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SCIENTIFIC PAPER

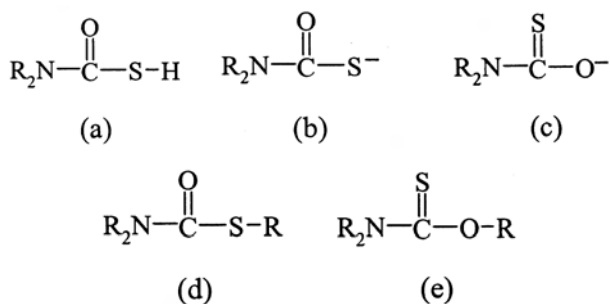
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KINETIC STUDY OF THE REACTION BETWEEN SODIUM ETHYL XANTHOGENACETATE AND ALKYLAMINE

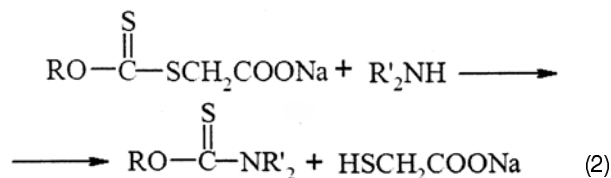
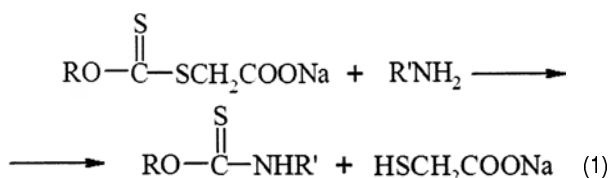
In this paper the kinetics of the reaction between sodium ethyl xanthogenacetate (NaEtXAc) and six amines was investigated. In order to determine the wavelength for following the reaction, the influence of the structures of reactants on the absorption (at 280 nm) was investigated. The values of rate constants for selected amines, at different temperatures were determined. It was confirmed that the reactions investigated are of the second-order. On the basis of the reaction rate constants and at the different temperatures, several thermodynamic parameters were calculated such as the energy of activation, the frequency factor, the activation entropy, Gibb's free-energy of the activation and the activation enthalpy. By evaluating the obtained results some assumptions that refer to the reaction mechanisms of nucleophilic attack of amine on the thiocarbonyl carbon, as well as forming of an activated complex as a critical step, were made.

Key words: Sodium ethyl xanthogenacetate, primary and secondary alkylamines, reaction rate constants, thermodynamic parameters.

Thionocarbamates, derivatives of thiocarbamine acid (Scheme 1a), are compounds of a significant biological activity [1–4]. Important derivatives of *N*-alkyl-*O*-ethylthionocarbamates and *N,N*-dialkyl-*O*-ethylthionocarbamates are thiocarbamine acid (s) salts (b and c), its esters thiol (d) and thionocarbamate (e) [1,2]:



The synthesis of thionocarbamates is based mainly on the reaction of alcohol and isocyanate [3], thioacylating of amines [4, 5], and thioacylating of alcohols and phenols are well known in literature [3, 6]. Also, the thionocarbamates can be prepared by the reaction between sodium-ethylxanthogenacetate (NaEtXAc) and alkylamines or dialkylamines presented by equations 1 and 2 [7]:



There are some literature data concerning thionocarbamates as extractants for preconcentration of trace and major amounts of Ag and Hg [8, 9]. As far as the solution properties of thionocarbamates as flotation collectors are concerned, potentiometric titrations, UV and Fourier transform IR (FTIR) spectroscopy were used for their investigation [10–12]. There are some data about the adsorption of thionocarbamates as flotation collectors, too. Namely, surface enhances Raman scattering (SERS) spectroscopy, followed by electrochemical control was used to elucidate the interaction of thionocarbamates with metal (Cu, Ag or Au) surfaces in flotation processes [13–15]. But, till nowadays there are no available data on the optimization of the synthesis and corresponding reaction kinetics data in literature. The present work represents a kinetic study of six amines including the reaction parameters followed by the analysis of the reaction mechanism. The thermodynamic parameters calculated are also discussed.

EXPERIMENTAL

Determination of kinetics parameters

Kinetic measurements were performed on UV-spectrophotometer SHIMADZU 1700 at 280 nm at temperatures of 25, 30, 35 and 40 °C. Water solutions were thermostated at the appropriate temperatures for at least 30 minutes prior to measuring. Solutions of an amine and NaEtXAc (5 cm³ of each) were mixed, and a part was poured in an adequate measuring cell and

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placed in a UV-spectrophotometer equipped with a thermostat. The initial concentrations were 1.734×10^{-5} and 4.686×10^{-2} mol/dm³ for NaEtXAc and each amine, respectively. The absorbance was monitored with time until no further change was observed. The results of the kinetic studies are presented in Table 1.

RESULTS AND DISCUSSION

The reactions of sodium-alkylxanthogenacetate and alkylamines or dialkylamines were rarely used for the synthesis of *N*-alkyl-*O*-ethylthionocarbamates and *N,N*-dialkyl-*O*-ethylthionocarbamates [7, 16]. There are no data on kinetic studies for these reactions. According to literature data, we suppose that for the similar type of the substitution reaction of diethylcarbonate and *S*-substituted-*O*-alkylxanthate by hydroxide ion and amines [17–19], the above reactions (Eqs. 1 and 2) are thioacyl nucleophile substitutions of NaEtXAc by amines. The nucleophile, namely amine, "attacks" thiocarbonyl carbon of NaEtXAc forming a tetrahedral intermediate. Our kinetic study in this work shows that this is the first-order reaction, with respect to both reactants, which indicates the proposed reaction mechanism where the formation of the transition state is probably a rate determination step.

In order to develop a kinetic measurement method, the absorbance of the system for every pair of NaEtXAc-amines in the range 200–800 nm was investigated. It was experimentally established that amines and corresponding products absorption in that range do not interfere with the absorption change of NaEtXAc having a maximum at 280 nm. According to this observation, the decrease of the absorbance of NaEtXAc at 280 nm can be measured as the reaction proceeds (Fig. 1). The absorption change of the above reaction system of NaEtXAc and EtNH₂ during (a) some period of the reaction time is shown in Fig. 2. An example of the absorbance change in function of the reaction time, at $t = 35^\circ\text{C}$, of the reaction system NaEtXAc (1.734×10^{-5} mol/dm³) and R'NH₂ or R'₂NH (4.686×10^{-2} mol/dm³) is presented in Fig. 3. The

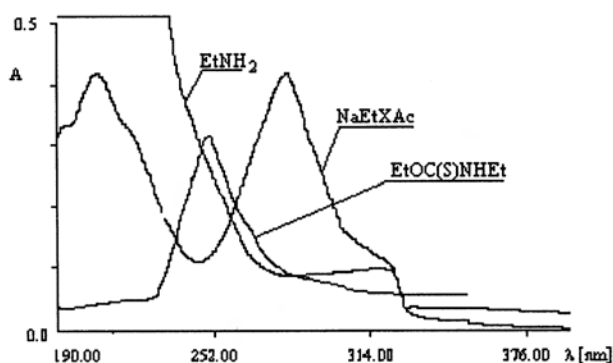


Figure 1. Absorption spectra of the starting compounds of NaEtXAc (1.734×10^{-5} mol/dm³) and EtNH₂ (4.686×10^{-2} mol/dm³) at $25 \pm 0.1^\circ\text{C}$

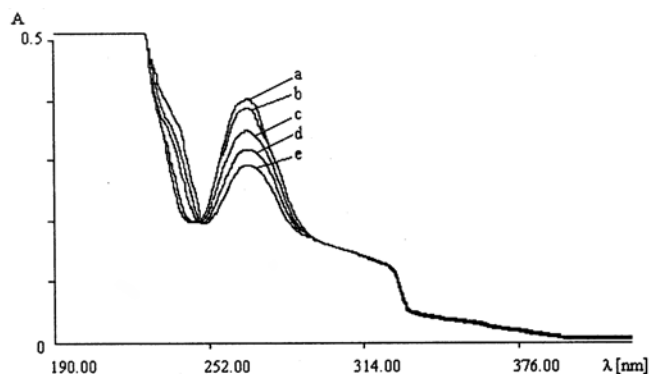


Figure 2. Absorption spectra of the reaction mixture NaEtXAc (1.734×10^{-5} mol/dm³) and EtNH₂ (4.686×10^{-2} mol/dm³) after a) 1 min, b) 2 min, c) 5 min, d) 8 min and e) 11 min from the beginning of the reaction at $25 \pm 0.1^\circ\text{C}$

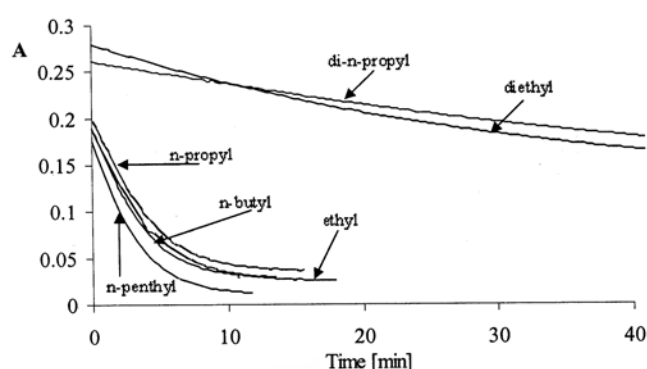


Figure 3. Dependence of the absorbance on the reaction time (35°C) in the reaction system of NaEtXAc (1.734×10^{-5} mol/dm³) and R'NH₂ or R'₂NH (4.686×10^{-2} mol/dm³)

Table 1. The second order rate constant at different temperatures ($k_2 \times 10^3$, dm³mol⁻¹s⁻¹)

Amine	Temperature, °C			
	25	30	35	40
Ethyl	49.61	70.20	107.41	133.73
n-Propyl	65.44	87.61	107.76	140.85
n-Butyl	69.46	93.85	128.75	141.20
n-Pentyl	70.56	97.50	119.14	179.61
Diethyl	6.12	8.07	9.85	16.39
Di-n-propyl	5.48	6.48	7.43	9.63

calculated second-order rate constants are presented in Table 1.

As the initial concentrations of the reactants were chosen to provide a pseudo-first order reaction, the processing of kinetics data has been done by first-order kinetic law [20]. The second order rate constants were calculated from the pseudo first-order constants. A high stoichiometric excess of amines to NaEtXAc was chosen to get a reliable reaction time for the kinetic measurements. Oppositely, a possible side effect can be a change of the reaction medium, which can significantly influence the reaction rate and the

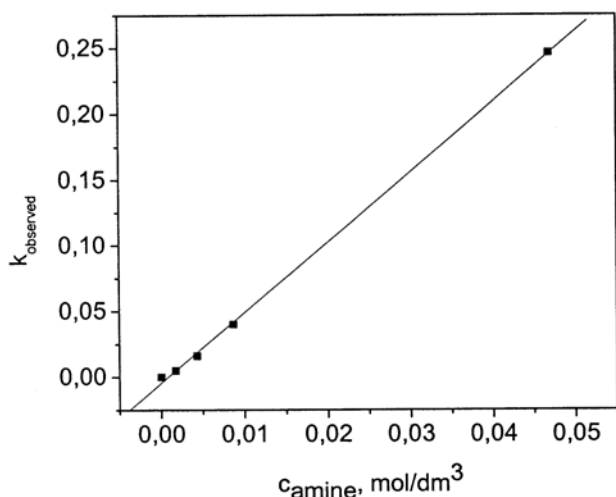


Figure 4. Correlation of the rate constants vs amine concentrations for the reaction between NaEtXAc and *n*-propylamine at 30°C

mechanism of the reaction. To check this assumption further, the experiment was conducted with a constant concentration of NaEtXAc (1.734×10^{-5} mol/dm³) and variable amine concentrations having the values as follows: 1.734×10^{-5} , 1.734×10^{-3} , 4.335×10^{-3} , 8.67×10^{-3} and 4.686×10^{-2} mol/dm³ (on 30°C). The first-order reaction constant was correlated with the amine concentration, where its slope corresponded to the first-order rate constant. Fig. 4 illustrates the case of *n*-propylamine, the second-order constant being calculated to be 88.48×10^{-3} dm³mol⁻¹s⁻¹, which is close to the value given in Table 1. A high linear correlation coefficient found for all amines studied (>0.988) undoubtedly showed that the reaction followed the second order kinetic law being independent of the high excess of an amine. All the reaction rate constants for all amines determined by the above method and the values from Table 1 agreed within 3% of the mean.

Based upon kinetic data, the activation parameters were calculated by using the second-order rate constants from Table 1: the energy of activation, the frequency factor, the entropy of activation, the Gibbs's free-energy of activation and the enthalpy of activation [20]. The calculated values of the activation parameters of all the reactions are presented in Table 2. Based on both high linear correlation coefficients for all amines

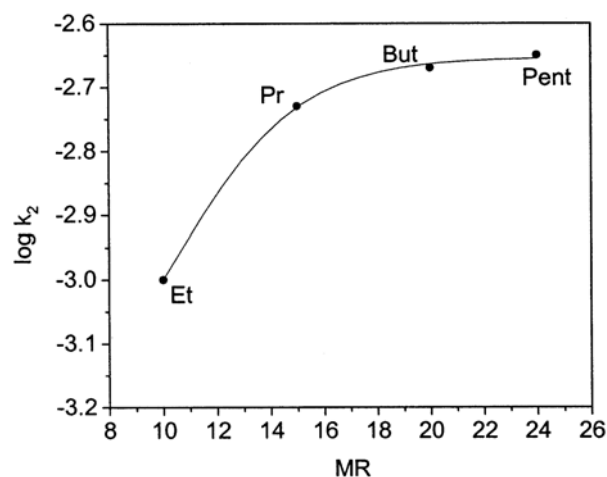


Figure 5. Correlation of $\log k_2$ of *n*-alkyl amines vs MR steric factor at 25°C

($r > 0.998$) and the calculated activation parameters, the reaction mechanism was proposed to involve the nucleophilic attack by amine followed by the creation of the activated complex as a rate determining step being the most likely one.

The kinetic and thermodynamic data (Table 1 and 2, respectively) indicate a large influence of the steric effect related to the alkyl groups of the attacking amines. Unexpectedly, longer alkyl chain amines react at a higher reaction rate, what is probably influenced by an additional solvent effect, where the amines having a longer alkyl chain of lower solubility [21] are forced to react more rapidly. The correlation of the reaction rate vs steric factor [22] MR gave the inversed exponential curve with a flat end going from ethyl to *n*-pethylamine (Fig. 5).

The high negative values of the activation entropy of activated complex with *n*-alkyl amines indicate that a high degree of arrangement is necessary for its formation. Two partially acidic hydrogen atoms bonded to nitrogen are capable of creating an intermolecular hydrogen bond to some extent, while a flexible alkyl chain is possible to adapt to a high ordered structure of the activated complex. Activation entropies for the activated complex with di-ethyl amine and di-*n*-propylamine exhibit high values showing a better arrangement of the activated complex.

Table 2. Thermodynamic parameters of the investigated reactions

Amine	E_a (kJ/mol)	A (dm ³ /mol·s)	ΔS^\ddagger_{25} (J/molK)	ΔH^\ddagger_{25} (kJ/mol)	ΔG^\ddagger_{25} (kJ/mol)
Ethyl	52.8 ± 4.1	$9.10 \cdot 10^7$	-93.12	50.4	78.2
<i>n</i> -Propyl	38.9 ± 1.6	$4.40 \cdot 10^5$	-137.50	36.5	77.5
<i>n</i> -Butyl	38.0 ± 5.4	$3.33 \cdot 10^5$	-139.93	35.6	77.3
<i>n</i> -Pentyl	46.6 ± 4.5	$1.01 \cdot 10^7$	-111.20	44.1	77.3
Diethyl	48.7 ± 11	$2.03 \cdot 10^6$	-124.31	46.3	83.4
Di- <i>n</i> -propyl	28.3 ± 4.4	$4.82 \cdot 10^2$	-193.87	25.8	83.6

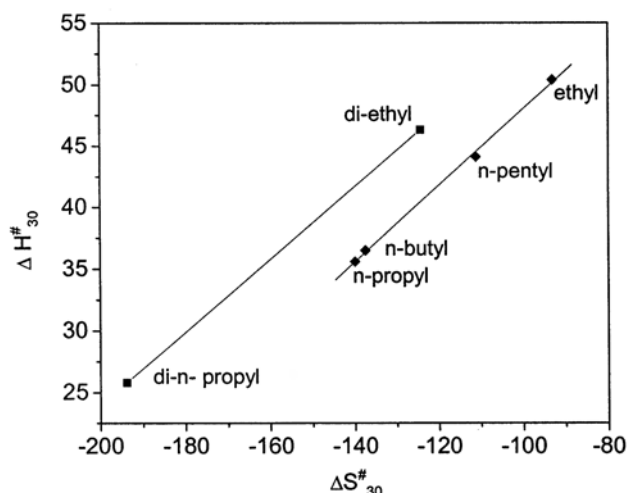


Figure 6. Correlations of the enthalpy of activation vs the entropy of activation for all amines studied

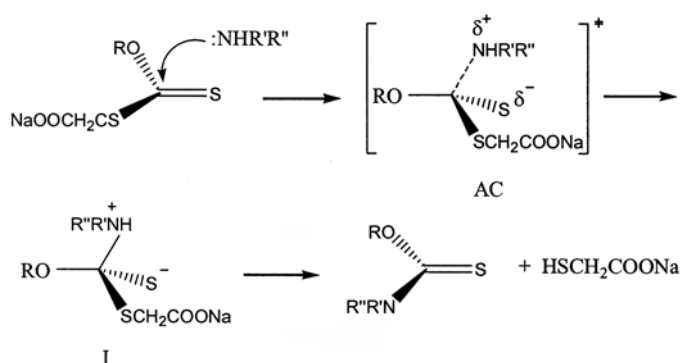


Figure 7. The most probable reaction pathway of the investigated reaction (AC – activated complex; I – intermediate)

Linear correlations of enthalpy of activation versus entropy of activation, as presented in Fig. 6, with a high correlation coefficient ($r > 0,995$), indicate the qualitative similarities of all amine–NaEtXAc systems investigated. However, the quantitatively structural influences of the amines are different [23]

Di-alkyl shows a strong influence of the steric effect of alkyl group being close to the reaction center. Generally, correlations show that amines with similar structural and spatial arrangement, having similar influences on the thermodynamic values of activated complex, belong to corresponding correlation lines. On the basis of the above results a probable reaction mechanism of the investigated reactions follows the reaction pathway as presented in Figure 7.

CONCLUSION

The calculated rate constants for the investigated reaction of amines and NaEtXAc are a summ of influences of the steric, inductive and solvent effects on the reaction rate. Also, the values of thermodynamic activation parameters are in accordance with the proposed reaction mechanism corroborating the

second-order rate law for all amines studied. The entropy of the activation reflects a high degree of the orderliness in the activated complex, especially in the case of the amines having a possibility to create an intermolecular hydrogen bond, and unexpectedly in the case of the di-n-alkylamines.

The kinetic results of the investigated reactions and calculated thermodynamic parameters indicate a complex reaction mechanism, and a more reliable mechanistic picture request a detailed further investigation.

SYMBOLS AND ABBREVIATIONS

A	– frequency factor
E_a	– energy of activation
ΔG_{25}^\ddagger	– Gibbs's free-energy of activation
ΔH_{25}^\ddagger	– enthalpy of activation
k	– constant reaction rate
ΔS_{25}^\ddagger	– entropy of activation
λ	– wavelength
NaEtXAc	– sodium-ethylxanthogenacetate

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