituted compounds *IV*, *V*, and *VI*, which again differ by the alkyl group as in the preceding case. Their polarographic curves are characterized by a maximum which is neither of the first nor of the second kind. Similar maxima can be observed also in the case of other bromo derivatives, whose peculiar behaviour is attributed to concurrent reactions related to a pronounced deformability of halogen atoms. These can function in certain electrode reactions as electron bridges and thus change the reaction mechanism, whereby the value of $E_{1/2}$ is shifted[4-6] or maxima are formed[7]. The reversibility of the reduction of these compounds was studied with the aid of the Kalousek switch and the result was analogous to the first group: small stability of the primary radical product evidenced by a small value of the anodic current of the switched curve. The transfer of another electron proceeded analogously with chloro and bromo derivatives; it was manifested by an irreversible diffusion wave with $E_{1/2}$ between $-2·65$ and $-2·7$.V (ref.[5]).

In contrast to compounds *I* – *VI*, the polarographic behaviour of substance *VII* which has a nitro group, was much different. The first wave was much more positive, $E_{1/2} = -0·896$ V, with a logarithmic slope 58 mV corresponding to a one-electron reversible process. This is in accord with the results obtained with the use of the Kalousek switch; the ratio of the height of the switched to that of the normal wave was determined as 2·55 at a frequency of switching of 6·25 Hz (Fig. 2) in good agreement with the theoretical value of 2·6 for a reversible wave according to Koutecký[9], an evidence that the primary reduction product is relatively stable. Similar results were obtained by Geske and Maki[10] who studied the reduction of nitrobenzene and nitrosobenzene, and Stradin and Reikhmanis[11], who found that the most positive reduction wave of nitrofuranes is reversible and corresponds to the formation of anion radicals of the type $[R\text{-}NO_2]^{\dot{-}}$. The second reduction wave with $E_{1/2} = -1·46$.V and with the ratio of the heights of the switched and normal curve 1·85 corresponds to the transfer of another electron, probably on the CO group, as discussed in ref.[12].

The results of polarographic measurements are in accord with the EPR spectra, which substantiated the formation of an anion radical in the first reduction step and

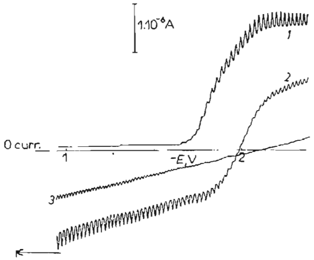


FIG. 1

Polarographic Curve for Compound *II* (1st Wave) with Kalousek Switch

1 Normal curve; *2* switched curve; *3* same for the base electrolyte; $c_{II} = 5 . 10^{-4}$ mol/l, 0·05 mol/l TBAP, $f = 12·5$ Hz, $E_{aux} = -2·3$ V.

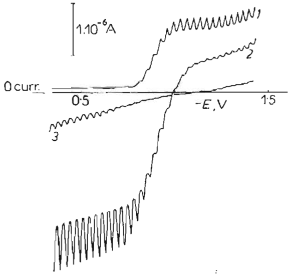


FIG. 2

Polarographic Curve for Compound *VII* (1st Wave) with Kalousek Switch

1 Normal curve; *2* switched curve; *3* same for base electrolyte; $c_{VII} = 5 . 10^{-4}$ mol/l 0·05 mol/l TBAP, $f = 6·25$ Hz, $E_{aux} = -1·2$ V.

revealed a difference between the stability of the radical formed by reduction of the nitro derivative and that of the radicals formed in other cases.

Substances *I*, *II*, and *III*, the spectra of whose radicals are shown in Fig. 3*d* − *c*, differ in their structure by the alkyl next to the CO group. The effect of the halogen substituent on the spectrum was practically negligible: the spectra did not change if the Cl atom was replaced by Br. The spectrum in Fig. 3*a* is by 0·91 mT wider than that in 3*b*; this difference between the spectra of compounds *I* and *II* follows from a strong interaction of the methyl and ethyl protons with the unpaired electron, is conditioned by its high spin population in the vicinity of these alkyls, and corresponds to the formation of ketyl radicals. A similar change of the spectral width of ketyl radicals of compounds with a methyl or ethyl next to the CO group was found and discussed in detail earlier[13].

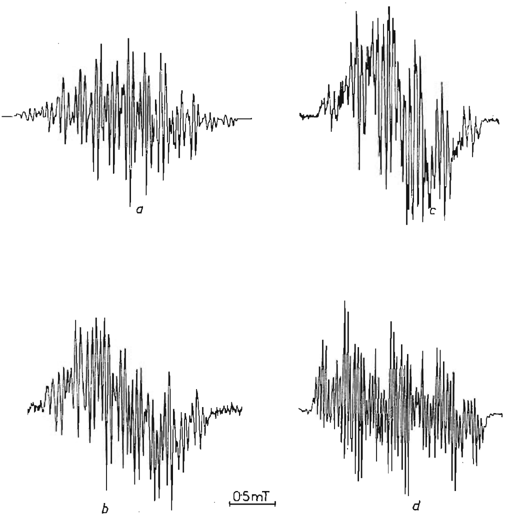


FIG. 3
EPR Spectra Obtained During Reduction of Compounds *I*(*a*), *II*(*b*), *III*(*c*), and *VII*(*d*)

The spectra of radicals of compounds *II* and *III* (Fig. 3*b*, *c*) have the same fine structure, but the spectral bands of compound *III* exert, in addition, a fine splitting corresponding to two small interaction constants of protons with 0·02 mT, and these are not observable in the spectrum of the radical *II*. Since the only difference between the structure of compounds *II* and *III* consists in that the former has an ethyl and the latter an n-propyl group bound to the CO group, the mentioned fine splitting can be attributed only to a γ-interaction of the methylene protons of the n-propyl group with the unpaired electron. Such interactions are caused by a hindrance of the rotation of the methylene protons of the n-propyl group. The observed γ-interaction suggests a high spin density of the unpaired electron on the CO group and substantiates the formation of ketyl radicals of the studied compounds.

The spectrum in Fig. 3*d* consists of a triplet, whose splitting constant is equal to 0·62 mT. It follows from approximately equal intensities of the bands of this triplet that they are due to an interaction of the unpaired electron with the nitrogen nucleus. Each band is splitted into another triplet, whose two splitting constants are approximately equal to 0·3 mT. The band intensities of this triplet are in the ratio of 1 : 2 : 1 and can be attributed to an interaction of the *ortho* protons of the phenyl group with the unpaired electron. Another fine splitting of the spectrum, whose splitting constants are smaller than 0·2 mT, can be attributed to the *meta* protons of the phenyl group and to wide-range interactions with the protons of the furane ring. These observations are in accord with the assumption that, in the case of compound *VII*, an anion radical is formed whose center of the unpaired electron is on the nitrogen nucleus.

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