

Electron-Transfer Effects in Conjugated Isothiocyanate Systems

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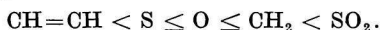
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Some effects of the substituents in 4'-substituted 4-isothiocyanato derivatives of stilbenes, phenyl ethers, diphenylmethanes, diphenyl sulfones, and diphenyl sulfides upon the polarographic reduction of the isothiocyanato group in Britton–Welford buffer have been studied. Under the working conditions —NCS group is reduced which shows itself by a double electron wave. In all systems studied there is a linear relationship between $E_{1/2}$ values of —NCS group and σ_p constants of the substituents. The found reaction constants $\rho_{\pi, R}$ were compared with those found by earlier authors. On the basis of these comparisons the electron-transfer effects in the conjugated systems are discussed. It has been found that the hindering effect of the linking groups upon the transfer of the electron effects in the studied systems is as follows:



The polarographic reductions of —NCS group on an aromatic ring have been studied by a number of workers [1–9]. The presented work relates to the study of the effect of the substituents upon the polarographic reduction of an isothiocyanato group under alkaline conditions in the series of 4'-substituted 4-isothiocyanatostilbenes (*I*), 4-isothiocyanato derivatives of phenyl ethers (*II*), diphenylmethanes (*III*), and diphenyl sulfones (*IV*). The 4-isothiocyanato derivatives of diphenyl sulfides (*V*) have previously been studied [8]. In the present paper their $E_{1/2}$ values in 2-propanol are included as found under our working conditions. The obtained results are compared with similar systems already described [6, 9, 10].

Experimental

Instruments

Polarographic measurements were carried out on an OH-102 Polarograph (Radelkis, Budapest) equipped with a modified Kalousek vessel and separate SCE. The out-flow velocity on the mercury drop electrode m at the mercury level $h = 69$ cm was 2.15 mg s^{-1} and drop time $t_1 = 2.8$ sec (in 0.1 M-KCl at 0 V). The pH of the buffers and of the investigated solutions was measured using a PHM-26 (Radiometer, Copenhagen) pH-meter

equipped with a glass electrode G 202B and K 100-type SCE. $E_{1/2}$ values of the compound under investigation were measured with an accuracy of ± 2 mV on QTK-compensator (Metra, Blansko) using three-electrode system with respect to nonpolarized SCE.

Chemicals

The synthesis of isothiocyanates of the series *I–V* was described earlier [11–15]. The purity of the compounds was verified by determination of physical constants. 2-Propanol was rid of electroactive substances by redistillation and chromatography on a column of Al_2O_3 . Reagent grade chemicals (Lachema, Brno) were used throughout.

Working conditions

The measurements were carried out using 0.2 mM solutions of the investigated compound mixed with an equal volume of supporting electrolyte (Britton–Welford buffer, KH_2PO_4 – $NaOH$, [16]). The concentration of the depolarizer in thus made solutions was 0.1 mM, concentration of alcohol 50% and pH 9.15. All measurements were run at 20°C.

To remove oxygen, purified (alkaline solution of pyrogallol) nitrogen was bubbled through the polarographed solutions for 5 minutes.

Results and Discussion

In investigations on polarographic reduction of isothiocyanates carried out previously [3, 6, 8, 9] methanolic solutions were used. However, the compounds in the series *I–I* are not equally soluble in common solvents (methanol, ethanol, propanol). Therefore our measurements were made in 2-propanol which was found the most suitable solvent. The final concentration of the depolarizer in the polarographed solutions (0.1 mM) does not affect the $E_{1/2}$ values of the derivatives in the investigated series to such an extent as it does in the case when concentration $c < 0.1$ mM.

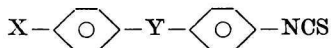
It has been found [3, 6, 8] that the working medium of pH above 9 has little effect upon $E_{1/2}$ values and that $-NCS$ groups do not hydrolyze yet when $pH \approx 9$. This makes the mentioned pH range more suitable for the correlation of $E_{1/2}$ with σ_p constants of the substituents.

It follows also from the previous works that the polarographic curves are, to a certain extent, disfigured by maxima, which make reading of $E_{1/2}$ values more difficult. These maxima appeared also when our compounds were investigated, mainly those of the series *I* and *II*, and partially also of others. Suppression of these maxima by addition of brucine [4] was found unsuitable as then a shift of $E_{1/2}$ to more negative values was observed [9]. As a result, the charge-transfer coefficients [17] exceed the range of tolerable scattering and the values of correlation coefficients become statistically less significant. Therefore, the values of $E_{1/2}$ (Table 1) were obtained by measurements without brucine.

As can be seen in Fig. 1 in individual series there is a reasonable linear relation between the $E_{1/2}$ values of $-NCS$ group and σ_p constants of the substituents. This follows also from the values of charge-transfer coefficients α (Table 1) which are in a quite narrow range allowing thus application of the correlations in the systems under investigation.

It follows from the comparison of the values $\rho_{\pi, R}$ summarized in Table 2 that the polarographic reduction of $-NCS$ group is much less affected by the substituents of compounds *I–V* and of *p*-substituted biphenyl isothiocyanates [9] than by those of *p*-substituted phenyl isothiocyanates [6, 10].

Table 1

Values of $E_{1/2}$ and of charge-transfer coefficients α of the series

Series	Y	No.	X	$-E_{1/2}$ (pH 9.15) [V(SCE)]	α^*
I	CH=CH	1	N(CH ₃) ₂	1.162	0.46
		2	NHOH	1.138	0.33
		3	OCH ₃	1.137	0.48
		4	CH ₃	1.128	0.45
		5	H	1.123	0.49
		6	Cl	1.109	0.48
		7	Br	1.105	0.47
		8	NCS	1.092	0.34
II	O	9	NHOH	1.192	0.28
		10	CH ₃	1.203	0.32
		11	H	1.184	0.31
		12	Cl	1.171	0.36
		13	Br	1.179	0.37
		14	NCS	1.168	0.29
III	CH ₂	15	N(CH ₃) ₂	1.034	0.42
		16	NHOH	1.022	0.39
		17	CH ₃	1.026	0.48
		18	NHCOCH ₃	1.010	0.44
		19	H	1.017	0.48
		20	NCS	0.991	0.43
		21	N(CH ₃) ₂	0.948	0.57
		22	NHOH	0.942	0.44
		23	CH ₃	0.952	0.53
IV	SO ₂	24	H	0.947	0.49
		25	Cl	0.944	0.52
		26	Br	0.941	0.50
		27	NCS	0.939	0.48
V	S	28	N(CH ₃) ₂	1.028	0.54
		29	CH ₃	1.009	0.51
		30	H	0.999	0.50
		31	Cl	0.986	0.51
		32	Br	0.983	0.51
		33	NCS	0.979	0.52

* The value of the coefficient was obtained graphically according to [17].

It ensues from the foregoing that in the systems I–V there exists a hindering effect of the linking groups $-\text{C}_6\text{H}_4-\text{Y}-$ ($\text{Y} = \text{CH}=\text{CH}$, S, O, CH₂, SO₂) upon the transfer of the electron effects of the substituents.

The values of the coefficient of the electron-transfer effects π' [19] investigated was calculated for each series separately. It can be seen from the presented data that the electron effects are transferred in the investigated systems to about one forth compared to the transfer occurring in substituted benzene derivatives (Table 2). The lowest value of π' was found for diphenyl sulfones ($\pi' = 0.03$). The low value of the correlation coeffi-

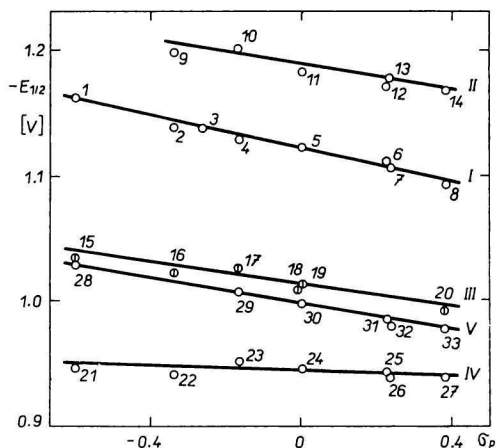


Fig. 1. Correlation of $E_{1/2}$ of substituted isothiocyanates in the series I–V with σ_p constants of the substituents [18].

cient shows that the dependence of $E_{1/2}$ upon σ_p constants is not linear because the r value (0.571) is beyond the statistical significance. The data for diphenyl sulfones are presented to give a complete picture about the electron-transfer effects in conjugated systems of isothiocyanates.

Electron-transfer effects through the linking atoms S and O were studied and compared in various kinds of compounds using different physicochemical methods [20–27]. It follows from some of the cited works [20, 22] that, in contrast to our findings, the atoms of sulfur and oxygen in diphenyl sulfides and phenyl ethers, respectively, have a positive linking effect if compared to biphenyl. This discrepancy may be caused by the fact that the object of the cited works was the interaction between NO_2 and NH_2 groups with pronounced electron-withdrawing and electron-repelling properties. Thus

Table 2

Reaction constants $Q_{\pi, R}$ of the conjugated systems of isothiocyanates

No.	System	$Q_{\pi, R}$ [V]				
1	benzene [6]	+0.22		0.96	1	
2	biphenyl [9]	+0.07			0.32	
3	stilbene	+0.065	0.003	0.989	0.003	0.30
4	diphenyl sulfide	+0.052	0.002	0.995	0.002	0.24
5	phenyl ether	+0.048	0.009	0.932	0.005	0.22
6	diphenylmethane	+0.042	0.007	0.940	0.006	0.49
7	diphenyl sulfone	+0.007	0.005	0.571	0.004	0.03

s_e — error of the line slope,

r — correlation coefficient,

s — standard deviation,

π' — coefficient of the electron-transfer effects.

the nature of the transfer of electron effects through the mentioned linking atoms may be different from that showing itself by the polarographic reduction of $-NCS$ group. This assumption is in agreement with the results obtained elsewhere [26].

It was found from the differences in values of $\rho_{\pi,R}$ constants as well as from the comparison of the electron-transfer coefficients π' that the hindering effect of the linking group upon the electron-transfer effect is, in the systems under investigation, as follows



This is in agreement with the results obtained from the IR studies [11–15].

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