

# Polarographic study of the effect of substituents in 5-arylthio- and 5-arylsulfonyl-2-furaldehydes

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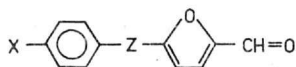
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The values of transfer coefficients  $\pi'$  were calculated on the basis of statistical parameters, obtained by correlation of half-wave potentials with  $\sigma$  constants of substituents for groupings: thio-furan, sulfonyl-furan, thio and sulfonyl groups. It has been found that the calculated values  $\pi'$  of the systems under investigation are in good accordance with those of the benzene analogues.

По статистическим параметрам, полученным корреляцией между потенциалами полуволн и константами  $\sigma$  заместителей были рассчитаны значения коэффициентов переноса  $\pi'$  через группировки: тио-фуран, сульфонил-фуран, тио- и сульфонильную группы. Было обнаружено, что полученные значения  $\pi'$  для изученных систем находятся в хорошем согласии с их бензольными аналогами.

Transfer coefficients  $\pi'$  through a furan ring of various series of furan derivatives were already reported [1—7]. The  $\rho$  constants calculated from wavenumbers, dissociation constants, and half-wave potentials indicate a hindering effect of the furan ring. To extend the knowledge concerning the transmission of electronic effects of substituents through bridging groups thio-furan and sulfonyl-furan the corresponding parameters were calculated from polarographic data, these being obtained by electroreduction of the carbonyl group in series of 5-(4-X-phenylthio)- (I) and 5-(4-X-phenylsulfonyl)-2-furaldehydes (II) of general formula



where  $Z = S$  in series *I* and  $SO_2$  in series *II*. Substituted benzaldehydes (*III*) were used as model compounds. The obtained values of the individual reaction constants were mutually compared with each other and with  $\rho$  values for series of substituted 4-isothiocyanatodiphenylsulfides and -sulfones [8].

## Experimental

### Chemicals

5-Arylthio-2-furaldehydes (*I*) were synthesized from the respective 4-substituted sodium benzenethiolates and 5-bromo-2-furaldehyde in ethanol or acetone [9], 5-arylsulfonyl-2-furaldehydes (*II*) from 4-substituted sodium benzenesulfonates and the same reagent in dimethylformamide [10]. Purity of products crystallized from appropriate solvents was verified by the determination of physical constants. Other chemicals used for the preparation of standard solutions and aldehydes of series *III* were anal. grade (Lachema, Brno).

### Instruments

Polarographic curves were recorded on an OH-102 polarograph (Radelkis, Budapest) in a modified Kalousek vessel with a separate SCE. The characteristic mercury-dropping electrode data: the operating reservoir height  $h = 60$  cm, flow rate  $m = 2.1$  mg s<sup>-1</sup>, the drop time  $t_1 = 3$  s (in 0.1 M-KCl at 0.0 V). The half-wave potential values were measured by a three-electrode system against the nonpolarized calomel electrode using QTK compensator (Metra, Blansko) with accuracy  $\pm 2$  mV. The pH of the polarographed solutions was measured with a PHM 26 pH-meter (Radiometer, Copenhagen) using glass electrode G 202 B and calomel electrode K 400. Constant temperature 20°C was maintained by ultrathermostat Wobster U8 (Prüfgeräte, Mädingen—Dresden). Parameters of linear correlations were calculated from statistical relations [11] by means of a Hewlett—Packard Calculator 9100 B.

### Measurements

Polarographic measurements were performed in aqueous-methanolic Britton—Robinson buffers of pH 2—12 and 0.1 mM concentration of depolarizer. The  $E_{1/2}$  values of all derivatives used for statistical evaluation were measured at pH 11.5. Oxygen from the polarographed solutions was removed by a stream of purified nitrogen passing through for 5 min.

## Results and discussion

Examination of the basic polarographic characteristics  $i = f(c, h^{1/2})$  of both series showed a linear course and lines intersecting the respective experimental points run

through the origin of the coordinate system. Basing upon these facts one can presume the processes proceeding on the mercury electrode to be governed by diffusion.

It has further been ascertained that derivatives of series *I* behave similarly as benzaldehydes *III* and 5-substituted-2-furaldehydes [12] depending on the pH. These substances reveal in acid medium one, in neutral medium two one-electron waves merging in alkaline medium ( $\text{pH} > 8$ ) in one two-electron wave. On the other hand, two one-electron waves associated with derivatives of series *II* keep their character even in alkaline medium unchanged (Fig. 1). Up to  $\text{pH} \sim 9$  the  $E_{1/2}$  values are dependent on the medium and the lines display a slope  $\sim 60$  mV per one pH unit. The values of half-wave potentials are pH independent in alkaline medium.

The  $E_{1/2}$  values of derivatives with sulfonyl group were found to be by  $\sim 200$  mV more positive (Table 1). This could be ascribed to enhanced electron-accepting properties of the  $\text{SO}_2$  group in relation to the thio group resulting in a decreased electron density at the carbon bearing the aldehyde group which, as a consequence, undergoes a more facile reduction. These facts are in accordance with behaviour of these groups (S and  $\text{SO}_2$ ) in aromatic systems [8].

On the basis of experimental results could be, moreover, presumed that all derivatives are reduced according the same mechanism as was found with the reduction of substituted benzaldehydes [13]. The final reduction products of substances under investigation are the corresponding 5-arylthio- and 5-arylsulfonyl-2-furfuryl alcohols.

Table 1

Polarographic characteristics of derivatives of series *I*, *II*, and *III*

No.	X	$-E_{1/2}$ , V			<i>i/c</i>	
		<i>I</i>	<i>II</i>	<i>III</i>	<i>I</i>	<i>II</i>
1	4-NO <sub>2</sub>	1.382	—	1.726	3.3	—
2	4-N(CH <sub>3</sub> ) <sub>2</sub>	—	1.132	1.728	—	4.2
3	4-OCH <sub>3</sub>	1.345	—	1.632	3.1	—
4	4-CH <sub>3</sub>	1.337	1.100	1.566	3.2	4.3
5	3,4-O <sub>2</sub> CH <sub>2</sub>	—	—	1.558	—	—
6	3-NHOH	—	—	1.528	—	—
7	4-NHCOCH <sub>3</sub>	1.326	1.092	—	3.2	3.9
8	H	1.328	1.094	1.530	3.0	4.5
9	3-OCH <sub>3</sub>	—	—	1.482	—	—
10	4-Cl	1.302	1.076	1.478	3.3	4.5
11	4-Br	1.305	1.082	1.486	2.9	3.2
12	3-Cl	—	—	1.422	—	—

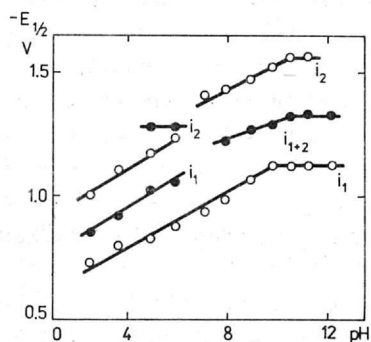


Fig. 1. Plot of  $E_{1/2}$  on pH of a chloro derivative of series I (●) and a fundamental derivative of series II (○).

$i_1$  — the first and  $i_2$  — the second alkaline cathodic wave.

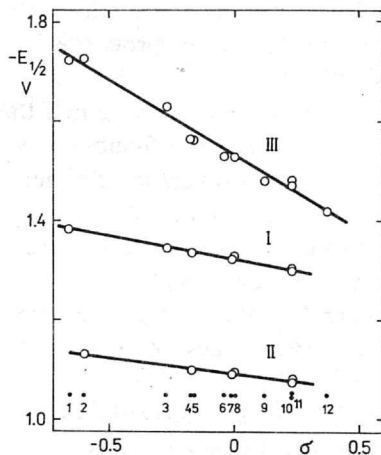


Fig. 2. Graphic dependence of  $E_{1/2}$  on  $\sigma$  constants for series investigated.

Numbering of derivatives coincides with that in Table 1. Value for amino group (I), to which the nitro group is preferentially reduced, was used.

The measured values of half-wave potentials for all three series were used for a statistical evaluation with  $\sigma$  constants of substituents [14]. The course of these dependences is shown in Fig. 2.

As it follows from the values of reaction constants  $\rho$  these are lower for series with a furan ring (Table 2). This indicates that the substituent effects on the reaction centre of derivatives I and II are partially hindered. Numerical values of the transfer coefficients  $\pi'$  were calculated from the equation  $\pi' = \rho/\rho_0$  in which

Table 2

Statistical parameters of linear relationships

Parameter	Series		
	I	II	III
$n$	7	6	11
$\rho \pm s_\rho$	$0.086 \pm 0.003$	$0.065 \pm 0.003$	$0.298 \pm 0.015$
$q \pm s_q$	$-1.324 \pm 0.000$	$-1.092 \pm 0.000$	$-1.532 \pm 0.004$
$r$	0.996	0.995	0.987
$s$	0.002	0.002	0.016

$n$  — number of derivatives in a series,  $\rho$  — slope and its error,  $q$  — calculated  $E_{1/2}$  value for a fundamental derivative and its error,  $r$  — correlation coefficient,  $s$  — standard deviation.

Table 3

Values of the transfer coefficients

Bridging group	$\pi'$	Ref.
—furan—	0.56—0.68	[1—7]
—S—furan	0.29	This paper
—SO <sub>2</sub> —furan	0.21	
—S—	0.48	
—SO <sub>2</sub> —	0.36	
—benzene—	0.27—0.32	[15, 16]
—S—benzene—	0.24	[8]
—SO <sub>2</sub> —benzene—	0.03	[8]

for  $\rho$  reaction constants for series *I* and *II* and for  $\rho_0$  values for 5-aryl-2-furaldehydes [6] and series *III* were substituted as seen in Table 3.

The results obtained confirm that after introducing another bridge (S and SO<sub>2</sub> in our case) into 5-aryl-2-furaldehyde system the values of coefficients  $\pi'$  are even lower. Comparison of the transfer coefficients of the series under investigation with those of the benzene analogues [8] showed a good agreement for the thio group. The disagreement for series with the bridging SO<sub>2</sub> group could be ascribed to the interactions on different reaction centres (CH=O and NCS).

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