HYDROLYSIS KINETICS AND MECHANISM OF DIARYLDITHIOCARBAMATES IN 20% AQUEOUS DIOXANE

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Nine diaryldithiocarbamates have been prepared. Kinetic study of their hydrolysis has revealed that this hydrolysis proceeds by ElcB mechanism in the pH range 2 to 12. Values of activation entropies, reaction constants, Brönsted coefficient, and comparison with reactivity of the corresponding N-methyl analogue have been used as criteria for the suggested mechanism. In acid media pH 2 to 0·4 and H_0 −0·6 the hydrolysis follows a mechanism analogous to $A_{Ac}2$. Results of hydrolyses of dithiocarbamates, thiocarbamates and carbamates are compared.

The dithiocarbamates studied in this paper are used as selective pesticides[1,2] and were suggested as corrosion inhibitors[3]. Hydrolytic stability of these compounds has not been studied yet. In acid media hydrolysis of the type $A_{Ac}2$ can be considered[4], whereas in basic media two kinetically indistinguishable mechanisms – $B_{Ac}2$ and ElcB – must be considered[5–7]. The aim of this work is to follow the hydrolysis kinetics of the diaryldithiocarbamates *Ia*–*Ii* in acidic, neutral and alkaline media and suggest the reaction mechanism. Aqueous 20% dioxane was chosen as the reaction medium, so that the results of kinetic measurements might be compared with the values found for oxygen analogues[5–9].

EXPERIMENTAL

Reagents

The diaryldithiocarbamates *Ia*–*Id* and *If*–*Ih* were prepared by mixing solutions of 0·05 mol substituted phenyl isothiocyanate in 10 ml benzene and 0·05 mol substituted benzenethiol in 10 ml benzene. After addition of 3 drops pyridine the mixture was heated in a sealed ampoule on water bath 1 h. After cooling the precipitated product was crystallized from n-heptane, washed with n-pentane and dried. The yields were within 60 to 90%. The melting points and results of elemental analyses are summarized in Table I. The described procedure failed in the case of the compound *Ie*.

Phenyl N-(*4-nitrophenyl*)*dithiocarbamate* (Ie). 1·89 g (0·01 mol) phenyl chlorodithiocarbonate in 5 ml benzene was mixed with 2·76 g (0·02 mol) 4-nitroaniline dissolved in 5 ml tetrahydrofurane at 20°C. The mixture was left to stand at 20°C for 20 days. The separated 4-nitroanilinium chloride was filtered off. After evaporation of solvents the product was decanted with n-pentane, and the precipitated product was collected by suction. Yield 1·9 g (65%), m.p. 144—146°C. This compound was further purified by crystallization from n-heptane. M.p. 146—146·5°C, the elemental analysis is given in Table I.

Phenyl N-*phenyl*-N-*methyldithiocarbamate* (Ii) was prepared according to ref.[10]; m.p. 98—99°C.

Kinetic Measurements

Hydrolysis rates of the diaryldithiocarbamates were followed spectrophotometrically in acetate, borax, phosphate, and carbonate buffers with ionic strength 0·1 or in solutions of sulphuric acid or sodium hydroxide in 20% aqueous dioxane. The measurements were carried out in the pH range 0·4 to 12 and at H_0 —0·6, the decreases of aryl N-phenyldithiocarbamates (*Ie—Ii*) and phenyl N-aryldithiocarbamates (*Ia—Id*) being measured in UV region at 310 nm and 260 nm, respectively. For the measurements 5 µl dioxane solution was injected into 2·5 ml 20% aqueous-dioxane buffer. The measurements were carried out at 25 to 85°C using a Specord UV VIS

TABLE I

Physical properties of diaryldithiocarbamates $XC_6H_4NHCS_2C_6H_4Y$ and results of elemental analyses

No	X Y	Formula (mol. mass)	M.p., °C	Found/Calculated		
				% C	% H	% S
Ia	H	$C_{13}H_{11}NS_2$	105—106[a]	68·61	4·29	27·07
	H	(245·4)		68·52	4·52	26·13
Ib	H	$C_{14}H_{13}NS_2$	120—121	64·55	5·01	24·79
	4-CH_3	(259·4)		64·85	5·02	24·73
Ic	H	$C_{13}H_{10}ClNS_2$	102—103	56·19	3·69	22·99
	4-Cl	(279·8)		55·82	3·57	22·92
Id	H	$C_{14}H_{10}F_3NS_2$	94—94	53·65	3·37	20·40
	3-CF_3	(313·4)		53·67	3·19	20·45
Ie	6-NO_2	$C_{13}H_{10}N_2O_2S_2$	146—146·5	53·41	3·15	22·43
	H	(290·4)		53·72	3·44	22·20
If	4-Br	$C_{13}H_{10}BrNS_2$	83—84	47·68	2·87	19·86
	H	(324·2)		48·16	3·08	19·78
Ig	4-CH_3	$C_{14}H_{13}NS_2$	71—72	64·93	5·16	25·05
	H	(259·4)		64·85	5·01	24·73
Ih	3-Cl	$C_{13}H_{10}ClNS_2$	58—59	55·82	3·40	22·99
	H	(279·8)		55·76	3·57	22·52

[a] Ref.[10] gives m.p. 104—106°C.

and a VSU 2 apparatus (Zeiss, Jena). Faster hydrolyses with halflives below 30 s were measured with a Durrum–Gibson model D-110 spectrophotometer. Very slow hydrolyses were followed at higher temperatures, and the rate constants found were converted to 25°C by means of the Arrhenius relation. The pH values of individual buffers were measured with a Standard PHM 62 apparatus (Copenhagen) at 25°C.

Balance Experiments and Products Identification

The hydrolysis products of diphenyldithiocarbamate formed on 1 h heating of 0·1 g sample in 70 ml 20% aqueous–dioxane buffer at 50°C were neutralized and extracted with ether. The extract was washed with water, concentrated, and submitted to chromatography on Silufol with light petroleum–methanol 19 : 1 as eluent. The hydrolysis products were compared chromatographically with benzenethiol, aniline and phenyl isothiocyanate. Similarly, the spectra of these standards were compared with those of the hydrolysis products. In this way products were identified from acid, neutral and alkaline hydrolysis at pH 0·4, 3·5, 6·5, 10·5 and H_0 −0·6. Ionisation constants of the diaryldithiocarbamates were determined as in previous communication[7].

RESULTS AND DISCUSSION

The dependences log k_{obs} *vs* pH are given in Figs 1 and 2 for the compounds *Ia* and *Ie*, respectively. The experimental points were interlaced by a curve corresponding to Eq. (*1*) for the observed rate constant of pseudomonomolecular reaction,

$$k_{obs} = k_H a_H + k_2 K_a/(K_a + a_H)\,, \tag{1}$$

where the expression $k_H a_H$ involves specific acid catalysis, and the last term cor-

TABLE II

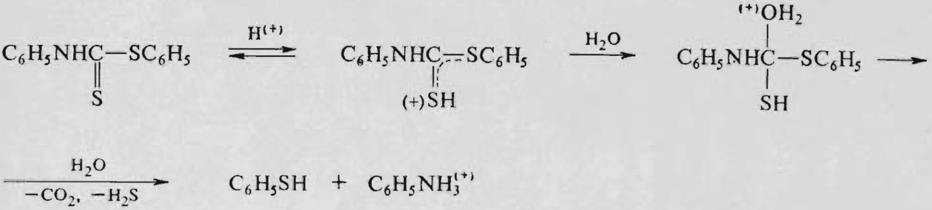
Rate constants of splitting of the conjugated bases and ionisation constants of diaryldithiocarbamates in 20% aqueous dioxane

Compound	log k_2	pK_a
Ia	−2·27	5·25
Ib	−2·45	5·30
Ic	−1·51	5·12
Id	−1·27	5·05
Ie	−1·35	4·90
If	−2·18	5·20
Ig	−2·50	5·50
Ih	−2·01	5·15

responds to base catalysis. In similar way pH profiles were constructed for the compounds *Ib – Ih*. The values log k_2 and pK_a are given in Table II.

Hydrolysis in Acid Medium

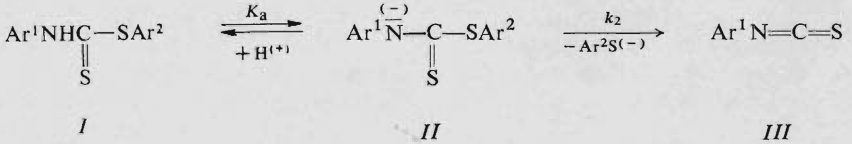
From Fig. 1 it can be seen that the hydrolysis rate constant of the dithiocarbamate *Ia* increases from pH 2 up to H_0 $-0{\cdot}6$, the slope of the dependences of log k_{obs} on these functions being about 1. From kinetic data it cannot be decided whether the hydrolysis follows the mechanism $A_{Ac}2$ or $A_{Ac}1$. From analogous hydrolyses of thiolbenzoate and thiobenzoate[4] in diluted aqueous solutions of sulphuric acid it can be presumed that, within the studied acidity range, the diphenyldithiocarbamate *Ia* is hydrolyzed by a mechanism analogous to $A_{Ac}2$ involving the rate-limiting nucleophilic attack of water on the protonated substrate at the thion sulphur atom (Scheme 1).



SCHEME 1

Hydrolysis in Neutral and Alkaline Media

Fig. 1 represents the pH profile of the dithiocarbamate *Ia*. It is obvious that spontaneous solvolysis does not take place (no "plateau" in the dependence log k_{obs} *vs vs* pH)), the hydrolysis being base-catalyzed from pH about 2 (the slope about 1). From pH about 5 the hydrolysis rate does not depend on hydroxyl ion concentration. This course is typical of the ElcB mechanism. The mechanism is further supported by the finding that phenyl N-phenyl-N-methyldithiocarbamate (*Ii*) is hydrolyzed 7 orders of magnitude slower by the $B_{Ac}2$ mechanism (Fig. 1). In analogy to hydrolysis of thiocarbamates[6,7] it can be presumed that the rate-limiting step consists in decomposition of the conjugated base *II* to the aryl isothiocyanate *III* (Scheme 2).



SCHEME 2

The latter compound was found and chromatographically isolated from the hydrolysis products. In accordance with the ElcB mechanism we could find for alkaline hydrolysis of diphenyldithiocarbamate the value $\Delta S^{\neq} = 79{\cdot}8\ \text{J mol}^{-1}\ \text{K}^{-1}$ (at pH 6·4) which agrees with the date of ref.[6], whereas a negative value $\Delta S^{\neq} = -81{\cdot}65\ \text{J}\,.\,\text{mol}^{-1}\ \text{K}^{-1}$ was found for the hydrolysis of phenyl N-phenyl-N-methyldithiocarbamate (*Ii*). Comparison of the pH profiles of phenyl N-(4-nitrophenyl)dithiocarbamate (*Ie*) and O- and S-phenyl N-(4-nitrophenyl)thiocarbamates[7] or phenyl N-(4-nitrophenyl)carbamate[9] in 20% aqueous dioxane (Fig. 2) reveals that the N—H bond in dithiocarbamates has the highest acidity in the compared series. From comparison with the oxygen analogues[7] it is obvious that the conjugated base of dithiocarbamates is split most slowly. For comparison with literature data we calculated the value of the Brönsted coefficient for the compounds *Ia*–*Id* ($\beta = -1{\cdot}13$). For the calculation we used the $\text{p}K_\text{a}$ values of benzenethiols taken from refs[7,11]. The calculated values β agree well with those given for hydrolyses of N,O-diarylthiocarbamates ($\beta = -1{\cdot}18$) (ref.[6]), S-aryl-N-(4-nitrophenyl)thiocarbamates ($\beta = -1{\cdot}22$) (ref.[7]), aryl N-phenylcarbamates ($\beta = -1{\cdot}17$) (ref.[8]), and aryl N-(4-nitrophenyl)carbamates ($\beta = -1{\cdot}36$) (ref.[9]). Magnitude of this constant presents another support for the ElcB mechanism, because the reactions following the $\text{B}_{\text{Ac}}2$ mechanism show the β values below 0·5 (refs[8,12]).

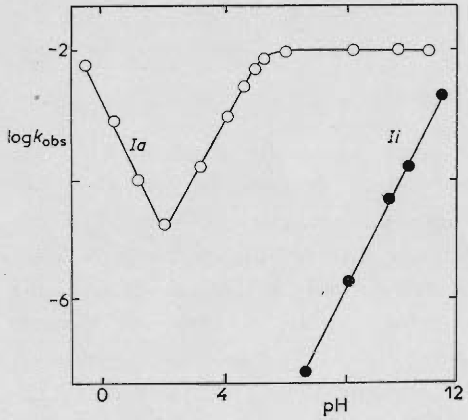


FIG. 1

Dependence log k_{obs} *vs* pH (or H_0) of hydrolyses of diphenyldithiocarbamate (*Ia*) and phenyl N-phenyl-N-methyldithiocarbamate (*Ii*) in 20% aqueous dioxane at 25°C

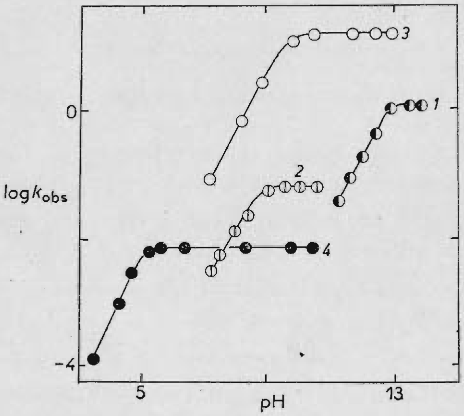


FIG. 2

Dependences log k_{obs} *vs* pH of hydrolyses of phenyl N-(4-nitrophenyl)carbamate *1*, O-phenyl N-(4-nitrophenyl)thiocarbamate *2*, S-phenyl N-(4-nitrophenyl)thiocarbamate *3*, and phenyl N-(4-nitrophenyl)dithiocarbamate *4* in 20% aqueous dioxane at 25°C

Substituent Effects on Acidity and Hydrolysis Rate of Diaryldithiocarbamates

Table II gives the k_{obs} values which were compared with the corresponding substituent constants σ using the Hammett equation. The calculated reaction constant for the C—S bond splitting is $\varrho = 1{\cdot}2$ for the substituents in the N-phenyl ring, which agrees with the value $\varrho = 1{\cdot}2$ found for S-arylthiocarbamates under the same conditions[7]. On the contrary, it is almost double what it was found[9] for carbamates ($\varrho = 0{\cdot}7$). Polar effects of substituents in the N-phenyl ring on the splitting of C—S bond are substantially greater than those of the C—O bond splitting, which is connected with the extent of the bond splitting in the corresponding activated complexes. The calculated reaction constant for the C—S bond splitting is $\varrho = 1{\cdot}9$ for the substituents in the S-phenyl ring, which is lower than that found[9] for the C—O bond splitting in carbamates ($\varrho = 2{\cdot}9$), but it is comparable with that found[6,7] for O- and S-arylthiocarbamates ($\varrho = 1{\cdot}5$ and $2{\cdot}2$, respectively).

The dissociation constants given in Table II were determined in similar way as in ref.[7]. Regression analysis of these values gave the constants $\varrho = 0{\cdot}6$ and $0{\cdot}4$ for the effects of substituents in the N- and S-phenyl rings, respectively, which is less than that found for ionisation of carbamates[9] ($\varrho = 1{\cdot}0$), O-arylthiocarbamates[6] ($\varrho = 0{\cdot}9$), or S-arylthiocarbamates[7] ($\varrho = 0{\cdot}7$). Transmission of polar effects through the atom groupings decreases in the order $\mathrm{O{-}\overset{|}{C}{=}O > O{-}\overset{|}{C}{=}S > S{-}\overset{|}{C}{=}O > \, > S{-}\overset{|}{C}{=}S}$.

REFERENCES

1. Ashton F. M., Crafts A. S.: *Mode of Action of Herbicides*, p. 382. Wiley, New York 1973.
2. Matsushima K., Miyamoto M.: Japan 6 821 055 (1968); Chem. Abstr. *70*, 57 389 (1969).
3. Railsback H. E., Reynolds W. B.: U.S. 2 956 043 (1960); Chem. Abstr. *55*, 18 546 (1961).
4. Edward J. T., Sin Cheong Wong, Welch G.: Can. J. Chem. *56*, 931 (1978).
5. Bränstad J. O., Ekberg G., Nilson J.: Acta Pharm. Suec. *10*, 1 (1973).
6. Sartoré G., Bergon M., Calmon J. P.: J. Chem. Soc., Perkin Trans. 2, *1977*, 650.
7. Mindl J., Balcárek P., Šilar L., Večeřa M.: This Journal *45*, 3130 (1980).
8. Williams A.: J. Chem. Soc., Perkin Trans. 2, *1973*, 1244.
9. Hegarty A. F., Frost L. N.: J. Chem. Soc., Perkin Trans. 2, *1973*, 1719.
10. Rivier M. H.: Bull. Soc. Chim. Fr. *1*, 733 (1907).
11. Chuchani G., Frühlich A.: J. Chem. Soc. (B) *1971*, 1417.
12. Hladká J., Mindl J., Večeřa M.: This Journal *42*, 3316 (1977).

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