Cathodic reduction of substituted 5-phenyl-2-furaldehydes in dimethylformamide

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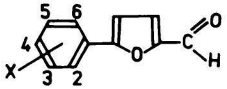
5-(H-, 4-CH_3-, 4-OCH_3-, 4-Cl-, 4-Br-, 3-Cl-, 3-Br-, 3-F-, 4-NO_2-, 3-NO_2-Phenyl)-2-furaldehydes were reduced reversibly to anion radicals in dimethylformamide on a dropping mercury electrode in one-electron step. These radicals were unstable and underwent subsequent reactions. The effect of the substituents on $E_{1/2}$, characterized by Hammett constants, was more significant than in aqueous media and was represented by the slope of + 0.2 V.

Восстановление 5-(H-, 4-CH_3-, 4-OCH_3-, 4-Cl-, 4-Br-, 3-Cl-, 3-Br-, 3-F-, 4-NO_2- и 3-NO_2-фенил)-2-фуральдегидов протекает в диметилформамиде на капельном ртутном электроде обратимо в одноэлектронной степени при образовании неустойчивых анионрадикалов, принимающих участие в последующих реакциях. Влияние заместителей на $E_{1/2}$ охарактеризовано константами Гаммета является более выразительным чем в водных средах и определяется наклоном + 0,2 В.

The present work is a continuation of studies [1—3] of electrochemical properties of furan derivatives and deals with the reduction of substituted 5-phenyl-2-furaldehydes on a dropping mercury electrode in anhydrous dimethylformamide. The formation of anion radicals in the initial step of the reduction and the effect of the substituents on the $E_{1/2}$ shift were investigated with the following derivatives



X = H, 4-CH_3, 4-OCH_3, 4-Cl, 3-Cl, 4-Br, 3-Br, 4-NO_2, 3-NO_2, 3-F

Experimental

Instruments

Polarographic curves were recorded with an OH-102 (Radelkis, Budapest) and an LP 60 (Laboratorní přístroje, Prague) polarographs. Potentiostatic reductions were carried out on a Unit OM 404/A (Radelkis, Budapest) potentiostat and the e.s.r. spectra were obtained on a Varian E3 spectrometer. At $h = 55$ cm, the dropping mercury electrode had the mercury flow rate of 1.24 mg s^{-1} and the drop time was 3.43 s. As reference electrode, 4 M-LiCl calomel electrode was used.

Solvents and chemicals

Dimethylformamide (DMF; Soyuzkhimexport) was purified after the method described by *Thomas* and *Rochow* [4]. Tetrabutylammonium perchlorate (TBAP), used in the basic electrolyte, was prepared by neutralization of tetrabutylammonium hydroxide (BDH-Chemicals, Ltd.) with perchloric acid (VEB Jenapharm GDR).

Results and discussion

A reversible reduction of the studied substituted 5-phenyl-2-furaldehydes proceeded on a dropping mercury electrode in dimethylformamide with 0.1 M-TBAP as basic electrolyte according to the scheme $S + e \rightleftharpoons S^{\cdot -}$. The

Table 1

Half-wave potentials $E_{1/2}$, values of the Hammett constants $\sigma_{m,p}$, $S_2 = i_p/i_d$ obtained by Kalousek commutator, and results of the logarithmic analysis of the first polarographic wave of *o*- and *p*-substituted 5-phenyl-2-furaldehydes

X	$E_{1/2}$ V	$\sigma_{m,p}$	S_2	$(E_{1/2} - E)/\log \frac{i}{i_d - i}$ mV
p-OCH_3	−1.73	−0.27	1.48	73.3
p-CH_3	−1.67	−0.17	1.47	73.1
H	−1.63	0.00	1.11	81.8
p-Cl	−1.59	0.23	1.27	72.5
p-Br	(−1.65)	0.23	—	—
m-F	−1.57	0.34	1.63	64.3
m-Cl	−1.55	0.37	1.67	64.3
m-Br	—	0.39	—	—
m-NO_2	−0.93	0.71	2.20	63.1
p-NO_2	−1.27	0.78	2.05	60.6

formation of anion radicals was observed by e.s.r. spectroscopy similarly as described in [1—3]. The reversibility of the process was studied by the method of Kalousek commutator. The obtained pulse curves showed a relatively high anodic current.

The values of the ratio $S_2 = i_p / i_d$ for the pulse frequency of 6.25 Hz [5, 6], $E_{1/2}$, and the results of logarithmic analysis of the first wave with the values of the corresponding Hammett constants $\sigma_{m,p}$ are presented in Table 1.

In spite of the relatively high anodic current of the pulse curve, which usually is the measure of the stability of the primary product of electrochemical reaction, it was impossible to obtain a good e.s.r. spectrum of the primary radical product because the formed anion radical, due to high reactivity of the aldehyde group, underwent chemical reactions giving more stable polymeric forms. The observed e.s.r. spectrum changed rapidly. For illustration we present a spectrum (Fig. 1) obtained at cathodic reduction of 5-phenyl-2-furaldehyde. The asymmetry of the

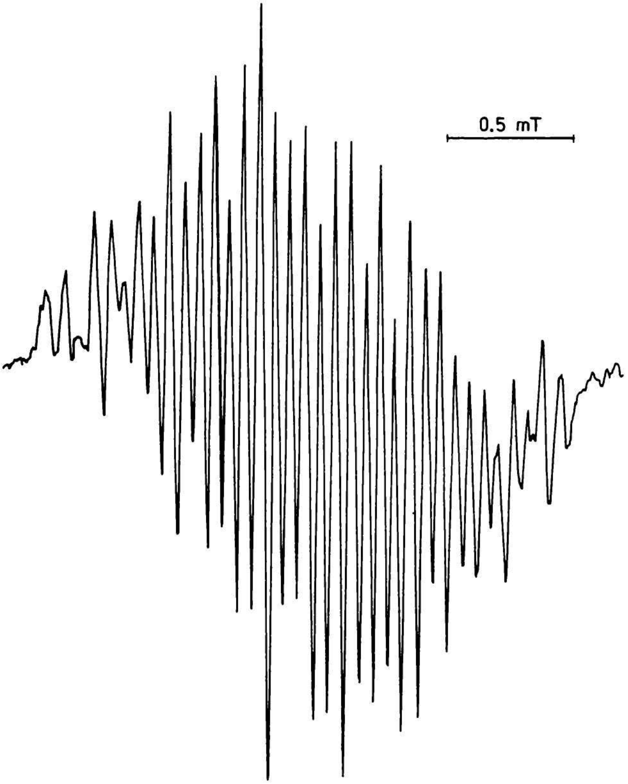


Fig. 1. ESR spectrum obtained at the reduction of 5-phenyl-2-furaldehyde.

spectrum and the changes of its shape during the reduction indicate that it is a sum of spectra of two radical products analogously as it was described in [3]. It was difficult to analyze this sum, because we failed to record the spectra of the individual radicals.

When studying the effect of the substituents on the shift of $E_{1/2}$, we followed the Hammett dependence in the form of $\Delta E_{1/2} = \varrho_{r,R}\sigma_X$. The value of the slope $\varrho_{r,R}$ was found to be $+0.2$ V (Fig. 2) which was higher than that obtained in aqueous alcoholic media [7]. A certain deviation was observed in the case of the derivative with the OCH_3 group. The deviation was more significant with *p*-bromo derivative where also the formation of a polarographic maximum was observed on the reduction curve. This was found also with other bromo derivatives [2] and could be probably assigned to more complicated reaction mechanism which is affected by the halogen atom [8]. The behaviour of the *m*-bromo derivative was different as well. Two waves were observed on its reduction curve with the components $E_{1/2}$ of -1.5 and -1.66 V, respectively.

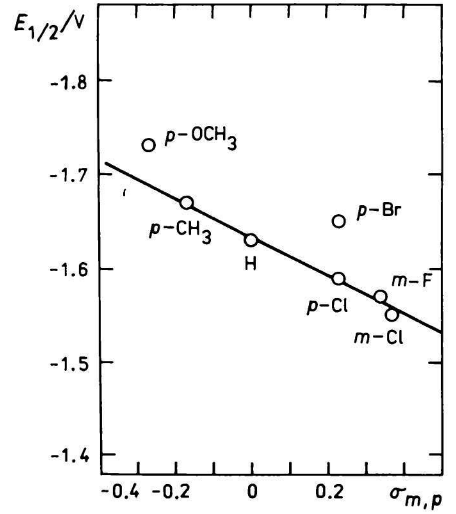


Fig. 2. Dependence of $E_{1/2}$ on the Hammett $\sigma_{m,p}$ constants of the substituents of the investigated *o*- and *p*-substituted 5-phenyl-2-furaldehydes.

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