

HYDROLYSIS KINETICS AND MECHANISM OF DIARYLTHIOCARBAMATES IN 20% AQUEOUS DIOXANE MEDIUM

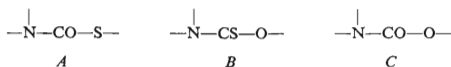
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Substituted S-aryl and O-aryl N-arylthiocarbamates have been synthesized. Kinetic studies of hydrolysis of these compounds in 20% aqueous dioxane prove the ElcB mechanism. The found Hammett reaction constants, activation entropy values, Brønsted coefficients, and comparison of reactivity with N-methyl analogues have been discussed as criteria of the mentioned mechanism. Hydrolysis results of thiocarbamates and carbamates in the same medium are compared.

The aim of this work is to compare behaviour of thiocarbamates type *A* and *B* and carbamates type *C* in hydrolyzing medium. For this purpose S-aryl N-arylthiocarbamates type *A* and O-aryl N-arylthiocarbamates type *B* were synthesized. The base-catalyzed hydrolysis can be presumed to go by ElcB mechanism with the sub-



strates having hydrogen atom at nitrogen, whereas with other substrates the $B_{Ac}2$ mechanism is operating¹⁻³. To ensure the necessary solubility of the studied compounds, and to ensure the comparison with hydrolysis of the structurally close carbamates³ type *C*, we have chosen 20% aqueous dioxane as the reaction medium.

EXPERIMENTAL

Reagents

Benzenethiol and its 4-methyl and 4-chlorosubstituted derivatives were prepared by standard procedure⁴ from the respective benzenesulphonyl chlorides, 4-nitrobenzenethiol was prepared from 4-nitrochlorobenzene⁵.

3-(Trifluoromethyl)benzenethiol: 1.6 g magnesium shavings was treated with 15 g 3-bromotri-fluoromethylbenzene in 75 ml ether, whereupon 1.9 g sulphur in 100 ml benzene was added with stirring during 30 min. The mixture was heated to boiling, cooled, and decomposed with solu-

tion of 20 ml conc. hydrochloric acid and 200 ml water. The organic layer was separated and treated with 5 g zinc powder and 100 ml water and 10 ml conc. hydrochloric acid with stirring at 25°C during 2 h. The mixture was steam-distilled, and the distillate was mixed with 50 ml 10% aqueous potassium hydroxide. The obtained solution was extracted twice with 50 ml ether. The aqueous phase was acidified and the separated product was removed with benzene. After drying the benzene phase, the product was obtained as a fraction boiling within 161 to 163°C under atmospheric pressure. Yield 7.2 g (60.7%), oil, n_D^{20} 1.4122. For $C_7H_5F_3S$ (178.2) calculated 47.14% C, 2.81% H, 0.56% acid hydrogen; found: 46.95% C, 3.00% H, 0.53% acid hydrogen. IR spectrum: $\nu(S-H)$ 3420 cm^{-1} .

4-Nitrophenyl isothiocyanate was prepared from 4-nitroaniline⁶.

Substituted O-arylthiocarbonyl chlorides were prepared from the corresponding phenols by reaction with thiophosgene according to Rivier⁷.

S-Aryl N-Arylthiocarbamates: Solution of 0.01 mol of the respective benzenethiol in 5 ml benzene was mixed with solution of 0.01 mol substituted phenyl isocyanate in 5 ml benzene. The mixture was heated at 120°C in a sealed ampoule 24 h. The product crystallized after evaporation of 7 ml benzene and was recrystallized from ethanol. As the thiocarbamates prepared from 4-chloro, 3-trifluoromethyl, and 4-nitrobenzenethiol by reaction with 4-nitrophenyl isocyanate underwent reesterification in ethanol to give ethyl N-(4-nitrophenyl)carbamate, the raw products were submitted to chromatographic separation on a silica gel column in benzene using benzene-ethyl acetate 5 : 1 as eluent. The yields were within 24 to 85%. Melting point and results of elemental analyses are given in Table I.

O-Aryl N-(4-Nitrophenyl)thiocarbamates: 0.022 mol 4-nitroaniline in 10 ml dioxane was mixed with 0.01 mol O-arylthiocarbonyl chloride in 5 ml dioxane. The mixture was heated at 70°C 30 min. After cooling the precipitated 4-nitroaniline hydrochloride was filtered off, and the filtrate was mixed with 150 ml 0.5% aqueous hydrochloric acid. After about 5 min stirring the obtained solid was collected by suction and crystallized from n-heptane. Yields of pure O-aryl N-(4-nitrophenyl)thiocarbamates were within 30 to 45%. Melting points and results of elemental analyses are given in Table I.

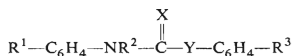
Materials Balance Tests

The hydrolysis products of S-aryl N-arylthiocarbamates, formed by heating the starting substances in 20% aqueous dioxane buffers for 1 h, were separated with ether and submitted to chromatography on Silufol, using benzene-ethyl acetate 5 : 1 as eluent. Positions of individual fractions were detected by UV light and compared with those of the expected hydrolysis products. Identification of products was also accomplished by comparison of UV spectra of the reaction mixture after hydrolysis with those of the model substances. Solution of sodium N-(4-nitrophenyl)-carbamate, which was used as a model substance, was prepared by mixing 4-nitrophenyl isocyanate with 20% aqueous dioxane solution of 5% sodium hydroxide. In similar way solution of sodium N-methyl-N-(4-nitrophenyl)carbamate was prepared from N-methyl-N-(4-nitrophenyl)-carbamoyl chloride. The hydrolysis products of O-aryl N-(4-nitrophenyl)thiocarbamates were obtained by 5 min heating of these substrates in 0.1M-NaOH in 50% aqueous dioxane or pure 50% aqueous dioxane at 50°C. From these solutions the products or intermediates were obtained by acidification to pH 5 and extraction in ether and its evaporation. The products and intermediates were separated chromatographically on Alufol using light petroleum-ethyl acetate 5 : 1 as eluent.

Kinetic Measurements

The hydrolysis of diaryl thiocarbamates was followed spectrophotometrically in media of chloride, chloroacetate, acetate, phosphate, borax, and carbonate buffers or in solutions of potassium

TABLE I
Results of Elemental Analyses and Melting Points of Diarylthiocarbamates



Denoted as	R ¹ R ³	R ²	X Y	Formula (m.mass)	M.p., °C	Found/Calculated		
						% C	% H	% N
<i>la</i>	H H	H	O S	C ₁₃ H ₁₁ NOS (229.3)	120—122 ^a	—	—	—
<i>lb</i>	4-CH ₃ H	H	O S	C ₁₄ H ₁₄ NOS (243.3)	159—160	69.98 69.10	5.45 5.38	5.71 5.76
<i>lc</i>	3-Cl H	H	O S	C ₁₃ H ₁₀ ClNOS (263.7)	111—112	59.10 59.19	3.70 3.82	5.15 5.30
<i>ld</i>	4-NO ₂ H	H	O S	C ₁₃ H ₁₀ N ₂ O ₃ (274.3)	138—139	57.12 56.93	3.64 3.67	10.22 10.21
<i>le</i>	4-NO ₂ 4-CH ₃	H	O S	C ₁₄ H ₁₂ N ₂ O ₃ S (288.4)	145—146	58.46 58.31	4.45 4.19	9.58 9.72
<i>lf</i>	4-NO ₂ 4-Cl	H	O S	C ₁₃ H ₉ ClN ₂ O ₃ S (308.7)	157—159	50.15 50.53	2.79 2.91	8.82 9.07
<i>lg</i>	4-NO ₂ 4-NO ₂	H	O S	C ₁₃ H ₉ N ₃ O ₅ S (319.3)	161—163	49.14 48.85	3.05 2.82	12.80 13.15
<i>lh</i>	4-NO ₂ 3-CF ₃	H	O S	C ₁₄ H ₉ F ₃ N ₂ O ₃ S (342.3)	122—124	49.50 49.12	2.60 2.63	8.39 8.18
<i>li</i>	4-NO ₂ H	CH ₃	O S	C ₁₄ H ₁₂ N ₂ O ₃ S (288.3)	69—70	58.32 58.31	3.98 4.19	10.03 9.72
<i>IIa</i>	4-NO ₂ H	H	S O	C ₁₃ H ₁₀ N ₂ O ₃ S (274.3)	118—119	56.75 56.93	3.72 3.67	10.41 10.21
<i>IIb</i>	4-NO ₂ 4-CH ₃	H	S O	C ₁₄ H ₁₂ N ₂ O ₃ S (288.4)	98—100	58.42 58.31	4.41 4.19	9.72 9.72
<i>IIc</i>	4-NO ₂ 3-Cl	H	S O	C ₁₃ H ₉ ClN ₂ O ₃ S (308.7)	108—110	50.50 50.53	2.93 2.91	9.06 9.08
<i>IIId</i>	4-NO ₂ H	CH ₃	S O	C ₁₄ H ₁₂ N ₂ O ₃ S (58.31)	95—97	58.62 58.31	4.40 4.19	9.85 9.72

^a Ref.¹⁶ gives m.p. 122—123°C.

hydroxide in 20% aqueous dioxane. We either measured continuously the thiocarbamate decrease in the reaction mixture within pH 2.1 to 13.1, or we adopted the method of withdrawing samples to measure the kinetic course of hydrolysis by increase of the substituted aniline after acidification of the reaction mixture. The reaction mixture was prepared by injection of 10 μ l dioxane solution of thiocarbamate to 3 ml 20% aqueous dioxane buffer solution in tempered cell or reaction vessel. This method was used for experiments having half-lives above 60 s at 25–85°C. The concentration changes of thiocarbamates or products or intermediates were determined spectrophotometrically using a Specord UV VIS apparatus (Zeiss, Jena). The reactions with the hydrolysis half-life below 60 s were carried out with a Durrum-Gibson model D-110 stopped-flow spectrophotometer by mixing equal volumes of aqueous-dioxane solutions of thiocarbamates of pH about 2 and buffer solutions of double concentration. The initial thiocarbamate concentration in the reaction mixture was within 1 to 2 $\cdot 10^{-5}$ M. The pH values of the individual solutions were determined with a pH Meter 4c (Radiometer, Copenhagen) at 25°C. The values ΔS^\ddagger were calculated from two to four k_{obs} values from the range 25 to 45°C. Values of the ionization constants of the benzenethiols were determined by the spectrophotometric method⁸ in buffer solutions with constant ionic strength ($\mu = 1.0$; KCl).

RESULTS AND DISCUSSION

Spectral analysis of reaction products of the compounds type *A* or their thin layer chromatography revealed that in the chosen reaction medium the hydrolysis of thiocarbamates *Ia* to *Ii* produces the respective benzenethiol and aniline or sodium *N*-arylcarbamate (at pH above 10). The same method proved that hydrolysis of thiocarbamates type *B* (compounds *IIa* to *IId*) produced the respective phenol, 4-nitrophenyl isothiocyanate and 4-nitroaniline. The corresponding benzenethiols could not be detected. From the mentioned experiments it follows that the isomerization observed under different conditions⁹ does not take place during preparation of the samples or hydrolysis.

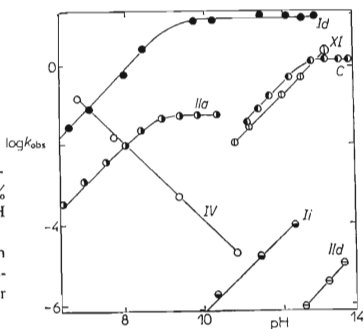


FIG. 1

Hydrolysis Rate of Thiocarbamates, Carbamates and Their Intermediates in 20% Aqueous Dioxane at 25°C at Various pH Values

The compounds *IV* and *XI* are sodium *N*-(4-nitrophenyl)carbamate and 4-nitrophenyl isothiocyanate, respectively, for the other numbers see Table I.

Measurement of the rate constants k_{obs} at various pH values enabled construction of pH profiles for the thiocarbamates *Id* and *Ila* (Fig. 1). The values K_a and k_2 were calculated from Eq. (1a) for the region $[\text{H}^+] \gg K_a$, and from Eq. (1b) for $[\text{H}^+] \ll K_a$.

$$\log k_{\text{obs}} = \log k_2 - pK_a + \text{pH}, \quad (1a)$$

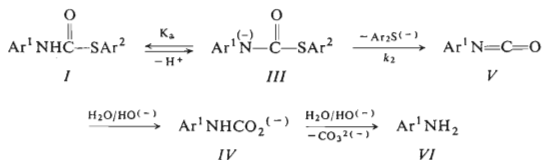
$$\log k_{\text{obs}} = \log k_2. \quad (1b)$$

The ionization constants pK_a found from kinetic data for the thiocarbamates *Id* and *Ila* are 9.3 and 8.9, respectively. The pK_a values of ionization of the N—H bond are lower by more than two units than those found for ionization of phenyl N-(4-nitrophenyl)carbamates³ ($pK_a = 12.5$). In our opinion the enhanced acidity of the thiocarbamate *Ila* is due to lowered tendency of carbon and sulphur to form C=S bonds by $2p_\pi - 3p_\pi$ overlap. A similar acidity increase was observed when comparing thiourea and urea in ammonia medium¹⁰.

In thiocarbamate *Id* cross-conjugation is obviously less important than in carbamates, which also increases its ability to split off the proton. The pK_a values of thiocarbamates *Iib* and *Iic* were calculated from Eq. (1a), and from these values the reaction constant $\rho = 0.9$ was obtained. The practically identical value $\rho = 1$ was found for ionization of carbamates³ in accordance with the fact that the substituent effects are transferred by the same atoms, *i.e.* carbon and oxygen. The reaction constant of ionization of thiocarbamates *Id–Ih* was assessed $\rho = 0.7$ (see below). This somewhat lower value agrees with the fact that the substituent effects are transmitted less easily by sulphur atom.

Mechanism of Hydrolysis of Thiocarbamates

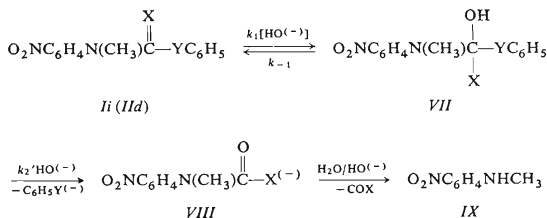
Figure 1 represents dependence of hydrolysis rate of S-aryl N-(4-nitrophenyl)thiocarbamate *Id* on pH values in 20% aqueous dioxane along with decarboxylation rate of its intermediate — sodium N-(4-nitrophenyl)carbamate (*IV*, Scheme A)



SCHEME A

in the same medium. The rate-limiting step consists in decomposition of the conjugated base of the substrate (*Id*, mechanism ElcB). At pH above 8 the subsequent

decarboxylation of sodium N-(4-nitrophenyl)carbamate is slow (Fig. 1), so that in the medium chosen the anion *IV* represents a stable intermediate¹¹. At pH below 7 the subsequent decarboxylation is fast, and 4-nitroaniline is the product¹¹. In accordance with the ElcB mechanism of the hydrolysis of the series of S-aryl N-arylthiocarbamates *Ia* to *Ih*, the respective ΔS^\ddagger values are positive (e.g. for *Id* it is $\Delta S^\ddagger = 10.4 \text{ J mol}^{-1} \text{ K}^{-1}$) (see also ref.¹). The hydrolysis rate constant of S-phenyl N-methyl-N-(4-nitrophenyl)thiocarbamate (*Ii*) was found lower by 8 orders of magnitude, which agrees with B_{Ac}2 mechanism of hydrolysis of this thiocarbamate (Scheme B). The bimolecular mechanism also agrees with the found negative value $\Delta S^\ddagger =$

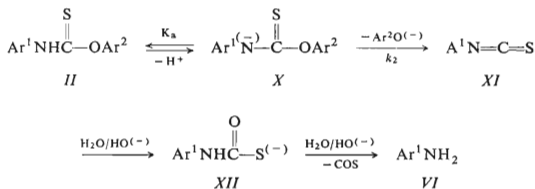


for *Ii*: X = O; Y = S, *IId*: X = S; Y = O

SCHEME B

$= -48.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Hydrolysis of *Ii* produces carbamate *VIII* as a relatively little stable intermediate which rapidly decarboxylates on acidification. O-Phenyl N-(4-nitrophenyl)thiocarbamate (*Iia*) is hydrolyzed, at pH 6–10, faster than phenyl N-(4-nitrophenyl)carbamate by about 2 orders of magnitude³, but it is hydrolyzed more slowly than the compound *Id* by 2 orders of magnitude (Fig. 1). The found value $\Delta S^\ddagger = 17.6 \text{ J mol}^{-1} \text{ K}^{-1}$ agrees with the ElcB mechanism of the hydrolysis². From the observed dependences of the hydrolysis rate of thiocarbamate *Iia* and that of 4-nitrophenyl isothiocyanate (*XI*) (Fig. 1) it is obvious that this compound is a stable intermediate of the hydrolysis (Scheme C). From kinetic data (Fig. 1) it follows that the compound *Iia* behaves in different way from that of isocyanate *XI*. Continuous recording of spectra during hydrolysis of 4-nitrophenyl isothiocyanate showed isosbestic points indicating that no intermediate is accumulated in the hydrolysis. We presume the splitting of sodium N-(4-nitrophenyl)thiocarbamate to be a fast reaction in these media, which agrees with literature data^{12,13}. The hydrolysis of the compounds *Iia* to *Iic* can be described by Scheme C. No sodium N-methyl-N-(4-nitrophenyl)carbamate was detected in hydrolysis of O-phenyl N-methyl-N-(4-nitrophenyl)thiocarbamate (*IId*), wherefrom it can be concluded that the reaction rate is limited by addition of hydroxyl ion to C=S group of the substrate *IId*,

and thiocarbamate VIII is transformed rapidly to N-methyl-4-nitroaniline (IX) (Scheme B). The found value is $\Delta S^\ddagger = -83.9 \text{ J mol}^{-1} \text{ K}^{-1}$ for hydrolysis of *IId*. This thiocarbamate is hydrolyzed more slowly than *Ila* by more than 8 orders of magnitude.



SCHEME C

Substituent Effects in Hydrolysis of Thiocarbamates

Figure 2 presents the values of the observed rate constants $\log k_{\text{obs}}$ of hydrolysis of the compounds type A and B at 25°C at various pH values. The found reaction constant of hydrolysis of the series of S-aryl N-(4-nitrophenyl)thiocarbamates *Id*–*Ih* at pH 5 was $\rho_{\text{obs}} = 2.9$. The constant ρ_{obs} corresponds to the value $\rho_1 + \rho_2$, where ρ_1 represents the effect of substituent in Ar^2 on the equilibrium constant K_a , and ρ_2 corresponds to splitting of the conjugated base *XII* (Scheme A). As the proton is split off from the third atom next to sulphur, the value $\rho_1 = 0.7$ can be obtained by assessment for this dissociation, if the value $\rho_1 = 1$ for the oxygen analogue is taken into account along with the lowered ability of sulphur (compared to oxygen)

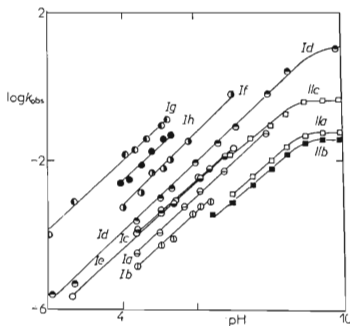


FIG. 2

Hydrolysis Rate of Diarylthiocarbamates in 20% Aqueous Dioxane at 25°C at Various pH Values

The rate constants k_{obs} are given in s^{-1} . For numbers of the individual thiocarbamates see Table I.

to transmit polar effects (see the value $\rho_{\text{PhSH}} = 1.8$ and $\rho_{\text{PhOH}} = 2.7$ in ref.¹⁴), *i.e.* the factor 0.7. Hence, the proper splitting has the value $\rho_2 = 2.9 - 0.7 = 2.2$. This constant is lower than that found for splitting of the oxygen analogue type C ($\rho_2 = 2.9$, ref.³). Therefore it follows that in the activated complex the splitting of C—S bond is less substituent-dependent than that of C—O bond, which is also connected with the fact that for correlations of the compounds type A and their oxygen analogues type C the substituent constants σ and σ^- , respectively, appear more suitable³. From the k_2 values of splitting of the conjugated bases of thiocarbamates *Ila–Ilc* we could estimate the constant $\rho_2 = 1.5$ which agrees with that of O-aryl N-phenylthiocarbamates² ($\rho = 1.3$), whereas the oxygen analogues have a higher reaction constant ($\rho = 2.9$)³. Therefrom it follows that bond splitting in the transition state of spontaneous splitting of the conjugated base of thiocarbamates *Ila–Ilc* is the least advanced among the investigated three series, and, therefore, substituents have the lowest effects. The lowered sensitivity is ascribed to dipolar character of carbon–sulphur bond, the positively charged carbon decreasing the splitting sensitivity to substituent effects. Effect of substituents in the benzene ring bound through nitrogen was studied with the thiocarbamates *Ia–Id*. The reaction constant found has the value $\rho = 1.2$ which is practically doubled as compared with that of the oxygen analogues³ ($\rho = 0.64$). The polar effects of the substituents from the ring Ar¹ on the investigated reaction rate, *i.e.* ionization and splitting of C—S bond are opposite. Compensation of the both effects is obviously substantially lower due to sulphur (as compared with the oxygen analogues), a substituent X affects the C—S bond splitting less than the C—O bond splitting, which is connected with the splitting progress in the activated complex and its position on the reaction coordinate.

TABLE II

Characteristical Constants of Hydrolysis of Thiocarbamates Type A and B and Carbamate Type C

Type	ρ_{obs}^a	ρ_{obs}^b	ρ_1	ρ_2	β^c	$\log k_2^c$	pK_a^c
A	1.2 ^d	2.9 ^e	0.7	2.2	-1.22	1.24	9.3
B	—	—	0.9 ^{f,h}	1.5 ^{g,h}	-1.18 ^h	-1.19	8.9
C	0.64	3.9	1.0	2.9	-1.36	0.19	12.5

^a Effects of substituents in Ar¹; ^b effects of the substituents in Ar²; ^c for the substrate having Ar¹ = O₂NC₆H₄ and Ar² = C₆H₅; ^d more accurately $\rho_{\text{obs}} = (1.24 \pm 0.21)$, $r_\rho = 0.998$, ^e more accurately $\rho_{\text{obs}} = (2.86 \pm 0.10)$, $r_\rho = 0.997$; ^f more accurately $\rho_1 = (0.86 \pm 0.04)$, $r_\rho = 0.999$; ^g more accurately $\rho_2 = (1.47 \pm 0.01)$, $r_\rho = 0.999$; ^h the value given has approximative character, because it was calculated from 3 points.

Dependence of Bimolecular Rate Constants of Hydrolysis on pK_a of the Leaving Groups

Value of the Brønsted coefficient $\beta = -1.22$ was calculated for the compounds *I*d–*I*h from Eq. (2) using the relations (3) and (4):

$$\log k_2 = \beta pK^{ArSH} + k', \quad (2)$$

$$\log k_2 = 2.2\sigma + 1.24, \quad (3)$$

$$pK^{ArSH} = -1.8\sigma + 6.81. \quad (4)$$

The pK_a values of the substituted benzenethiols were taken from ref.¹⁴ or were determined in 20% aqueous dioxane medium (3-trifluoromethylbenzenethiol pK_a 6.02, 4-nitrobenzenethiol pK_a 5.35). The calculated β value agrees well with those given for hydrolysis of O-aryl N-arylthiocarbamates ($\beta = -1.35$, ref.²), aryl N-(4-nitrophenyl)carbamates³ ($\beta = -1.36$), aryl N-phenylcarbamates¹⁵ ($\beta = -1.17$), and it represents another support for the ElcB mechanism. The value $\beta = -0.25$ was calculated for the hydrolysis of aryl N-methyl-N-phenylcarbamates (series *I*Ia to *I*Ic) going by $B_{Ac}2$ mechanism¹⁵.

Similarly the value of the Brønsted coefficient was calculated for the compound series *I*Ia–*I*Ic ($\beta = -1.18$), using the pK values of phenols from ref.¹³. The found β value also corresponds to the ElcB mechanism.

The described investigation allows to draw the following conclusions about behaviour of thiocarbamates type *A* and *B* and carbamates type *C*: a) in all the three series the compounds containing ionisable N—H bond are hydrolyzed by ElcB mechanism; substitution of this hydrogen by methyl group results in the hydrolysis mechanism being changed to $B_{Ac}2$. b) The fundamental difference between carbamates and thiocarbamates lies in higher acidity of the latter (3 orders of magnitude), which is manifested by increased hydrolysis rate of thiocarbamates by ElcB mechanism in the pH region where the substrates are not completely ionized. c) Decomposition rate of the conjugated bases decreases in the compound series S-aryl N-(4-nitrophenyl)thiocarbamates (type *A*) > O-aryl N-(4-nitrophenyl)thiocarbamates (type *B*) > aryl N-(4-nitrophenyl)carbamates (type *C*). d) The found constants describing the hydrolysis of the investigated compound series *A*, *B*, *C* in 20% aqueous dioxane by ElcB mechanism are summarized in Table II.

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