Isothiocyanates. XXXIV.
On polarography of some isothiocyanates

ᵃA. BEŇO, ᵇJ. SURÁ, ᵇA. MARTVOŇ, and ᵇM. UHER

ᵃ*Department of Analytical Chemistry, Faculty of Natural Sciences,
Komenský University, 801 00 Bratislava*

ᵇ*Department of Organic Chemistry, Slovak Technical University,
880 37 Bratislava*

Dedicated to Professor S. Stankoviansky on his 65th birthday

The polarographic reduction of the three series of isothiocyanates containing $N=N$, CO, COO, and OCO groups was studied in dependence on pH. In these systems also the influence of substituents on the shift of the half--wave potential of $-NCS$ group was investigated. In all studied series there were found linear correlations between $E_{1/2}$ values and Hammett σ constants. Using the slopes of Hammett correlations the coefficients of the electron-transfer effects for each above-mentioned group were calculated.

Previous polarographic studies [1—4] of the reduction of isothiocyanates and the electron-transfer effects of substituents on $-NCS$ group were devoted to conjugated systems with unreducible bridges only.

In the present paper the behaviour of 4-X-4'-isothiocyanatoazobenzenes (*I*), 4-X-4'--isothiocyanatobenzophenones (*II*), 4'-isothiocyanatophenyl-4-X-benzoates (*III*), and 4-X-phenyl-4'-isothiocyanatobenzoates (*IV*) (Scheme 1) in dependence on the pH of

Scheme 1

Britton—Robinson buffers was studied by polarography. Moreover, in these systems the substituent effects on the shift of $E_{1/2}$ of $-NCS$ group were investigated and the values of half-wave potentials were correlated with Hammett σ constants. From the calculated reaction constants $\varrho_{\pi,R}$ the coefficients of the electron-transfer effects, π', were calculated for each series.

Experimental

Instruments

The polarographic curves were recorded on an OH-102 polarograph (Radelkis, Budapest) in Kalousek vessel with separated SCE. The working height of the Hg-reservoir was 60 cm, the out-flow velocity 1.9 mg s⁻¹, and the drop time $t_1 = 3$ sec (at 0,0 V

in 0.1 M-KCl). The pH of polarographic buffers were measured with a PHM-26 (Radio-meter, Copenhagen) pH meter using a glass electrode G 202B and K 400 type SCE. The $E_{1/2}$ values were measured using three-electrode system with respect to nonpola-rized SCE on a QTK-compensator (Metra, Blansko) the accuracy being ±3 mV. The para-meters of linear correlations were computed from unapproximated statistic relations [5] on a computer 9100 B (Hewlett—Packard).

Chemicals

The synthesis of isothiocyanates of the series $I-IV$ was described earlier [6—8]. The compounds were recrystallized and their purity was checked by determining the physical constants before use. Other chemicals used were anal. grade (Lachema, Brno).

Working conditions

0.5 mM methanolic solutions of all compounds studied were prepared. These solutions were mixed with Britton—Robinson buffers in the range of pH 2—12 to give 0.1 mM of depolarizer and 50% of methanol in the final polarographic solution. All the measure-ments were carried out at 20°C. Oxygen was eliminated by nitrogen purified by alkaline solution of pyrogallol for 5 minutes at 100 mmH$_2$O overpressure.

Results and discussion

The study of the nature of limiting currents of compounds in the series $I-IV$ showed that they are controlled by diffusion. Their dependence on the square root of height of the Hg-reservoir and on the concentration of depolarizer in the range of 0.04—0.25 mM is expressed by the lines which go through the origin of the coordinated system.

The course of the polarographic reduction of —NCS group of substituted isothio-cyanates in the series $I-IV$ is analogous to that of the corresponding parent compounds. In the acid region a four-electron wave appears and with the increasing pH it splits in two double electron waves. The first of them corresponds to the reduction of N=C bond in —NCS group and does not change in the alkaline region. The second wave represents the reduction of C=S bond and disappears in neutral region [1, 9].

As the bridging groups (Y) in compounds $I-IV$ are reducible, they partially influence the reduction of the —NCS group. For this reason the polarographic curves become complicated and their evaluation, mainly in the acid region, rather difficult. It is char-acteristic of the series II, III, and IV that the $E_{1/2}$ values of —NCS group in the region of pH < pK' depend on the pH (the ratio of $\Delta E_{1/2} : \Delta$pH being ∼75 mV). The $E_{1/2}$ values of —NCS group in the region where pH > pK' are approximately constant. However, those of reducible additional groups depend on pH. The pK' values for these series are in the region 4.7—5.9.

In the compounds of series I in the measured pH range the azo group is reduced to hydrazo group before —NCS group. The $\Delta E_{1/2} : \Delta$pH ratio is ∼75 mV. The —NCS group exhibits one wave at pH < 6; however, in the pH region 6—8 it manifests itself by two waves with $\Delta E_{1/2}$ ∼ 150 mV. The second wave disappears at pH 8 and the first becomes independent of pH.

In the series II the first wave corresponding to reduction of the N=C bond of —NCS group is in the acid region partially separated from the second wave of C=S bond, which in this region merges with a wave corresponding to the reduction of the CO group.

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The splitting of this wave takes place at pH > 4 with $\Delta E_{1/2} \sim 100$ mV, whereby the wave with the more negative potential at pH $\sim$ 7 disappears (the second wave of $-$NCS group).

In the alkaline region compounds of the series I and II exhibit two waves of approximately the same height (as follows from the values of the limiting currents in Table 1). The wave corresponding to the reduction of $-$NCS group in the series I with more negative $E_{1/2}$ and in the series II with more positive $E_{1/2}$ disappears at pH 12. The waves of CO group (series II) in the range of pK' < pH < pK'' have a slope of ~ 35 mV : ΔpH. The pK'' values for the individual derivatives are in the range $9.5-10.5$.

The polarographic behaviour of compounds in the series III in the acid region is similar to that in the series IV. The difference between the polarographic behaviour of compounds

Table 1

Polarographic data of the waves of $-$NCS (A) and N$=$N, CO, OCO (B) groups in compounds of the series $I-IV$

Series	No.	X	$-E_{1/2}$ [V (SCE)]		i_d/c [μA mmol^{-1} l]	
			A	B	A	B
$I_{N=N}$	1	4-N(CH$_3$)$_2$	1.170	0.572	3.8	3.6
	2	4-OCH$_3$	1.160	0.550	4.4	4.5
	3	4-CH$_3$	1.162	0.537	4.7	4.7
	4	3-CH$_3$	1.156	0.522	4.8	4.8
	5	H	1.152	0.512	4.8	4.8
	6	4-Cl	1.150	0.494	4.2	4.1
	7	4-Br	1.148	0.496	4.4	3.9
	8	3-Cl	1.148	0.475	4.5	3.9
	9	4-NCS	1.140	0.480	4.2	4.1
	10	3-Br	1.144	0.467	4.3	4.1
	11	4-NHOH, NO$_2^*$	1.168	0.424*	4.5	4.3
II_{CO}	12	4-OCH$_3$	1.008	1.273	4.8	3.9
	13	4-CH$_3$	1.001	1.251	4.8	4.8
	14	H	0.994	1.220	4.5	4.8
	15	4-Br	0.980	1.168	3.0	3.2
	16	4-NCS	0.970	1.157	2.8	2.8
	17	4-NHOH	1.007	1.285	2.5	2.9
III_{COO}	18	4-OCH$_3$	1.018		4.8	
	19	4-CH$_3$	1.012		4.3	
	20	4-CH(CH$_3$)$_2$	1.012		4.5	
	21	3-CH$_3$	1.009		5.2	
	22	H	1.006		5.0	
	23	4-Cl	1.002		3.8	
	24	4-Br	0.998		3.1	
	25	4-I	0.994		2.8	
	26	4-NCS	1.038		7.5	
IV_{OCO}	27	4-OCH$_3$	1.076	1.664	3.8	3.1
	28	4-C(CH$_3$)$_3$	1.082	1.662	3.8	2.9
	29	4-CH$_3$	1.082	1.652	4.0	3.0
	30	3-CH$_3$	1.078	1.650	4.1	3.0
	31	H	1.074	1.648	3.9	2.9
	32	4-Cl	1.070	1.645	4.0	3.0
	33	4-Br	1.068	1.644	4.0	3.1
	34	3-Cl	1.068	1.636	3.6	2.8
	35	4-COCH$_3$	1.065	1.625	4.3	3.1

in these series was found in alkaline media. With the compounds of series IV immediately after disappearance of the second wave of $-NCS$ group at pH 7 a new wave appeared at $E_{1/2}$ by about 500 mV more negative than $E_{1/2}$ of the first wave of $-NCS$ group. The value $\Delta E_{1/2} : \Delta pH$ was ~ 30 mV for derivatives of this series if $pK' < pH < pK''$ values being in the region of 10.5—11.1. With derivatives of the series III this wave does not appear and their behaviour is similar to the other conjugated systems studied earlier [4]. The limiting currents of a new wave of the compounds in the series IV decrease with the increasing pH and in strong alkaline media (pH 12) the new wave as well as the wave of $-NCS$ group disappear.

Different behaviour of the derivatives of the series IV compared with those of III could be explained by different ability of bridges to transfer the effects of the substituents and of $-NCS$ group. It is supposed that the bridging group in the series IV acts as another reaction centre. This is supported by the following circumstances.

a) The electron-acceptor effect of $-NCS$ group simplifies the electroreduction of the CO group.

b) The substituents X do not substantially influence the polarity of the CO group because the oxygen atom between phenyl and carbonyl groups operates as an insulator of substituent effects.

In the case of compounds of the series III where the 4'-isothiocyanatophenyl group is separated from the CO group by an oxygen bridge the transfer of electron-acceptor effect of the $-NCS$ group on the CO group is less efficient than with the compounds of the series IV. It was found by the kinetic measurements that the compounds of the series IV undergo in alkaline media, besides the addition of OH^- ions to $-NCS$ group [2], also hydrolytic cleavage of esters to give corresponding phenols and anions of 4-isothiocyanatobenzoic acids [10].

From the above-mentioned facts it follows that the second wave of compounds of the series IV which appeared in alkaline media represents the reduction of the CO group in OCO bridge. This wave decreases and finally disappears with the increasing pH as a result of hydrolytic cleavage of corresponding esters.

Table 2

Statistical parameters of linear correlations of $E_{1/2}$ for NCS, N=N, CO, and OCO groups with σ constants of substituents in the studied series

Series	Group	n	$\varrho_{\pi, R}$	s_ϱ	s	π'
I	NCS	11	+0.027	±0.003	0.959	0.003	0.12
II	NCS	6	+0.053	±0.003	0.992	0.002	0.24
III	NCS	8	+0.037	±0.004	0.971	0.002	0.17
IV	NCS	9	+0.021	±0.004	0.910	0.003	0.095
I	N=N	11	+0.105	±0.005	0.988	0.007	
II	CO	6	+0.187	±0.001	0.995	0.006	
IV	OCO	9	+0.042	±0.001	0.954	0.004	0.22

n — number of compounds in correlation,
$\varrho_{\pi, R}$ — slope of the regression line,
s_ϱ — error of the line slope,
r — correlation coefficient,
s — standard deviation,
π' — coefficient of the electron-transfer effects.

The results of polarographic measurements of the compounds of the series $I-IV$ at pH 9.2 are listed in Table 1. The data obtained for these groups confirm the results of polarographic studies with similar systems published earlier [11—13].

Since the $E_{1/2}$ values for —NCS group of all studied compounds of the series $I-IV$ in alkaline region are independent of pH they can be correlated with Hammett σ constants of substituents [14] (Table 2, Fig. 1). It follows from the comparison of the values of $\varrho_{\pi.R}$ calculated statistically that the influence of substituents on the polarographic reduction
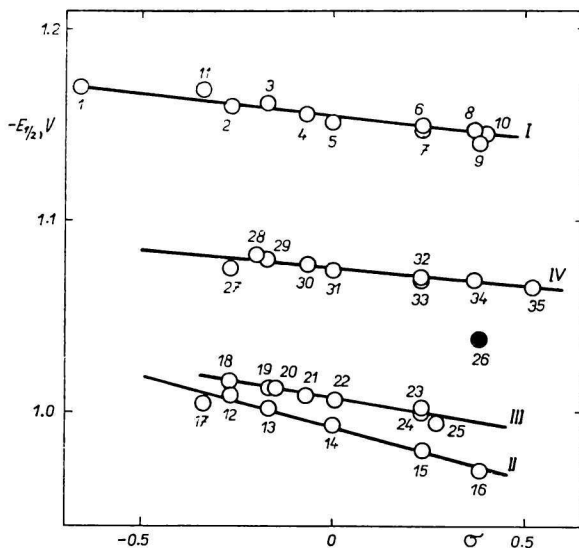
Fig. 1. Dependence of $E_{1/2}$ of —NCS group for derivatives in the series $I-IV$ on σ constants of the substituents. The numbering of the series and the experimental points are the same as in Table 1.
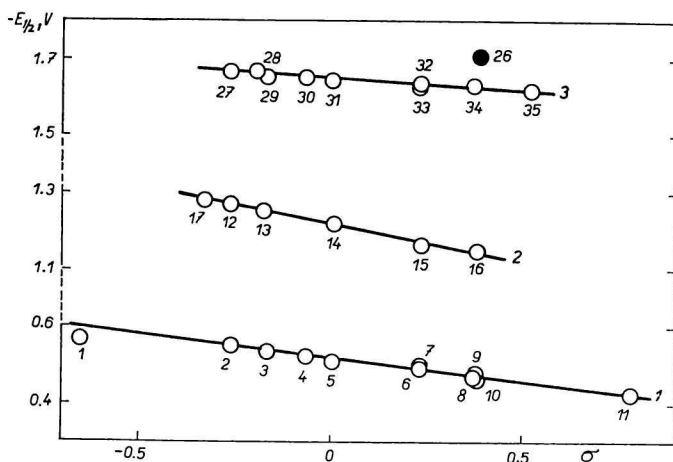

Fig. 2. Correlations of $E_{1/2}$ with σ constants for groups N=N (*1*), CO (*2*) and OCO (*3*).

of −NCS group in compounds of the series $I-IV$ is substantially lower than in the case of substituted phenyl isothiocyanates [13, 15]. This indicates that the above-mentioned bridging groups (Y) considerably hinder the electron-transfer effects on −NCS group. The hindering effect is the most pronounced with compounds of the series IV and is the least marked in the case of the series II.

For each series the coefficients of the electron-transfer effects, π', [16] through considered bridging groups were calculated. The comparison of π' values (considering also their calculated errors) showed that the hindering effect of the individual bridges attached to benzene ring increases in the order CO < COO < NH−NH < COO.

When comparing our results with the systems published earlier [4] the hindering effects of the bridging groups increase in the following order:

$$CH{=}CH < S \leqslant O \leqslant CO < CH_2 < COO < NH{-}NH < OCO < SO_2 \,.$$

These results are in a good agreement with those obtained by i.r. spectral measurements for isothiocyanato derivatives [6−8]. The $E_{1/2}$ values representing the reduction of N=N, CO. and OCO groups (Table 1; B) were used also for correlations with σ constants of substituents. The graphical evaluation of these relations is given in Fig. 2 and the values of their reaction constants are summarized in Table 2. From the comparison of slopes for the series II and IV it can be seen that the introduction of the oxygen atom between the phenyl and CO groups makes the influence of substituents substantially less efficient. If we calculate the transfer coefficient π' using the relations of slopes $\varrho_{IV}/\varrho_{II}$ we obtain the value 0.22, which agrees with that for diphenyl ether systems [4].

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