Polarography of 4-Substituted 4'-Isothiocyanatodiphenyl Sulfides

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The polarographic reduction of seven 4-substituted 4'-isothiocyanatodiphenyl sulfides was investigated in Britton—Robinson buffer solutions. The characteristic polarographic data were either measured or calculated and the $\varrho_{\pi,R}$ reaction constant, obtained from the correlation of half-wave potentials with Hammett σ constants was found to be 0.03 V.

The electron effect transfer of the —NCS group in polarographic reduction was so far studied in benzene, biphenyl, stilbene and diphenyl oxide systems [1—4]. In the present work isothiocyanates of general formula
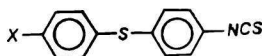
were investigated, where $X— = H$, CH_3, Cl, Br, $N(CH_3)_2$, NCS, NO_2.

Experimental

Chemicals and apparatus

Isothiocyanates described in this paper were prepared applying thiophosgene method to the starting amines according to [5, 6]. Physicochemical constants were measured to check the purity of compounds used.

Britton—Robinson buffer solutions of pH 2—11 were used as basic electrolytes. To those solutions an equal volume of freshly prepared methanolic solution of depolarizer was added. All chemicals were of p. a. grade and their purity was also checked by recording the $i—E$ curves of the basic electrolyte without the depolarizer.

Polarographic curves were recorded by means of polarograph LP 60 (Laboratorní přístroje, Prague). The flow-rate of the dropping mercury electrode was $m = 2.3$ mg/s, the drop time $t = 3$ s, the height of the mercury in the reservoir $h = 80$ cm. Kalousek vessel with a saturated calomel electrode was used. Oxygen was removed from the polarographic solutions by a stream of nitrogen purified through alkaline pyrogallol solution for 5 minutes at 10 cm water pressure. The $E_{1/2}$ values were measured with a three-electrode system towards a non polarized SCE by means of a QTK-compen-

sator (Metra, Blansko). The pH values of the polarographed solutions were measured with a PHM 22 pH Meter (Radiometer, Copenhagen) using a glass electrode G 202 B towards K 100 type SCE.

Results and Discussion

The investigated compounds were soluble in water to a small extent only, but the solubility was substantially better in methanol. All derivatives were possible to be prepared either in 1 mM methanolic solutions, or in no more than 0.1 mM methanol—water (1 : 1, v/v) solutions. Consequently, the half-wave potentials were measured with 0.05 mM depolarizer solutions, excepting the diisothiocyanato derivative, the concentration of which could be 0.03 mM only.

The general behaviour of derivatives under study in polarographic reduction is analogous to that of other aromatic isothiocyanates [1—4, 7—9]. In a strong acidic medium, the formal number of electrons needed for reduction of the isothiocyanato group is more than four. The less acidic solution, the less the number of electrons taking part in reduction and in a mild alkaline medium the number is equilibrated at a constant value $n = 2$. The limiting currents are still less in stronger alkaline solutions. A further decrease of the wave-height in this case is due to the addition of the OH^- ion to the isothiocyanate to form a thiocarbamate anion [1, 2] and not to the decrease of the number of electrons involved in the reduction.

The limiting currents of compounds being polarographically investigated in this paper were found to be linearly proportional to the square root of the height of the mercury in the reservoir, as well as to the depolarizer concentration. Essential results are summarized in Table 1.

Table 1

Basic polarographic characteristics of 4-X-4'-isothiocyanatodiphenyl sulfides

X—	$-E_{1/2}$ (pH 9.1) [V (SCE)]	α	$\Delta E_{1/2}/\Delta$pH (pH $<$ pK') [V/pH]	p$K'^{a)}$	$\bar{i}_d/c$ [μA mmole^{-1} l]
H	0.994	0.62	0.040	5.2	6.8
CH$_3$	1.001	0.57	—	—b)	6.1
Cl	0.991	0.61	0.060	4.5	7.7
Br	0.990	0.61	0.060	4.5	6.5
(CH$_3$)$_2$N	1.014	0.57	0.085	5.6	4.1
NCS	0.982	0.56	0.055	4.6	7.3
NO$_2$	0.989	0.37	0.095	6.4	4.1

a) pK' and $\Delta E_{1/2}/\Delta$pH were estimated from the $E_{1/2}$ on pH dependence by graphic method. The $\Delta E_{1/2}/\Delta$pH reading was accurate to ± 5 mV.

b) See Fig. 3.

A typical reduction course was observed with chloro, bromo and diisothiocyanato derivatives which reveal one wave in the acidic region; its more negative section discloses a steeper slope than the start does (Fig. 1). The first wave is perfectly separated from the second one at pH 3.5. The dimethylamino derivative reveals a distinctly separated first two-electron reduction wave throughout the entire pH
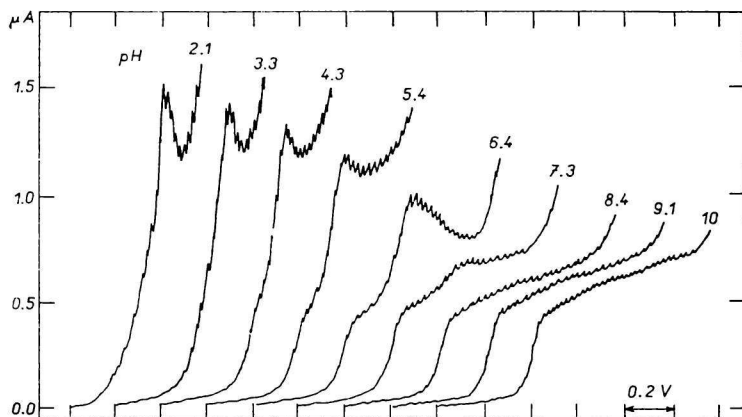
Fig. 1. The polarographic curves of 4-chloro-4'-isothiocyanatodiphenyl sulfide in Britton —
— Robinson buffer solutions.
Depolarizer concentration $c = 5 \times 10^{-5}$ M, 50% CH_3OH, zero position of curves at
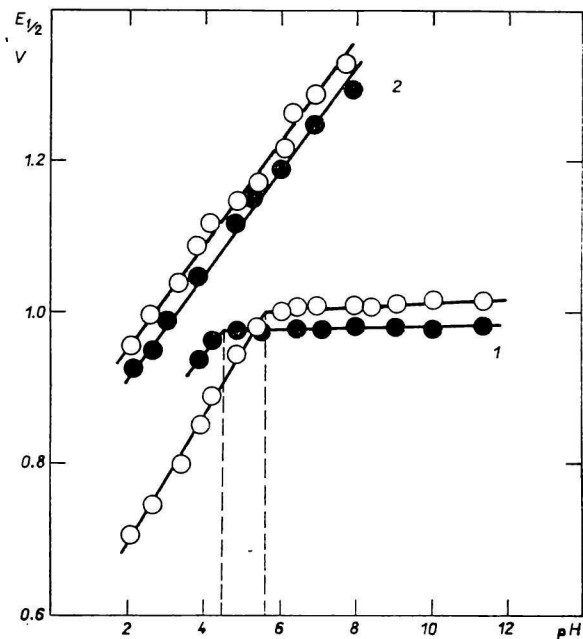-0.6 V; sensitivity 7.15×10^{-8} A cm^{-1}.

Fig. 2. The $E_{1/2}$ on pH shift dependence of (○) 4-dimethylamino-4'-isothiocyanato-
diphenyl sulfide; (●) 4,4'-diisothiocyanatodiphenyl sulfide.
1. first wave; *2.* second wave.

range (Fig. 2). The nitro derivative is reduced with six electrons in the alkaline region, four of which being consumed in the $-NO_2$ group reduction (reduction of this group to afford hydroxylamino group can be observed throughout the entire pH range). Coming from the alkaline to the acid region a third wave can be noticed already in the neutral medium. Likewise the second wave the third one becomes more pronounced when the medium grows acidic.

A special anomaly has been observed with the fundamental derivative, as well as with the methyl derivative. In the 2—10 pH range a little prewave occurs the height of which corresponds to one fourth of the two-electron reduction wave of isothiocyanates. Its half-wave potential was found to be 0.6—0.7 V more positive
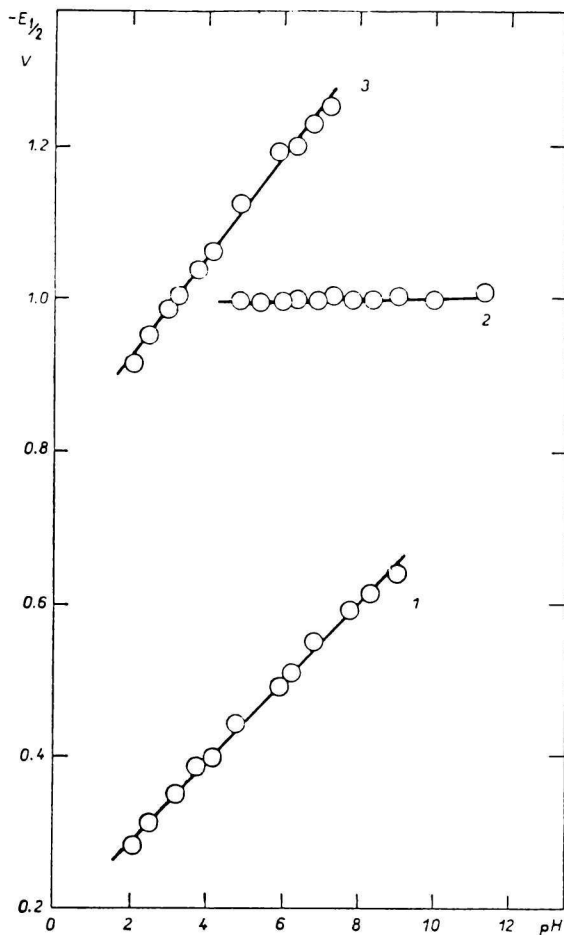

Fig. 3. The $E_{1/2}$ on pH shift dependence of 4-methyl-4′-isothiocyanatodiphenyl sulfide. *1.* prewave; *2.* first wave; *3.* second wave.

than that of the main reduction wave. The height of this wave keeps constant even in solutions several days old which one cannot say about waves associated with the reduction of —NCS group since these waves become lower as the solution grows old (reaction of isothiocyanate with alcohol; Fig. 3). In spite of the fact that we have not been able to disclose the nature of this electrode process which might be attributed to this half-wave; it can be assumed that an other site of molecule is involved than that of the isothiocyanato group (Fig. 4).
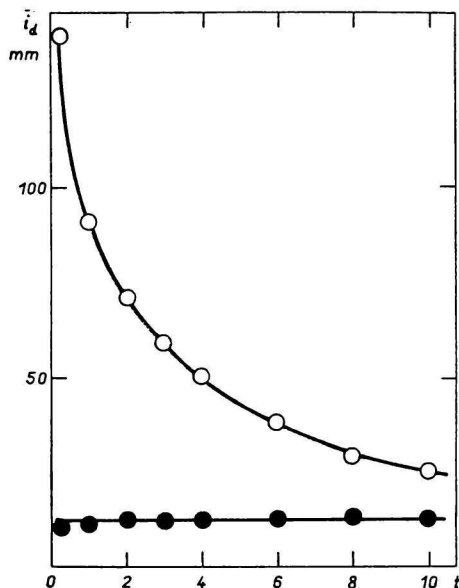

Fig. 4. The time dependence of waves of 4-methyl-4'-isothiocyanatodiphenyl sulfide at pH 4.8, 50% CH_3OH; depolarizer concentration $c = 5 \times 10^{-5}$ м.
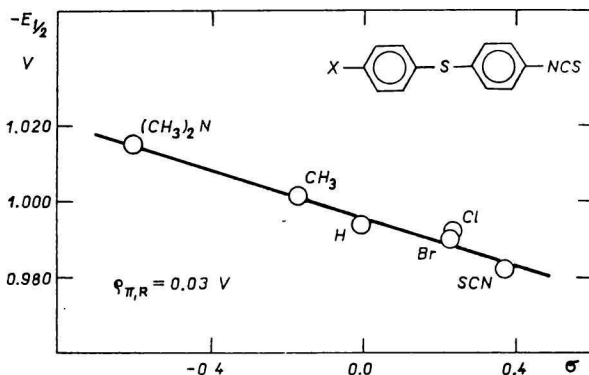● the prewave height; ○ the isothiocyanate wave height. Time in days.

Fig. 5. The correlation of half-wave potentials with Hammett constants of substituents.

Half-wave potentials of derivatives the electrode process irreversibility of which is characterized by charge transfer coefficient $\alpha = 0.59 \pm 0.03$ were selected for correlation with the Hammett constants of substituents. The correlation did not imply the nitro derivative the transition coefficient of which is substantially lower. As it follows from the reaction constant value $\varrho_{\pi,R} = 0.03$ V (Fig. 5), the electron effect transitions through the sulfide bond are very small in the polarographic reduction of the NCS group, as yet the lowest in the series of systems so far investigated. (Reaction constants: benzene 0.22 V, stilbene 0.08 V, diphenyl oxide 0.07 V, biphenyl 0.07 V.)

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