

Isothiocyanates. XL.

Reaction kinetics of isothiocyanates having a longer conjugated system with OH^- anions and NH_2 group of glycine

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The reactivity of isothiocyanates of conjugated stilbene, azobenzene, and diphenyl oxide systems with OH^- anions and NH_2 group of glycine was examined. The rate constants of addition, calculated from kinetic measurements, were correlated with σ_p constants of substituents. The electron transfer in the systems under study is discussed on the basis of comparison of the line slopes in particular systems.

The reactivity of the $-\text{NCS}$ group, bound to various systems, with OH^- anions, NH_2 and SH groups has already been reported [1–5].

This paper refers to the interaction of electrons in longer conjugated systems on the basis of reactivity of the $-\text{NCS}$ group measured kinetically. So far, we have investigated various isothiocyanates [6–9] and have shown that the effect of substituents could be seen both on the position of the asymmetric $-\text{NCS}$ vibration absorption band in the infrared spectrum ($2000\text{--}2200\text{ cm}^{-1}$) and on the values of polarographic half-wave potentials. The obtained results, although a good linear dependence was observed, are not fully substantiated from the thermodynamic point of view [10, 11] and therefore we consider the solution of this problem by means of kinetic measurement more significant; in this case the effect of substituent is manifested immediately in the moment of reaction.

Experimental

Chemicals

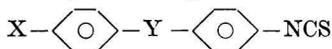
Isothiocyanates under study (Table 1) were prepared according to [6–8]. Before use, they were recrystallized and their purity checked chromatographically. Some of thiourea-decarboxylic acids, serving for identification of the reaction products of isothiocyanates with glycine, were synthesized according to [3]. The identity of products obtained from the reaction with OH^- anions was verified by comparison with the appropriate electronic spectra [1]. All solvents and buffer constituents were of analytical grade (Lachema, Brno). Dioxan and methanol for spectral and kinetic measurements were purified in the usual manner [12]. Glycine (A.R. Nutritional Biochemical Corporation) was used directly.

Apparatuses

The electronic spectra of isothiocyanates in methanol were measured with a Specord UV VIS Zeiss apparatus at $25 \pm 0.2^\circ\text{C}$. The solubility and rate constants of additions

Table 1

Values of rate constants of glycine and OH^- addition on substituted isothiocyanates of general formula



Series	Y	No.	X	k_{NH_2} [$\text{l mol}^{-1} \text{min}^{-1}$]	k_{OH} [$\text{l mol}^{-1} \text{min}^{-1}$]	$S \cdot 10^{-7}$ [mol l^{-1}]
I	-CH=CH-	1	H	25.69 ± 0.54	9.41 ± 0.24	3.13
		2	CH ₃	21.63 ± 0.48	6.84 ± 0.22	2.27
		3	Cl	31.30 ± 0.39	12.75 ± 0.23	3.07
		4	Br	30.70 ± 0.43	11.99 ± 0.26	2.95
		5	NCS	38.60 ± 0.68	14.82 ± 0.32	1.98
		6	NO ₂	52.48 ± 0.23	20.42 ± 0.51	2.03
		7	CH ₃ O	20.28 ± 0.51	5.96 ± 0.31	2.29
		8	(CH ₃) ₂ N	15.33 ± 0.32	4.81 ± 0.17	2.38
II	-N=N-	1	H	34.30 ± 0.28	25.45 ± 0.49	3.64
		2	CH ₃	26.71 ± 0.41	22.04 ± 0.53	2.30
		3	Cl	42.00 ± 1.05	28.16 ± 0.56	4.08
		4	Br	40.30 ± 0.84	29.51 ± 0.32	4.20
		5	NCS	51.30 ± 1.13	35.90 ± 0.33	2.87
		6	NO ₂	63.09 ± 1.39	46.80 ± 0.77	3.38
		7	CH ₃ O	24.20 ± 0.53	16.49 ± 0.44	2.16
		8	(CH ₃) ₂ N	22.10 ± 0.17	13.40 ± 0.61	2.74
III	-O-	1	H	9.81 ± 0.42	6.03 ± 0.34	3.19
		2	CH ₃	10.23 ± 0.51	6.17 ± 0.36	2.57
		3	Cl	13.49 ± 0.61	7.08 ± 0.31	3.05
		4	Br	13.19 ± 0.62	8.51 ± 0.39	2.06
		5	NCS	13.81 ± 0.54	10.23 ± 0.58	1.42
		6	NO ₂	14.81 ± 1.17	12.03 ± 0.63	1.47

were determined spectrophotometrically on a Specord UV VIS and VSU-1 Zeiss, Jena apparatuses in heatable cells. The pH values of reaction mixtures were measured using glass and calomel electrodes and a Radelkis pH meter.

Kinetics measurements

The reaction between the particular isothiocyanate and glycine was examined in a reaction mixture composed of methanol (9.9 ml), pH 9.8 borate buffer solution (8 ml, 0.1 M) and an aqueous solution of glycine (2 ml; 5×10^{-2} M). The kinetics of the OH^- anions addition was investigated in a reaction mixture containing methanol (9.9 ml) and sodium hydroxide solution (10 ml; 5×10^{-3} to 1×10^{-1} M); a stock solution of isothiocyanate in dioxan (0.1 ml; $1-5 \times 10^{-3}$ M) was added into the heatable reaction mixture. The concentration decrease of isothiocyanate or the concentration increase of the reaction product were determined spectrophotometrically in regular time intervals at $25 \pm 0.2^\circ\text{C}$ up to the end of the reaction. The dissociation constant value $\text{p}K$ 9.778 was used when calculating the concentration of glycine as reactant in the form of a free base [13].

The solubility of isothiocyanates was determined spectrophotometrically by the downward saturation method [14]. The calibration curves were constructed using the

absorbancy values of solutions at 25°C with 10% of methanol added. Each derivative was measured three times: Table 1 lists the average values of molar solubilities thus obtained in water.

Results and discussion

The kinetics of addition of both OH^- anions and NH_2 group of glycine to substituted isothiocyanates of stilbene, azobenzene, and diphenyl ether, given in Table 1, was measured in order to investigate the electron effect of various substituents in positions 4 and 4' on the $-\text{NCS}$ functionality. The reaction conditions satisfy the pseudounimolecular course. The apparent rate constants, which are dependent either on the concentration of glycine or on OH^- anions, were calculated from the line slope of the $\log(E - E_\infty)$ or $\log(E_\infty - E)/\text{time}$ function. Instead of the effective values of isothiocyanate or reaction product concentration changes the equivalent values of absorbancy changes were substituted. The effective values of rate constants were calculated from the concentration of the added component. To obtain reliable results, each derivative was measured three times at least.

As seen from the values of rate constants, the reaction rate raises with the increase of electron-accepting character of the substituent, whereas electron-donating substituents decrease the reaction rate. The observed dependence well reflects the fact that the reaction under study is a nucleophilic addition subject to an attack at the carbon atom

of the $-\text{NCS}$ group bearing a partial positive charge $\text{R}-\overset{\delta+}{\text{N}}=\overset{\delta-}{\text{C}}=\text{S}$. It is obvious that the reaction rate, under constant reaction conditions, depends on the magnitude of the positive charge on the carbon atom of the $-\text{NCS}$ group. The magnitude of this charge varies and is, in the systems considered, substituent dependent.

It has been found that all isothiocyanates in question react more easily with glycine than with OH^- anions. The difference is greater with stilbene and azobenzene derivatives and almost none with those of diphenyl ethers.

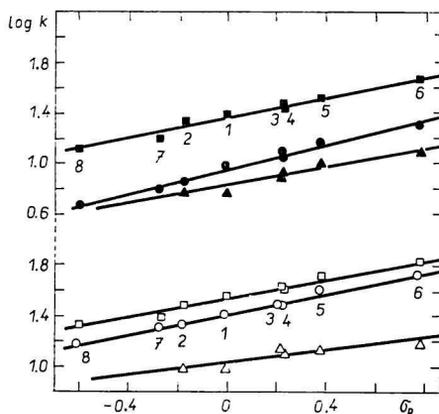


Fig. 1. The dependence of rate constants of glycine addition (full points) and addition of OH^- anions (void points) upon Hammett σ constants of substituents. The values ρ (slopes) and r (correlation coefficients) are listed in Table 2. The plot shows derivatives of stilbene (\bullet), azobenzene (\blacktriangle), and diphenyl ether (\square); the numbering of derivatives is identical with that in Table 1.

A linear dependence has been obtained when logarithms of rate constants were correlated with σ_p constants of substituents in order to evaluate quantitatively the effect of substituent on the reaction rate (Fig. 1). Values of correlation coefficients r (Table 2) indicate a good agreement of $\log k$ values with σ_p constants of substituents.

Table 2

Values of line slopes ρ and correlation coefficients r characteristic of the dependence of logarithms of rate constants of addition of glycine and OH^- anions on σ constants of substituents (n = number of compounds in particular series)

Series	Y		ρ_{NH_2}			ρ_{OH}	
I	—CH=CH—	8	0.38	0.995	8	0.48	0.984
II	—N=N—	8	0.35	0.972	8	0.39	0.984
III	—O—	6	0.19	0.866	6	0.35	0.936

As evidenced by the values of reaction constants, ρ , the greatest effect of substituent, due to electron transfer in systems under study, on the reaction rate has been found with derivatives of stilbene, whereas diphenyl ether system exhibits the greatest "retardation" effect. A low value of the reaction constant, ρ , characteristic of the reactions examined, indicates the bimolecular mechanism of the addition reaction in which no strong polarizing groups are involved in the transition or rate-determining step.

The transfer coefficient, π' , found in our series of compounds is in accordance with that reported for this type of reaction [11] (Table 2).

When comparing reaction rates of 4-isothiocyanatoazobenzene and isothiocyanatostilbene derivatives it becomes apparent that the former series react more easily. This fact agrees with the statement that the azobenzene system is more electron-accepting than that of stilbene, whereas in electron transfer process it exhibits a greater retardation effect [15].

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