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Solvolysis of Thioamides in Alkaline Region in the System of Water—Ethanol

†J. MOLLIN and E. KARÁSKOVÁ

*Department of Inorganic and Physical Chemistry, Faculty of Natural Sciences,
Palacký University, CS-771 46 Olomouc*

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The rate constants of alkaline solvolysis of *N,N*-diphenylthiobenzamide and 4-chloro-*N,N*-dimethylthiobenzamide have been measured. The change in the reaction order with respect to the base concentration, conditioned by change in composition of the solvent, has been discussed on the basis of Taft's mechanisms and equilibrium between the hydroxide and ethoxide ions.

Alkaline solvolysis of thioamides was studied many times [1–6] and the literature agrees in that the reacting component is the neutral thioamide molecule. In aqueous medium the reaction is of first order with respect to concentration of OH ions [1–4, 6], while in the mixture of water—ethanol the reaction order with respect to the total base concentration was found, in some cases, to be higher [5, 6] and changing also with the change of the solvent [6]. Therefore, it seemed to be of interest to gather further data in experiments using solvents with higher content of ethanol and tertiary thioamides as reacting substrates, so that the result was not loaded with error due to possible dissociation of the electrophile.

EXPERIMENTAL

N,N-Diphenylthiobenzamide [7] and 4-chloro-*N,N*-dimethylthiobenzamide [8] were prepared according to the respective literature. The purity of the compounds was checked by determination of melting points and by elemental analysis. The

5×10^{-4} M solutions of the presented compounds were prepared in the mixture of water—ethanol (*N,N*-diphenylthiobenzamide in mixtures of 30, 70, and 90 mass % of ethanol in water and 4-chloro-*N,N*-dimethylthiobenzamide in mixtures of 70 and 90 mass % of ethanol in water). The pH of the solution was adjusted by NaOH solution in the same solvent. For preparation of solutions distilled water, ethanol for UV measurement and NaOH of anal. grade (both from Lachema, Brno) were used. The pH of the reaction mixture could not be measured directly due to substrates interfering in setting of a reproducible potential of the hydrogen electrode.

Therefore, the solutions were prepared without the substrate in the same solvent of the same concentration of NaOH as in the respective reaction mixture. The pH of these solutions were measured by using hydrogen and silver chloride electrodes, while the function of the electrode system was checked by series of buffers [9–11].

The reacting system was analyzed by an E-7 polarograph (Laboratorní přístroje, Prague) with mercury drop electrode (drop time = 2.6 s).

Application of this method was substantiated by existence of a well developed diffusion wave, described in the literature [8].

For kinetic measurements the ampoule technique was used. The ampoules after filling were put into an ultrathermostat the temperature of which was maintained with the accuracy of $\pm 0.1^\circ\text{C}$. Solvolysis of *N,N*-diphenylthiobenzamide proceeded at 89.5°C and solvolysis of 4-chloro-*N,N*-dimethylthiobenzamide at 91.5°C . After suitable time the ampoules were withdrawn, cooled, and their content was analyzed polarographically. The rate constant (k) of the reaction was calculated after introducing the found currents into the equation $\ln(I_0/I_t) = k t$, where I_0 and I_t are the currents of diffusion waves at the beginning of the reaction and in time t , respectively.

RESULTS AND DISCUSSION

The found rate constants are presented in Tables 1 and 2. Figs. 1 and 2 illustrate the dependence of logarithms of rate constants upon pH, together with the data taken from the previous communications [5, 6].

Interpretation of the experimental results may be provided on the basis of the so-called Taft's mechanisms [12] and the unambiguously proved equilibrium [13–15] between the hydroxide and ethoxide ions according to the equation



Table 1. Rate Constants of Solvolysis of *N,N*-Diphenylthiobenzamide in Mixtures of Water–Ethanol at 89.5°C

		w(Ethanol)/%					
		30		70		90	
pH	$k \cdot 10^4/\text{s}^{-1}$	pH	$k \cdot 10^4/\text{s}^{-1}$	pH	$k \cdot 10^4/\text{s}^{-1}$	pH	$k \cdot 10^4/\text{s}^{-1}$
12.73	0.525	13.18	0.515	13.19	0.278		
12.98	0.673	13.43	0.734	14.00	0.575		
13.10	1.20	13.62	1.30	14.17	1.15		
13.30	2.37	13.72	2.17	14.66	2.09		
13.49	5.18	13.87	4.16	14.70	3.16		

Table 2. Rate Constants of Solvolysis of 4-Chloro-*N,N*-dimethylthiobenzamide in Mixtures of Water–Ethanol at 91.5°C

		w(Ethanol)/%			
		70		90	
pH	$k \cdot 10^4/\text{s}^{-1}$	pH	$k \cdot 10^4/\text{s}^{-1}$	pH	$k \cdot 10^4/\text{s}^{-1}$
13.01	0.806	14.10	0.611		
13.08	0.905	14.23	1.07		
13.27	2.25	14.52	2.57		
13.42	4.15	14.69	4.16		
13.59	6.50	14.77	6.19		

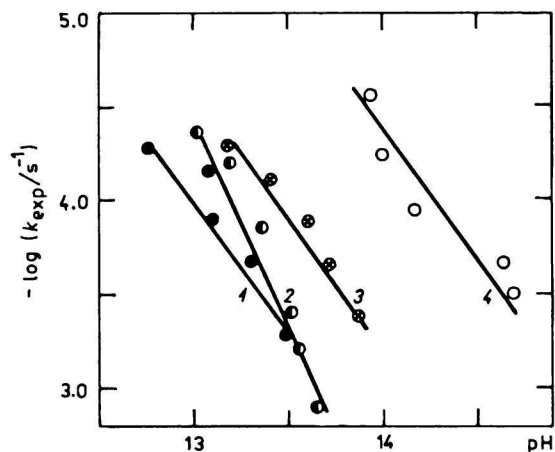


Fig. 1. pH Dependence of $-\log k_{\text{exp}}$ of solvolysis of *N,N*-diphenylthiobenzamide in mixtures of water–ethanol. w(Ethanol)/%: 1. 30, 2. 50, 3. 70, 4. 90.

The reactions expressing both conceptions are shown in Scheme 1, where C_{B^-} represents the total base concentration ($C_{\text{B}^-} = C_{\text{OH}^-} + C_{\text{EtO}^-}$). The reaction products of our experiments have not been argued.

By using the method of quasi-stationary concentrations, for the experimentally found rate constant we obtain the following expression

$$k_{\text{exp}} = k_4 C_{\text{OH}^-} + \frac{k_1 k_3}{k_2 + k_3} C_{\text{EtO}^-} - \frac{k_4 k_5 k_8 K_{\text{w}}^{\text{S}}}{(k_5 + k_6)(k_8 C_{\text{H}^+} + k_9) + k_7 k_9 C_{\text{B}^-}} - \frac{k_4 k_5 k_9 K_{\text{w}}^{\text{S}}}{(k_5 + k_6)(k_8 C_{\text{H}^+} + k_9) C_{\text{H}^+} + k_7 k_9 K_{\text{S}}} \quad (1)$$

where K_{w}^{S} is the ion product of water in the given solvent and K_{S} is the ion product of the solvent. From eqn (1) it is evident that the experimentally found rate constant is a complicated function of

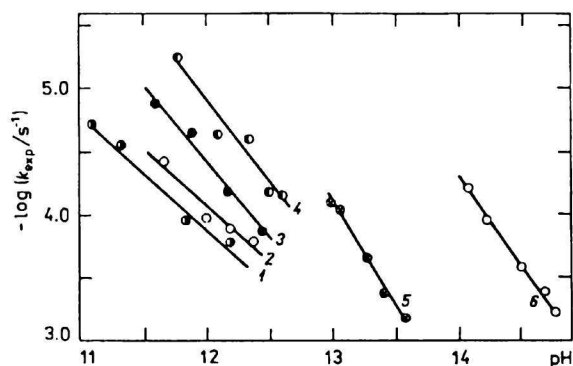
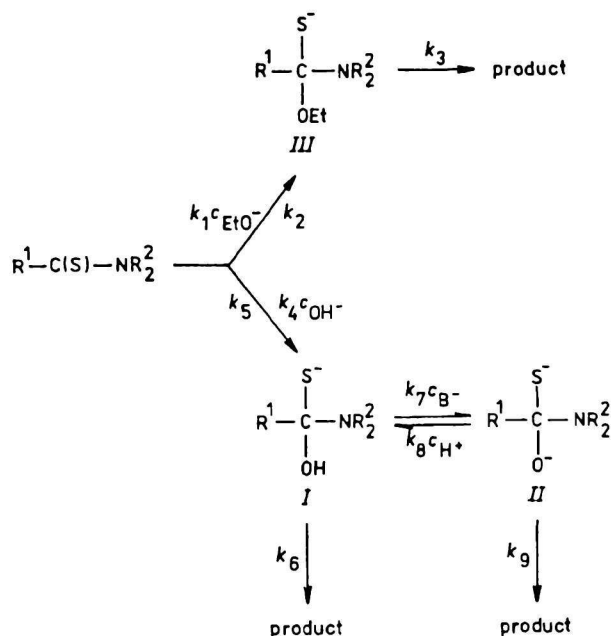


Fig. 2. pH Dependence of $-\log k_{\text{exp}}$ of solvolysis of 4-chloro-*N,N*-dimethylthiobenzamide in mixtures of water–ethanol. w(Ethanol)/%: 1. 0, 2. 10, 3. 30, 4. 50, 5. 70, 6. 90.

pH, and may be approximated by a straight line only in a narrow concentration range of H⁺ ions (Figs. 1 and 2).

The changes of the reaction order with respect to the total base concentration brought about by the change of the medium cannot be explained on the basis of the expression for k_{exp} , obtained by the Bodenstein method. It is advantageous to discuss this effect by using Scheme 1. In accor-



Scheme 1

dance with the experiment, in water and water-rich mixtures mainly hydrolysis proceeds under formation of one intermediate only, *i.e.* monoanion *I*. In this case the reaction order with respect to the total base concentration is close to one, which has been proved experimentally [1—4, 6]. With the increasing portion of alcohol in the mixture, decomposition of the dianion *II* to reaction products becomes kinetically significant and the reaction order increases. The reaction orders, calculated by the least squares method, are presented in Table 3. Further increase in concentration of alcohol in the mixture brings about a significant shift of the equilibrium in eqn (A) in favour of the ethoxide ions [16]. Thus, ethanolysis becomes kinetically important. The reaction proceeds also by decomposition of monoanion *III* to reaction products and with the increasing portion of ethanolysis the reaction order with respect to the total base concentration decreases. The aforementioned explanation is in qualitative agreement with Figs. 1 and 2, and with the reaction order with respect to the total base concentration, summarized in Table 3. The reaction order of the

Table 3. Reaction Order of Alkaline Solvolysis of Tertiary Thioamides with respect to Total Base Concentration in Mixtures of Water—Ethanol

w(Ethanol)/%	<i>N,N</i> -Diphenylthio- benzamide	4-Chloro- <i>N,N</i> -di- methylthiobenzamide
0	—	1.02 ^a
10	—	1.33 ^a
30	1.34	1.41 ^a
50	2.36 ^b	1.81 ^a
70	1.31	1.66
90	1.10	1.43

a) Ref. [18]; b) Ref. [5].

solvolytic reaction of *N,N*-diphenylthiobenzamide in the mixture with 50 mass % of ethanol, exceeding the proposed value, is probably associated with experimental error in pH measurements of the least diluted base solutions. Unfortunately, quantitative explanation of the k_{exp} dependence upon pH cannot be given on the basis of Scheme 1 because the dependence of the individual k_i on the medium is unknown. Therefore, only qualitative explanation may be the subject of this communication. Nevertheless, this provides also interesting information on the reaction mechanism.

Lately, we have pointed out many times [13, 17] that the equilibrium in water—ethanol systems in terms of eqn (A) must not be neglected generally. In this work studied changes of the reaction order with respect to the total base concentration, conditioned by the change of the solvent composition, are a further example when neglecting the equilibrium mentioned above would lead to misinterpretation of the experimental data.

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Synergetic Effects in the Extraction of Rare-Earth Ions by Mixed Organic Solvents

I. The Systems of Benzyltributylamine with Bis(2-ethylhexyl) Hydrogen Phosphate or Tributyl Phosphate

L. KOMOROVÁ and NHU HUNG TRAN

Department of Chemistry, Faculty of Metallurgy, Technical University, CS-043 85 Košice

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The objective of this paper was to determine the behaviour of the rare-earth ions during their extraction from the aqueous solutions by the organic extractants diluted in benzene. The organic extractant was either one-component (TBP, DEHPA, BDBuN) phase or a mixed (TBP—BDBuN or DEHPA—BDBuN) organic phase, always diluted with benzene.

Experiments showed that distribution ratios of La, Pr, Nd, and Sm obtained when extracting with DEHPA—BDBuN mixed organic phase were much higher than the corresponding distribution ratios in case of single-component extractant (either DEHPA or BDBuN) and aqueous solution only in such a case when the salting-out agent ($8.5 \text{ mol dm}^{-3} \text{ NH}_4\text{NO}_3$) was added to it prior to extraction. The synergetic coefficients of each element tested were very high. Extraction by TBP—BDBuN mixed organic phase was somewhat less satisfactory although the synergetic effect was also observed. The magnitudes of the synergetic coefficients of each rare-earth ion were lower than in the previous case.

The occurrence of the synergetic phenomena in extraction has been known for some time. It involves an enhancement of the extraction of a metal ion from the aqueous phase to the organic phase by the addition of another extractant to the organic phase. The solvent extraction of rare-earth metal ions by an extractant, e.g. tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) was the subject of investigation of several researchers [1—5]. Benzyltributylamine (BDBuN) was used for extraction by authors of papers [1, 6, 7]. On the other hand, the systematic study of the synergetic effects in the systems that consisted of the mixed organic solvents has been rather scarce [8].

The objective of this paper therefore is to contribute to the investigation of the synergetic effects in the systems BDBuN with DEHPA (bis(2-ethylhexyl) hydrogen phosphate) resp. TBP during the extraction of the following lanthanoids La, Pr, Nd, and Sm.

EXPERIMENTAL

The following organic solvents were used: TBP, DEHPA, and BDBuN (The Research Institute of Chemical Technology, Bratislava), benzene (Lachema, Brno). Rare-earth element (REE) salts of anal. grade were in the form of nitrates (Ventron, FRG).

The aqueous solutions of the REE nitrates were prepared by dissolving nitrate in the distilled water so that its concentration was $5 \times 10^{-2} \text{ mol dm}^{-3}$. Nitric acid was added to each solution so that its final concentration in all of them would be 0.5 mol dm^{-3} . Two sets of solutions were prepared: one without the salting-out agent and another with 8.5 mol dm^{-3} of NH_4NO_3 . The organic phase consisted either of one-component organic extracting agent, i.e. TBP, BDBuN, and DEHPA diluted with benzene or their mixture. Equal volumes of the organic and aqueous phases were taken and intimately mixed by mechanically shaking the test